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Correlations of organic solution scintillators and chemical constitution

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CORRELATIONS OF ORGANIC SOLUTION SCINTILLATORS AND CHEMICAL CONSTITUTION

by

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INTRODUCTION

With the emergence of the many interesting applications of radioactivity in all fields of scientific research, there has arisen an accompanying need for more sensitive and accurate systems of measuring radiation. Many methods of measurement have been developed, the most sensitive of which depend on scintillation, i.e., conversion of wave energy (or kinetic energy of subatomic particles) into light energy.

The materials employed to effect this conversion (scintillators) fall into four general classes:

1. Ionic crystals, zinc sulfide being the classic example, were the first materials in which the phenomenon of scintillation was observed.[1] Although this observation was reported in 1903, zinc sulfide is still widely used to count alpha particles, with the use of a photomultiplier as the only important refinement. Sodium and lithium iodide have been used for both alpha and neutron counting.
2. Covalent crystals, particularly anthracene and stilbene, have been used in recording beta and gamma radiation.
3. Organic solutions have been modified to respond to all types of radiation. A spectacular use of this

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[1] W. Crookes, Chem. News, 87, 157 (1903).

class of scintillation system is the counting of cosmic rays by Harrison,[2] who used a solution of p-terphenyl in a large bulk of toluene.

4. Plastic scintillators, a modification of the solution class, combine the large volume and rapid response of solution scintillators with the structural rigidity of the crystalline types. p-Terphenyl in polyvinyltoluene is the best of a series prepared and studied by Buck and Swank.[3]

This work is concerned only with solution scintillators. These systems, unlike ionic or covalent solids, can be prepared in large volume units to permit applications utilizing low external radiation fluxes or low cross section interactions. Homogeneous incorporation of materials to be counted within the system is an important advantage, as well as great transparency and dissolution of many useful compounds without quenching.

The purpose of this investigation is a threefold organic chemistry problem: (a) the synthesis of a wide variety of aromatic compounds as potential scintillator solutes, (b) a concentrated effort to incorporate various functional groups and heterocyclic systems into proven scintillator molecules,

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[2] F. B. Harrison, Nucleonics, 10, No. 6, 40 (1952).

[3] W. L. Buck and R. K. Swank, Nucleonics, 11, No. 11, 48 (1953).

and (c) the correlation of the efficiency of light production of these solutes with their chemical constitution in hopes of laying the foundation upon which a general theory of the scintillation process may be constructed.

HISTORICAL

The Scintillation Process

As previously mentioned, the first observation of scintillation was that of Crookes. A crude scintillation counter was devised in 1908 by Regener.[4] Scintillation of solutions was reported by Ageno, et al.,[5] in 1949 and was looked upon as an interesting novelty until the cosmic ray counting experiment of Harrison brought the versatility of solution counters to the attention of experimentalists in all fields. In the subsequent five years these systems have become widely accepted and give every indication of being the ideal measuring device for practical laboratory use. For this reason it is desirable to know more of the effect of radiation on the solution itself in order to insure reliable application. According to the calculations of Reynolds[6] only a few volts are required to produce one photon of light, but 150 volts are passed into a terphenyl-toluene solution for each photon emitted. It is far too pessimistic to say that there is an intrinsic limit to the efficiency of this energy conversion without more intimate knowledge of the process.

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[4] E. Regener, Ber. physik. Ges., 6, 78 (1908).

[5] M. Ageno, M. Chizzotto, and R. Querzoli, Atti. Accad. nazl. Lincei, Rend. 6, 626 (1949) [C. A. 44, 9810 (1949)].

[6] G. T. Reynolds, Nucleonics, 10, No. 7, 46 (1952).

Early speculation on the mechanism of the scintillation process by Förster[7] divided the problem into three stages: (a) excitation, (b) energy transfer, and (c) emission. The reasoning leading to this division follows directly from a few observations of the characteristics of common solution scintillators. The comparison of the quantity of luminescence to the quantity of fluorescent molecules shows that the energy must be initially absorbed by the solvent. The spectra of the light emitted is characteristic of the solute, even when diluted to one part in ten thousand. If a second solute, having an emission peak at a longer wavelength than the first, is added in concentrations of the order of one-hundredth of the first, the spectra will be characteristic of this secondary solute. The entire process requires less than 10^{-7} second. High concentrations of solute give rise to some form of quenching of the light. The maximum rate of photon emission (relative peak height) of a terphenyl-toluene system is 30% greater than that of a stilbene crystal scintillator. It is interesting to note, however, that this ratio is reversed when the time constants of the electronic measuring circuit are of the order of 10^{-8} second or greater. The reason proposed by Post[8] is that the slower circuit records the total (integrated)

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[7] T. Förster, Naturwiss., 33, 166 (1946).

[8] R. F. Post, Phys. Rev., 79, 735 (1950).

output. In fast counting, of course, the peak height is the more significant measurement.

The absorption of radiation energy by the solvent of a solution may take place in many ways, depending on the nature of the radiation. Charged particles impart kinetic energy to electrons in their path and may even break some covalent bonds. The commonly encountered uncharged radiation, gamma rays and neutrons, function differently. Gamma rays set a Compton scattering process in operation. This is a result of ejection of an electron from a molecule by the ray, and the transfer of some of the original energy to this secondary electron. Both the activated electron and the slightly less energetic gamma can further excite electrons by the charged particle mechanism and further Compton scattering, respectively. Obviously large volume liquid scintillators are well suited to this type of counting.

Fast neutrons collide with protons in the solution, and the scintillation results from the action of these recoil protons. Thermal neutrons are not sufficiently energetic to excite scintillator molecules of themselves. Muehlhause and Thomas[9] developed a system containing methyl borate to count these particles indirectly. Natural boron contains 18.4% B^{10} which has an exceptionally high thermal neutron cross section.

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[9] C. O. Muehlhause and G. E. Thomas, Jr., Nucleonics, 11, No. 1, 44 (1953).

Following the neutron capture, an alpha particle and a gamma ray are emitted as shown below and can be observed in the

$$_5B^{10} + {}_0n^1 \longrightarrow {}_3Li^7 + {}_2He^4 + \gamma \qquad \text{(Eq. 1)}$$

usual fashion. An interesting sidelight is the use of the few microsecond delay between the proton recoil caused by a fast neutron and subsequent capture of the resulting thermal neutron to distinguish the fast neutron signal.

There has been suggested a number of paths by which the excited solvent molecules may dissipate their energy. The early proposal of Förster[7] involves a double molecule at a lower energy state, having a certain binding energy which stabilizes the excitation energy. This double molecule is incapable of fluorescence and will eventually quench the excess energy in the form of heat liberated by impact with the surroundings. The decreased chance of photon emission from this double molecule increases the chance of dissipation of energy as heat. The possibility of dissociation and alteration of solvent molecules by the collision energy of the incident radiation was studied by Reynolds.[6] Mass spectrographic analysis, however, did not bear this out. The theory currently accepted (with reservations and slight variations) is that of Kallmann and Furst,[10] which attributes an excitation level to

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[10]H. Kallmann and M. Furst, Phys. Rev., 79, 857 (1950).

the excited solvent molecule that is considerably higher than the pure electronic level of the solute molecule. Reynolds added that the solvent states are probably coupled through vibrational states and are reduced to the lowest vibrational state of the first excited level in a time interval of about 10^{-12} second. Photon emission from this state can be shown to be highly improbable.

A similar problem arises in the consideration of the mode of transfer of excitation energy to the fluorescent molecule. Here it is important to consider the numerous processes that are possible once the solvent molecules have been excited. Using the symbolism of Reynolds,[6] wherein

S represents a solvent molecule,

F represents a fluorescent solute molecule,

$h\nu$ represents a photon of energy,

S* represents an excited solvent molecule, and

F* represents an excited fluorescent molecule,

the following processes are potentially feasible:

(1) $S + h\nu_1 \longrightarrow S^*$

(2) $S^* \longrightarrow S + h\nu_2$

(3) $S^* + S \longrightarrow S + S^*$

(4) $S^* + F \underset{b}{\overset{a}{\rightleftharpoons}} S + F^*$

(5) $F^* \longrightarrow F + h\nu_3$

as are the radiationless processes:

(6) $S^* + S \longrightarrow S + S + \text{heat}$ (or $S^* \longrightarrow S + \text{heat}$)

(7) $F^* + S \longrightarrow F + S + \text{heat}$ (or $F^* \longrightarrow F + \text{heat}$)

The extension of these processes to include a secondary solute is a needless complication that can be visualized readily.

Process 2 above can be readily eliminated as the simple aromatic solvents employed are known not to fluoresce. The third reaction is a strong possibility in view of the easy access of an excited solvent molecule to unexcited solvent molecules. This type of resonance would also contribute to the stability of the excited solvent molecules. The reaction also represents a refinement of the double molecule theory. Step 4a above is critical, and must be irreversible for all practical purposes, although 4b may become important in the case of some poor scintillator solutes. The scintillation itself is represented by 5.

The ideal conditions for step 4a above were summarized by Kallmann and Furst.[10] The solvent radiation must be weak, the excited solvent must have sufficient lifetime to permit appreciable transfer, and the fluorescent molecules must be able to trap the energy. In the case of toluene the excitation energy is reported[6] to have a lifetime of 3×10^{-10} second, and the energy dissipation is non-radiative; thus fulfilling the first

two conditions. If the energy is not released as radiation from pure toluene, it is reasonable to eliminate photon emission from solvent, followed by absorption by solute, as the transfer mechanism. Subsequent work by Birks[11] led him to the conclusion that such energy transfers are possible in the case of ultraviolet excitation. The value of the fluorescence techniques employed by Birks in the study of scintillation spectra is sufficiently questionable to restrain conclusions based on this approach.[12] Reynolds[6] eliminated this mechanism on the grounds that the time interval was too short for such "carrying-around of the energy" in the solution.

Energy transfer by a dipole-dipole interaction was suggested by Förster[13] on the basis of analogy to a similar transfer in dye solutions. According to Reynolds, these weak dipoles require distances considerably shorter than those present in the very dilute scintillator solutions. Reynolds concludes the energy exchange must be quantum mechanical and cites calculations to show that this could be effected in a time interval of 3×10^{-11} second, well below the lifetime of an excited toluene molecule.

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[11] J. B. Birks, Phys. Rev., 94, 1567 (1954).

[12] For a discussion of the major discrepancies involved, see D. G. Ott, F. N. Hayes, V. N. Kerr, and R. W. Benz, Science, 123, 1071 (1956).

[13] T. Förster, Ann. Physik, 2, 55 (1948).

The conclusions reached by Kallmann and Furst are compatible, although arrived at in a different fashion. These workers restricted their quantitative considerations to the quenching of scintillation.[10] The shift of emission spectrum was shown to be the critical effect in preventing quenching. They calculated that the probability of quenching by excited solvent molecules was very high, and by fluorescent molecules much lower. They were also able to determine that the excited solvent molecule has a higher excitation level than the pure electronic level of the fluorescent molecule. The energy transfer would then raise the fluorescent molecule to a state in which atomic vibrations are also excited. The excited atomic vibrations are then transferred to other atomic vibrations and thereby decoupled from the electronic excitation of the fluorescent molecule. The remaining excitation, being purely electronic, is insufficient to re-excite solvent molecules. This process accounts, in a qualitative fashion, for both the similarities and differences in the scintillation and ultraviolet-excited spectra. Explicit also, is the irreversibility of the energy transfer, although no attempt is made to correlate this fact with the higher wavelength of the fluorescence. In their studies on secondary solutes both Birks[11] and Roser[14] pointed out the vital importance of this relationship.

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[14] F. X. Roser, Science, 121, 806 (1955).

The approach to the mechanism of scintillation through quenching by the solution itself or by foreign bodies has been adopted by a number of workers since the original empirical considerations of Kallmann and Furst.[10,15] In this latter report these workers attributed the difference between the three isomers of terphenyl (see Table 2) to a difference in internal quenching probability. Quenching by the solution itself had previously been observed by Harrison and Reynolds[16] who observed that emission is more intense if measured near the slit at which the excitation is admitted than at the opposite side. Displacement of dissolved oxygen by nitrogen was reported[17] to give noticeable increases in relative pulse height of terphenyl-toluene scintillator solutions. Ott, Hayes, and coworkers[18,19] carried out a quantitative comparison of quenching via light absorption by the solvent, measuring the wavelength at which the mean free path had a specific length in forty-four different solvents. When argon was used to replace dissolved oxygen, there was a 20-25% increase in

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[15] H. Kallmann and M. Furst, Phys. Rev., 81, 853 (1951).

[16] F. B. Harrison and G. T. Reynolds, Phys. Rev., 79, 732 (1950).

[17] R. W. Pringle, B. L. Funt, L. D. Black, and S. Sobering, Phys. Rev., 92, 1582 (1953).

[18] F. N. Hayes, B. S. Rogers, and P. C. Sanders, Nucleonics, 13, No. 1, 46 (1955).

[19] D. G. Ott, F. N. Hayes, J. E. Hammel, and J. F. Kephart, Nucleonics, 13, No. 5, 62 (1955).

efficiency of light production by terphenyl or 2,5-diphenyloxazole in toluene. The drop in scintillation efficiency at high solute concentrations was attributed to "self-quenching" by solute molecules themselves. A quenching study was later carried out in more detail by these same workers,[20] which confirmed the observation of Kallmann and coworkers[21] that quenching by heavy elements is due mainly to a quenching of the excited solvent molecule, although no information has been presented concerning Kallmann's use of naphthalene and biphenyl as intermediate transfer agents.

Concurrent with this work on the phenomenon of scintillation was a series of studies concerned with the make-up of the best available solution scintillator systems. The process consisted of measuring the scintillation from a variety of solvents containing the same solute, or a variety of solutes in the same solvent, using a standard, reproducible source of excitation. The efficiency of light production can then be compared to some arbitrary standard. In this work the standard of comparison will be that chosen by Hayes and coworkers,[18] a solution of 2,5-diphenyloxazole in toluene at a concentration of 3 g./l., which is assigned the arbitrary pulse-height value of 1.00.

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[20] V. N. Kerr, F. N. Hayes, and D. G. Ott, International Journal of Applied Radiation and Isotopes, 1, 284 (1957).

[21] H. Kallmann, M. Furst, and F. H. Brown, Nucleonics, 14, No. 4, 48 (1956).

Scintillation Solvents

Ninety-nine per cent of the liquid scintillator is solvent. It follows that the first considerations in an attempt to idealize conditions for scintillation are the criteria of a good solvent. Most of these criteria are implicit in the discussion of the role played by the solvent and a few practical considerations. The solvent should be aromatic to permit electronic excitation; it must, of course, have some solvent power for the high molecular weight aromatic solutes; it should be readily available and of consistently high purity;[22] it must have high transparency for the emitted light, particularly in large bulk applications such as neutrino detection[23] and human counting;[24] it must have high hydrogen density for counting of fast neutrons by proton recoil; and it should have a melting point at least 20° below zero because of frequent application in totally refrigerated systems.

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[22]The effect of trace impurities is illustrated by the value reported by Kallmann and Furst for mesitylene, < 0.10, and the subsequent report by Hayes and coworkers, 0.83, for the purified solvent; see Table 1.

[23]C. L. Cowan, Jr., F. Reines, F. B. Harrison, E. C. Anderson, and F. N. Hayes, Phys. Rev., 90, 493 (1953).

[24]E. C. Anderson, R. L. Schuch, J. D. Perrings, and W. H. Langham, Nucleonics, 14, No. 1, 26 (1956).

The most efficient solvents examined to date are all alkyl benzenes.[25,26] Many other classes of compounds have been tested as solvents, and all that have been reported in the literature before January 1, 1957 are listed in Table 1. Those reported for the first time in this thesis were tested in the pulse-height analyzer described by Hayes, et al.[27] The relative pulse height is the ratio of the maximum pulse height recorded for the system being examined to that of the diphenyloxazole standard. The values reported by Kallmann and Furst have been multiplied by the necessary factor derived from an average ratio of identical systems tested by both. In these instances both values are given since this factor is not too reliable. Solvents for which the reports were greatly different were not used in deriving the approximating factor since one or the other was undoubtedly working with a contaminated solution. Terphenyl was assumed to have an efficiency 96% of that of diphenyloxazole.[26] Kallmann used terphenyl as a standard solute in nearly all of his solvents.

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[25] H. Kallmann and M. Furst, Nucleonics, 8, No. 3, 32 (1951).

[26] F. N. Hayes, Los Alamos [New Mexico] Scientific Laboratory Report No. LA-1639, 56, 61 (1953).

[27] F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, Nucleonics, 13, No. 12, 38 (1955).

Table 1. Solvent relative pulse heights

Name of compound	RPH	Ref.
Acetic acid	<0.10	18
Acetone	<0.10	18
Acetophenone	<0.10	18
2-Amino-p-cymene	<0.10	25
2-Amino-dimethylbenzene (*sic*)	<0.10	25
4-Amino-1,3-dimethylbenzene	<0.10	25
Aniline	0.16	25
Anisole	0.80 0.83	25 18
Benzalacetone	<0.10	25
Benzaldehyde	<0.10	25
Benzalmethylamine	<0.10	25
Benzene	0.88 0.85	25 18
Benzyl alcohol	0.13 0.42	25 18
Benzylamine	<0.10	25
Benzyldimethylamine	<0.10	25
Benzyl ether	0.12	25
Benzylsilane	0.39	28
Bromobenzene	<0.10	18

[28]Not previously reported.

Table 1. (Continued)

Name of compound	RPH	Ref.
Bromocyclohexane	<0.10	18
1-Butanol	<0.10	18
Butyrophenone	<0.10	25
n-Butylbenzene	0.88	18
1-(n-Butyl)naphthalene	0.92	28
Carbon tetrachloride	<0.10	25
α-Chloronaphthalene	<0.10	25
Chlorobenzene	<0.10	18
Chlorocyclohexane	<0.10	18
Cumene	0.59 0.80	25 18
Cyclohexane	0.20 0.31	25 18
Cyclohexanol	<0.10 <0.10	25 18
Cyclohexanone	<0.10 <0.10	25 18
Cyclohexene	<0.10 <0.10	25 18
Cyclohexylamine	<0.10	25
Cyclohexylcarbinol	<0.10	25
Cyclopropyl methyl ketone	<0.10	25
p-Cymene	0.58 0.80	25 18
Dibenzylamine	<0.10	25

Table 1. (Continued)

Name of compound	RPH	Ref.
Di-n-butylamine	<0.10	25
N,N-Di-n-butylaniline	<0.10	25
o-Dichlorobenzene	<0.10	25
m-Dichlorobenzene	0.12	25
Dicyclohexyl	0.49	18
N,N-Diethyl-α-naphthalamine	<0.10	25
N,N-Diethyl-o-toluidene	<0.10	25
p-Difluorobenzene	0.54	18
Di-isobutylene (sic)	<0.10	25
m-Dimethoxybenzene	0.38	18
1,1-Dimethoxyethane	<0.10	18
N,N-Dimethylaniline	0.20	25
N,N-Dimethyl-o-toluidine	<0.10	25
1,4-Dioxane	0.54 0.20	25 18
Dipentene (sic)	<0.10	25
Diphenylmethane	<0.10	25
Diphenyl ether	1.24	25
n-Dodecane	0.16	25
Ethanol	<0.10 <0.10	25 18
Ethylbenzene	0.96	18
Ethyl ether	<0.10	25

Table 1. (Continued)

Name of compound	RPH	Ref.
Fluorobenzene	0.65	18
Fluorocyclohexane	0.20	18
o-Fluorotoluene	0.74	18
m-Fluorotoluene	0.68	18
p-Fluorotoluene	0.69	18
n-Heptane	0.14	25
n-Hexadecane	0.29	25
Hexane (sic)	0.12 0.27	25 18
1-(n-Hexyl)naphthalene	0.52	28
Isodurene	1.09	25
Ligroin	0.20	25
Mesitylene	<0.10 0.82	25 18
Methanol	<0.10	18
Methyl benzoate	<0.10	25
2-Methylbenzothiazole	<0.10	25
2-Methylbenzoxazole	0.20	25
Methylbenzylaniline (sic)	<0.10	25
Methyl borate	<0.10	18
Methylcyclohexane	0.35	18
2-Methylfuran	0.18	18
2-Methyltetrahydrofuran	<0.10	18

Table 1. (Continued)

Name of compound	RPH	Ref.
Mineral oil	0.26	18
Morpholine	<0.10	25
Naphthalene monobromide (sic)	<0.10	25
1-Ethoxynaphthalene	<0.10	25
n-Octane	0.19	25
Paraffin oil	0.11	25
Phenetole	0.76	25
Phenylcyclohexane	1.24 1.02	25 18
Phenylethylene oxide	<0.10	25
β -Phenylethylamine	<0.10	25
dl- α-Phenylethylamine	<0.10	25
Phenylsilane	0.77	28
3-Picoline	<0.10	18
Piperidine	<0.10	18
n-Propylal (sic)	<0.10	25
N-(n-Propyl)aniline	<0.10	25
p-(i-Propyl)benzaldehyde	<0.10	25
n-Propylbenzene	0.11	25
i-Propyl benzoate	<0.10	25
Pyridine	<0.10 <0.10	25 18
Pyrrole	<0.10	25

Table 1. (Continued)

Name of compound	RPH	Ref.
Quinoline	<0.10	25
Styrene	<0.10	25
Tetrahydrofuran	<0.10	25
Tetrahydronaphthalene	0.55	25
Thiophene	<0.10	25
Toluene	1.00	25
	1.00	18
m-Toluidine	<0.10	25
Triethylbenzene	0.96	18
2,2,4-Trimethylpentane	<0.10	25
Xylene	1.09	25
	1.07	18
o-Xylene	0.98	18
m-Xylene	1.09	18
p-Xylene	1.12	18

Scintillation Solutes

The investigation of scintillation solutes, including those reported for the first time in this work, has been carried out systematically. The early report of Ageno[5] was an

extension of current investigation concerned with the effect of impurities on the scintillation of anthracene crystals. Since it was generally held that impurities such as phenanthrene, fluorene, and others were responsible for the scintillation, the anthracene crystals had come to be looked upon as solid solutions. The work with solutions followed naturally, using these same impurities as solutes.

In their broad survey of solutions Kallmann and Furst[25] examined many solutes, especially as xylene solutions, and all of these results are to be found in Table 2. Also in Table 2 are all other compounds tested as scintillation solutes before January 1, 1957, many reported during 1957, and a group of compounds heretofore unreported. As a result of their data, Kallmann and Furst suggested the apparent importance of resonance in the solute molecule, with special reference to that peculiar to "chain-type" polyaryls, as a criterion of light production efficiency. Terphenyl was the most efficient of all the compounds they examined.

As the broad utility of terphenyl-toluene scintillators became obvious, a study was undertaken by Hayes and his coworkers[27] to refine scintillation solutions to the point of maximum practical sensitivity for the homogeneous counting of C^{14} and H^{3}. They decided on toluene as solvent and Cs^{137} as excitation source in order to insure uniformity and reproducibility. Early observations on chain-type molecules

containing the oxazole and the thiazole ring[29] led them to concentrate their efforts on the former. The choice was based on a number of favorable characteristics of these oxazole derivatives.

The replacement of benzene by the oxazole ring in a chain of simple aromatic rings gave rise to a considerable decrease in melting point and corresponding increase of solubility in toluene. This permitted measurement at a wider range of concentrations. It is important to note in this respect that the relative pulse height of terphenyl in toluene is still increasing with concentration at the limit of its solubility[30] (8 g./l.). The extension by one more ring to p-quaterphenyl results in a solubility of less than 1 g./l., which is too low to provide an effective evaluation. These workers have extended the chain of rings to seven (with 1,4-di-[5-(4-biphenylyl)-2-oxazolyl]benzene) before the solubility drops to 1 g./l.

Early observations showed that some oxazole and oxadiazole derivatives have higher light production efficiency than terphenyl. At this time the highest reported relative pulse height is that of 2-(4-biphenylyl)-5-phenyl-1,3,4-oxadiazole, which Hayes and coworkers[27] measured as 1.28 at 10 g./l. in toluene.

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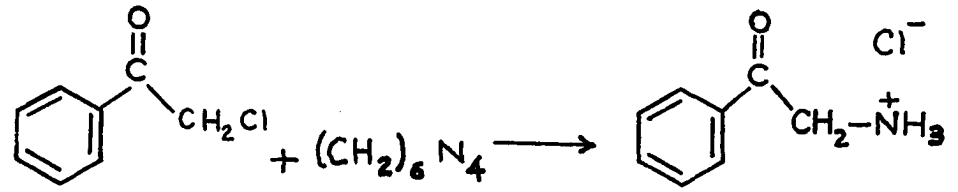
[29]F. N. Hayes, L. C. King, and D. E. Peterson, J. Am. Chem. Soc., 74, 1106 (1952).

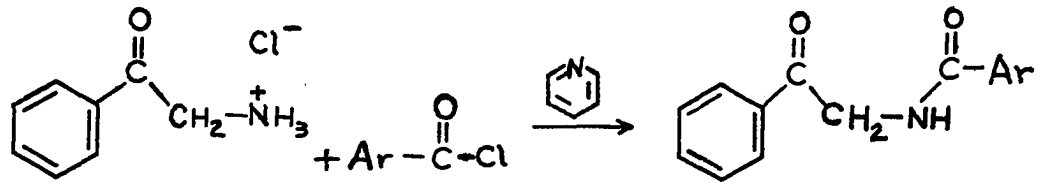
[30]Reference 26, p. 55.

The emission spectra of the oxazole derivatives was also a determining factor. Most of the simple 2,5-diaryloxazoles have a maximum in the emission spectra around 380-430 mμ.[31] This shows good correspondence to the range of maximum sensitivity of most commercial photomultipliers. The RCA 5819, for example, reaches maximum efficiency at 480 mμ.[32] The maximum in the emission spectrum of terphenyl is at 354 mμ, where the sensitivity of the 5819 is only 65%.

Finally the synthesis of a broad scope of aryloxazoles appeared feasible from the series of reactions shown below:[33]



(Eq. 2)



(Eq. 3)

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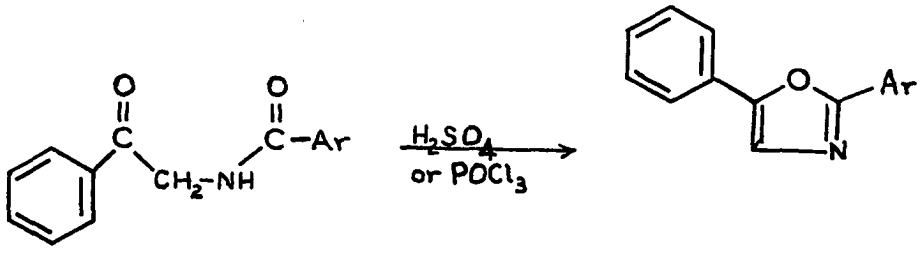
[31] D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, J. Am. Chem. Soc., 79, 5448 (1957).

[32] R. W. Engstrom, R. G. Stoudenheimer, and A. M. Glover, Nucleonics, 10, No. 4, 58 (1952).

[33] F. N. Hayes, B. S. Rogers, and D. G. Ott, J. Am. Chem. Soc., 77, 1850 (1955).



(Eq. 4)

Apparently any number of derivatives with the phenyl group in the 5-position could be synthesized by this process, as the only necessary starting material was the carboxylic acid of the aromatic system desired for the 2-position. The remarkable success of these workers can be seen from the large number of interesting oxazole derivatives listed in Table 2.

This orderly series of closely related compounds permitted a few preliminary generalizations regarding the correlation between molecular structure and relative pulse height of liquid scintillator solutes:

1. Linkage of four rather than three rings in a molecule yields a better scintillator, partly because of its longer wavelength spectrum.

2. Four and five-ring compounds have sufficient solubility for scintillation applications when they incorporate heterocyclic ring systems such as oxazole.

3. Generally beneficial ring systems are benzene, naphthalene, furan, pyrrole, oxazole, 1,3,4-oxadiazole, pyridine, indole, and benzoxazole. Poor ones are

thiophene, thiazole, 1,3,4-thiadiazole, pyrazine, pyridazine, and benzothiazole.

4. Substituent groups causing no difficulty are methyl, methoxy, fluoro, and chloro. Undesirable ones are bromo, iodo, nitro, and phenolic hydroxyl.[27]

The researchers were careful to note that sweeping generalizations of this type consistently fail because of "the diverse processes which contribute to this ability." This reservation was well taken for almost simultaneously Arnold[34] reported remarkable pulse heights for two compounds which had structures containing apparently undesirable groups. 2-(p-Dimethylaminophenyl)benzothiazole, produced a relative pulse height of 0.90 in spite of the fact that it was a sulfur heterocycle. 7-Diethylamino-4-methylcoumarin was reported at 0.93. Although no specific statement had been made with regard to the reduction of scintillation values by the carbonyl function in general, or the ester linkage in particular, all of the compounds tested by Kallmann and Furst[25] containing carbonyl linkages gave poor values. Hayes[35] attributes the remarkable values observed by Arnold to a strongly beneficial effect of the dialkylamino function. A possible explanation of this effect was suggested in subsequent studies[31] of the variation of intensity of absorption and fluorescence caused

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[34] J. R. Arnold, Science, 122, 1139 (1955).

[35] F. N. Hayes, Private communication to Dr. H. Gilman.

by such groups. This report noted a striking bathochromic shift in the spectra of molecules containing the dimethylamino function, along with increased intensity for both absorption and fluorescence. The increased intensity of fluorescence was attributed to a decreased lifetime of the excited fluorescent molecule, which in turn is a result of the high absorption intensity.[36] It follows that this shorter lifetime diminishes the probability of internal quenching since there is a shorter period during which the excited molecule may encounter the sides of the vessel or another like molecule. Both of these processes have been postulated as means of non-radiative energy dissipation.[6,7]

A further observation in this study was the fact that introduction of the dialkylamino function into a compound which already has high fluorescence efficiency does not increase this efficiency. The authors hold that this substitution "may be expected to be detrimental."[31] No reason is given for this expectation, but examples are pointed out.

Table 2 of all solutes tested for scintillator activity before January, 1957 follows. Nomenclature used is in accordance with the recommendations of Leonard T. Capell and Mary A. Magill of Chemical Abstracts as expressed in letters dated Dec. 6, 1956, Apr. 25, 1957, Oct. 21, 1957, and Nov. 14, 1957.

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[36] W. West, "Fluorescence and Phosphorescence," in W. West, ed., "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 709.

Table 2. Primary-solute relative pulse heights

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
1	Acridine	<0.10	25	37
2	10-Allylphenothiazine	<0.10	28	38
3	2-Aminobiphenyl	0.16	28	37
4	2-Amino-p-cymene	<0.10	25	37
5	2-Aminodibenzo-p-dioxin	<0.10	28	39
6	6-Amino-2,3-di-(4-methoxyphenyl)-quinoxaline	<0.10	28	40
7	2-Aminophenanthrene	0.23	28	41
8	3-Aminophenanthrene	0.20	28	42

[a]Relative pulse height versus solution of 3 g./l. of 2,5-diphenyloxazole in toluene (arbitrarily called 1.00).

[b]Reference to report of relative pulse height.

[c]Reference to synthesis or source of sample tested.

[37]Commercially available.

[38]H. Gilman and D. A. Shirley, J. Am. Chem. Soc., 66, 888 (1944).

[39]M. Tomita, J. Pharm. Soc. Japan, 55, 1060 (1935) [C. A., 31, 6661 (1937)].

[40]H. Gilman and H. S. Broadbent, J. Am. Chem. Soc., 70, 2620 (1948).

[41]W. E. Bachmann and C. H. Boatner, J. Am. Chem. Soc., 58, 857 (1936).

[42]J. Schmidt, Ber., 34, 3533 (1901).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
9	2-(m-Aminophenyl)-5-phenyloxazole	0.40	31	31
10	2-(p-Aminophenyl)-5-phenyloxazole	0.80	31	31
11	2-(3-Aminostyryl)pyridine	0.49	28	43
12	2-(3-Aminostyryl)quinoline	0.51	28	43
13	4-Amino-p-terphenyl	0.85	28	44
14	4-Amino-m-xylene	<0.10	25	37
15	2-Amino-p-xylene	<0.10	25	37
16	Aniline	<0.10	25	37
17	Anthracene	0.20 0.18	25 27	37 37
18	Anthranilic acid	0.48	25	37
19	Azobenzene	<0.10	25	37
20	Benzalacetophenone	<0.10	25	37
21	Benzalacetophenone dibromide	<0.10	25	37
22	Benzalaminophenol (sic)	<0.10	25	37
23	Benzalaniline	<0.10	25	37
24	Benzalazine	<0.10	25	37
25	Benzamide	<0.10	25	37
26	Benzanilide	<0.10	25	37

[43] H. Gilman and G. Karmas, J. Am. Chem. Soc., 67, 342 (1945).

[44] This thesis.

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
27	Benz[a]anthracene	0.10	25	37
28	Benz[b]anthracene-7,12-dione	<0.10	25	37
29	3,4-Benzocoumarin	<0.10	28	37
30	Benzoic acid	<0.10	25	37
31	Benzoic anhydride	<0.10	25	37
32	Benzoin	<0.10	25	37
33	Benzo[h]quinoline	<0.10	28	45
34	4-Benzoyl-p-terphenyl	<0.10	28	46
35	4-Benzoyl-p-terphenyl oxime	<0.10	28	47
36	Benzylamine	<0.10	25	37
37	4-Benzylbiphenyl	<0.10	28	48
38	2-Benzyldibenzo-p-dioxin	<0.10	28	49
39	Benzyl ether	<0.10	25	37
40	Benzyl-1-naphthyl ether	<0.10	25	37

[45]H. Skraup, Monatsh., 2, 163 (1881).

[46]H. Gilman and E. A. Weipert, J. Org. Chem., 22, 446 (1957).

[47]Sample through the courtesy of B. J. Gaj of this Laboratory.

[48]K. Goldscheniedt, Monatsh., 2, 443 (1881).

[49]J. J. Dietrich, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1957.

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
41	Bibenzyl	<0.10	25	37
42	1,1'-Bidibenzo-p-dioxin	0.15	28	49
43	2,2'-Bidibenzo-p-dioxin	0.59	28	49
44	2,2'-Bidibenzofuran	0.14	28	50
45	4,4'-Bidibenzothiophene	<0.10	28	51
46	1,1'-Binaphthyl	0.87	28	52
47	2,2'-Binaphthyl	0.25	28	53
48	Biphenyl	<0.10	25	33
49	N-(4-Biphenylyl)aniline	0.63	28	54
50	2-(4-Biphenylyl)benzoxazole	0.96	31	31
51	2-Biphenylyl 4-biphenylyl ether	<0.10	28	55
52	9-(4-Biphenylyl)carbazole	0.35	28	56

[50] H. B. Willis, Iowa State Coll. J. Sci., 18, 98 (1943).

[51] H. Gilman and G. R. Wilder, J. Org. Chem., 22, 523 (1957).

[52] H. Gilman and C. G. Brannen, J. Am. Chem. Soc., 71, 658 (1949).

[53] F. Ullman and R. Gilli, Ann., 332, 50 (1904).

[54] F. Ullman and O. Lowenthal, Ann., 332, 67 (1904).

[55] Sample through the courtesy of Dow Chemical Co.

[56] H. Gilman and J. B. Honeycutt, J. Org. Chem., 22, 226 (1957).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
53	N-(4-Biphenylyl)diphenylamine	0.39	28	57
54	2-(4-Biphenylyl)indole	0.51	27	58
55	1-(2-Biphenylyl)isoquinoline	<0.10	28	59
56	1-(4-Biphenylyl)isoquinoline	<0.10	28	59
57	5-(4-Biphenylyl)-2-(4-methoxyphenyl)-1,3,4-oxadiazole	1.24	27	33
58	5-(4-Biphenylyl)-2-(4-methoxyphenyl)-oxazole	1.19	27	33
59	5-(4-Biphenylyl)-2-(1-naphthyl)-oxazole	1.08	27	33
60	10-(4-Biphenylyl)phenothiazine	<0.10	28	60
61	10-(4-Biphenylyl)phenoxazine	<0.10	28	61
62	1-(2-Biphenylyl)-2-phenylcyclohexene	0.25	28	44
63	1-(4-Biphenylyl)-2-phenylcyclohexene	0.58	28	44
64	2-Biphenylyl phenyl ether	0.16	28	55

[57] J. Piccard, Helv. Chim. Acta, 7, 789 (1924).

[58] H. M. Kissman, D. W. Farnsworth, and B. Witkop, J. Am. Chem. Soc., 74, 3948 (1952).

[59] T. S. Soddy, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1957.

[60] R. O. Ranck, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1957.

[61] H. Gilman and L. O. Moore, J. Am. Chem. Soc., 79, 3485 (1957).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
65	4-Biphenylyl phenyl ether	0.16	28	55
66	2-(4-Biphenylyl)-5-phenyl-1,3,4-oxadiazole	1.28	27	33
67	2-(4-Biphenylyl)-5-phenyloxazole	1.18	27	33
68	5-(4-Biphenylyl)-2-phenyloxazole	1.16	27	33
69	2-(4-Biphenylyl)-6-phenylpyridine	0.47	28	44
70	3-(4-Biphenylyl)-6-phenyl-2-pyrone	<0.10	62	62
71	2-(4-Biphenylyl)pyridine	0.12	28	63
72	Bis-4-biphenylylamine	0.95	28	57
73	Bis-(4-biphenylyl)phenylamine	0.61	28	57
74	p-Bis(9-carbazolyl)benzene	0.27	28	56
75	4,4'-Bis(9-carbazolyl)biphenyl	0.93	28	56
76	2,6-Bis(p-diethylaminophenyl)-pyridine	0.15	28	64
77	2,3-Bis(3,4-dimethoxystyryl)-quinoxaline	0.29	28	65

[62] R. H. Wiley, C. H. Jarboe, and F. N. Hayes, J. Am. Chem. Soc., 79, 2602 (1957).

[63] J. Evans and C. Allen, Org. Syn., 18, 70 (1938).

[64] H. Gilman and D. Shirley, J. Am. Chem. Soc., 72, 2181 (1950).

[65] H. Gilman and H. S. Broadbent, J. Am. Chem. Soc., 70, 3316 (1948).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
78	Bis(p-dimethylaminophenyl)-diphenyllead	<0.10	28	66
79	Bis(p-dimethylaminophenyl)-p-terphenyl-4-ylcarbinol	0.12	28	44
80	4,4'-Bis(2-methyl-1-cyclohexen-1-yl)biphenyl	0.60	28	67
81	4,4'-Bis(3-methyl-1-cyclohexen-1-yl)biphenyl	1.01	28	67
82	p-Bis(10-phenothiazinyl)benzene	<0.10	28	60
83	p-Bis(10-phenoxazyl)benzene	<0.10	28	61
84	4,4'-Bis(10-phenoxazyl)biphenyl	<0.10	28	61
85	2,5-Bis(5-phenyl-2-oxazolyl)-pyridine	0.63	31	31
86	3,3'-Bis-[β-(2-quinolyl)vinyl]-azobenzene	<0.10	28	43
87	4,4'-Bis(trimethylsilyl)biphenyl	0.30	28	68
88	9,9-Bis(trimethylsilyl)fluorene	0.12	28	69
89	4,4''-Bis(trimethylsilyl)-p-terphenyl	0.99	28	47

[66] P. R. Austin, J. Am. Chem. Soc., 54, 3726 (1932).

[67] H. Gilman and E. A. Weipert, J. Am. Chem. Soc., 79, 2281 (1957).

[68] H. A. Cook, British Patent 671,553 (1952) [C. A., 47, 4909 (1953)].

[69] Sample through the courtesy of M. B. Hughes of this Laboratory.

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
90	2-Bromodibenzo-p-dioxin	<0.10	28	70
91	1-(4-Bromophenyl)-5-methyl-2-phenylpyrrole	<0.10	28	71
92	10-(o-Bromophenyl)phenoxazine	<0.10	28	61
93	10-(p-Bromophenyl)phenoxazine	<0.10	28	61
94	2-(2-Bromophenyl)-5-phenyloxazole	<0.10	27	33
95	2-(3-Bromophenyl)-5-phenyloxazole	0.45	27	33
96	2-(4-Bromophenyl)-5-phenyloxazole	0.28	27	33
97	4'-Bromo-m-terphenyl	<0.10	28	72
98	4-Bromo-p-terphenyl	0.22	28	73
99	2-(t-Butyl)dibenzo-p-dioxin	<0.10	28	49
100	4-Carboxy-p-terphenyl	<0.10	28	46
101	Carotene	<0.10	25	37
102	2-Chlorodibenzo-p-dioxin	<0.10	28	70
103	1-Chloronaphthalene	<0.10	25	37

[70] H. Gilman and J. J. Dietrich, J. Am. Chem. Soc., 79, 1439 (1957).

[71] J. F. Nobis, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1948.

[72] C. K. Bradsher and I. Swerlick, J. Am. Chem. Soc., 72, 4189 (1950).

[73] J. v. Braun, G. Irmisch, and J. Nelles, Ber., 66B, 1471 (1933).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
104	2-(2-Chlorophenyl)-5-phenyloxazole	0.79	27	74
105	2-(3-Chlorophenyl)-5-phenyloxazole	0.93	27	74
106	2-(4-Chlorophenyl)-5-phenyloxazole	0.96	27	33
107	3-Chloro-p-terphenyl	0.83	28	44
108	4-Chloro-p-terphenyl	0.93	28	44
109	Chrysene	0.11	27	37
110	Cinnamalazine	<0.10	25	37
111	2-Cyclohexyl-5-phenyloxazole	0.28	27	33
112	2,7-Diaminodibenzo-p-dioxin	<0.10	28	49
113	2,8-Diaminodibenzofuran	0.14	28	75
114	Dibenzalacetone	<0.10	25	37
115	Di(2-benzenesulfonylphenyl)-diphenyltin	<0.10	28	76
116	Dibenzo-p-dioxin	<0.10	28	70
117	1-(2-Dibenzo-p-dioxinyl)-1,2-diphenylethanol	<0.10	28	49
118	Dibenzofuran	0.10	28	37

[74]S. Minovici, C. D. Nenitzescu, and B. Angelescu, Bull. soc. chim. Romania, 10, 149 (1928) [C. A., 23, 2716 (1929)].

[75]J. Swislowsky, Iowa State Coll. J. Sci., 14, 92 (1939).

[76]L. A. Gist, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1956.

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
119	Dibenzylamine	<0.10	25	37
120	2,5-Di(4-biphenylyl)-1,3,4-oxadiazole	0.89	27	33
121	2,5-Di(4-biphenylyl)oxazole	0.81	27	33
122	1,4-Di[5-(4-biphenylyl)-2-oxazolyl]benzene	0.12	27	33
123	2,5-Di(4-bromophenyl)-1,3,4-oxadiazole	0.41	27	77
124	4,4''-Dibromo-p-terphenyl	<0.10	28	73
125	N,N-Di-n-butylaniline	0.12	25	37
126	o-Dichlorobenzene	<0.10	25	37
127	m-Dichlorobenzene	<0.10	25	37
128	4,7-Dichloro-2-(4-methoxyphenyl)quinoline	0.17	28	78
129	2,3-Di(o-chlorophenyl)-6-(2,5-dimethyl-1-pyrryl)quinoxaline	<0.10	28	40
130	2,5-Di(4-chlorophenyl)oxadiazole	0.94	27	33
131	2-(2,4-Dichlorophenyl)-5-phenyloxazole	0.69	27	33
132	2-(3,4-Dichlorophenyl)-5-phenyloxazole	0.88	27	33
133	7-Diethylamino-4-methylcoumarin	0.93	34	37

[77] R. Stolle, J. prak. chim., 69, 480 (1903).

[78] H. Gilman and R. A. Benkeser, J. Am. Chem. Soc., 69, 124 (1947).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
134	2-(β-Diethylamino-α-phenylethoxy)benzoxazole	<0.10	28	79
135	2-(β-Diethylamino-α-phenylethoxy)benzthiazole	<0.10	28	79
136	2-(p-Diethylaminophenyl)-6-methoxyquinoline	0.59	28	64
137	2-(m-Diethylaminophenyl)-8-methylquinoline	0.57	28	64
138	2-(p-Diethylaminophenyl)-5-phenyloxazole	0.85	31	31
139	2-(p-Diethylaminophenyl)pyridine	0.45	28	64
140	2-(m-Diethylaminophenyl)quinoline	<0.10	28	64
141	2-(p-Diethylaminophenyl)quinoline	0.50	28	64
142	4-Diethylamino-p-terphenyl	1.03	28	44
143	Diethyl-1-naphthylamine	0.23	25	37
144	Diethyl-o-toluidine	<0.10	25	37
145	2,5-Di(4-fluorophenyl)-1,3,4-oxadiazole	0.82	27	33
146	2,5-Di(2-furyl)-1,3,4-oxadiazole	0.94	27	33
147	Dihydrocollidine (sic)	<0.10	25	37
148	2,3-Di(4-hydroxyphenyl)quinoxaline	<0.10	28	40
149	6,6'-Dimethoxy-2,2'-bidibenzofuran	0.46	28	50

[79] B. Hofferth, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1950.

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
150	2,2'-Dimethoxybiphenyl	0.14	28	80
151	4,4'-Dimethoxybiphenyl	0.20	28	54
152	2,8-Dimethoxydibenzofuran	0.27	28	81
153	4,6-Dimethoxydibenzofuran	0.24	28	82
154	2,2'-Dimethoxy-3,3'-dimethylbiphenyl	<0.10	28	80
155	2,3-Dimethoxyphenanthrene	0.14	28	83
156	2,5-Di(4-methoxyphenyl)-1,3,4-oxadiazole	1.01	27	33
157	2,3-Di(4-methoxystyryl)quinoxaline	0.18	28	65
158	Dimethylamine hydrochloride	<0.10	25	37
159	3-Dimethylaminodibenzofuran	0.79	28	84
160	4-Dimethylamino-3-isopropylphenol	0.10	28	85

[80] H. Gilman, J. Swiss, and L. C. Cheney, J. Am. Chem. Soc., 62, 1963 (1940).

[81] H. Gilman, J. Swiss, H. B. Willis, and F. A. Yoeman, J. Am. Chem. Soc., 66, 798 (1944).

[82] H. Gilman and L. C. Cheney, J. Am. Chem. Soc., 61, 3149 (1939).

[83] H. Gilman and T. H. Cook, J. Am. Chem. Soc., 62, 2813 (1940).

[84] W. H. Kirkpatrick and P. T. Parker, J. Am. Chem. Soc., 57, 1123 (1935).

[85] J. R. Stevens and R. H. Beutel, J. Am. Chem. Soc., 63, 308 (1941).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
161	9-(p-Dimethylaminophenyl)acridine	0.26	28	64
162	2-(p-Dimethylaminophenyl)-benzthiazole	0.90	34	37
163	2-(p-Dimethylaminophenyl)-6-chloroquinoline	0.63	28	64
164	2-(p-Dimethylaminophenyl)-5-phenyloxazole	0.95	31	31
165	2-(p-Dimethylaminophenyl)pyridine	0.80	28	86
166	(p-Dimethylaminophenyl)-triphenyltin	<0.10	28	87
167	2-(p-Dimethylaminostyryl)quinoline	<0.10	28	43
168	4-(p-Dimethylaminostyryl)quinoline	<0.10	28	43
169	Dimethylaniline	0.16	25	37
170	p-Dimethylarsenobenzoic acid	<0.10	28	88
171	Dimethylbenzylamine	<0.10	25	37
172	Dimethyldi(p-terphenyl-4-yl)silane	0.81	28	89
173	Dimethylnaphthalene (sic)	<0.10	25	37

[86]H. Gilman and J. T. Edwards, Can. J. Chem., 31, 464 (1953).

[87]H. Gilman and C. E. Arntzen, J. Org. Chem., 15, 994 (1950).

[88]H. Gilman and S. Avakian, J. Am. Chem. Soc., 76, 4031 (1954).

[89]Sample through the courtesy of R. Tomasi of this Laboratory.

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
174	N,N-Dimethyl-1-naphthylamine	0.21	25	37
175	10,10-Dimethylphenothiasilin-5-dioxide	<0.10	28	90
176	10,10-Dimethylphenoxasilin	<0.10	28	91
177	6-(2,5-Dimethyl-1-pyrryl)-2,3-di(4-methoxyphenyl)quinoxaline	<0.10	28	40
178	2-[3-(2,5-Dimethyl-1-pyrryl)-styryl]pyridine	<0.10	28	43
179	2-[3-(2,5-Dimethyl-1-pyrryl)-styryl]quinoline	<0.10	28	43
180	2,2'''-Dimethyl-p-quaterphenyl	0.90	28	67
181	3,3'''-Dimethyl-p-quaterphenyl	1.13	28	67
182	4,4'''-Dimethyl-p-quaterphenyl	0.26	28	67
183	4,4''-Dimethyl-p-terphenyl	0.99	28	47
184	N,N-Dimethyl-o-toluidine	<0.10	25	37
185	Di-β-naphthol (sic)	<0.10	25	37
186	5,5'-Di(2-naphthyl)-2,2'-bioxazolyl	0.49	31	31
187	2,5-Di(1-naphthyl)-1,3,4-oxadiazole	1.04	27	33
188	2,5-Di(2-naphthyl)-1,3,4-oxadiazole	0.96	27	33
189	2,5-Di(1-naphthyl)oxazole	1.06	27	33

[90] K. Oita and H. Gilman, J. Org. Chem., 22, 336 (1957).

[91] K. Oita and H. Gilman, J. Am. Chem. Soc., 79, 339 (1957).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
190	2,5-Di(2-naphthyl)oxazole	1.06	27	33
191	Di-2-naphthyl-p-phenylenediamine	<0.10	25	37
192	Diphenylacetic acid	<0.10	25	37
193	Diphenylamine	<0.10	25	37
194	Diphenylbenzidine (sic)	<0.10	25	37
195	5,5'-Diphenyl-2,2'-bi(1,3,4-oxadiazolyl)	0.22	27	31
196	5,5'-Diphenyl-2,2'-bioxazolyl	0.75	27	33
197	1,4-Diphenylbutadiene	0.33	25	37
198	1,5-Diphenylcarbohydrazide	<0.10	25	37
199	5,5-Diphenyldibenzosilole	0.15	28	92
200	5,10-Diphenyl-5,10-dihydrophenazine	<0.10	28	49
201	Diphenyldi-p-terphenyl-4-ylsilane	0.86	28	47
202	9,9-Diphenylfluorene	0.14	28	93
203	6,6-Diphenylfulvene	<0.10	28	94

[92]R. D. Gorsich, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1957.

[93]R. G. Clarkson and M. Gomberg, J. Am. Chem. Soc., 52, 2881 (1930).

[94]V. Grignard and C. Courtot, Compt. rend., 158, 1766 (1914).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
204	2,5-Diphenylfuran	0.89	27	95
205	1,3-Diphenylguanidine	0.13	25	37
206	1,6-Diphenylhexatriene	0.52	25	37
207	Diphenylmethane	<0.10	25	37
208	1,8-Diphenyloctatetrene	<0.10	25	37
209	2,5-Diphenyl-1,3,4-oxadiazole	0.87	27	96
210	1,4-[2-(5-phenyl-1,3,4-oxadiazolyl)]benzene	<0.10	27	33
211	2,5-Diphenyloxazole	1.00	27	97
212	1,4-Di[2-(5-phenyloxazolyl)]benzene	0.81	27	33
213	10,10-Diphenylphenothiasilin-5-dioxide	<0.10	28	90
214	10,10-Diphenylphenoxasilin	<0.10	28	91
215	10,10-Diphenylphenoxastannin	<0.10	28	76
216	1,3-Diphenyl-1,3-propanedione	<0.10	25	37
217	2,5-Diphenylpyrazine	<0.10	27	98
218	3,6-Diphenylpyridazine	<0.10	27	99

[95] W. H. Perkin and A. Schlosser, J. Chem. Soc., 944 (1890).

[96] R. Stolle, Ber., 32, 798 (1899).

[97] E. Fischer, Ber., 29, 207 (1896).

[98] F. Kunckell and F. Vossen, Ber., 35, 2295 (1902).

[99] C. Paal and E. Dencks, Ber., 36, 491 (1903).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
219	2,6-Diphenylpyridine	<0.10	28	86
220	3,6-Diphenyl-2-pyrone	<0.10	62	62
221	2,5-Diphenylpyrrole	0.95	27	100
222	2,3-Diphenylquinoxaline	<0.10	28	40
223	1,5-Diphenyltetrazole	<0.10	27	37
224	2,5-Diphenyl-1,3,4-thiadiazole	<0.10	27	96
225	2,5-Diphenylthiazole	0.22	27	101
226	2,5-Diphenylthiophene	0.18	27	100
227	2,5-Di(β-styryl)-1,3,4-oxadiazole	0.47	27	33
228	2,5-Di(2-thienyl)-1,3,4-oxadiazole	0.77	27	33
229	2,5-Di(p-tolyl)-1,3,4-oxadiazole	0.98	27	102
230	n-Dodecyltri(p-terphenyl-4-yl)-silane	0.88	28	89
231	1,4-Endoxynaphthalene	<0.10	28	103
232	Ethoxytri-1-naphthylsilane	<0.10	28	104

[100] S. Kapf and C. Paal, Ber., 21, 3006 (1888).

[101] S. Gabriel, Ber., 43, 134 (1910).

[102] R. Stolle, J. prak. chim., 69, 377 (1903).

[103] H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 79, 2625 (1957).

[104] H. Gilman and C. G. Brannen, J. Am. Chem. Soc., 73, 4640 (1951).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
233	Ferrocene	<0.10	28	105
234	Fluoranthrene	0.27	27	37
235	Fluorene	0.12	25	37
236	Fluorenone	<0.10	25	37
237	2-(2-Fluorophenyl)-5-phenyloxazole	0.94	27	33
238	2-(3-Fluorophenyl)-5-phenyloxazole	0.94	27	33
239	2-(4-Fluorophenyl)-5-phenyloxazole	0.98	27	33
240	4-Fluoro-p-terphenyl	0.91	28	44
241	Furfuralazine	<0.10	25	37
242	2-(2-Furyl)-5-phenyl-1,3,4-oxadiazole	0.93	27	33
243	2-(2-Furyl)-5-phenyloxazole	0.95	27	33
244	Hexaethylbenzene	<0.10	25	37
245	2-Hydroxy-8-methoxydibenzofuran	0.21	28	81
246	4-(α-Hydroxy-α-methylbenzyl)-6-methoxy-2-phenylquinoline	0.13	28	106
247	4-(α-Hydroxy-α-methyl-p-dimethylaminobenzyl)-6-methoxy-2-phenylquinoline	<0.10	28	106
248	4-(1-Hydroxy-1-methoxypropyl)-6-methoxy-2-phenylquinoline	0.13	28	106

[105] T. J. Kealy and P. L. Pauson, Nature, 168, 1039 (1951).

[106] R. A. Benkeser, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1947.

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
249	2-Hydroxyphenyl benzenephosphinate	<0.10	28	107
250	2-(2-Hydroxyphenyl)benzoxazole	<0.10	27	37
251	2-(2-Hydroxyphenyl)-5-phenyloxazole	0.28	31	31
252	2-(3-Hydroxyphenyl)-5-phenyloxazole	0.66	31	31
253	2-(4-Hydroxyphenyl)-5-phenyloxazole	0.31	31	31
254	4-Hydroxy-p-terphenyl	0.30	28	44
255	1-Indenyltriphenyltin	<0.10	28	108
256	2-Iododibenzo-p-dioxin	<0.10	28	70
257	2-(2-Iodophenyl)-5-phenyloxazole	<0.10	27	33
258	2-(3-Iodophenyl)-5-phenyloxazole	<0.10	27	33
259	2-(4-Iodophenyl)-5-phenyloxazole	<0.10	27	33
260	4-Iodo-p-terphenyl	<0.10	28	44
261	2-Mesityl-5-phenyloxazole	1.03	31	31
262	2-Mesitylquinoline	<0.10	28	109
263	p-Methoxybenzoic acid	<0.10	28	37
264	2-(4-Methoxyphenyl)-5-(1-naphthyl)-1,3,4-oxadiazole	0.98	27	33

[107] R. D. Nelson, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1951.

[108] H. Gilman and L. A. Gist, J. Org. Chem., 22, 250 (1957).

[109] W. Oldham and I. Johns, J. Am. Chem. Soc., 61, 3291 (1939).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
265	2-(4-Methoxyphenyl)-5-(2-naphthyl)-1,3,4-oxadiazole	0.95	27	33
266	2-(4-Methoxyphenyl)-5-(2-naphthyl)oxazole	1.04	27	33
267	2-(2-Methoxyphenyl)-5-phenyloxazole	1.00	27	33
268	2-(3-Methoxyphenyl)-5-phenyloxazole	0.95	27	33
269	2-(4-Methoxyphenyl)-5-phenyloxazole	0.91	27	33
270	3-(4-Methoxyphenyl)-6-phenyl-2-pyrone	<0.10	62	62
271	Methyl p-aminobenzoate	<0.10	25	37
272	N-Methylanthranilic acid	0.44	25	37
273	Methyl benzoate	<0.10	25	37
274	4-Methylbenzo[f]quinoline	0.14	25	37
275	2-Methylbenzothiazole	<0.10	25	37
276	2-Methylbenzoxazole	<0.10	25	37
277	Methyl o-benzoylbenzoate	<0.10	25	37
278	5-Methyl-10-(4-biphenylyl)-5,10-dihydrophenazine	<0.10	28	49
279	4-(2-Methyl-1-cyclohexenyl)-p-terphenyl	0.98	28	67
280	4-(3-Methyl-1-cyclohexenyl)-p-terphenyl	0.82	28	67
281	4-(4-Methyl-1-cyclohexenyl)-p-terphenyl	1.02	28	67

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
282	1-Methyl-2,5-diphenylpyrrole	1.03	27	110
283	2-(3,4-Methylenedioxyphenyl)-5-phenyloxazole	0.99	27	74
284	Methyl 2-methoxy-3-dibenzofurancarboxylate	0.13	28	111
285	5-Methyl-10-phenyl-5,10-dihydrophenazine	<0.10	28	49
286	4-Methyl-2-phenylquinoline	<0.10	28	112
287	2-(1-Methyl-4-piperidyl)-5-phenyloxazole	0.10	31	31
288	2-Methyl-p-quaterphenyl	0.94	28	67
289	3-Methyl-p-quaterphenyl	0.97	28	67
290	4-Methyl-p-quaterphenyl	0.62	28	67
291	2-Methyl-p-terphenyl	0.68	28	46
292	3-Methyl-p-terphenyl	0.97	28	46
293	4-Methyl-p-terphenyl	0.96	28	46
294	9-Methyl-9-(trimethylsilyl)fluorene	<0.10	28	69
295	Methyltri(p-terphenyl-4-yl)silane	0.85	28	89

[110] R. Lukes and V. Prelog, Chem. Listy, 22, 244 (1928) [C. A., 23, 1408 (1929)].

[111] S. Avakian, Unpublished Ph.D. Thesis, Iowa State College, Ames, Iowa, 1944.

[112] D. Tarbell, J. Burnett, R. Carbin, and V. Wystrach, J. Am. Chem. Soc., 67, 1584 (1945).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
296	Morpholine	<0.10	25	37
297	Naphthacene	<0.10	25	37
298	Naphthalene	<0.10	25	37
299	1-Naphthol	0.13	25	37
300	2-Naphthol	0.21	25	37
301	Naphtholbenzein	<0.10	25	37
302	1-Naphthonitrile	0.12	25	37
303	α-Naphthoquinoline (sic)	<0.10	25	37
304	β-Naphthoquinoline (sic)	<0.10	25	37
305	1-Naphthylamine	0.51	25	37
306	2-Naphthylamine	0.40	25	37
307	2-Naphthyl benzoate	<0.10	25	37
308	2-(1-Naphthyl)benzoxazole	0.78	27	113
309	N-(1-Naphthyl)ethylenediamine dihydrochloride	<0.10	25	37
310	1-Naphthyl ethyl ether	0.21	25	37
311	2-Naphthyl ethyl ether	0.21	25	37
312	2-(2-Naphthyl)indole	0.74	27	114
313	1-Naphthyl methyl ether	<0.10	25	37

[113] S. Skraup, Ann. Chem. Indus. Liebig, 419, 1 (1919).

[114] R. Brunck, Ann. Chem. Indus. Liebig, 272, 204 (1893).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
314	2-Naphthyl methyl ether	0.21	25	37
315	5-Methyl-2-(1-naphthyl)oxazole	0.59	27	31
316	2-(1-Naphthyl)-5-(2-naphthyl)oxazole	0.99	27	33
317	2-(1-Naphthyl)-5-phenyl-1,3,4-oxadiazole	0.82	27	33
318	2-(2-Naphthyl)-5-phenyl-1,3,4-oxadiazole	0.58	27	33
319	2-(1-Naphthyl)-5-phenyloxazole	0.92	27	115
320	2-(2-Naphthyl)-5-phenyloxazole	1.14	27	33
321	5-(1-Naphthyl)-2-phenyloxazole	1.00	27	33
322	5-(2-Naphthyl)-2-phenyloxazole	1.01	27	33
323	3-(2-Naphthyl)-6-phenyl-2-pyrone	<0.10	62	62
324	1-Naphthyltriphenylsilane	<0.10	28	104
325	2-Naphthyltriphenylsilane	0.14	28	116
326	2-(3-Nitrophenyl)-5-phenyloxazole	<0.10	27	115
327	2-(4-Nitrophenyl)-5-phenyloxazole	<0.10	27	115
328	4-Nitro-p-terphenyl	<0.10	28	44
329	10-(1-Oxo-2-pyridyl)phenothiazine-5-dioxide	<0.10	28	60

[115] J. Lister and R. Robinson, J. Chem. Soc., 1297 (1912).

[116] H. Gilman, C. G. Brannen, and R. K. Ingham, J. Am. Chem. Soc., 77, 3917 (1955).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
330	Perylene	0.24	28	117
331	Phenanthrene	0.15	25	37
332	Phenazine	<0.10	28	118
333	Phenetole	<0.10	25	37
334	Phenol	<0.10	25	37
335	Phenoxazine	<0.10	28	61
336	dl-β-Phenylalanine	<0.10	25	37
337	2-Phenylbenzo[g]quinoline	0.27	28	119
338	2-Phenylbenzothiazole	<0.10	27	37
339	2-Phenylbenzoxazole	0.84	27	120
340	9-Phenylcarbazole	0.24	28	56
341	2-Phenyldibenzo-p-dioxin	0.40	28	49
342	N-(o-Phenyldiphenylmethyl)aniline	0.13	28	121

[117] J. Weitzenbock and R. Seer, Ber., 46, 1996 (1913).

[118] H. Waterman and D. Vivian, J. Org. Chem., 14, 289 (1949).

[119] H. Gilman and R. D. Nelson, J. Am. Chem. Soc., 70, 3316 (1948).

[120] D. W. Hein, R. J. Alheim, and J. J. Leavitt, J. Am. Chem. Soc., 79, 427 (1957).

[121] H. Gilman, J. E. Kirby, and C. R. Kinney, J. Am. Chem. Soc., 51, 2252 (1929).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
343	2,2'-p-Phenylenebis[5-(2-naphthyl)-oxazole]	0.22	31	31
344	2,2'-m-Phenylenebis(5-phenyloxazole)	0.89	31	31
345	p-Phenylenebis[triphenylsilane]	<0.10	28	122
346	p-Phenylenebis[triphenyltin]	<0.10	28	122
347	m-Phenylenediamine	<0.10	25	37
348	p-Phenylenediamine	<0.10	25	37
349	β-Phenylethylcinnamate	<0.10	25	37
350	9-Phenylfluorene	0.18	28	123
351	1-Phenylisoquinoline	<0.10	28	124
352	N-Phenyl-1-naphthylamine	0.65	25	37
353	N-Phenyl-2-naphthylamine	0.21	25	37
354	6-Phenylphenanthridine	<0.10	28	119
355	2-Phenylphenanthroxazole	0.67	27	125
356	10-Phenylphenothiazine	<0.10	28	126

[122] H. Zimmer and H. G. Mosle, Ber., 87, 1255 (1954).

[123] F. Ullman and R. v. Wurstenberger, Ber., 37, 74 (1904).

[124] K. Ziegler and H. Zeiser, Ann., 485, 174 (1931).

[125] A. Schönberg, J. Chem. Soc., 373 (1950).

[126] H. Gilman, P. R. Van Ess, and D. A. Shirley, J. Am. Chem. Soc., 66, 1214 (1944).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
357	10-Phenylphenothiazine-5-dioxide	<0.10	28	127
358	10-Phenylphenothiazine-5-oxide	<0.10	28	38
359	10-Phenylphenoxazine	<0.10	28	61
360	5-Phenyl-2-(2-phenyl-4-quinolyl)oxazole	0.37	31	31
361	2-Phenylpyridine	<0.10	28	63
362	2-Phenylquinoline	<0.10	28	124
363	5-Phenyl-2-(2-quinolyl)oxazole	0.74	31	31
364	5-Phenyl-2-(6-quinolyl)oxazole	0.84	31	31
365	2-(α-Phenylstyryl)dibenzo-p-dioxin	<0.10	28	49
366	5-Phenyl-2-styryloxazole	0.64	27	115
367	Phenyl-p-terphenyl-4-ylmethyl ethyl ether	<0.10	28	47
368	5-Phenyl-2-(p-terphenyl-4-yl)oxazole	0.90	28	44
369	2-Phenyl-5-(2-thienyl)-1,3,4-oxadiazole	0.55	27	33
370	1-Phenyl-1-(p-tolyl)-1,2-dihydroisoquinoline	<0.10	28	59
371	5-Phenyl-2-(o-tolyl)oxazole	1.00	27	115
372	5-Phenyl-2-(m-tolyl)oxazole	0.90	27	115

[127] C. Finzi, Gazz. chim. ital., 62, 175 (1932) [C. A., 26, 4338 (1932)].

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
373	5-Phenyl-2-(p-tolyl)oxazole	1.00	27	115
374	Phenyltri-p-terphenyl-4-ylsilane	0.91	28	89
375	2-Phenyl-5-(2,5-xylyl)oxazole	0.99	31	31
376	5-Phenyl-2-(2,5-xylyl)oxazole	0.97	31	31
377	Piperazine	<0.10	25	37
378	Polystyrene	<0.10	25	37
379	2-(i-Propyl)dibenzo-p-dioxin	<0.10	28	49
380	Pyrene	0.23 0.21	25 27	37 37
381	9-(2-Pyridyl)carbazole	0.20	28	56
382	10-(2-Pyridyl)phenothiazine	<0.10	28	60
383	10-(2-Pyridyl)phenothiazine-5-dioxide	<0.10	28	60
384	10-(2-Pyridyl)phenothiazine-5-oxide	<0.10	28	60
385	2-(2-Pyridyl)-5-phenyloxazole	0.93	27	33
386	2-(3-Pyridyl)-5-phenyloxazole	0.92	27	33
387	2-(4-Pyridyl)-5-phenyloxazole	0.78	27	33
388	1,1'-2',1''-2'',1'''-Quaterphenyl	<0.10	28	128
389	1,1'-3',1''-3'',1'''-Quaterphenyl	<0.10	28	128
390	p-Quaterphenyl	<0.10	28	128

[128]G. T. Bowden, J. Chem. Soc., 1111 (1931).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
391	9-(2-Quinolyl)carbazole	0.14	28	56
392	Spiro[anthracene-9(10H),9'-fluorene]	0.17	28	93
393	Spiro[anthracene-9(10H),9'-xanthene]	<0.10	28	93
394	5,5'-Spirobi[dibenzogermole]	<0.10	28	92
395	5,5'-Spirobi[dibenzosilole]	0.17	28	92
396	9,9'-Spirobifluorene	0.14	28	93
397	10,10'-Spirobiphenoxasilin	<0.10	28	91
398	10,10'-Spirobiphenoxastannin	<0.10	28	76
399	9,9'-Spirobixanthene	<0.10	28	93
400	Spiro[fluorene-9,9'-xanthene]	<0.10	28	93
401	Stilbene	0.10 <0.10	25 26	37 37
402	Styrene	0.19 <0.10	25 26	37 37
403	o-Terphenyl	<0.10	25	37
404	m-Terphenyl	0.43 0.17	25 35	37 37
405	p-Terphenyl	1.00 1.00	25 27	37 37
406	p-Terphenyl-4-yldiphenylcarbinol	0.84	28	46
407	2-(p-Terphenyl-4-yl)quinoline	0.12	28	59
408	1,2,4,5-Tetrachlorobenzene	<0.10	27	37

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
409	2,3,7,8-Tetrachlorodibenzo-p-dioxin	<0.10	28	70
410	1,2,3,4-Tetrahydro-6-methoxy-4-oxobenzo[b]naphtho[1,2-d]furan	<0.10	28	111
411	1,2,3,4-Tetrahydro-7-methoxy-1-oxocycloocta[klm]dibenzofuran	<0.10	28	111
412	Tetrahydronaphthalene	<0.10	25	37
413	Tetrakis(3-biphenylyl)silane	<0.10	28	129
414	Tetrakis(4-biphenylyl)silane	0.29	28	130
415	Tetrakis(p-dimethylaminophenyl)lead	<0.10	28	66
416	Tetrakis(p-dimethylaminophenyl)-silane	<0.10	28	131
417	Tetrakis(p-methoxyphenyl)lead	<0.10	28	132
418	N,N,N',N'-Tetramethylbenzidine	0.28	28	37
419	1,1,4,4-Tetraphenyl-1,3-butadiene	<0.10	27	37
420	1,2,3,4-Tetraphenylcyclopentadiene	<0.10	25	37

[129] H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 21, 1307 (1956).

[130] W. C. Schumb, J. Ackerman, and C. M. Saffer, J. Am. Chem. Soc., 60, 2486 (1938).

[131] H. Gilman and M. A. Plunkett, J. Am. Chem. Soc., 73, 1686 (1951).

[132] H. Gilman and J. C. Bailie, J. Am. Chem. Soc., 61, 731 (1939).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
421	Tetraphenylfuran	0.47	28	133
422	Tetraphenylgermane	<0.10	28	134
423	Tetraphenyllead	<0.10	28	135
424	Tetraphenylmethane	<0.10	28	136
425	Tetraphenylpyrazine	<0.10	27	37
426	Tetraphenylsilane	<0.10	28	137
427	Tetraphenyltin	<0.10	28	37
428	Tetra-p-terphenyl-4-ylsilane	0.22	28	47
429	Thianthrene-5-dioxide	<0.10	28	138
430	Thianthrene-5,10-dioxide (α)	<0.10	28	139
431	Thianthrene-5-oxide	<0.10	28	140

[133] R. Putter and W. Dilthey, J. prakt. Chem., 149, 183 (1937).

[134] D. L. Tabern, W. R. Orndorff, and L. M. Dennis, J. Am. Chem. Soc., 47, 2039 (1925).

[135] H. Gilman and J. Robinson, J. Am. Chem. Soc., 49, 2315 (1927).

[136] M. Gomberg and L. H. Cone, Ber., 39, 1463 (1906).

[137] A. Polis, Ber., 19, 1013 (1886).

[138] K. Fries and W. Vogt, Ann., 381, 312 (1911).

[139] E. Bergman and M. Tschudnowsky, Ber., 65, 457 (1952).

[140] H. Gilman and D. R. Swayampati, J. Am. Chem. Soc., 77, 3388 (1955).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
432	Thianthrene-5,10-tetraoxide	<0.10	28	141
433	Thianthrene-5,5,10-trioxide	<0.10	28	142
434	2-(2-Thienyl)-5-phenyloxazole	0.39	27	33
435	10-(o-Tolyl)phenothiazine	<0.10	28	143
436	m-Toluidine	<0.10	25	37
437	2-(p-Tolyl)-4,7-dichloroquinoline	<0.10	28	78
438	Tris-4-dibenzofurylcarbinol	0.13	28	75
439	2-(3-Trifluoromethylstyryl)-quinoline	<0.10	28	43
440	p-Trimethylsilylbenzeneboronic acid anhydride	<0.10	28	47
441	9-(Trimethylsilyl)fluorene	0.11	28	69
442	2-(p-Trimethylsilylphenyl)quinoline	<0.10	28	59
443	Trimethyl(m-terphenyl-4-yl)silane	<0.10	28	89
444	Trimethyl(p-terphenyl-4-yl)silane	1.01	28	47
445	Triphenylamine	<0.10	25	37

[141] J. B. Cohen and F. W. Skirrow, J. Chem. Soc., 75, 887 (1899).

[142] K. Fries, H. Koch, and H. Stuckenbrock, Ann., 468, 162 (1929).

[143] H. Gilman, R. D. Nelson, and J. F. Champaign, Jr., J. Am. Chem. Soc., 74, 4205 (1952).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
446	2,4,5-Triphenyl-3-(p-dimethylaminophenyl)cyclopentadiene	<0.10	25	144
447	Triphenylene	<0.10	28	145
448	Triphenylhydrazine	<0.10	28	146
449	2,4,5-Triphenylimidazole	0.24	27	147
450	Triphenylmethane	<0.10	25	37
451	Triphenylphosphine	<0.10	28	37
452	Triphenylphosphine oxide	<0.10	28	37
453	p-Triphenylsilylbenzeneboronic acid	<0.10	28	47
454	Triphenyl-p-terphenyl-4-ylgermane	0.73	28	69
455	Triphenyl-p-terphenyl-4-yllead	<0.10	28	69
456	Triphenyl-p-terphenyl-4-ylsilane	0.89	28	47
457	Triphenyl-p-terphenyl-4-yltin	0.38	28	69
458	Tris(4-biphenylyl)amine	0.58	28	57
459	Tris(2-biphenylyl)arsine	<0.10	28	148

[144] Not reported.

[145] C. F. H. Allen and F. P. Pingert, J. Am. Chem. Soc., 64, 1365 (1942).

[146] H. Gilman and J. C. Bailie, J. Org. Chem., 2, 84 (1937).

[147] R. Radziszewski, Ber., 15, 1493 (1882).

[148] D. E. Worrall, J. Am. Chem. Soc., 62, 2514 (1940).

Table 2. (Continued)

No.	Compound	RPH[a]	Ref.[b]	Syn.[c]
460	Tris(4-biphenylyl)arsine	<0.10	28	149
461	Tris(2-biphenylyl)phosphine	<0.10	28	148
462	Tris(4-biphenylyl)phosphine	<0.10	28	150
463	Tris(2-biphenylyl)stibine	<0.10	28	148
464	Tris(4-biphenylyl)stibine	<0.10	28	151
465	Tris(p-dimethylaminophenyl)(p-methoxyphenyl)silane	<0.10	28	131
466	Valerophenone semicarbazone	<0.10	28	47
467	Xanthone	<0.10	25	37

[149]D. E. Worrall, J. Am. Chem. Soc., 52, 664 (1930).

[150]D. E. Worrall, J. Am. Chem. Soc., 52, 2933 (1930).

[151]D. E. Worrall, J. Am. Chem. Soc., 52, 2046 (1930).

Synthesis of Chain-Type Polyaryls

In view of the clear superiority of chain-type polyaryls as scintillation solutes, it is necessary to review the properties and methods of synthesis of these compounds. It is important to remember in this discussion that many good solutes, although not completely condensed systems, may contain condensed rings as individual members of the chain.

As stated in the consideration of the properties of solutes, solubility is an important factor. While concentration of the order of 5 g./l. in toluene does not seem to be a difficult criterion to satisfy, many systems containing more than three rings are extremely insoluble. The most symmetric compounds, as might be expected, are the least soluble; certain functional groups also contribute to decreased solubility. Fortunately these same functional groups are generally harmful to scintillation efficiency. Carboxylic acids, nitro derivatives, phenols, and derivatives containing elements beyond the first period generally have poor solubility and are poor scintillators as well. Some interesting exceptions will be treated in the Discussion section of this work under the heading "Functional Groups."

The high melting points of these systems give rise to some experimental difficulties, but most are white when pure, sublime readily under reduced pressure, and are reasonably stable toward heat.

Many of the compounds of three or more rings acquire a strong electrostatic charge when dry which makes handling difficult. Crystal formation is poor; the compounds occasionally take the form of shiny platelets, but more frequently come out of solution as finely divided powders.

Some have been screened for carcinogenic activity.[152] While p-quaterphenyl and both symmetrical binaphthyls showed no activity, 1,3,5-triphenylbenzene produced carcinogens in 12 of 60 mice exposed. In view of the notorious activity of 4-aminobiphenyl in this respect, it is surely wise to handle other amino polyphenyls carefully.

The most widely-known synthetic methods used in the preparation of polyaryls are certainly the Ullman and the Gomberg reactions. The former is handicapped in that it is only convenient for symmetrical derivatives, but it does provide good yields and it is easily carried out on any scale.[153] The latter is not electronically influenced and results in a mixture of isomers unless the ring used to build the chain is symmetrical.[154]

A third convenient route is the reaction of an organometallic reagent with cyclohexanone or a substituted cyclohexanone.[67,73,155] The resulting carbinol can be dehydrated,

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[152]Private communication to Dr. H. Gilman from Prof. L. Fieser.

[153]For a detailed discussion see P. E. Fanta, Chem. Revs., 38, 139 (1946).

[154]The Gomberg reaction is thoroughly reviewed by W. E. Bachmann and R. A. Hoffman in R. Adams, ed., "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

[155]G. F. Woods and F. T. Reed, J. Am. Chem. Soc., 71 1348 (1949).

then dehydrogenated to the aromatic system. This procedure was found to be the best practical approach to 4-bromo-p-terphenyl,[73] employing p-dibromobenzene, magnesium, and 4-cyclohexylcyclohexanone in equimolar portions. The organolithium derivative from 4-bromo-p-terphenyl is reported as a versatile reagent in the synthesis of derivatives of p-terphenyl.[46]

Polyaryls containing an heterocyclic ring have been synthesized from a number of different routes, most of which involve formation of the heterocyclic ring as the ultimate step. Interesting examples would include the aryl oxazoles of Hayes and coworkers,[33] the aryl pyrones of Wiley and coworkers,[62] and the recently reported benzoxazoles, -thiazoles, and -imidazoles by the method of Hein and coworkers.[120] A notable exception is the addition of organolithium reagents to the azomethine linkage of many aza-aromatic heterocycles as suggested by the work of Ziegler and Zeiser.[124] This method, although simple and direct, restricts one to α-substituted derivatives.

EXPERIMENTAL

Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents. Tetrahydrofuran was further dried by distillation from lithium aluminum hydride. All melting points are uncorrected. The infrared spectra were obtained through the courtesy of the Ames Laboratory of the Atomic Energy Commission, and special thanks for the determination of the spectra are due Messrs. V. A. Fassel, R. A. McCord, and E. M. Layton.

Derivatives of p-Terphenyl from the Gomberg Reaction

4-Nitro-p-terphenyl[156]

A warm solution of 4.0 g. (0.019 mole) of 4-acetamidobiphenyl in a mixture of 60 ml. of glacial acetic acid and 15 ml. of acetic anhydride was chilled with rapid stirring to 10° in order to precipitate a fine, white suspension. Nitrous fumes, generated by slowly dropping concentrated nitric acid on sodium nitrite, were passed through the suspension for two hours. The resulting green solution was poured into 500 ml.

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[156] H. France, I. M. Heilbron, and D. H. Hey, J. Chem. Soc., 1364 (1938).

of water and stirred vigorously. The yellow nitroso derivative was filtered and dried on an aspirator. This product was allowed to stand with 120 ml. of nitrobenzene over 10 g. of sodium sulfate for 24 hr. At the end of this period the dark red solution was steam distilled to remove the bulk of the solvent. The residue was extracted with chloroform; the extract was dried and freed of solvent. The gummy, orange residue was chromatographed on alumina and eluted with benzene. Evaporation of the solvent left a gummy residue which solidified, when washed free of traces of nitrobenzene with petroleum ether (b.p. 60-70°), and melted at 164-183°. Two recrystallizations from 1:1 benzene-petroleum ether afforded 1.2 g. (23%) of white powder, m.p. 212.5-213.5°. Reported[156] m.p. 211-212°.

4-Fluoro-p-terphenyl

The nitroso derivative from 7.0 g. (0.033 mole) of 4-acetamidobiphenyl, obtained in the manner described above was allowed to stand 48 hr. with 70 ml. of fluorobenzene. The solvent was distilled, and last traces stripped with the aid of an aspirator. The remaining dark solid was distilled at 140-160° (0.01 mm.), and 2.92 g. (36%) of yellow, waxy solid was collected. Recrystallization from ethanol afforded 2.45 g. (30%) of yellow plates, melting at 159-164°. Further

crystallization from ethanol did not improve this melting range, nor did sublimation at reduced pressure. Seven recrystallizations from glacial acetic acid eventually produced a pure product, m.p. 176.5-178°. The remaining mixture of isomers in the mother liquors could not be resolved.

Anal. Calcd. for $C_{18}H_{13}F$: C, 86.09; H, 5.24. Found: C, 85.77, 86.05; H, 5.30, 5.04.

4-Chloro-p-terphenyl

The procedure described above was repeated using 10.0 g. (0.048 mole) of 4-acetamidobiphenyl and 200 ml. of chlorobenzene. Subsequent to steam distillation, the residue was extracted with chloroform, the solution dried, and the solvent stripped with an aspirator. Distillation of the dark material remaining at 0.003 mm. gave 3.2 g. (25%) of crude product boiling at 145-153°. Recrystallization twice from glacial acetic acid afforded 1.38 g. of a fraction melting at 189-206°. Two recrystallizations of this product afforded 0.97 g. (8%) of pure material, m.p. 225-226°. Reported[156] m.p. 220-221°.

Fractional crystallization of the material remaining in the mother liquors ultimately produced 0.15 g. of 3-chloro-p-terphenyl, m.p. 137.5-138.5°. Reported[156] m.p. for this product is 136-137°.

4-Methoxy-p-terphenyl (attempted)

The procedure above was repeated substituting anisole for chlorobenzene. The only material isolated was 3.24 g. (32%) of 4-acetamidobiphenyl, m.p. and mixed m.p. with pure starting material 175.5-176°. A second attempt employing a five-hour nitrosation period also failed.

4-Dimethylamino-p-terphenyl (attempted)

The same reaction with dimethylaniline as solvent resulted in a thick, red-orange oil which could not be resolved into any identifiable material by sublimation, crystallization, or chromatography.

Derivatives of p-Terphenyl from p-Terphenyl-4-yllithium

4-Carboxy-p-terphenyl

The previously described preparation and carbonation of p-terphenyl-4-yllithium,[46] when run on a 0.10 mole scale produced yields up to 78%.

p-(4-Biphenylyl)benzoyl chloride

To 30 ml. of warm thionyl chloride was added 10.96 g. (0.04 mole) of 4-carboxy-p-terphenyl in small portions. The mixture was gently refluxed for 12 hr. Excess thionyl chloride was stripped at reduced pressure, and the residue crystallized from benzene to give 8.62 g. (74%) of yellow-white powder, m.p. 192-194°. Further crystallization failed to effect this constant and gave rise to traces of the acid unless carried out in a strictly anhydrous atmosphere.

p-Terphenyl-4-carboxamide

To a solution of 1.46 g. (0.005 mole) of p-(4-biphenylyl)benzoyl chloride in 150 ml. of benzene was passed gaseous ammonia until precipitation was complete. The insoluble material was boiled with methyl cellosolve and filtered. The filtrate deposited shiny, near-white plates on cooling, m.p. 318-320°. Two recrystallizations left 1.16 g. (85%), m.p. 320-321°.

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.50; H, 5.53. Found: C, 83.32, 83.21; H, 5.64, 5.47.

Ethyl p-terphenyl-4-carboxylate

To a solution of 1.46 g. (0.005 mole) of p-(4-biphenylyl)benzoyl chloride in 150 ml. of benzene was added 50 ml. of absolute ethanol. The solvents were evaporated, and the residue recrystallized from ethanol as shiny, colorless plates, m.p. 184-185.5°. One recrystallization from ethanol left 1.38 g. (89%) of pure product, m.p. 184.5-185.5°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 82.74, 82.72; H, 6.36, 6.12.

α-[p-(4-Biphenylyl)benzamido]acetophenone

A mixture of 7.50 g. (0.027 mole) of 4-carboxy-p-terphenyl and 50 ml. of thionyl chloride was refluxed until solution was complete (2 hr.). The thionyl chloride was thoroughly stripped with an aspirator. The residual acid chloride was stirred with 60 ml. of pyridine while 5.16 g. (0.03 mole) of powdered phenacylammonium chloride was added. The mixture was refluxed 30 min., cooled to 15°, and filtered. The product was washed thoroughly with cold benzene and with cold ethanol. The remaining gray powder was extracted with 300 ml. of boiling methyl cellosolve, which deposited 3.87 g. (36%) of tan powder, melting at 252-257°, on cooling. Sublimation at 240° (0.10

mm.) gave a pale yellow powder, m.p. 262-265°. Two recrystallizations from methyl cellosolve raised this to 277-278°.

Anal. Calcd. for $C_{27}H_{21}NO_2$: C, 82.86; H, 5.37. Found: C, 82.73, 82.64; H, 5.39, 5.17.

5-Phenyl-2-(p-terphenyl-4-yl)oxazole

A mixture of 4.0 g. of α-[p-(4-biphenylyl)benzamido]-acetophenone (0.01 mole) and 30 ml. of phosphorous oxychloride gave a dark solution after refluxing 24 hr. The mixture was cooled and poured slowly into 300 ml. of water containing crushed ice. There was obtained 3.95 g. (100%) of crude, tan product, melting at 212-216°. Two recrystallizations of this material from methyl cellosolve afforded 3.10 g. (82%) of nearly white needles, m.p. 220-220.5°.

Anal. Calcd. for $C_{27}H_{19}NO$: C, 86.86; H, 5.09. Found: C, 86.90, 87.00; H, 5.07, 5.15.

2-(p-Terphenyl-4-yl)benzoxazole (attempted)

A smooth paste of 1.09 g. (0.01 mole) of o-aminophenol, 2.93 g. (0.01 mole) of p-(4-biphenylyl)benzoyl chloride, and 40 ml. of polyphosphoric acid was heated gradually to 250°. Hydrogen chloride was evolved at about 150°. The mixture was held at 250° for 3 hr., cooled to 100°, and poured into 600

ml. of rapidly stirred ice water. The dark solid obtained was filtered, washed with water, slurried with 10% sodium carbonate, and filtered again. The only product obtained from attempted crystallization or sublimation was a dark brown solid which decomposed above 200°.

Diphenyl-p-terphenyl-4-ylmethyl ethyl ether

This product was isolated in the course of an attempt to reduce diphenyl-p-terphenyl-4-ylcarbinol to the hydrocarbon by the method of Gilman, Kirby, and Kinney.[157] A mixture of 1.5 g. (0.0036 mole) of the carbinol, 100 ml. of ethanol, and 25 ml. of concentrated hydrochloric acid was stirred at gentle reflux 24 hr. After cooling, the deposited white solid was filtered and fractionally crystallized from benzene-ethanol. The least soluble material, melting at 207-211°, was impure starting material (mixed m.p. 211-213°). From the mother liquors was isolated 1.23 g. (78%) of impure ethyl ether, melting at 137-145°. Three recrystallizations from ethanol afforded 0.65 g. (41%) of pure material, m.p. 150-151°.

Anal. Calcd. for $C_{33}H_{28}O$: C, 89.72; H, 6.54. Found: C, 90.21, 90.12; H, 6.39, 6.40.

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[157] H. Gilman, J. E. Kirby, and C. R. Kinney, J. Am. Chem. Soc., 51, 2252 (1929).

Bis(p-dimethylaminophenyl)-p-terphenyl-4-ylcarbinol

To a stirred solution of p-terphenyl-4-yllithium[46] (0.010 mole) in 50 ml. of ether was added a solution of 2.95 g. (0.011 mole) of Michler's ketone in 50 ml. of benzene. The mixture was stirred at gentle reflux for 30 min., hydrolyzed with 50 ml. of water, and diluted with 50 ml. of benzene to effect complete solution. Concentration of the organic layer, followed by dilution with ethanol, produced 1.70 g. (34%) of pale green powder, melting at 146-151°. From the mother liquor there was obtained 1.48 g. (30%) of tiny, pale green needles, m.p. 170-172°. Recrystallization of this product from ethanol gave 1.04 g. (22%) of nearly white needles, m.p. 171-172°.

Anal. Calcd. for $C_{35}H_{34}N_2O$: C, 84.31; H, 6.87. Found: C, 84.19; H, 7.28.

9-(p-Terphenyl-4-yl)-9-fluorenol

A solution of 4.14 g. (0.023 mole) of fluorenone in 50 ml. of benzene was added, over a period of 10 min., to a stirred solution of 0.010 mole of p-terphenyl-4-yllithium in ether. After refluxing 30 min. Color Test I[158] was negative,

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[158] H. Gilman and J. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

and the mixture was hydrolyzed with 40 ml. of 5% hydrochloric acid. The organic layer was washed with water and concentrated to a volume of 30 ml. Cooling this solution to 0° afforded 5.12 g. (62%) of pale yellow powder, melting at 213-221°. Repeated recrystallization from benzene left 4.18 g. (51%) of pure product, m.p. 225-226°.

Anal. Calcd. for $C_{31}H_{22}O$: C, 90.75; H, 5.37. Found: C, 90.47; H, 5.74.

Phenylbis(p-terphenyl-4-yl)carbinol

To a stirred solution of 0.010 mole of p-terphenyl-4-yllithium in ether was added a solution of 0.75 g. (0.005 mole) of ethyl benzoate in 20 ml. of ether. A heavy, white precipitate formed immediately, and Color Test I was negative after stirring 15 min. at gentle reflux. Hydrolysis was effected with 50 ml. of 5% hydrochloric acid, the aqueous layer was separated, and the organic layer diluted with 100 ml. of benzene, washed with water, and dried by azeotroping residual water. The hot solution was filtered from a trace of insoluble material and allowed to cool slowly. The product was a white powder melting at 239-247°; crude yield: 2.41 g. (85%). After three recrystallizations from benzene there was isolated 0.90 g. (35%) of glassy prisms, m.p. 254-255.5°.

Anal. Calcd. for $C_{43}H_{32}O$: C, 91.49; H, 5.67. Found: C, 91.38; H, 5.72.

2-(p-Terphenyl-4-yl)ethanol (attempted)

A stream of ethylene oxide was passed slowly over a stirred solution of 0.015 mole of p-terphenyl-4-yllithium in 150 ml. of ether at 0-5°. After 45 min. Color Test I was negative, and the mixture was hydrolyzed with 50 ml. of water. The resulting thick, white suspension was filtered, and the white solid product recrystallized repeatedly from acetone and from benzene. Only a small amount, less than 0.03 g., of pure product, m.p. 225-226°, was isolated. The infrared spectra had absorption peaks at 2.8μ (weak) and 3.5μ, indicative of O-H and aliphatic C-H, respectively.

4-Styryl-p-terphenyl (attempted)

A solution of 3.0 g. (0.025 mole) of styrene oxide in 50 ml. of ether was added dropwise to a stirred solution of 0.015 mole of p-terphenyl-4-yllithium in 100 ml. of ether. After refluxing 2 hr. Color Test I was negative, and the mixture was hydrolyzed with 50 ml. of 5% hydrochloric acid. The resulting thick emulsion was filtered, and the organic layer in the filtrate evaporated to dryness. The solid remaining from

this solution was combined with the insoluble material and extracted with 100 ml. of hot benzene. The benzene solution was refluxed 1 hr. with 40 ml. of Lucas reagent. The layers were separated, and the organic layer washed with water, sodium bicarbonate, and water again. Evaporation of this solution left a pale yellow solid from which there was obtained 2.70 g. (54%) of yellow powder, melting at 170-185°. Repeated attempts at recrystallization from ethanol, from benzene, and from petroleum ether (b.p. 77-115°) failed to improve this melting range.

4-Iodo-p-terphenyl

A solution of 0.010 mole of p-terphenyl-4-yllithium in 50 ml. of ether was added dropwise to a stirred suspension of 3.81 g. (0.030 g. atom) of iodine in 50 ml. of ether at 0°. After stirring 30 min., Color Test I was negative, and the mixture was hydrolyzed with 50 ml. of water. The aqueous layer was discarded, and the organic layer washed free of excess iodine with sodium bisulfite. The ether insoluble product was filtered and dried. Two recrystallizations from benzene afforded 1.72 g. (48%) of white powder, m.p. 252-254°. Reported[159] m.p. 248-249°.

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[159] H. Gerngoss and R. Dunkel, Ber., 57, 746 (1924).

4-Mercapto-p-terphenyl (attempted)

To a stirred solution of 0.020 mole of p-terphenyl-4-yllithium in 100 ml. of ether at 0° was added 0.70 g. (0.022 g. atom) of finely powdered sulfur in small portions. After warming to room temperature, Color Test I was negative and the mixture was hydrolyzed with 50 ml. of 10% sulfuric acid. Most of the aqueous layer was drawn off and the remaining organic suspension washed free of acid. The pale yellow powder was filtered and dried. From this material (2.65 g., melting at 255-270°) there could be isolated no pure product. Some small fractions were separated with 3° melting ranges, but none was constant and none showed an absorption band near 3.8 μ in the infrared spectra, indicative of an S-H bond.

4-Hydroxy-p-terphenyl

To a stirred solution of 0.015 mole of p-terphenyl-4-yllithium in 200 ml. of ether was added a solution of 0.030 mole of n-butylmagnesium bromide in 40 ml. of ether. The pink lithium reagent faded to a dark gray during this addition. With this mixture cooled to 0-5°, oxygen gas was allowed to pass over the surface while stirring. After 30 min. the mixture had turned to a thick, white suspension, and Color Test I was negative. Hydrolysis was effected with 75 ml. of 5%

hydrochloric acid. The insoluble material was filtered and extracted with 100 ml. of hot toluene. Cooling of the extract afforded 0.90 g. (24%) of tiny white needles, m.p. 267-270°. Two recrystallizations from ethyl acetate left 0.47 g. (13%) of pure product, m.p. 273.5-275°. Reported[160] m.p. 264-265°.

4-Amino-p-terphenyl

To a stirred solution of 0.020 mole of p-terphenyl-4-yllithium in 100 ml. of ether was added a solution of 0.47 g. (0.010 mole) of methoxyamine in 10 ml. of ether. After stirring 30 min., the pink color had been replaced by an orange color and a yellow precipitate; Color Test I was negative. Subsequent to hydrolysis with 50 ml. of water and dilution with 100 ml. of benzene, the organic layer was separated and filtered from undissolved p-terphenyl. Treatment of the filtrate with dry hydrogen chloride precipitated a tan powder. This material was stirred at gentle reflux with 100 ml. of ethanol and 50 ml. of concentrated ammonia for 12 hr. The product was filtered and recrystallized twice from ethanol to give 0.45 g. (18%) of nearly white plates, m.p.

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[160] H. France, I. M. Heilbron, and D. H. Hey, J. Chem. Soc., 1283 (1939).

198-199.5°. Reported[161] m.p. 198°. The pure material is highly electrostatic.

4-(N-Methylamino)-p-terphenyl (attempted)

A solution of 0.04 mole of p-terphenyl-4-yllithium was held at -20 ± 5° and stirred slowly during the dropwise addition of a solution of 1.22 g. (0.02 mole) of O,N-dimethylhydroxylamine in 30 ml. of ether. The pink color of the solution faded to a light gray which gradually turned yellow on warming to room temperature. Color Test I was positive after stirring 6 hr., but negative after 12 hr. Hydrolysis was effected with 50 ml. of water, and 200 ml. of benzene was added to facilitate separation of the phases. Undissolved p-terphenyl (m.p. 212-214°) was filtered, the filtrate dried over sodium sulfate, and dry hydrogen chloride was passed through the solution to precipitate a gummy yellow solid; yield, 5.82 g. (98%). The amine was liberated by treatment with warm, 10% potassium hydroxide and crystallized from ethanol-benzene. The product was a yellow powder, melting at 148-156°, which showed a violet fluorescence in ethanol; yield, 3.64 g. (68%). After three recrystallizations the product melted at 153.5-154.5°. The infrared spectra showed bands at

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[161] R. Pummerer and K. Bittner, Ber., 57, 85 (1924).

3.3, 3.5, 7.4, 8.3, 12.4, and 13.1μ, characteristic of aromatic C-H, aliphatic C-H, aliphatic C-N, aromatic C-N, monosubstituted benzene, and p-disubstituted benzene, respectively. There was no band characteristic of N-H.

Anal. Calcd. for $C_{19}H_{17}N$: C, 88.00; H, 6.61. Found: C, 86.98, 87.00; H, 7.27, 7.43.

2-(p-Terphenyl-4-yl)pyridine (attempted)

To a stirred solution of 0.013 mole of p-terphenyl-4-yllithium in 60 ml. of ether was added a solution of 1.58 g. (0.02 mole) of pyridine in 40 ml. of ether. The mixture refluxed gently and turned deep red during addition. After stirring overnight the mixture was light purple and Color Test I was negative. Oxidation was effected by a stream of dry air as suggested by Gilman and Edwards[86]. The thick, white suspension resulting from hydrolysis was filtered, and the yellow solid remaining was crystallized from methyl cellosolve. The yellow powder obtained (3.35 g., melting at 205-235°) resisted all attempts at purification.

N-[Phenyl(p-terphenyl-4-yl)methyl]aniline (attempted)

To a stirred solution of 0.015 mole of p-terphenyl-4-yllithium in 100 ml. of ether was added a solution of 3.26 g.

(0.018 mole) of benzalaniline in 50 ml. of ether. The mixture turned to a thick yellow suspension, and Color Test I was negative after stirring 15 min. Subsequent to hydrolysis and separation of the organic layer with the aid of 100 ml. of benzene, the organic solvents were evaporated to leave a gummy, yellow solid. Recrystallization from a variety of solvents invariably brought about some decomposition of the product, as evidenced by a violet fluorescence in the hot solution and the progressively darker yellow color of the product.

p-Terphenyl-4-boronic acid (attempted)

To a stirred solution of 5.75 g. (0.025 mole) of tri-n-butyl borate in 50 ml. of ether at -70° was added a solution of 0.010 mole of p-terphenyl-4-yllithium in 50 ml. of ether over a period of 30 min. A milky white suspension formed immediately, but Color Test I was positive. After stirring overnight, the mixture was permitted to warm to room temperature, and Color Test I was negative. The aqueous layer resulting from hydrolysis with 10% hydrochloric acid was separated, and the white solid in the organic layer filtered. Extraction of this material with hot glacial acetic acid afforded only 1.34 g. (49%) of p-terphenyl, m.p. and mixed m.p. with pure p-terphenyl 212-213.5°.

Direct Substitution of p-Terphenyl

4-Bromo-p-terphenyl (attempted)

Direct bromination was carried out according to the method suggested by France and coworkers.[156] To a gently refluxing solution of 2.3 g. (0.01 mole) of p-terphenyl in 230 ml. of glacial acetic acid, was added a crystal of iodine, followed by 4.8 g. (0.03 mole) of bromine. Refluxing was continued for 6 hr., during which time the red solution had faded to a yellow-orange color. The material which crystallized on cooling was apparently a mixture of p-terphenyl and various polybromo derivatives. The only pure substance isolated after repeated attempts at fractional crystallization from ethanol, glacial acetic acid, toluene, and ethyl acetate was the unsubstituted hydrocarbon.

4,2',4''-Trinitro-p-terphenyl

Nitration was carried out at the conditions by which Allen and Pingert[162] effected mononitration of o-terphenyl. A warm solution of 4.6 g. (0.02 mole) of p-terphenyl in 100 ml. of acetic anhydride was chilled to 5° in order to

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[162] C. F. H. Allen and F. P. Pingert, J. Am. Chem. Soc., 64, 2641 (1942).

precipitate a thick suspension. To this suspension was added 1.30 ml. of concentrated nitric acid (den., 1.44). The mixture was warmed slowly to a clear orange solution at 85°, then allowed to cool slowly. The product which crystallized was in the form of yellow needles and melted at 195.5-197°. One recrystallization from ethyl acetate gave 2.60 g. (35%) of trinitro derivative, m.p. 197-198°. From the mother liquors there was recovered 1.56 g. (34%) of p-terphenyl, m.p. and mixed m.p. with a pure sample 213-215°.

4-Chloromethyl-p-terphenyl (attempted)

Run 1. Following the procedure of Cambron[163] for the chloromethylation of naphthalene, a mixture of 11.5 g. (0.05 mole) of p-terphenyl, 2.0 g. (0.065 mole) of paraformaldehyde, 6.5 ml. of concentrated hydrochloric acid, 100 ml. of glacial acetic acid, and 3 ml. of syrupy phosphoric acid was heated at gentle reflux 18 hr., then poured over crushed ice. The precipitated white solid was filtered, washed with ethanol, and recrystallized from benzene. There was isolated 11.0 g. (96%) of p-terphenyl, m.p. and mixed m.p. 213-214°.

Run 2. A second attempt, employing chloromethyl ether as suggested by Vavon, Bolle, and Calin,[164] was equally

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[163] A. Cambron, Can. J. Research, 17B, 10 (1939).

[164] G. Vavon, J. Bolle, and J. Calin, Bull. soc. chim., (5)6, 1025 (1939).

unsuccessful. Chloromethyl ether was prepared according to the method of Reyschuler.[165] A stream of dry hydrogen chloride was passed rapidly into a mixture of 30 g. of paraformaldehyde and 40 ml. of methanol, keeping the temperature below 5° with an ice-bath. When the paraformaldehyde had gone into solution, the layers were separated. The upper layer was washed with concentrated hydrochloric acid, dried over calcium chloride, and distilled. The fraction boiling at 56-61° was collected and redistilled twice, collecting only the material boiling at 58-59°; yield 11.5 g. (29%).

A mixture of 11.5 g. (0.05 mole) of p-terphenyl, 6.04 g. (0.075 mole) of chloromethyl ether, 250 ml. of glacial acetic acid, and 10 ml. of acetic anhydride was stirred at 60-65° for 4 days. The mixture was poured over crushed ice, and the resulting white solid shown to be p-terphenyl. Recovery after purification was 11.22 g. (98%), m.p. 213-214°.

4-(Dimethylaminomethyl)-p-terphenyl (attempted)

N,N,N',N'-Tetramethyldiaminomethane was prepared by the modification of Lindsay and Hauser.[166] To a stirred solution of 162 g. (2.0 moles) of 37% formaldehyde solution at 10° was

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[165] J. Reyschuler, Bull. soc. chim., (4)1, 1195 (1907).

[166] J. K. Lindsay and C. R. Hauser, J. Org. Chem., 22, 355 (1957).

added 722 g. (4.0 moles) of 25% dimethylamine solution. The temperature was kept below 15° during the addition, which required 2 hr., and the solution was stirred 2 hr. after addition was complete. A large quantity (about 100 g.) of solid potassium hydroxide was added, and the clear upper layer was separated and dried over solid potassium hydroxide. The product was distilled to give 62 g. (40%) of pure product, b.p. 81°, which was used in the following experiment.

A mixture of 10.20 g. (0.10 mole) of the material prepared as described above and 3.16 g. (0.05 mole) of paraformaldehyde in 350 ml. of glacial acetic acid was warmed to effect solution, and 23.0 g. (0.10 mole) of p-terphenyl was added. The mixture was stirred and refluxed 72 hr. The white solid which crystallized on cooling was filtered and dried to give 22.6 g. (97%) of recovered starting material, m.p. and mixed m.p. 213-214°.

4-Dimethylamino-p-terphenyl

Dimethylamine was passed slowly over a stirred solution of 0.030 mole of n-butyllithium[167] at 0° until Color Test I was negative (40 min.). To this suspension of lithium dimethylamide was added a slurry of 6.18 g. (0.02 mole) of

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[167] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, J. Am. Chem. Soc., 71, 1499 (1949).

4-bromo-p-terphenyl in 200 ml. of tetrahydrofuran. The ice-bath was removed, and the mixture was stirred at gentle reflux for 4 hr. At the end of this period the solution was pale violet in color. Hydrolysis was effected with 50 ml. of water. The aqueous layer was separated and washed with 50 ml. of benzene. The combined organic solution was dried and treated with dry hydrogen chloride. The precipitated solid was filtered, triturated with 50 ml. of ethanol, and refluxed gently with 50 ml. of concentrated ammonia overnight. The resulting yellow powder was extracted with 100 ml. of hot ethanol, leaving 1.20 g. (19%) of starting bromide, m.p. 235-238°. When cooled to room temperature, another 0.15 g. of starting material separated. After concentration to 30 ml. and cooling to 0°, there was deposited 0.52 g. (9%) of pale yellow plates, m.p. 108.5-110°. Three recrystallizations from ethanol left 0.31 g. (6%) of nearly white plates, m.p. 111-111.5°. Concentration of all mother liquors gave small amounts of less pure product, but no evidence of another isomer.

Anal. Calcd. for $C_{20}H_{19}N$: C, 87.87; H, 7.01. Found: C, 86.93, 87.03; H, 7.15, 7.28.

4-Diethylamino-p-terphenyl

A suspension of lithium diethylamide was prepared by addition of 0.06 mole of diethylamine to a solution of 0.03

mole of n-butyllithium in 30 ml. of ether. A slurry of 4.64 g. (0.015 mole) of 4-bromo-p-terphenyl in 100 ml. of tetrahydrofuran was added, and the mixture was refluxed 2 hr. Hydrolysis, precipitation of hydrochloride, and liberation of the free amine as described above afforded 1.70 g. of yellow powder, melting at 103-120°. Recrystallization from 110 ml. of ethanol (trace insoluble) gave 0.57 g. (11%) of yellow needles, m.p. 147-149°. Two recrystallizations provided an analytical sample, melting at 148.5-149°.

Anal. Calcd. for $C_{22}H_{23}N$: C, 87.66; H, 7.69. Found: C, 87.15, 87.16; H, 7.79, 7.58.

Combination and concentration of the mother liquors provided a second product which, after two recrystallizations from methanol, melted at 64-65°.

Anal. Calcd. for $C_{22}H_{23}N$: C, 87.66; H, 7.69. Found: C, 86.93; H, 7.48.

An infrared absorption band at 12.9μ indicated that this latter compound is the 3-isomer.

Polyphenyls by Other Routes

1-(2-Biphenylyl)-2-phenylcyclohexene

To a stirred solution of 8.7 g. (0.05 mole) of 2-phenylcyclohexanone[168] added a solution of 0.05 mole of 2-biphenylyl-

[168] M. S. Newman and R. Farbman, J. Am. Chem. Soc., 66, 1551 (1944).

lithium in 100 ml. of ether. When addition was complete, Color Test I was negative, and hydrolysis was effected with 50 ml. of 10% hydrochloric acid. The water layer was discarded and 100 ml. of benzene was added to the organic layer. The ether was distilled, and residual water azeotroped from this solution. After cooling, 25 ml. of Lucas reagent was added, and the mixture stirred at gentle reflux for 1 hr. The benzene layer was separated, washed with water, sodium bicarbonate solution, and water again; then dried over sodium sulfate. Removal of solvent left a thick, yellow oil. Crystallization from 100 ml. of ethanol afforded 0.25 g. (2%) of pale yellow needles, melting at 203-207°. The mother liquors contained a mixture of biphenyl and 2-phenylcyclohexanone. Two recrystallizations of the product raised the m.p. to 207-208°.

Anal. Calcd. for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.48; H, 7.34.

1-(4-Biphenylyl)-2-phenylcyclohexene

Employing the same conditions and quantities as described above with 4-biphenylyllithium, there was obtained 0.80 g. (7%) of crude product, melting at 130-133°. After sublimation at 125° (0.01 mm.), which removed traces of non-volatile

yellow contaminant, and three recrystallizations from ethanol, the pure material melted at 133-134°.

Anal. Calcd. for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.59; H, 7.37.

1,1'-2',1''-4'',1'''-Quaterphenyl (attempted)

Oxidation of 0.40 g. of the above material with two equivalents of chloranil in boiling xylene as described by Crawford and Nelson[169] produced only an intractable glass.

2-Phenyltriphenylene

A solution of 0.098 mole of 2-biphenylyllithium in 500 ml. of ether was added to 20.0 g. (0.10 mole) of 4-cyclohexylcyclohexanone in 40 ml. of ether over a period of 30 min. After refluxing 2 hr. Color Test I was negative, and the mixture was hydrolyzed with 50 ml. of 10% hydrochloric acid. The layers were separated, and the ether removed from the organic layer. The remaining oil was taken up in 125 ml. of benzene and treated with Lucas reagent as described above. The product from this treatment was an orange oil. Distillation at reduced pressure afforded 5.83 g. (39%) of biphenyl, boiling

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[169] H. M. Crawford and H. B. Nelson, J. Am. Chem. Soc., 68, 134 (1946).

at 119-123° (17 mm.), 2.44 g. (14%) of 4-cyclohexylcyclohexanone, boiling at 117-121° (4 mm.), and 3.61 g. (12%) of a viscous, yellow oil, boiling at 157-160° (0.01 mm.). This latter fraction was heated with 5 equivalents (4.58 g., 0.057 g. atom) of selenium at 300-350° for 24 hr. The solidified melt was broken up and extracted with hot benzene. Concentration of the extract to 30 ml. and addition of an equal quantity of petroleum ether (b.p. 60-70°), precipitated 0.36 g. (10%) of tan needles, melting at 177-182°. Two recrystallizations from this mixture produced a pure sample, m.p. 185-186°.

Anal. Calcd. for $C_{24}H_{16}$ (2-phenyltriphenylene): C, 94.70; H, 5.30. Calcd. for $C_{24}H_{18}$ (1,1'-4',1''-2'',1'''-quaterphenyl): C, 94.07; H, 5.93. Found: C, 94.68, 94.64; H, 5.33, 5.27. The analytical data indicates that the quaterphenyl, if formed, underwent further dehydrogenation to the triphenylene derivative. This oxidation is common with compounds related to o-terphenyl.[162]

1,1'-2',1''-2'',1'''-Quaterphenyl

This compound was prepared by the Ullman reaction as described by Bowden.[128] A mixture of 7.0 g. (0.025 mole) of 2-iodobiphenyl and 7.0 g. (0.109 g. atom) of copper powder was heated slowly to 250°, at which temperature the reaction became exothermic and turned lumpy. The cooled melt was broken

up and extracted with benzene. Evaporation of the solvent and three recrystallizations of the residue from ethanol gave 2.03 g. (53%) of glassy prisms, m.p. 117-118°. Reported[128] m.p. 118-119°.

3-Iodobiphenyl

To a stirred solution of 30.0 g. (0.23 g. atom) of iodine in 400 ml. of ether was added a solution of 0.10 mole of 3-biphenylyllithium. Color Test I was negative after stirring 40 min. The mixture was hydrolyzed with 100 ml. of water, and the layers were separated. The ether layer was washed with sodium bisulfite, filtered, and dried over sodium sulfate. Removal of the solvent and distillation at reduced pressure produced 18.8 g. (67%) of product, b.p. 163-165° (3.5 mm.).

1,1'-3',1''-3'',1'''-Quaterphenyl

The process described above for 2-iodobiphenyl was repeated using 11.95 g. (0.043 mole) of 3-iodobiphenyl and 12.0 g. (0.19 g. atom) of copper powder. The crude product was an oil which solidified when thinned with 3 ml. of carbon disulfide and covered with 150 ml. of ethanol. The resulting yellow powder, melting at 66-71° formed an oil during recrystallization. After refluxing 1 hr. with 100 ml. of ethanol,

the ethanol solution was decanted and cooled carefully. When cooled to 0°, the solution deposited 1.60 g. (25%) of white powder, m.p. 86-87°. Reported[128] m.p. 86°.

4-Cyclohexyl-1-(p-dimethylaminophenyl)cyclohexene

A solution of p-dimethylaminophenyllithium containing 0.067 mole in 80 ml. of ether was added dropwise to a stirred solution of 11.5 g. (0.064 mole) of 4-cyclohexylcyclohexanone in 50 ml. of ether. Color Test I was faint after stirring 30 min., and the mixture was hydrolyzed with 50 ml. of water. The layers were separated; the organic layer was washed with water, diluted with 100 ml. of benzene, and distilled to remove ether and residual water. Treatment with Lucas reagent as described above left a dark oil which was crystallized from 75 ml. of ethanol. The product was 2.98 g. (17%) of white plates, m.p. 122-126°. Two recrystallizations from ethanol afforded an analytical sample, m.p. 126-127°.

Anal. Calcd. for $C_{20}H_{25}N$: C, 84.74; H, 10.31. Found: C, 84.37; H, 11.05.

4-Dimethylamino-p-terphenyl (attempted)

By the unsymmetrical Ullman reaction. A mixture of 8.40 g. (0.03 mole) of 4-iodobiphenyl, 7.44 g. (0.03 mole) of

p-iododimethylaniline, and 11.4 g. (0.18 g. atom) of copper powder was heated slowly to 190° with frequent manual stirring. At this point the reaction became exothermic and stirring became difficult. When the initial reaction had subsided, the mixture was held at 200-210° for 1 hr. After cooling the mixture was pulverized and extracted with 4-50 ml. portions of hot toluene. The cooled extract deposited 0.47 g. of shiny platelets, m.p. and mixed m.p. with pure quaterphenyl 305-308°. Treatment of the filtrate with dry hydrogen chloride precipitated a dark, gummy solid. Crystallization of this material from hot 1% hydrochloric acid gave tiny, pale green needles that filtered with great difficulty. Treatment of this hydrochloride with ammonia, followed by crystallization of the free base, left only a small amount of purple powder which decomposed above 200°.

By coupling of an aryllithium reagent with an aryl halide. Following a procedure suggested by the report of Gilman and Gaj[170] concerning an unusual coupling of organometallic compounds with aryl halides in tetrahydrofuran, an attempt was made to couple 4-biphenylyllithium with p-iododimethylaniline. A solution of 0.052 mole of 4-biphenylyllithium in 125 ml. of ether was added to a stirred solution of 13.84 g. (0.052 mole) of p-iodo-N,N-dimethylaniline in 125 ml.

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[170] H. Gilman and B. J. Gaj, J. Org. Chem., 22, 447 (1957).

of tetrahydrofuran. After stirring 22 hr. between -10 and 0°, Color Test I was faint, and the mixture was hydrolyzed with 50 ml. of water. The aqueous layer was extracted with 50 ml. of ether, and the combined organic layer filtered and dried. The insoluble material was a trace of impure p-quaterphenyl, melting at 298-305°. The organic layer was treated with hydrogen chloride, and the precipitate shaken with a 1:1 mixture of benzene and 6M ammonia. Evaporation of the benzene layer left a dark, oily residue which was chromatographed on alumina, using petroleum ether as eluant. The bulk of the material was p-iododimethylaniline, 1.10 g. (8%), m.p. 77-80°.

A second attempt employing a solution of 0.02 mole of p-dimethylaminophenyllithium and 5.60 g. (0.02 mole) of 4-iodobiphenyl in 100 ml. of tetrahydrofuran, and stirring for 20 hr. between -10 and -20°, left only unreacted starting material.

By coupling of two different Grignard reagents. Activated magnesium was prepared by gradual addition of 0.75 g. of iodine to 1.50 g. of magnesium while heating with an open flame and shaking. To this material was added 8.0 g. of cupric chloride and 50 ml. of ether. A solution of 6.99 g. (0.03 mole) of 4-bromobiphenyl and 6.00 g. (0.03 mole) of 4-bromodimethylaniline in 100 ml. of ether was then added dropwise, and the mixture was stirred at reflux overnight.

Subsequent to hydrolysis with saturated ammonium chloride and precipitation of basic material from ether with dry hydrogen chloride, the aminoid material was chromatographed on alumina and proved to be a mixture of dimethylaniline and a small amount of 4-bromodimethylaniline.

By coupling of two different lithium reagents. A solution of 0.03 mole of 4-biphenylyllithium in 100 ml. of ether was thoroughly mixed with a solution of 0.03 mole of p-dimethylaminophenyllithium in 60 ml. of ether; and this mixture was added dropwise to a suspension of 8.0 g. of cupric chloride in 50 ml. of ether. After stirring at gentle reflux overnight, Color Test I gave a pale green color, but this same color was observed when the test was run without Michler's ketone. Subsequent to hydrolysis and work-up as described for the Grignard reaction above, there was isolated 1.02 g. of quaterphenyl, m.p. and mixed m.p. 306-309°. The only aminoid product was dimethylaniline.

By dehydrogenation of 4-cyclohexyl-1-(p-dimethylaminophenyl)cyclohexene. A mixture of 2.79 g. (0.0098 mole) of this decahydro derivative and 3.90 g. (0.049 g. atom) of selenium was heated slowly to 300°, then held at 300-330° for 6 hr. The cooled residue was broken up and extracted with benzene. The only product isolated from the residue was 0.96 g. (36%) of crude material melting at 186-190°. Three recrystallizations from ethanol raised the m.p. to 201-202°.

The infrared spectra of this material was superimposable with that of 4-amino-p-terphenyl, and the mixed m.p. with an authentic specimen was not depressed.

Anal. Calcd. for $C_{18}H_{15}N$: C, 88.12; H, 6.16. Found: C, 88.37; H, 6.31.

Demethylation of N,N,N',N'-tetramethylbenzidine (attempted)

In order to examine the generality of the demethylation observed above, attempts were made to demethylate tetramethylbenzidine with hydrogen selenide generated from another molecule.

Run 1, with selenium and tetralin. A mixture of 1.92 g. (0.008 mole) of N,N,N',N'-tetramethylbenzidine, 12.6 g. (0.16 g. atom) of selenium, and 21.1 g. (0.16 mole) of tetralin was refluxed 24 hr. The unused selenium was filtered and extracted with hot benzene. Dilution of filtrate and extract with petroleum ether (b.p. 60-70°) precipitated tetramethylbenzidine, m.p. 194-195.5°.

Run 2, with selenium and dicyclohexenylbiphenyl. To a stirred solution of 0.23 mole of n-butyllithium in 170 ml. of ether was added a suspension of 31.2 g. (0.10 mole) of 4,4'-dibromobiphenyl in 200 ml. of benzene at 0°. The thick suspension was stirred 3 hr. before 22.0 g. (0.23 mole) of cyclohexanone was added. After refluxing overnight Color

Test I was negative, and hydrolysis was effected with 50 ml. of water. The layers were separated with the aid of an additional 100 ml. of benzene, and the organic layer was distilled to a volume of 200 ml. Dehydration with Lucas reagent, followed by concentration of the benzene solution to 100 ml. and dilution with ethanol to the point of incipient crystallization afforded 13.7 g. (32%) of fine white needles, melting at 190-201°. Further recrystallization did not improve this range; the product turned yellow while melting.

A mixture of 3.14 g. (0.01 mole) of this crude 4,4'-di(cyclohexen-1-yl)biphenyl, 3.16 g. (0.04 g. atom) of selenium, and 1.13 g. (0.0046 mole) of tetramethylbenzidine was maintained at 300-320° for 24 hr. with no apparent reaction. Extraction of the reaction mixture with hot benzene and subsequent separation of the amine with hydrogen chloride, effected 93% recovery of tetramethylbenzidine.

1-(4-Biphenylyl)-2-dimethylaminocyclohexene (attempted)

To a stirred solution of 28.42 g. (0.20 mole) of 2-dimethylaminocyclohexanone in 100 ml. of ether was added a solution of 0.143 mole of 4-biphenylyllithium in 250 ml. of ether over a period of 1 hr. After stirring an additional hour, Color Test I was negative, and the mixture was hydrolyzed with 60 ml. of water. The organic layer was separated,

filtered from a trace of solid, and dried over sodium sulfate. The solvents were removed, and the residual oil stirred at 50-60° with 100 ml. of 20% sulfuric acid for 2 hr. After cooling, the mixture was diluted with 200 ml. of water, made alkaline with potassium hydroxide, and extracted with benzene. This solution was dried over sodium sulfate, and the solvents were stripped. Fractionation of the residue at 14 mm. gave 4.02 g. (20%) of recovered 2-dimethylaminocyclohexanone at 78-82°, and 8.88 g. (41%) of crude biphenyl at 113-116°. Further distillation at 0.02 mm. afforded a waxy, yellow solid at 150-155°, and a thick, yellow oil at 175-180°. The waxy solid appeared, upon attempts at recrystallization, to be a mixture of two compounds, one melting at about 150° the other at about 165°. No pure material could be isolated, however.

4-Dimethylamino-o-terphenyl (attempted)

A solution of 0.05 mole of p-dimethylaminophenyllithium in 50 ml. of ether was added dropwise to a stirred solution of 8.70 g. (0.05 mole) of 2-phenylcyclohexanone in 50 ml. of ether. After refluxing 30 min., Color Test I gave the pale green color characteristic of these dialkylarylamines. The layers were separated and the aqueous layer extracted with benzene. The combined organic solutions were distilled until all ether and residual water were removed, then stirred at

gentle reflux with 40 ml. of Lucas reagent for 1 hr. The acid layer was separated and made strongly basic with 20% potassium hydroxide. The oily amine that resulted was extracted with ether and distilled. After a forerun of dimethylaniline, a thick yellow oil (3.15 g.) was collected at 148-151°. This product was heated with 5.41 g. (0.022 mole) of chloranil in 40 ml. of refluxing xylene for 6 hr. The mixture became very dark and the only product isolated (other than dihydrochloranil) was a glassy, black resin. This material was thought to be a complex formed between the amine and dihydrochloranil, but was uneffected by warm alkali.

2-(2-Biphenylyl)pyridine

To a stirred solution of 8.70 g. (0.13 mole) of pyridine in 50 ml. of ether was added a solution containing 0.12 mole of 2-biphenyllithium in 135 ml. of ether. Color Test I was negative after stirring at gentle reflux overnight. A rapid stream of dry air was bubbled through the mixture before hydrolysis. Dilution with 100 ml. of benzene facilitated separation of the organic layer. Distillation at reduced pressure afforded 4.8 g. (26%) of recovered biphenyl, boiling at 70° (0.15 mm.) and melting at 67-70°. The product was a yellow oil collected at 115-120° (0.18 mm.); yield 4.10 g. (15%). The compound tended to oil out of solvents from

concentrated solutions. Repeated crystallization from petroleum ether (b.p. 60-70°) eventually produced 0.8 g. (3%) of white rosettes, m.p. 92.5-93.5°.

Anal. Calcd. for $C_{17}H_{13}N$: C, 88.27; H, 5.66. Found: C, 87.99, 88.20; H, 5.66, 5.70.

2,6-Bis(4-biphenylyl)pyridine (attempted)

To a stirred solution of 4.62 g. (0.02 mole) of 2-(4-biphenylyl)pyridine in 60 ml. of xylene was added a solution of 0.023 mole of 4-biphenyllithium in 50 ml. of ether. After refluxing overnight, the mixture was cooled, and a stream of dry air was bubbled through. After 15 min. the dark brown color had faded to a yellow-green. The mixture was poured into 50 ml. of ice water, and the organic layer was separated, filtered, and dried over sodium hydroxide pellets. Concentration of this solution to 15 ml. produced a tan powder which decomposed gradually above 230°. After two recrystallizations from benzene there remained 0.24 g. (3.5%) of yellow product, which melted at 249-255° to a red liquid. Further recrystallization failed to remove the color or to improve the melting point.

2,5-Diphenylpyrazine

This compound resulted as a bi-product in an attempt to effect condensation and cyclization of benzoic acid and phenacylammonium chloride to 2,5-diphenyloxazole in one step, rather than the usual three. A smooth paste of 4.88 g. (0.02 mole) of benzoic acid, 6.88 g. (0.02 mole) of phenacylammonium chloride, and 40 ml. of polyphosphoric acid was heated slowly with stirring to 250°. The sublimed benzoic acid was scraped back into the mixture with a spatula. After 2 hr. at 250°, the mixture was cooled to 100° and poured slowly into 100 ml. of water. The water was decanted through a filter, and the tarry residue chromatographed in benzene. The only product obtained from the eluate was 0.4 g. (9%) of 2,5-diphenylpyrazine, m.p. 196-197°. Reported[98] m.p., 195-196°.

Miscellaneous Reactions

4-Cyclohexylcyclohexanone

To a stirred solution of 48.5 g. (0.266 mole) of Eastman technical grade 4-cyclohexylcyclohexanone in 300 ml. of glacial acetic acid was added a solution of 17.8 g. (0.178 mole) of chromic anhydride in 300 ml. of glacial acetic acid, keeping the temperature below 20° with the aid of an ice-bath. After

stirring overnight, the mixture was poured into 1 l. of ice water, and the product extracted with three 200-ml. portions of ether. After drying and removal of solvents, there was obtained 29.1 g. (61%) of product, b.p. 139-141° (14 mm.). In another experiment in which all the materials were mixed initially, the reaction took place with a short flash of flame through the condenser.

2-Bromofluorene-9-carboxylic acid (attempted halogen-metal-interconversion of 2-bromofluorene)

Over a period of 15 min. a solution of 0.05 mole of n-butyllithium in 42 ml. of ether was added to a stirred solution of 12.25 g. (0.05 mole) of 2-bromofluorene[171] in 200 ml. of ether. The solution turned reddish-brown and refluxed gently during addition. When addition was complete, Color Test I was positive and Color Test II[172] was negative. The mixture was carbonated by pouring jetwise onto a stirred Dry Ice-ether slurry. The mixture was hydrolyzed with water, and the organic layer extracted with 20 ml. of 5% potassium hydroxide. Combined alkaline solutions were acidified with 10% hydrochloric acid, and the resulting crude acid was filtered

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[171] J. T. Thurston and R. L. Shriner, J. Am. Chem. Soc., 57, 2163 (1935).

[172] H. Gilman and J. Swiss, J. Am. Chem. Soc., 62, 1847 (1940).

and dried; yield 13.3 g. (92%), melting at 226-230°. Three recrystallizations from ethanol afforded 8.7 g. (60%) of pure acid, m.p. 239-240°.

Anal. Calcd. for $C_{14}H_9BrO_2$: N. E., 289. Found: N. E., 291, 291.

Repitition of this experiment at 0, -30, and -65° gave progressively lower yields of this compound, but no evidence of fluorene-2-carboxylic acid.

Fluorene-2-carboxylic acid

As reported by Miller and Bachman,[173] 2-bromofluorene could not be made to react with either magnesium or lithium in ether or ether-toluene. The Grignard reagent did form in tetrahydrofuran, however.

A mixture of 4.90 g. (0.02 mole) of 2-bromofluorene, 1.21 g. (0.05 g. atom) of magnesium, 50 ml. of tetrahydrofuran, and a crystal of iodine was stirred at gentle reflux 8 hr. to give a blood red solution, which gave a positive Color Test I. Carbonation and work-up as described above produced 0.50 g. (12%) of white powder which decomposed and sublimed above 260°. The methyl ester was prepared by refluxing with thionyl chloride and subsequent treatment with methanol as described by

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[173] H. F. Miller and G. B. Bachman, J. Am. Chem. Soc., 57, 766 (1935).

Fortner.[174] After recrystallization from methanol the pure derivative melted 127-127.5°. Reported[174] m.p. 120°.

4-Amino-4'-nitrobiphenyl

Reduction of 4,4'-dinitrobiphenyl as described Guglialmelli and Franco[175] was found to produce large amounts of benzidine. The reduction was successfully carried out, though in poor yield, by titanous chloride following the procedure of van Duin.[176]

To a stirred suspension of 6.10 g. (0.025 mole) of 4,4'-dinitrobiphenyl in 300 ml. of boiling ethanol was added 115.8 g. of 20% titanous chloride solution (0.150 mole) over a period of 30 min. The mixture was refluxed 1 hr. and concentrated to 100 ml. in order to coagulate titanium dioxide and other insoluble material. This insoluble material was extracted with 100 ml. of hot, 20% hydrochloric acid. The combination of filtrate and extract was made basic and extracted with 1:1 benzene-toluene. Evaporation of this extract left a red solid which gave 1.30 g. (24%) of orange plates on recrystallization from ethanol, m.p. 198-200°. Reported[175] m.p. 197-198°.

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[174] M. Fortner, Monatsh., 25, 448 (1904).

[175] L. C. Guglialmelli and M. R. Franco, Anal. Assoc. Quim. Argentina, 17, 340 (1929) [C. A., 24, 3235 (1930)].

[176] C. F. van Duin, Rec. trav. chim., 39, 578 (1920).

N-Methylmethoxyamine

Methoxyamine was distilled from a solution of the hydrochloride (25 g.) and excess alkali. The free amine was allowed to stand in ether with excess methyl chloride under a Dry Ice condenser. After addition of 20 ml. of 10% hydrochloric acid, excess methyl chloride and ether were allowed to evaporate. The free amine was liberated by addition of alkali and distilled at 42-44°; yield 6.07 g. (33%).

N,N-Dimethylmethoxyamine

Repetition of the above experiment, beginning with N-methylmethoxyamine, afforded 4.57 g. (61%) of the completely alkylated product, b.p. 32-34°.

Reaction of phenyllithium with N,N-dimethylmethoxyamine

A solution of 7.50 g. (0.10 mole) of N,N-dimethylmethoxyamine, 0.10 mole of phenyllithium, 100 ml. of ether, and 100 ml. toluene was refluxed 24 hr. At the end of this time Color Test I was still positive. Subsequent to hydrolysis, extraction, and removal of solvents, there was obtained 0.22 g. of yellow oil, b.p. 98-101° (0.17 mm.), which did not form a picrate. The infrared spectra of this material had a band at

2.98μ, indicative of a secondary amine, and another band at 13.3μ, indicative of a phenyl ring; but a small amount of p-toluenesulfonamide derivative melted at 177-180°. The corresponding derivative of N-methylaniline melts at 93-94°.

4-Dimethylaminodibenzofuran (attempted)

When the above reaction was carried out with 4-dibenzofuryllithium[177] instead of phenyllithium, no basic material was isolated.

Reaction of phenyllithium with N-methylmethoxyamine

A solution of 0.105 mole of phenyllithium in 120 ml. of ether was stirred at 0-10° during the addition of 3.17 g. (0.052 mole) of N-methylmethoxyamine in 20 ml. of ether. After stirring 1 hr. at room temperature, Color Test I was positive; after refluxing overnight it was negative. The mixture was hydrolyzed with 50 ml. of water; the organic layer was separated and dried; and the solvents distilled. Distillation of the residue at 17 mm. afforded 1.94 g. (35%) of N-methylaniline at 79-82°. The p-toluenesulfonamide prepared

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[177]H. Gilman and R. D. Gorsich, J. Org. Chem., 22, 687 (1957).

from this material melted at 92-93.5° and was not depressed when admixed with an authentic sample.

N-Methylcyclohexenimine (attempted)

A solution of 1.22 g. (0.02 mole) of N-methylmethoxyamine and 16.4 g. (0.20 mole) of cyclohexene in 50 ml. of ether was stirred at 0° during the addition (30 min.) of 0.020 mole of phenyllithium in 20 ml. of ether. The mixture was stirred at reflux overnight, then hydrolyzed with 50 ml. of water. The organic layer was washed with water, dried, and distilled. All material boiled below the boiling point of cyclohexene (81°). There was no evidence of either N-methylaniline or N-methylcyclohexenimine.

Triphenylphosphinemethylimine (attempted)

To a stirred solution of 3.05 g. (0.050 mole) of N-methylmethoxyamine and 16.11 g. (0.061 mole) of triphenylphosphine in 100 ml. of benzene was added a solution of 0.050 mole of phenyllithium in 50 ml. of ether, keeping the temperature below 5° during the addition. The solution became yellow as the reaction progressed, and a gas was evolved. A few pieces of dry ice were added to convert the unstable product, if formed, to triphenylphosphine oxide and

methylisocyanate.[178] The mixture was distilled in a nitrogen atmosphere into a flask containing 2 ml. of aniline. Evaporation of the ether from this receiver and dilution of the residual oil with petroleum ether and a few drops of benzene failed to produce any evidence of methylphenylurea. The undistilled material was hydrolyzed and filtered. The insoluble material was a mixture of lithium carbonate and recovered triphenylphosphine. There was no triphenylphosphine oxide in the mixture. Evaporation of the aqueous filtrate to near dryness left 0.15 g. of white material which decomposed above 260° and smelled of formaldehyde when heated on a spatula. The material is undoubtably hexamethylenetetramine.

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[178] H. Staudinger and E. Hauser, Helv. Chim. Acta, 4, 861 (1921).

DISCUSSION

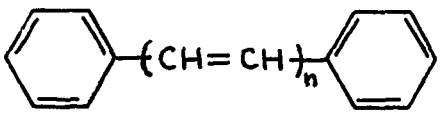
Ring Systems

Many ring systems have been incorporated in potential scintillator solutes in order to examine the alteration of physical and spectral properties of the resulting molecule. These properties are best considered in the light of the corresponding carbocycles.

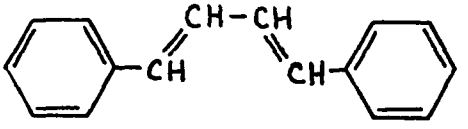
As pointed out previously, the best of a series of potential solutes examined by Kallman and Furst[25] was p-terphenyl. This molecule, however, has two undesirable characteristics, viz., a limited solubility in toluene and a poor spectral match with commercial photomultipliers. While the other two isomers, o- and m-terphenyl, have much greater solubility, both are inefficient light producers. p-Quaterphenyl has good spectral characteristics and is apparently able to convert atomic radiation energy to light energy with reasonable efficiency, but is remarkably insoluble in toluene. The other two isomers of quaterphenyl reported herein (388 and 389 in Table 2) are quite soluble in toluene, but are poor scintillator solutes. These poor values are presumably the result of the lack of continuous resonance throughout the molecule. When the rings are substituted in the ortho position, resonance is forbidden by lack of coplanarity, while the

odd atom separating the rings in the meta substituted molecule has the same effect.

The series of compounds built from two benzene rings linked by vinyl groups (I) rises and falls quickly in scintillation ability as the chain grows (see compounds 48, 401, 197, 206, and 208 in Table 2). When "n" in I is zero or one, the



I



II

compound does not respond to excitation. When "n" is two (II), the relative pulse height is 0.33. An interesting sidelight is the similarity of this compound (in the trans configuration shown) to p-terphenyl. Although the most efficient solute in this series is the hexatriene (n=3, RPH 0.52), the response for the next member (n=4) again drops too low to permit significant measurement. In this series there is a regular increase of the wavelength of the emitted light with "n", and it seems likely that the last compound is an example of a molecule with a wavelength too long to be efficiently received by the photomultiplier.

A multitude of condensed carbocyclic systems has been examined, only to find that these excellent covalent crystal

scintillators[179] are consistently poor as solutes. The highest value observed was that of 0.27 for fluoranthrene. The remarkably high value, 0.87, of compound 46 must be classed as a peculiar abnormality in view of the low values, 0.25 and 0.24, for 47 and 331, respectively. Further, all other instances in which corresponding 1- and 2-naphthyl derivatives have been screened (compounds 187-190, 264, 265, 299, 300, 305, 306, 310, 311, 317-322, 324, and 325 in Table 2) show little difference in the response of the isomers. The lone exception is the pair of amines, 352 and 353, the values for which, 0.65 and 0.21, again reflect a superiority of the 1-isomer.

The few examples of molecules containing the cyclopentadiene ring (202, 203, 235, 350, 392, 396, and 420) show no exceptionally good values, but none contains more than two distinct aromatic rings joined directly. The fluorene compounds with an aromatic ring on the methylene carbon, however, show a positive response, which is not true of the "open" analogs, tri- and tetraphenylmethane.

A number of derivatives of some novel cyclic systems containing elements of Group IVB are listed in Table 2. These heterocycles are currently under investigation, and the

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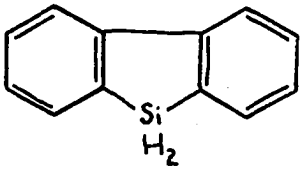
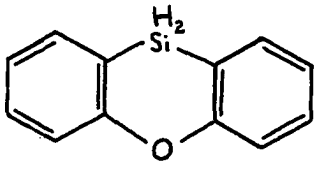
[179]R. Sangster, U. S. Office of Naval Research, Mass. Inst. of Tech. Bulletin No. 55 (1952).

limited number of derivatives screened to this date forbid any general statements. From early indications, however, it would seem that the heavier metals are detrimental to scintillation. This is in line with the quenching studies of Kerr, Hayes, and Ott[20] which assigned organotin and -lead compounds to the class of "strong quenchers". Derivatives of dibenzosilole (III) appear to be of the same order of efficiency as the analogous fluorene compounds, but synthetic techniques have



III



IV

not produced the necessary variety for complete investigation. Derivatives of phenoxasilin (IV), the corresponding heterocycle in which the two benzene rings are joined through an oxygen are clearly less effective (compare compounds 199 and 214, 395 and 397).

Nitrogen heterocycles fall into two general classes: those related to pyridine, commonly referred to as aza-aromatic heterocycles, and those related to pyrrole. Molecules having a heterocycle of either of these types in a chain of aromatic

rings generally have considerably greater solubility in aromatic solvents than those consisting entirely of carbocycles.

Aryl derivatives of aza-aromatic heterocycles are readily formed by the addition of aryllithium reagents to the C=N linkage of the heterocycle, and subsequent oxidation of the resulting dihydro derivative.[124] This mode of preparation restricts one to α-substituted derivatives, but this series appears to be most promising on the basis of the three 2-pyridyl-5-phenyloxazoles in Table 2 (compounds 385-387). In this instance the α-isomer registered a pulse height of 0.93, the β-isomer 0.92, and the γ-isomer 0.78. Heterocycles of this class in which 1,2-addition is not reasonable, such as acridine, readily undergo 1,4-addition.

This class of compounds is inferior in every instance thus far reported to the analogous carbocycles and to the corresponding pyrrole-type compounds. As evidence of this compounds 56, 71, 217, and 218 fail to give a significant response, even though all are closely related to p-terphenyl. 2,6-Diphenylpyridine, which may be thought of as an analog of 2,5-diphenylpyrrole as well as m-terphenyl, fails to give a measurable response. The latter two have been reported as 0.97 and 0.44, respectively. The bisaza-aromatic compounds screened thus far, derivatives of quinoxaline and phenazine (compounds 200, 222, 278, and 285), show even less potentiality.

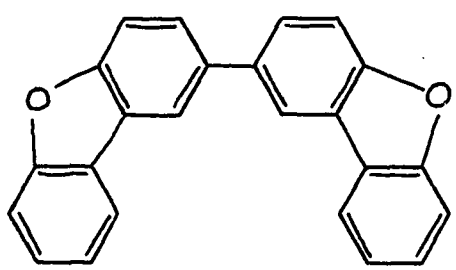
The only derivative of pyrrole, other than the one mentioned above, that has been screened is the 1-methyl-2,5-diphenyl compound (compound 282, RPH 1.03). Two arylindoles are found in Table 2 (54 and 312) and both have good values. All examples of carbazole derivatives tested have aryl groups on the nitrogen atom (52, 74, 75, 340, 381, and 391). Each of these compounds has some ability to scintillate, and compound 75 has a relative pulse height of 0.93. This value is interesting in view of the fact that, although this compound has six benzene rings, no more than two are linked directly to one another at any point in the molecule. This compound has a solubility of 5 g./l. in toluene, which is also remarkable in view of the number of aromatic rings and the symmetry of the molecule.

A further point of interest is the series of di- and triarylamines closely related to these N-arylcarbazoles. Triphenylamine, for example, fails to give any value while the extra bridge in 9-phenylcarbazole gives rise to a relative pulse height of 0.24. With one more ring in the molecule (compounds 52 and 53) the values are about the same (0.35 and 0.39). The carbazole derivatives (2-phenyl and 2,7-diphenyl) related to the two secondary amines with very good values (49 and 72, RPH 0.63 and 0.95) are not known.

The systems containing a polynitrogen heterocycle (compounds 217, 218, 223, 425, and 449 in Table 2) are all poor

solutes, even though each compound has at least three aromatic rings. No other heterocycles containing Group VB elements have been screened.

Most of the oxygen heterocycles in Table 2 have functional groups, but a few have been included in a series of rings and appear to be of considerable interest. 2,5-Diphenylfuran (204) and 2,5-di(2-furyl)oxazole (146), for example, have high values (0.89 and 0.94, respectively), but dibenzofuran just reaches the limit of measurement (0.10). Tetraphenylfuran registers only 0.47 on this scale and appears to be another example of a molecule in which the lack of coplanarity (and resultant lack of continuous resonance) effects a decrease in scintillation efficiency. The low value (0.14) of 2,2'-Bidibenzofuran (V) is reminiscent of the analogous quaterphenyl (389) which failed to scintillate. The oxygens in this molecule are apparently beneficial.



V

Only a few examples of pyran-type heterocycles are found in Table 2, and all of these have a carbonyl group in the

ring. These compounds, coumarins and pyrones, are lactones and will be considered as esters in the discussion of the effect of functional groups on scintillation.

The dibenzo-p-dioxin compounds without a functional group (compounds 42, 43, 116, 341, and 365) are poorer solutes in every instance than the corresponding dibenzofuran derivatives. The only unexpected value is that of 0.59 for 2,2'-Bidibenzo-p-dioxin, although it is the low value of the dibenzofuran compound, rather than this good value, which is more unusual.

Although some of the 2-thienyl compounds examined by Hayes and coworkers[27] did scintillate, all sulfur heterocycles screened and reported to this time are poorer scintillators than the corresponding oxygen compounds. The sulfoxide and sulfone derivatives which have been tested have all failed to scintillate. No heterocycles containing selenium or tellurium have been examined, but it is likely that they would tend to quench scintillation.

The most popular, and apparently most effective, heterocyclic systems reported are those containing both oxygen and nitrogen. The simplest of these and the focal point of the extensive investigation[18-20,26,27,29,31,33] by Hayes, Ott, and coworkers is oxazole. Polyaryls incorporating the oxazole ring appear to have the best combination of good solubility, fine spectral match with photomultiplier efficiency peaks,

efficient light production, and low quenching factor. By incorporating other aromatic rings into a chain including an oxazole ring, a number of notable indications concerning the other rings became apparent. With only one or two noticeable variations, the 1- and 2-naphthyl radicals appear to be equally good in their contribution to scintillation. The 4-pyridyl radical was found to be less effective than the other two isomers, which were equal, but all were poorer than the phenyl derivative. The 2-furyl radical was generally in the same range as the corresponding molecule with a phenyl radical. Derivatives of 1,3,4-oxadiazole are occasionally a little better than those of oxazole, but the differences are neither great nor consistent. Many of the oxazole compounds screened contained functional groups and will be considered under that heading.

Condensed heterocycles containing both oxygen and nitrogen are less effective. None of the derivatives of phenoxazine that have been screened (compounds 61, 92, 93, 335, and 359) have been found to scintillate at all. This failure, however, may be a side effect attributable to the persistent color of these compounds, which probably results in some self-quenching.

The thiazole, benzothiazole, and phenothiazine derivatives tested have been very poor solutes with but one exception. This compound, 2-(p-dimethylaminophenyl)benzothia-

zole, as previously mentioned, very likely owes its good light production efficiency to the dimethylamino function. As yet no heterocycles containing both oxygen and sulfur have been screened, but a few selected derivatives of phenoxathiin are to be tested in the near future.

Functional Groups

The effect of halogens on the scintillation efficiency of polyaryls is well substantiated by the agreement between the halogen derivatives of 2,5-diphenyloxazole reported by Hayes and coworkers[27] and the 4-halo-p-terphenyls reported herein. With the halogen in the 4-position of the phenyl group on carbon "2" of the oxazole ring, the values from fluorine through iodine are 0.98, 0.96, 0.28, and <0.10. In the same order the terphenyl derivatives showed pulse heights of 0.91, 0.93, 0.22, and <0.10. All three fluoro derivatives of diphenyloxazole reported (compounds 237-239) were equally good. 2-(3-Chlorophenyl)-5-phenyloxazole was approximately as good as the 4-chloro isomer, but the 2-chloro compound showed a drop to 0.79. 3-Chloro-p-terphenyl had a value of only 0.83 (compared to 0.93 for the 4-isomer), but a pure sample of the 2-chloro compound was not isolated (see the Gomberg Reaction under Experimental). The 3-bromo derivative of diphenyloxazole had a higher value (0.45) than the

4-isomer (0.28), but this value was much lower than any of the chloro derivatives.

Miscellaneous halogen derivatives of other systems reflect this same general trend. The ortho-substituted compounds are regularly the poorest solutes. Once again it is interesting to recall in this respect the postulation[27] of continuous resonance throughout the system as an important criterion of an efficient scintillator. The interference with coplanarity of a chain-type polyaromatic molecule caused by an ortho-substituent would have increasing significance as the substituent increases in size. The small fluorine atom in compound 237 has no detrimental effect.

Another possibility worthy of consideration is the ease of bond rupture by high-energy radiation, especially in the case of the carbon-iodine bond. It has also been shown[180] that organic iodides absorb ultraviolet light at wavelengths only slightly below the wavelength of the photon emission of solution scintillators.

Among the oxygen-containing functions, those having an oxygen attached to another element by a double-bond are all detrimental to scintillation. None of the nitro derivatives tested has shown any response, and the only carbonyl

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[180] E. L. Cochran, W. H. Hamill, and R. R. Williams, Jr., J. Am. Chem. Soc., 76, 2145 (1954).

derivatives which were found to scintillate are anthranilic acid and the dialkylaminocoumarin of Arnold (compound 133). Each of these compounds also contains an amine function, which undoubtably contributes to the observed scintillation.

The phenolic derivatives examined thus far are uniformly poor solutes. The three hydroxydiphenyloxazoles screened have low values, as does 4-hydroxy-p-terphenyl. An added difficulty is the low solubility of these derivatives in toluene.

Little investigation of compounds with an hydroxy function on a side chain has been carried out, but one example in Table 2 (compound 406, RPH 0.84) would make it appear as though these compounds are superior to the phenolic types, and they are considerably more soluble in toluene.

Values reported for methoxy derivatives are most encouraging in nearly every instance. The methoxyphenyloxazoles are particularly outstanding. All the various combinations and isomers screened by Hayes and his coworkers[27] have values above 0.95, and one, 5-(4-biphenylyl)-2-(4-methoxyphenyl)oxadiazole, has an exceptionally good relative pulse height of 1.24. Simple methoxy-substituted biphenyls (compounds 150, 151, and 154) have been shown to scintillate. Phenanthrene gives some response when substituted with methoxy groups (compound 155). Dibenzofuran becomes an active molecule with this substituent (compounds 149, 152, 153, and 284). A remarkable increase is noted in the instance of the two

bidibenzofurans (compounds 44 and 149). The relative pulse height is increased from 0.14 to 0.46 in the case of the molecule with a methoxy group on each dibenzofuran nucleus. An increase from 0.50 to 0.59 is also noted in the two quinoline compounds (136 and 141), which must be attributed to the methoxy function in the 6-position of the former.

Up to the present time alkoxy derivatives of scintillation solutes other than methoxy have not been investigated, but they have good potential in view of the results with methoxy compounds and the characteristic facile solubility of the higher homologs.

Aryl ethers have good solubility and spectral characteristics, but only three examples have been screened (compounds 51, 64, and 65). The values for these three molecules (< 0.10, 0.16, and 0.16, respectively) are not impressive, but the third compound, 4-biphenylyl phenyl ether, is an interesting molecule from the standpoint of its relationship to p-terphenyl. The observed decrease in scintillation efficiency brought about by separation of the rings with an oxygen atom is surprisingly great. The nitrogen analog, N-(4-biphenylyl)aniline (compound 49), has a relative pulse height of 0.63, and the carbon analog, 4-benzylbiphenyl (compound 37) has no measurable response. The temptation to speak of these values in terms of resonance between rings via the atom separating the rings makes the latter two examples reasonable,

but hardly accounts for the poor value of the ether. Previously there has been no mention of the hydrogen atom of secondary amines as a factor in the scintillation process, but the high value of this amine and the much lower response (0.39) of (4-biphenylyl)diphenylamine (compound 53) tend to leave an impression in this direction. Another example is the case of the two amines 72 and 73, in which the secondary amine has a value of 0.95 even though there are only two benzene rings joined directly to one another. The other, bis(4-biphenylyl)phenylamine, has a relative pulse height of 0.61.

Amine functions of all types appear to have interesting effects on scintillation. The primary amine derivatives of good solutes (compounds 9, 10, and 13) seem to have a slight, adverse effect on the values, but there are isolated examples (compounds 11, 12, and 18, RPH 0.49, 0.51, and 0.48, respectively) in which the primary amine function seems to contribute to efficient light production.

The single example of a secondary amine with both alkyl and aryl groups is N-methylanthranilic acid which has a value (0.44) nearly the same as anthranilic acid (0.48). Both are remarkable in that no other carboxylic acid has been found to scintillate.

Dimethyl- and diethylamino functions are the most interesting of all. There is a myriad of derivatives listed in Table 2 from which a few generalizations are apparent. In

most of the molecules which contain less than three aromatic rings, that are otherwise inefficient solutes, the substitution of a dialkylamino function enhances the pulse height. Sometimes this increase in considerable, such as the case of the two compounds reported by Arnold[34] (133 and 162). Replacement of hydrogen by a dialkylamino group in some of the systems which have been previously established as excellent solutes does not enhance the efficiency of these compounds and in two cases (138 and 164) decreases efficiency to a small extent.

Some isolated examples of the effect of this substituent are interesting. 4-Dimethylamino-3-isopropylphenol (compound 160, RPH 0.10) is the only substance, other than anthranilic acid and its N-methyl derivatives, that has a single aromatic ring and gives a measurable response. Three pyridine derivatives (76, 139, and 165) are interesting in view of the fact that 2-phenylpyridine does not scintillate at all. The decrease from 0.80 to 0.45 between the dimethylamino derivative and the diethylamino is far out of line for the slight structural difference, and is very likely the result of trace impurities in the latter compound. Either a pronounced spectral change or interference with the resonance stability of the activated intermediate may be responsible for the drop to 0.15 observed for the 2,6-disubstituted compound (76). Such changes are rather common in m-substituted aromatic systems.

The exceptional value of 0.79 for 3-dimethylaminodibenzofuran (compound 159) is unfortunately isolated. Screening of the corresponding derivatives of biphenyl, fluorene, carbazole, and dibenzothiophene would certainly be rewarding.

The only attempt at a theoretical explanation for the unusual properties of dialkylamino derivatives is the discussion[31] of the effect of absorption intensity on the lifetime of the excited state of the scintillator molecule. The great increase in fluorescence is attributed to a decreased lifetime of the excited intermediate, which sharply reduces the probability of internal quenching. The lifetime of the excited intermediate is shortened by the increased intensity of absorption. This reasoning adds strength to the conclusion that functions such as dialkylamino increase the pulse height of poor scintillator molecules, but have little or no effect on good solutes. Molecules which are poor solutes are precisely those which have some structural feature capable of quenching fluorescence. When this effect is overcome, the compound may be an efficient solute. In the case of the better scintillator solutes there is no internal quenching with which to be concerned, and consequently, no increased efficiency brought about by a shorter-lifetime excited state.

Aryl derivatives of the other elements of Group VB have failed to show any fluorescence. The tris(4-biphenylyl) derivatives of phosphorous, arsenic, and antimony do not

scintillate even though tris(4-biphenylyl)amine is reasonably efficient (RPH 0.58).

Metals and Metalloids

Two interesting series of compounds containing elements of Group IVB have been prepared and screened. The first (compounds 454, 455, 456, and 457) serves to incorporate the four elements beyond carbon into the p-terphenyl molecule. The effect of these metals is pronounced and consistent. With three phenyl groups and one p-terphenylyl moiety bonded to the metal, the relative pulse height decreases through the series silicon, germanium, tin, and lead from 0.89 to 0.73, 0.38, and <0.10. In an earlier quenching study[20] employing the tetraphenyl derivatives of these elements, it was reported that silicon and germanium were "mild quenchers" while tin and lead were "strong quenchers." The values of the p-terphenylyl derivatives indicate the silanes are not quenchers at all. This is brought out more clearly by the value of 1.11 for compound 456 at 10 g./l.[35] Self-quenching at higher concentrations is a characteristic of all the most efficient scintillators with a wide solubility range. The values for the other three compounds in this series would appear to classify the metals as mild, strong, and very strong quenchers, respectively. Further investigation of the other three p-terphenylyl-

phenyl combinations of silicon (compounds 201, 374, and 428) substantiates the impression that the silicon atom is not detrimental to scintillation. The only low value (0.22 for compound 428) was measured on a saturated solution of the material in toluene; the solubility limit is only 0.2 g./l.

The other series of interest is that of the novel cyclic compounds of Group IVB elements. Although these compounds show little prospect of practical application as scintillation solutes, a few observations are evident. As noted in the general discussion of ring systems, the cyclic systems containing a phenyl-phenyl linkage give a measurable pulse height while those with an oxygen or sulfur bridge (phenoxasilin and phenothiasilin) do not. It is also interesting that triphenylmethane, tetraphenylmethane, and tetraphenylsilane all fail to fluoresce, but 9-phenylfluorene, 9,9-diphenylfluorene, 9,9'-spirobifluorene, 5,5-diphenyldibenzosilole, and 5,5'-spirobi[dibenzosilole] give values between 0.14 and 0.18. The silicon atom in these molecules appears to have no more detrimental effect on scintillation than carbon. 5,5'-Spirobi[dibenzogermole], however, does not fluoresce.

Various aromatic systems containing other elements, such as boron, arsenic, selenium, and iron, have also been screened with no success, but none of these elements has been included in a molecule with a sufficiently extensive aromatic system to

provide a basis for a positive statement regarding their effect on fluorescence.

Synthetic Methods

Direct substitution of p-terphenyl in order to introduce functional groups of interest is of little or no utility. The two most useful reactions, nitration and bromination, apparently fail for the same reason. The nucleus is easily di- or trinitrated and dibrominated, but attempts to limit either of these reactions to the monosubstituted derivative have failed. The general nature of the molecule is undoubtedly of importance in this respect. The introduction of a substituent, even an electron withdrawing group like $-NO_2$, in the 4-position seemingly does not effect the 4''-position, although the resonance structure (VII) would predict deactivation

VI VII

toward electrophilic reagents. Experimental results indicate that this deactivation cannot operate through such an extensive

system, but there is no obvious reason why structure VI should be more susceptible to substitution than the hydrocarbon. The only convenient distinction in reactivity is the greater solubility of VI in the nitrating mixture than the hydrocarbon, and consequent greater contact with the reagent.

A similar situation predominates in bromination. When the temperature of the reaction mixture is sufficient to dissolve a significant quantity of p-terphenyl and initiate the reaction, the 4-bromo-p-terphenyl formed is at least equally soluble and equally reactive. The result is a mixture of unsubstituted hydrocarbon and the mono- and dibromo derivatives. As a result of the polar nature of the functional groups, 4,4''-dinitro-p-terphenyl is probably much more soluble in the strong acid medium than the hydrocarbon and is further substituted.

Of the other general methods employed in this investigation, the Gomberg reaction appears to be the most simple and direct. The nitrosation procedure developed by France, Heilbron, and Hey[156] permits one to carry out all three steps (acetylation, nitrosation, and coupling) without isolation of an intermediate. There is little question of the superiority of this process for simple phenylation of an aromatic amine. Unfortunately attempts to introduce versatility into the reaction destroy the simplicity. The coupling is completely random and affords a single product only in the case of a

symmetrical molecule to be coupled. Resolution of isomeric mixtures is a difficult process with large polyaryls, as the hydrocarbon structure of the molecule begins to dominate the physical properties, and the position of the substituent does not provide an outstanding difference in solubility.

The syntheses of 4-fluoro- and 4-chloro-p-terphenyl by this method provide a good example of this difficulty. In both cases the 4-substituted derivative was sufficiently less soluble than the other two isomers to provide separation and purification. In the first case the crude separation itself was unusually complicated, and final purification required extensive recrystallizations. The other two isomers could not be separated from each other and from remaining small amounts of 4-fluoro-p-terphenyl. In the latter instance the 4-isomer was separated rather easily, but the 3-isomer was very difficult to free from remaining amounts of the other two. Changes in the aromatic substitution bands (12-13.5μ) of the infrared spectra after each successive recrystallization provided an excellent means by which the stages of purity could be estimated. 2-Chloro-p-terphenyl was not isolated in the pure state.

Even with these difficulties it can be seen that this reaction is a source of small amounts of some materials inaccessible by other routes. The reaction is, of course, well suited to the preparation of 2,5-disubstituted derivatives

from a p-disubstituted benzene. A further improvement suggested by France, Heilbron, and Hey[181] is the use of nitrosyl chloride, which would reduce the hours required for nitrosation to minutes.

The speed of reaction and relative simplicity of work-up in the formation of polyaryls from lithium reagents make these compounds fine intermediates in the preparation of many potential scintillation solutes. The versatility of organometallic reagents is so broad in scope as to make a detailed discussion prohibitive. The methyl-p-quaterphenyls prepared from p-terphenyl-4-yllithium and 4,4'-biphenylenedilithium[67] are excellent solutes, and the method employed is nearly as general as the variety of cyclohexanones available. While some simple derivatives, such as nitro, fluoro, and chloro, are not available from the organolithium reagent, the acid obtained on carbonation of p-terphenyl-4-yllithium is a potentially useful intermediate, especially by way of the acid halide.

There appeared to be four routes to the synthesis of 4-dimethylamino-p-terphenyl, a molecule of considerable interest in this work.

The Gomberg reaction between N-nitroso-4-acetamidobiphenyl and dimethylaniline, which seemed to be the most

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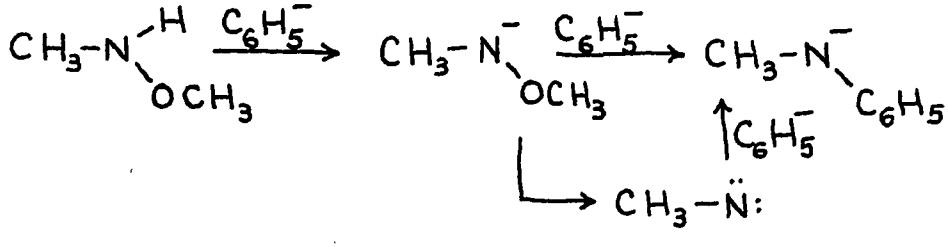
[181]H. France, I. M. Heilbron, and D. H. Hey, J. Chem. Soc., 369 (1940).

obvious approach, produced only a dark red oil which could not be resolved.

Condensation of p-dimethylaminophenyllithium and 4-cyclohexylcyclohexanone, followed by dehydration, afforded a poor yield of the expected olefin. Attempted dehydrogenation of this compound with selenium produced a mixture of products from which the only pure material isolated was 4-amino-p-terphenyl. A search of the literature concerning sulfur and selenium dehydrogenation revealed that there had been no previous observation of N- or O-dealkylation as a side reaction in this type of oxidation. The parallel, however, with dealkylation by hydrogen iodide is obvious. Two attempts to determine the generality of this reaction were made. The first, employing tetralin as both solvent and source of hydrogen selenide, was unsuccessful because of the failure to generate the gas at the temperature of refluxing tetralin. The second, employing a dicyclohexenylbiphenyl with selenium, also failed to bring about the demethylation of tetramethylbenzidine. Hydrogen selenide was generated in this latter case as evidenced by the formation of quaterphenyl in the reaction mixture and the deposit of selenium in an hypochlorite absorption tower connected to the outlet at the top of the condenser.

An attempt was made to carry out a displacement of methoxide ion from N,N-dimethylmethoxyamine using p-terphenyl-4-yllithium. The failure of this reaction led to an

investigation of the formation of amines from the reaction of organometallic reagents with methoxyamine. Phenyllithium affords good yields of aniline and N-methylaniline with methoxyamine and N-methylmethoxyamine, respectively, but could not be made to react with N,N-dimethylmethoxyamine. Apparently the initial proton abstraction must then be essential to the reaction. The reaction may then proceed through facile loss of methoxide aided by the approach of the carbanion. The alternative mechanism is suggested by the postulation by Stieglitz[182] of an electron-deficient nitrogen as an intermediate in the Hofmann and Curtius reactions. The loss of methoxide ion in the case of N-methylmethoxyamide would leave "methylimine" (or "methylnitrene" by analogy to carbene intermediates). Subsequent attack by phenyllithium would produce the lithium salt of N-methylaniline.



(Eq. 5)

An attempt was made to establish the presence or absence of this reactive intermediate by running the reaction with one

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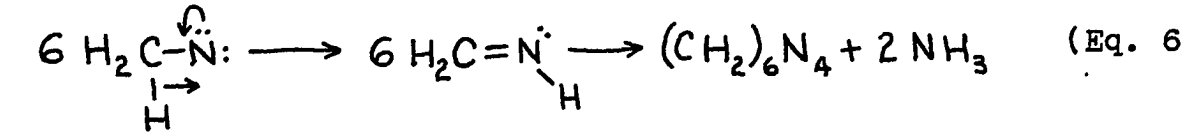
[182]J. Stieglitz, Am. Chem. J., 29, 49 (1901).

equivalent of phenyllithium in the presence of an excess of a nucleophilic reagent presumed to be too weak to displace methoxide from the initially formed anion. It was reasoned that methylimine would react with simple olefins such as cyclohexene to produce the cyclic imine, N-methylcyclohexenimine in this case, but the reaction did not take place. A second possibility was the formation of N-methyl-P,P,P-triphenylphosphinimide by generation of methylimine in the presence of excess triphenylphosphine. Staudinger and Hauser[183] isolated this product from the reaction of methyl azide with triphenylphosphine. Again the product was not isolated. In this reaction, however, evolution of a gas was observed during addition of phenyllithium to the alkoxyamine solution, and a trace of hexamethylenetetramine was isolated. This material could result from a shift of hydride ion from carbon to nitrogen in the intermediate, followed by loss of ammonia in a manner similar to that undergone in the preparation of this compound from ammonia and formaldehyde.



(Eq. 6)

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[183] H. Staudinger and E. Hauser, Helv. Chim. Acta, 4, 861, (1921).

4-Dimethylamino-p-terphenyl was formed, though in very poor yield, from 4-bromo-p-terphenyl and lithium dimethylamide in tetrahydrofuran. The reaction did not proceed in ether or in ether-benzene.

With the intention of extending polyaryl synthesis by the organometallic process to the fluorene molecule, 2-bromofluorene was prepared and conditions for halogen-metal-interconversion investigated. In spite of the fact that previously described conditions for metallation of fluorene involve 16- to 18-hour reflux periods,[173,184,185] and the halogen-metal-interconversion of aryl bromides is generally complete in 10-15 minutes, 2-bromofluorene was metallated in the 9-position in high yields at 30°, 0°, -30°, and -70° in a very short time. After carbonation there was no evidence of fluorene-2-carboxylic acid (from interconversion) or fluorene-9-carboxylic acid (from metallation by the interconversion product, followed by metallation of the resulting fluorene), 2-bromofluorene-9-carboxylic acid being the only product isolated. The Grignard reagent was prepared from 2-bromofluorene in 12% yield in refluxing tetrahydrofuran. As previously observed by Miller and Bachman, "2-Bromofluorene does not

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[184]H. Gilman, R. A. Benkeser, and G. E. Dunn, J. Am. Chem. Soc., 72, 1690 (1950).

[185]H. Gilman and J. W. Morton, Jr. in R. Adams, ed., "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 265.

react with lithium or magnesium in boiling ether or ether—xylene."[173]

Suggestions for Future Research

There remain three important hydrocarbon scintillation solute systems that require investigation. The first is the arylated derivatives of fluorene. 2-Phenylfluorene, for example is an analog of p-terphenyl in which the methylene bridge would provide increased solubility and fix two of the rings in a plane. The second is the series of unsaturated derivatives of good solutes. The cyclohexene derivatives, prepared as intermediates in the route to quaterphenyls, were good scintillators even before aromatization. The third system is the series of long chain alkyl derivatives, which would be expected to provide good solubility in large aromatic systems.

There are potentially a number of phenylated heterocycles which could be modeled on the p-polyphenyls. 3-Phenyl- and 3,7-diphenyldibenzofuran are interesting analogs of p-terphenyl and p-quaterphenyl, respectively. Both could be prepared by the Gomberg reaction if the required amines are made available. The convenient synthesis of benzoxazoles and benzimidazoles suggested by Hein, Alheim, and Leavitt[120] introduces

two new systems in which the whole range of functional derivatives could be re-examined.

Further work with the alkoxy and dialkylamino functions is indicated. Longer alkyl chains will surely be of interest. Cyclic amino derivatives, pyrrolidyl and piperidyl for example, have not been screened as yet, but are dialkylamino derivatives in the broad sense. Monoalkylamino functions offer another series of importance in view of the superiority of secondary aryl amines over corresponding tertiary compounds.

The isolated instance of hydrogen selenide dealkylation merits further investigation. Aromatization with selenium and sulfur is a generally accepted reaction used in structure determination and proof. In view of this important use it is necessary that research workers be aware of all potential side reactions that may lead to erroneous conclusions.

Better insight into the nature of the intermediates in the organometallic-alkoxyamine reaction is a necessary requisite to its general synthetic application. Related reactions of chloroamines surely proceed by the same path and offer a greater variety of starting materials.

The enhanced reactivity of metals and metal amides in tetrahydrofuran, as evidenced by the preparation of 2-fluorenylmagnesium bromide and 4-diethylamino-p-terphenyl, presents the fundamental idea for a whole new concept of the role of the solvent in organometallic reactions.

A final suggestion concerns the physics involved in quenching of scintillation. The effect of high energy radiation on chemical bonds is a field of current interest in physics and physical chemistry. It is reasonable to expect that quenching by heavy metal atoms is very likely related bond distortion of some type as there is apparently no interference with fluorescence.

SUMMARY

An history of investigations into the nature of the scintillation process was presented. All solvents and solutes screened for potential scintillator application were tabulated. Previously employed methods of synthesis of chain-type polyaryls and derivatives were reviewed.

Several new compounds of this general type were synthesized by a variety of methods, and their properties examined.

Correlations between the constitution and scintillation ability of these compounds were discussed with reference to ring systems and functional groups.

The general methods of synthesis employed were discussed with respect to simplicity and versatility.

An unusual dealkylation reaction of hydrogen selenide was encountered and attempts were made to establish its generality.

An attempt was made to determine the nature of the intermediate in the reaction between organometallic reagents and alkoxyamines.

Enhanced reactivity of metals and metal amides in tetrahydrofuran was observed in two instances.

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