1925

I. Organic oxygen antiseptics, II. The constitution of aliphatic diazo compounds, III. Anti-knock compounds

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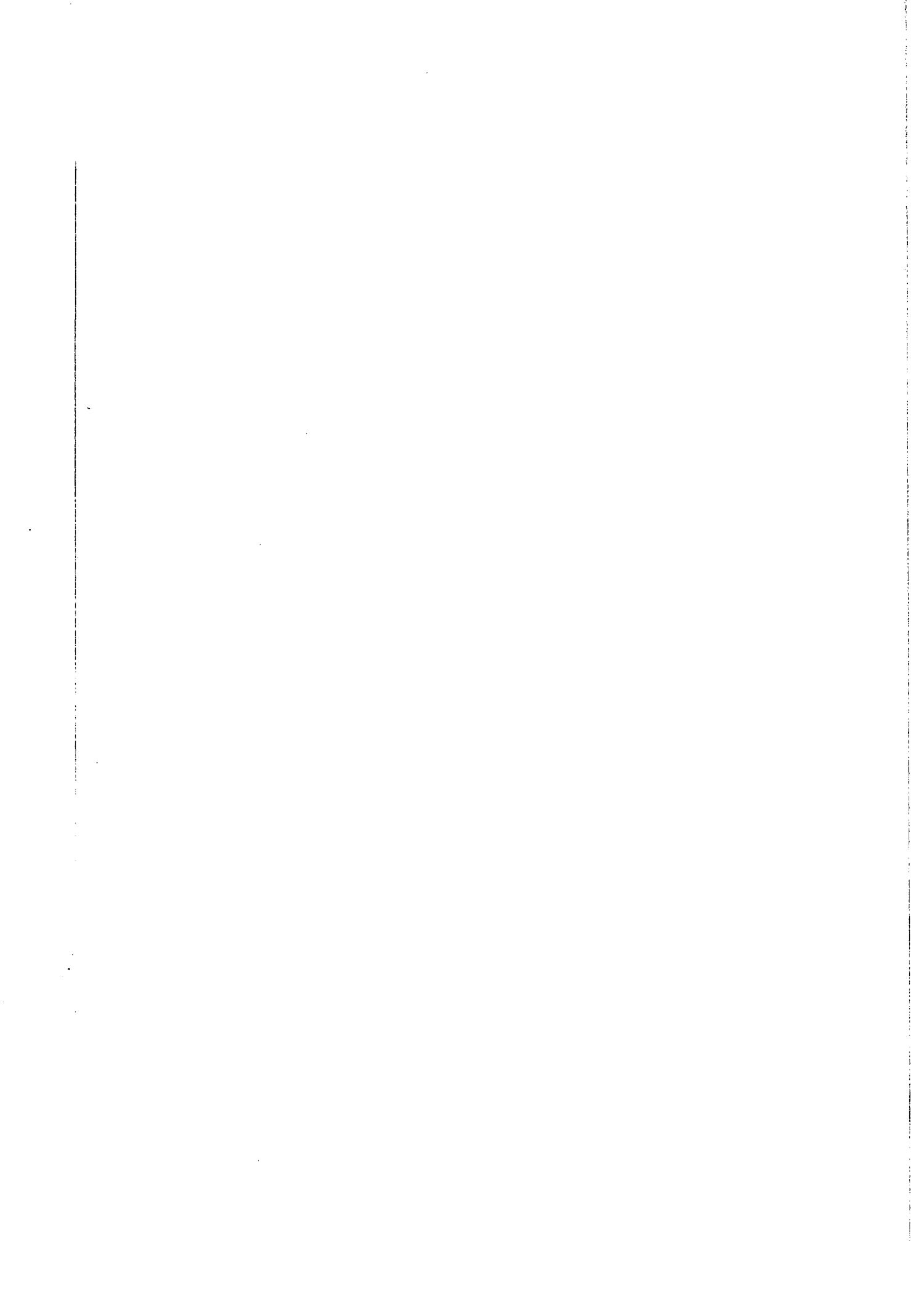
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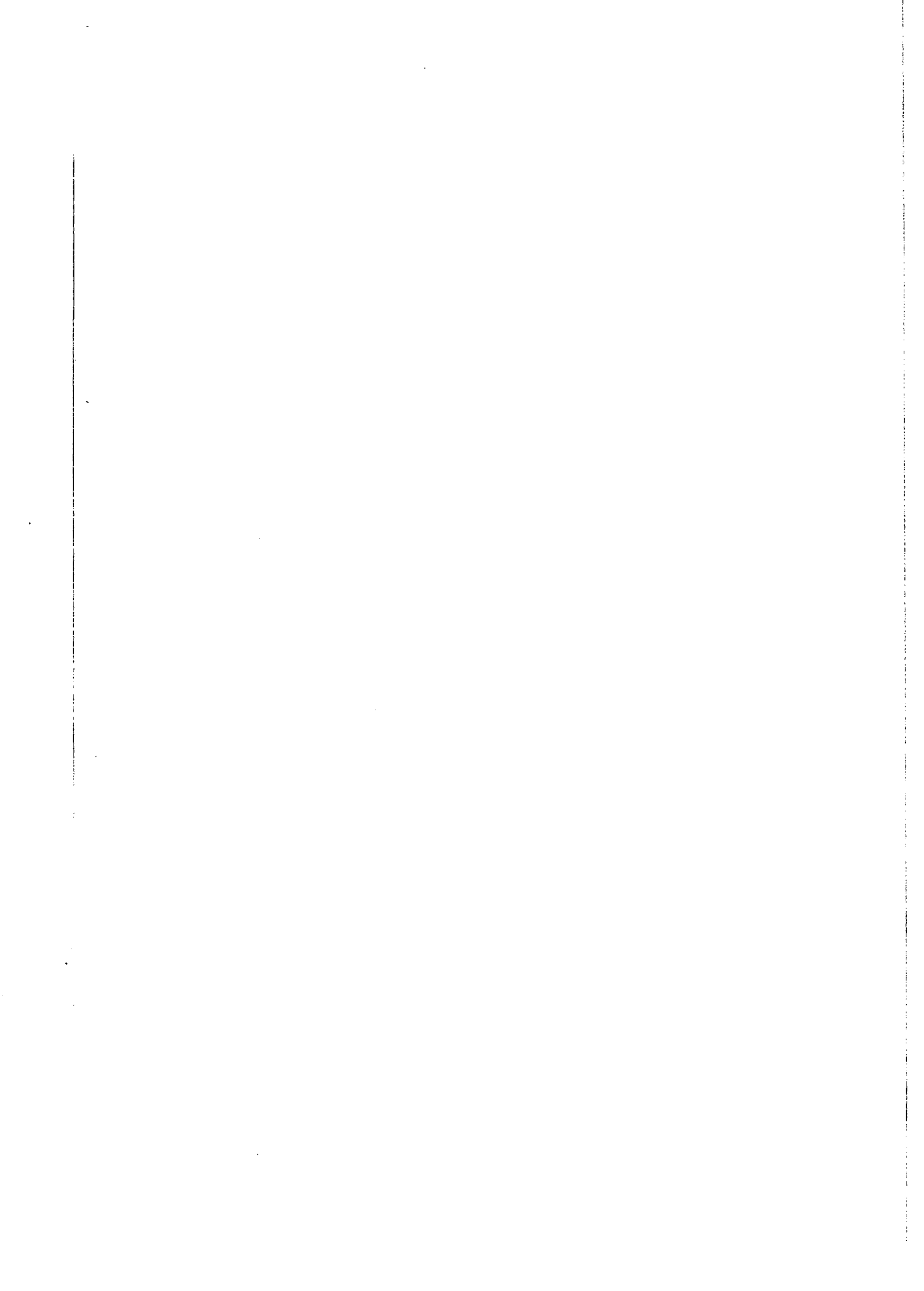
I. ORGANIC OXYGEN ANTISEPTICS

II. THE CONSTITUTION OF ALIPHATIC DIAZO COMPOUNDS

III. ANTI-KNOCK COMPOUNDS

A Dissertation
Submitted to the Graduate
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BY

Chester Elgin Adams

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Graduate Dean

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III.

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PART I.

ORGANIC OXYGEN ANTISEPTICS

Introduction

It has long been known that hydrogen peroxide and certain of its derivatives have strong antiseptic properties. The compounds of this type so far known, find application only for external use. It would be highly desirable to prepare a peroxide possessing the same bactericidal action but to a somewhat lesser degree. Such a compound might lend valuable aid in combating pathogenic organisms, especially if it was suitable for internal use.

As the result of attempts to prepare new oxygen antiseptics, an investigation has been made of the reaction between some typical organic peroxides and the Grignard reagent.

Theoretical

Reaction does not take place with every peroxide, and the rate of reaction varies appreciably with different peroxides. The following is a general expression of the course of reaction:

$$ROOR + R'MgX \longrightarrow ROR' + ROMgX \quad \dots\dots\dots\dots\dots\dots(I)$$
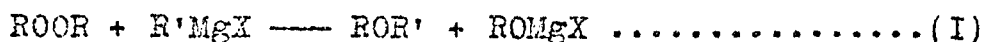
Wuyts (1) has reported an analogous reaction between disulfides and the Grignard reagent. Studies have been made on the reaction between hydrogen peroxide and organomagnesium halides. Oddo (2) obtained a variety of alcohols from the reaction between a concentrated hydrogen peroxide solution in water and alkylmagnesium halides. Durand and Naves (3) got an 80% yield of phenylhydroxylamine from the reaction between bromomagnesium aniline ($C_6H_5NHMgBr$) and hydrogen peroxide. Inorganic peroxides with phenylmagnesium bromide give phenol in a yield smaller than that obtained from dry oxygen (4).

With equivalent molecular quantities of dibenzoyl peroxide and RMgX compound the splitting reaction represented in (I) takes place. When an excess of Grignard

1. Wuyts, Bull. soc. chim., 35, 166 (1906). He predicted a like reaction with diselenides and also probably with peroxides.
2. Oddo and Binaghi, Gazz. chim. ital., 51, II, 343 (1921). C. A. 16, 1424 (1922).
3. Durand and Naves, Compt. rend., 180, 521 (1925).
4. Unpublished results of work done by Agnes Wood.

reagent is used the phenyl benzoate that is first formed undergoes the normal reaction of esters and RMgX compounds and a tertiary alcohol (5) is formed, namely, triphenyl carbinol. Gelissen and Hermans (6) found recently that a small amount of phenyl benzoate in addition to other compounds is obtained when dibenzoyl peroxide is heated in benzene. However, all experiments in this work with dibenzoyl peroxide were carried out at low temperatures (0° to -5°) because of the vigor of the reaction. Significant quantities of phenol were also obtained.

Succinic peroxide (7) underwent no reaction with phenylmagnesium bromide. This may be due in large part to the insolubility of this peroxide in solvents that are insensitive towards RMgX compounds. Attempts to force the reaction at moderately elevated temperatures invariably resulted in rapid decompositions that approximated mild explosions.

5. Although good yields of tertiary alcohols are obtainable, the reaction merits little consideration from a synthetic viewpoint. Un published results show that acid chlorides, from which peroxides are prepared either directly or indirectly, give better yields of tertiary alcohols when treated with RMgX compounds.
6. Gelissen and Hermans, Ber., 58, 285 (1925)
7. The author wishes to express his appreciation to Frederick Stearns and Co., of Detroit for ample supplies of this compounds.

Triacetone peroxide with an excess of phenylmagnesium bromide gave, in addition to a large amount of phenol, the tertiary alcohol that results from the reaction between acetone and phenylmagnesium bromide.

Diethyl peroxide underwent an unusual reaction in the sense that large amounts of diphenyl were formed. However, the typical splitting reaction (I) also took place. Diethyl peroxide is not to be confused with the ether peroxide $(CH_3C(H)(OOH)(OC_2H_5))$ described by Clover (8) in his work on the autoxidation of ether. This peroxide or its products of decomposition (acetaldehyde, in particular) give secondary alcohols with Grignard reagents (4).

Triphenylmethyl peroxide does not react to any appreciable extent under ordinary conditions with phenylmagnesium bromide. When the reaction is carried out at elevated temperatures the triphenylmethyl peroxide undergoes the known high temperature rearrangement to tetraphenyl-sym-diphenoxyethane $((C_6H_5)_2C(OC_6H_5)-)_2$. It is interesting to recall in this connection that Wuyts (1), in some preliminary experiments, found no reaction between the Grignard reagent and disulfides of high molec-

8. Clover, J. Amer. Chem. Soc., 44, 1107 (1922).

ular weight like benzhydryl disulfide $((C_6H_5)_2CHSSCH$
$(C_6H_5)_2)$ and bornyl disulfide.

It has long been known that oxygen produces chemi-
luminescence with arylmagnesium halides, in particular (9).
Those peroxides (dibenzoyl, triacetone and diethyl) that
react with phenylmagnesium bromide also give rise to the
phenomenon of chemiluminescence.

9. Evans and Dufford, ibid., 45, 278 (1923); Dufford,
    Calvert and Nightingale, ibid., 45, 2058 (1923);
    and, most recently, Dufford, Nightingale and Calvert,
    ibid., 47, 95 (1925).

Experimental

In the experiments with benzoyl peroxide the Grignard reagent was added slowly to a solution of the peroxide in benzene cooled to 0 to -5°. Reaction took place at once and the mixture was hydrolysed by dilute hydrochloric acid. The ether-benzene layer was separated; washed with dilute alkali to remove phenol and benzoic acid; dried over sodium sulfate; concentrated by distilling most of the ether and benzene in a vacuum; and the products were then worked up by crystallization or vacuum distillation. The alkali washings were acidified to obtain phenol and benzoic acid.

Varying conditions were used for the other peroxides.

All yields are based on the original quantities of peroxides.

TABLE I.

REACTION OF PEROXIDES WITH GRIGNARD REAGENTS.

PEROXIDE	MOLES	RX COMPOUND	MOLES[e]	COMPOUNDS FORMED (YIELD %)
Dibenzoyl[b]	.416	Bromobenzene	.41	Phenyl benzoate (28%); Benzoic acid
Dibenzoyl	.416	Bromobenzene	.82	Phenyl benzoate (3.6%);Triphenyl carbinol(23%)[c]
Dibenzoyl	.2	Ethyl bromide	.25	Ethyl benzoate (10%)[d]
Dibenzoyl[e]	.083	n-Butyl bromide	.43	Di-n-butyl phenyl carbinol (72%)
Dibenzoyl	.04	Benzyl chloride	.2	Dibenzyl phenyl carbinol (73%)[f]
Succinic	.2	Bromobenzene	.2	- - - - - - -
Triacetone	.09	Bromobenzene	.8	Dimethyl phenyl carbinol (25%) Phenol (66%)
Diethyl	.5	Bromobenzene	.63	Phenetole (84%); Diphenyl (30%)[l]
Triphenyl-methyl[j]	.03	Bromobenzene	.05	- - - - - - -

(Footnotes for Table I)

a. The quantity of RMgX used was approximately that actually present (Gilman and McCracken, J. Amer. Chem. Soc., 45, 2462 (1923)).

b. The yield of benzoic acid was 70 g. This high yield is due undoubtedly to the hydrolysis of some unchanged benzoyl peroxide.

   In an earlier experiment there was no evidence of reaction when phenylmagnesium bromide was added to an equivalent of peroxide in benzene-ether solution cooled by immersion in carbon dioxide snow in ether.

   In another experiment, carried out at about $-5°$, the precipitated reaction product in the red colored medium was extracted with benzene prior to hydrolysis. Concentration of this benzene solution gave phenyl benzoate. The solid residue after extration with benzene was practically pure bromomagnesium benzoate ($C_6H_5CO_2$ MgBr). This was determined from the weight of benzoic acid obtained on acidification.

c. 50 g. or 98% of benzoic acid was also obtained, in addition to 10 g. or 28% of phenol. The phenyl benzoate was obtained from an oil which might have contained, in addition, some benzophenone.

   A 50% yield of triphenyl carbinol was obtained when phenyl benzoate was treated with 4 equivalents of phenylmagnesium bromide under the approximate conditions of the peroxide experiment.

d. In addition some unchanged benzoyl peroxide was recovered.

e. The peroxide in benzene was added to the RMgX compound, and after standing over night the mixture was refluxed for an hour. 8.4 g. or 80% of benzoic acid was also obtained.

   The di-n-butyl phenyl carbinol was compared with the product obtained from the reaction between ethyl benzoate and n-butylmagnesium bromide. The constants of the two compounds agreed: b, 125-126° (7 mm.); $d_4^{?}$, 0.9319; n_D^{31}, 1.4824. At room temperatures the tertiary alcohol is a thick colorless oil. The temperatures recorded in this paper are uncorrected.

f. The dibenzyl phenyl carbinol melted at 84-85° and was confirmed by a mixed melting point determination with the same compound prepared according to Klages and Heilmann, Ber., 37, 1456 (1904).

g. In one experiment, the reaction mixture was refluxed in ether for 16 hours. The only product obtained was a very small amount of an alkali soluble compound that crystallized in long needles and melted at 90-94°. This compound may have been the monophenyl ester of succinic acid. A repeat experiment wherein refluxing was carried out for 18 hours in benzene-ether gave no solid product.

 The ether was largely replaced by anisole in a third experiment, and after heating for several hours at 95° sudden decomposition took place. On working up the solid reaction product a small amount of a solid was obtained that melted at 199° when recrystallized from acetone. A mixed melting point determination showed this compount was not α,δ -dihydroxy-$\alpha,\alpha,\delta,\delta$-tetraphenyl butane $((C_6H_5)_2C(OH)CH_2CH_2C(OH)(C_6H_5)_2)$. It is possible that the 199° compound may be a dehydration product of the dihydroxy butane: namely, tetraphenyl butadiene that melts at 202°.

 The obvious inertness of succinic peroxide in its reaction with phenylmagnesium bromide is not to be confused with its great instability at elevated temperatures. In several experiments a violent explosion took place when the reaction mixture was heated between 110-120°, even though the temperature was not permitted to rise above 110°.

h. No reaction takes place in ether and the peroxide is recovered. In one experiment, benzene was added to the reaction mixture and before most of the ether had been removed by distillation violent decomposition set in.

 In a third experiment the ether was replaced in large part by anisole. To this solution of the RMgX compound there was added an anisole solution of the peroxide. The peroxide was added slowly with stirring because of the vigor of the reaction. Subsequent to acid hydrolysis and alkali extractions to remove phenol, the ether layer was vacuum distilled.

i. The peroxide was added slowly with rapid stirring and at room temperature to the ether solution of phenylmagnesium bromide. In addition to phenetole and diphenyl,

less than one-half a gram of phenol was obtained. Phenetole was identified by its boiling point, density, refractive index and a mixed melting point with p-nitrophenetole.

In another experiment where 0.3 moles of peroxide and 0.67 moles of phenylmagnesium bromide was used, 35% of phenetole and 18% of diphenyl were obtained. Diphenyl was identified in both experiments by mixed melting point determinations.

j. After refluxing in an ether-benzene mixture at about 75° for 5 hours, 85% of the triphenylmethyl peroxide was recovered. In addition, a small quantity of a dark red oil was obtained.

A second experiment was carried out in boiling toluene for four hours. The chief product obtained after hydrolysis was tetraphenyl-sym-diphenoxyethane. This was identified by a mixed melting point with the same compound prepared according to Wieland, Ber., 44, 2550 (1911). The residual red oil in the first run very probably contained this compound.

CONSTITUTION OF DIETHYL PEROXIDE

Several formulas have been proposed for hydrogen peroxide. Closely related to these are the formulas suggested for organic peroxides. In his study of the reaction between hydrogen peroxide and RMgX compounds, Oddo (2) has considered the following formulas for hydrogen peroxide:

$$H-O-O-H \qquad\qquad H-O\overline{=}O-H \qquad\qquad O=O=H_2$$
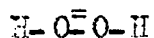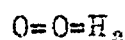
$$\text{(A)} \qquad\qquad\qquad \text{(B)} \qquad\qquad\qquad \text{(C)}$$

Oddo admits that no decisive answer concerning the constitution of hydrogen peroxide can be made as yet. On the basis of his work he inclines towards formulas (B) and (C). He postulates with (B) and one molecule of RMgX compound the following hypothetical addition compound:

$$(MgX)HO=OH(R)$$

In this connection, Gelissen and Hermans (10) have directed attention very recently to some analogies between organic peroxides and azo compounds. Their correlations would probably support formulas (A) and (B), and because of the unsaturated nature of the azo grouping preference might be given to (B).

The only peroxide in the present study that may be interpreted as having formula (B) is diethyl peroxide. The

10. Gelissen and Hermans, Ber., 58, 984 (1925).

unusual quantities of diphenyl formed in the reaction be-
tween diethyl peroxide and phenylmagnesium bromide suggest-
ed at once that an analogy might truly exist between perox-
ides and azo compounds (11). Gilman and Pickens (12) found
that the following reaction takes place between azobenzene
and phenylmagnesium bromide:

$$C_6H_5N = NC_6H_5 + 2C_6H_5MgBr \longrightarrow C_6H_5N(MgBr)N(MgBr)C_6H_5 +$$
$$C_6H_5 \cdot C_6H_5 \dots \dots \dots \dots \dots (II)$$
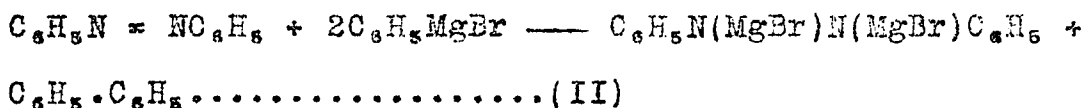
If we admit the correctness of Oddo's conjecture that
addition of RMgX may take place to hydrogen peroxide, and
if we admit also the correctness of the analogy between per-
oxides and azo compounds made by Gelissen and Hermans, then
the following reaction may occur between diethyl peroxide
and phenylmagnesium bromide:

$$C_2H_5O = OC_2H_5 + 2C_6H_5MgBr \longrightarrow C_2H_5O = O-C_2H_5 + C_6H_5 \cdot C_6H_5 \dots (III)$$
$$ MgBr \quad MgBr$$
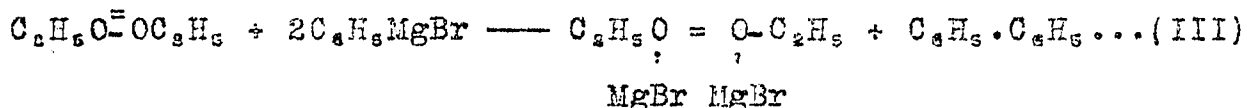
Certain it is that diethyl peroxide behaves differently
towards RMgX compounds than the other peroxides. The forma-
tion of phenetole shows that some of the splitting reaction
of (I) occurs. However, none of the other peroxides gave

11. Porter and Steel, J. Amer. Chem. Soc., 42, 2650 (1920),
    found that the quantity of diphenyl present in the pre-
    paration of phenylmagnesium bromide is not altered by
    passing oxygen through the ether solution
12. Gilman and Pickens, unpublished work.

any more than the usual quantities of diphenyl found in
an ordinary preparation of phenylmagnesium bromide. Fur-
thermore, the quantity of phenol obtained in the experi-
ments with diethyl peroxide is that normally found in the
customary preparation of phenylmagnesium bromide (4,11).
Dibenzoyl and triacetone peroxides gave decidedly signifi-
cant quantities of phenol. · The formation of phenol from
these two peroxides is very probably due in large part to
the reaction between phenylmagnesium bromide and the inter-
mediate compounds containing the phenoxy ($-OC_6H_5$) group,
such as phenyl benzoate when dibenzoyl peroxide is used.
The absence of any conclusive evidence for the direct oxi-
dation of RMgX compounds (such as is observed when oxygen
or air is used) would militate against formula (C) (13).

SUMMARY

The following reaction takes place between peroxides
and the Grignard reagent: ROOR + R'MgX —— ROR' + ROMgX.
The unusual quantities of diphenyl formed in the reaction
between diethyl peroxide and phenylmagnesium bromide suggest
a correspondence in structure between this peroxide and azo
compounds.

The possible importance of new peroxides as antiseptics
has been discussed.

13. An aid to the solution of this problem may be found in
the studies now in progress on the reaction between sul-
fenic esters (R-S-O-R) and the Grignard reagent.

PART II.

THE CONSTITUTION OF ALIPHATIC
DIAZO COMPOUNDS

Introduction.

The first member of the series known as Aliphatic
Diazo Compounds and having the general formula $R_2C = N_2$
was prepared by Schiff and Meissen (1) in 1881; namely, di-
azo camphor from camphorimide. They did not appreciate the
true nature of the compound, so it remained for Curtius
to demonstrate the existence of this very interesting class
of compounds.

In 1883 Curtius (2) succeeded in diazotizing the ethyl
ester of glycocoll, obtaining the now well known diazoacetic
ester. Later he prepared a number of other derivatives of
this new class of compounds, and has been one of the princi-
pal workers in this field.

Immediately following the discovery of diazo acetic es-
ter by Curtius, a number of other investigators turned their
attention to this new class of compounds in an attempt to
throw light on the general structure and mechanism of re-
action. As a result of these many investigations our know-
ledge of this special field of organic chemistry has been

1. Schiff and Meissen, Gazz. chim. ital., 35, 171 (1881)
    Cain, The Chemistry and Technology of the Diazo-com-
    pounds (1920), p. 120.
2. Curtius, Ber., 16, 2230 (1883)

greatly increased. However, in spite of the many researches so far carried out, the question of structure still remains in doubt.

Historical

Curtius showed that the two nitrogen atoms of diazo acetic ester are attached to the carbon, by treating the compound with free iodine, obtaining $\alpha,\alpha,$ diiodo acetic ester and nitrogen, and by reduction to obtain the original glycocoll and ammonia.

$$C_2H_5-O-CO-CH-N_2 + I_2 = C_2H_5-O-CO-CHI_2 + N_2$$

$$C_2H_5-O-CO-CH-N_2 + 5H = C_2H_5-O-CO-CH-NH_2 + NH_3$$
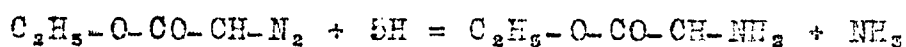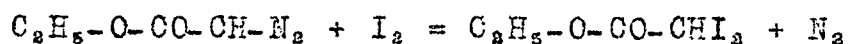
Since both nitrogens were linked to a single carbon he suggested the following configuration (4):

$$\begin{array}{c} R \\ \\ R \end{array} \diagdown C \diagup \begin{array}{c} N \\ \| \\ N \end{array}$$
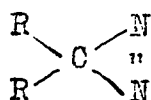
Angeli (5) in 1907 and Thiele (6) in 1911 proposed as a more probable structure, one in which the nitrogen atoms are in a straight chain with one of them pentavalent, thus:

$$\begin{array}{c} R \\ \\ R \end{array} \diagdown C = N \equiv N$$
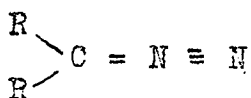
One of the most typical reactions of aliphatic diazo compounds is that in which free nitrogen is eliminated.

3. Curtius, J. prakt. Chem. (2), 38, 401 (1888)
4. Curtius, J. prakt. Chem. (2), 39, 107 (1889)
5. Angeli, Atti accad. Lincei (2), 16, 790 (1907)
6. Thiele, Ber., 44, 2522 (1911)

This takes place, in general, if a member of the series is treated with water, acids, alcohols, amines, and halogens (3), for example:

$$R_2C=N_2 + H_2O = R_2=CHOH + N_2$$

$$R_2C=N_2 + HX = R_2=CHX + N_2$$

$$R_2C=N_2 + ROH = R_2=CHOR$$

Either structure explains the above reactions provided the assumptions concerning intermediate compound formation are allowed. The reactions may be explained by the Curtius formula in three possible ways:

1.

2.   (7).

3.
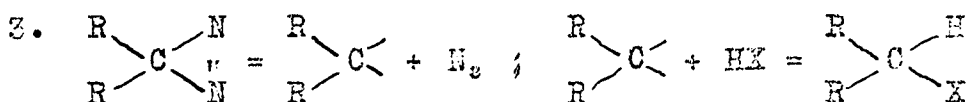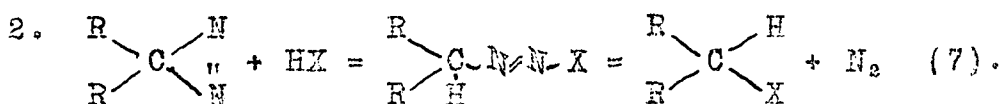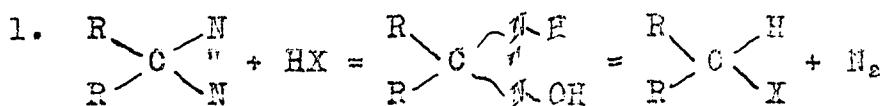
The Angeli-Thiele formula may have addition take place at either of the two unsaturated linkages, but it has been considered to take place at the ultimate and ante-penultimate (8) position. Also dissociation into nitrogen and di-valent carbon, followed by addition, may be assumed as in

7.   Staudinger and Gaule, Ber., 49, 1897 (1916)
8.   Staudinger, Helvetica Chim, Acta, 5, 87 (1922)

the case of the cyclic formula:

1.

$$R_2C=N\equiv N + H_2O = R_2\underset{H}{C}-N=N-OH = R_2C\underset{OH}{\overset{H}{<}} + N_2$$

2.

$$R_2C=N\equiv N = R_2C< + N_2 \;;\; R_2C< + H_2O = R_2C\underset{OH}{\overset{H}{<}}$$
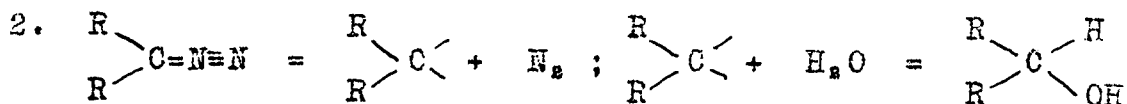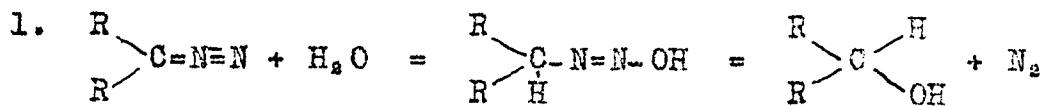
The reactions with ethylenic and acetylenic compounds to form pyrazolines (9)(10)(11) and pyrazoles (12)(13)(14) (15) may also be explained by both structures:

$$R_2C=N\equiv N + RCH=CHR \longrightarrow$$
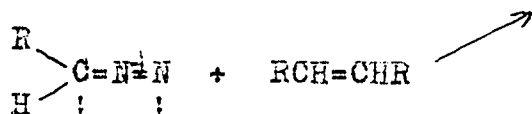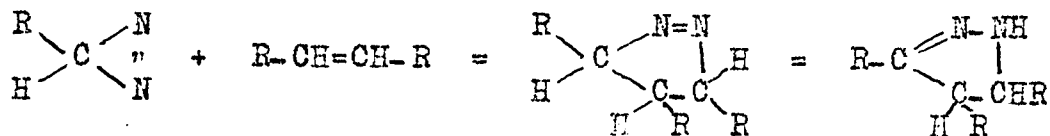
The reaction with acetylenic compounds is interpreted analogously.

From the above discussion it is seen that any reaction that can be explained by ultimate and ante-penultimate addition is of little use in choosing between one or the other of the structures so far mentioned.

9. Buchner and Dessauer, Ber., 26, 258 (1893)
10. Buchner and Feide, ibid., 34, 345 (1901)
11. Darapsky, ibid., 43, 1095 (1910)
12. Buchner, Fritsch, Papendieck and Witter, Ann., 273,226(1893)
13. Von Pechmann, Ber., 31, 2950 (1898)
14. Von Pechmann,and Burkard, ibid., 33, 3594 (1900)
15. Buchner and Lehmann, ibid., 35, 35 (1902)

Aliphatic diazo compounds are easily and smoothly reduced to the corresponding hydrazones (16). There seems to be little doubt but that the structure,

$$\begin{matrix} R \\ \\ R \end{matrix} \Big> C=N-NH_2$$
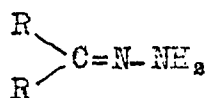
is the correct one (17) rather than the hydrazi configuration,

$$\begin{matrix} R \\ \\ R \end{matrix} \Big> C \begin{matrix} N-H \\ \\ N-H \end{matrix}$$
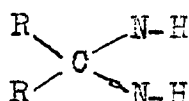
If we are to interpret the reaction assuming the cyclic structure for diazo compounds it is necessary to consider the formation of the hydrazi form as the most probable intermediate compound followed by a rearrangement to the hydrazone, thus:

$$\begin{matrix} R \\ \\ R \end{matrix} \Big> C \begin{matrix} N \\ " \\ N \end{matrix} + 2H = \begin{matrix} R \\ \\ R \end{matrix} \Big> C \begin{matrix} N-H \\ | \\ N-H \end{matrix} = \begin{matrix} R \\ \\ R \end{matrix} \Big> C=N-NH_2$$
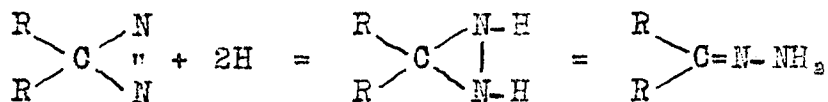
Taking the straight chain formula for the diazo compounds, the reaction is very simply and satisfactorily explained by the reduction of the triple bonded nitrogen in this manner,

$$\begin{matrix} R \\ \\ R \end{matrix} \Big> C=N\equiv N = \begin{matrix} R \\ \\ R \end{matrix} \Big> C=N=N \atop \quad\quad H \ H = \begin{matrix} R \\ \\ R \end{matrix} \Big> C=N-NH_2$$
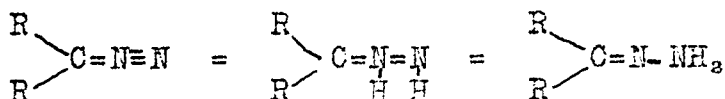
16. Staudinger, Helvetica Chim. Acta, 4, 212 (1921)
17. Staudinger and Kupfer, Ber. 44, 2202 (1911)

The intermediate hydrazi form has never been shown
to exist though attempts have been made to establish its
presence during the reaction (16).   From that evidence
the Angeli-Thiele structure seems the more probable, be-
cause it has the same C=N linkage as the resulting hydra-
zones.

The existence of optically active aliphatic diazo-
compounds, as shown by Marvel and Noyes(18), Chiles and
Noyes (19), and Levene and Mikeska (20), lends little
aid in deciding between these two possible structures, for
either one may be written so as to show the absence of a
plane of symmetry:

$$\begin{array}{ccc} R \diagdown & \diagup N \\ & C^x \\ R \diagup & \diagdown N \end{array} \quad or \quad \begin{array}{c} R \\ C+\diagup N\equiv N \\ R \end{array}$$
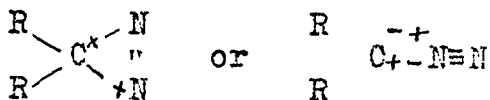
Assuming the electronic conception of valence, in both
cases there are four unlike valences attached to carbon,
and the necessary condition for optical activity is ful-
filled.

Evidence from absorption spectra (21) seems to indi-
cate that both nitrogens of the diazo group are trivalent.

18. Marvel and Noyes, J. Amer. Chem. Soc., 42, 2259 (1920)
19. Chiles and Noyes, ibid, 44, 1798 (1922)
20. Levene and Mikeska, J. Biol. Chem., 52, 485 (1922);
       54, 101 (1922); 55, 795 (1923)
21. Hantzsch and Lifschitz, Ber., 45, 3022 (1912)

This is directly against the Thiele formula, which has
one nitrogen pentavalent, and supports the Curtius struc-
ture.

Aside from absorption spectra evidence the Thiele
formula has been opposed on the ground that since it con-
tains a pentavalent nitrogen, the aliphatic diazo com-
pounds should be highly ionized, as is the case with other
compounds containing pentavalent nitrogen, with the ex-
ception of certain nitro compounds. The aliphatic diazo
compounds are nonpolar.

Forster and Cardwell (22) treated diazo camphor and
diazodesoxybenzoin with Grignard reagents obtaining the
corresponding hydrazones. Their work led them to favor
the straight chain formula. Their work appears to be
little more convincing than other evidence advanced in
support of that structure because of the presence of a
mobile hydrogen after hydrolysis. The reaction might take
place as follows, depending on which structure is assumed:

$$\begin{array}{c} R \\ R \end{array}\!\!>\!C=N\equiv N \; + \; RMgX \; = \; \begin{array}{c} R \\ R \end{array}\!\!>\!C=N=N-R \atop \quad MgX$$

$$\begin{array}{c} R \\ R \end{array}\!\!>\!C=N=N-R \atop \quad MgX \; + \; H_2O \; = \; \begin{array}{c} R \\ R \end{array}\!\!>\!C=N=N-R \atop \quad H$$
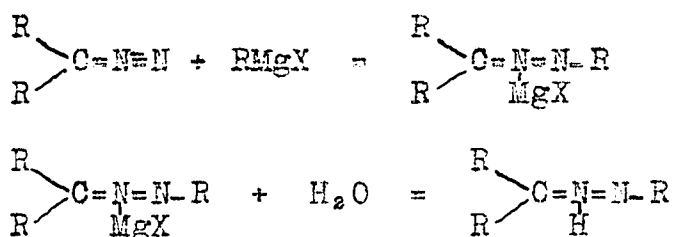
22. Forster and Cardwell, J. Chem. Soc., 103, 861 (1913)

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!=\!N\!=\!N\!-\!R \quad = \quad \begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!=\!N\!-\!N\!\!<\!\begin{matrix}R\\\\H\end{matrix}$$
$$\qquad\quad \overset{|}{H}$$

or,

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!=\!N\!\equiv\!N \;+\; RMgX \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{MgX}{C}\!-\!N\!=\!N\!-\!R$$

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{MgX}{C}\!-\!N\!=\!N\!-\!R \;+\; HOH \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{H}{C}\!-\!N\!=\!N\!-\!R$$

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{H}{C}\!-\!N\!=\!N\!-\!R \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!=\!N\!-\!N\!\!<\!\begin{matrix}R\\\\H\end{matrix}$$
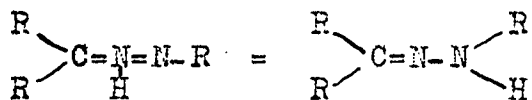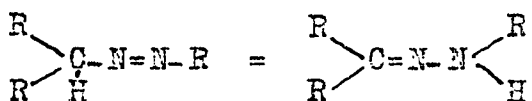
Taking the cyclic structure as the more probable one,
the mechanism might be considered to be this,

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!\!<\!\!\begin{matrix}N\\\\ ''\\\\N\end{matrix} \;+\; RMgX \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!\!<\!\!\begin{matrix}N\!-\!R\\\\ |\\\\N\!-\!MgX\end{matrix}$$

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!\!<\!\!\begin{matrix}N\!-\!R\\\\ |\\\\N\!-\!MgX\end{matrix} \;+\; H_2O \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!\!<\!\!\begin{matrix}N\!-\!R\\\\ |\\\\N\!-\!H\end{matrix} \;+\; Mg(OH)X$$

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!\!<\!\!\begin{matrix}N\!-\!R\\\\ |\\\\N\!-\!H\end{matrix} \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!=\!N\!-\!N\!\!<\!\!\begin{matrix}R\\\\H\end{matrix}$$
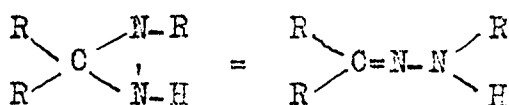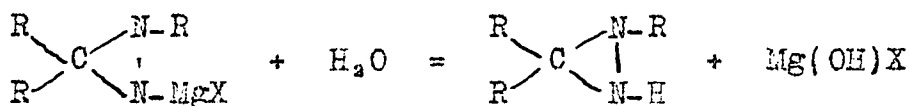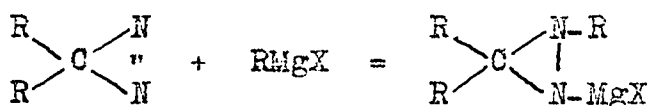
or this in which ring splitting takes place at once,

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!\!<\!\!\begin{matrix}N\\\\ ''\\\\N\end{matrix} \;+\; RMgX \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{MgX}{C}\!-\!N\!=\!N\!-\!R$$

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{MgX}{C}\!-\!N\!-\!NR \;+\; H_2O \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{H}{C}\!-\!N\!=\!N\!-\!R \;+\; Mg(OH)X$$

$$\begin{matrix}R\\\\R\end{matrix}\!\!>\!\underset{H}{C}\!-\!N\!=\!N\!-\!R \;=\; \begin{matrix}R\\\\R\end{matrix}\!\!>\!C\!=\!N\!-\!N\!\!<\!\!\begin{matrix}R\\\\H\end{matrix}$$
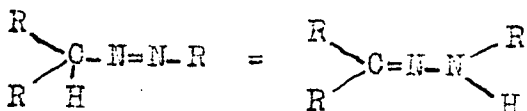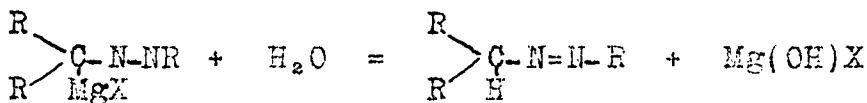
In the same year Zerner (23) published the results
of a similar research in which he attempted to decide be-
tween the two proposed structures. Zerner started the
work in the hope that he might be able to isolate the
intermediate compound,

$$R \diagdown C \diagup N-R$$
$$R \diagup \diagdown N-H$$
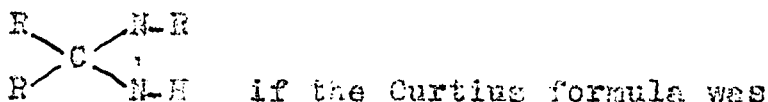
if the Curtius formula was
the correct one. He was unsuccessful, being only able to
obtain the hydrazones from the different Grignard reagents
and diazo compounds used. As a result, his work was no more
significant , one way or the other, than that of Forster
and Cardwell. Zerner advanced the theory, however, that
probably both the Curtius and the Angeli-Thiele formulae
were incorrect. Instead of the cyclic structure, or the
straight chain structure with pentavalent and trivalent
nitrogens, he proposed the configuration,

$$R \diagdown C=N-N \diagup$$
$$R \diagup$$
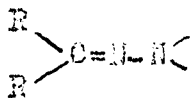
in which the penultimate nitrogen is trivalent and the
ultimate nitrogen is monovalent.

In 1910 Forster and Zimmerli (24) proposed a mechan-

23. Zerner, Monatshefte, 34, 1609, 164 (1913)
24. Forster and Zimmerli, J. Chem. Soc., 97, 2156 (1910)

ism for the formation of diazo compounds from hydrazones by oxidation with mercuric oxide in which they postulated the formula later suggested by Zerner as an intermediate product, as follows:

$$\begin{matrix} R \\ R \end{matrix} C{=}N{-}NH_2 \ - \ H_2 \ = \ \begin{matrix} R \\ R \end{matrix} C{=}N{-}N \ = \ \begin{matrix} R \\ R \end{matrix} C \overset{N}{\underset{N}{\lVert}}$$
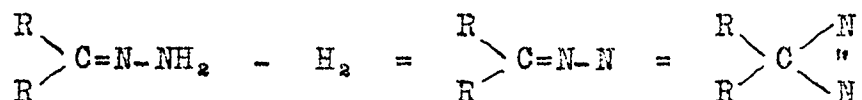
They evidently did not believe such an arrangement would be a stable one for they still regarded the structure of Curtius to be the form in which aliphatic diazo compounds existed in the free state.

The Zerner formula explains very simply the action of the Grignard reagent by having addition take place at the end nitrogen, and making unnecessary any assumption of re-arrangement whatever.

$$\begin{matrix} R \\ R \end{matrix} C{=}N{-}N \ + \ RMgX \ = \ \begin{matrix} R \\ R \end{matrix} C{=}N{-}N \begin{matrix} R \\ MgX \end{matrix}$$

$$\begin{matrix} R \\ R \end{matrix} C{=}N{-}N \begin{matrix} R \\ MgX \end{matrix} \ + \ H_2O \ = \ \begin{matrix} R \\ R \end{matrix} C{=}N{-}N \begin{matrix} R \\ H \end{matrix} \ + \ Mg(OH)X$$
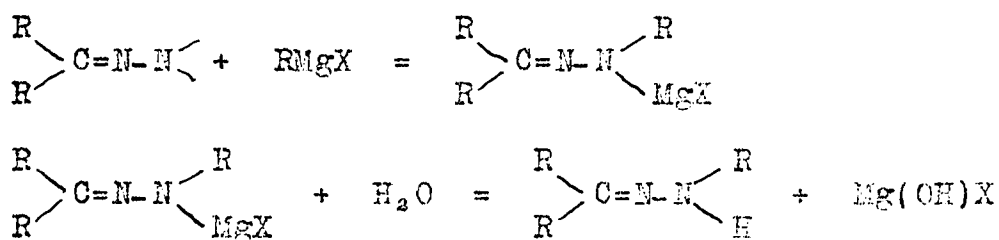
It also explains very well the action of trisubstituted phosphines to form phosphazines which has been investigated by Staudinger and co-workers (26).

26. Staudinger and Meyer, Helvetica Chim. Acta, 2, 619 (1919)

$$\begin{array}{l}R \\ \diagdown \\ C=N-N\diagup + PR_3 = C=N-N=PR_3 \\ R\diagup \end{array}$$
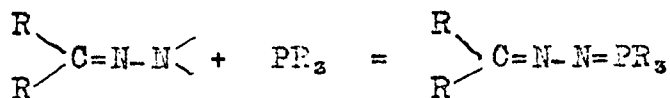
There is nothing in Zerner's work to give his proposed formula preference over the other two discussed, for they will explain the reaction with the Grignard reagent just as well if a rearrangement is allowed.

From the behavior of related compounds this assumption of rearrangement is very well founded. Fischer (26) and Bamberger and Pemsel (27) found that phenylazoethane rearranges easily to acetaldehydephenylhydrazone,

$$C_6H_5N=N-CH_2-CH_3 \xrightarrow{\text{rearr.}} C_6H_5NH-N=CH-CH_3$$
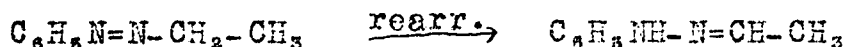
and other cases of rearrangement of azo compounds have been observed (28) (29) (30).

Staudinger (8) is of the opinion that the Thiele formula should be the preferred one. According to his point of view there are two points of reactivity in the molecule depending upon the kind of reagent with which it is treated. One point is the ultimate-antepenultimate position and the other the ultimate nitrogen alone:

$$\begin{array}{l}R \\ \diagdown \\ C=N=N \quad \text{and} \quad C=N=N \\ R\diagup \end{array}$$
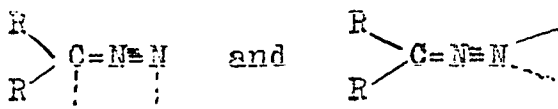
26. Fischer, Ber., 29, 794 (1896)
27. Bamberger and Pemsel, ibid., 36, 46 (1903)
28. Thiele, Liebig's Ann., 376, 239 (1910)
29. Japp and Klingemann, Ber., 20, 3398 (1887)
30. Meyer, ibid., 24, 1241 (1891)

He bases this conception on the effect of other groups in the molecule on the degree of reactivity. Acids, acid chlorides, alcohols, etc. are considered to react at the ultimate-antepenultimate position because the rate of reaction with different aliphatic diazo compounds varies depending upon what kind of group is attached to the carbon at the antepenultimate position. With phosphines, Grignard reagents and nascent hydrogen the point of reactivity is considered to be at the ultimate nitrogen because no matter what group may be attached to the carbon the reactions proceed with equal ease.

Although this is a plausible explanation, the possibility of addition taking place at the same position, no matter what the reagent used, is not necessarily rejected. The influence of other groups in the molecule may have a more marked effect on the reaction rate with one type of reagent than with another, and still have preliminary addition take place in the same manner.

This interpretation by Staudinger and the other interpretations of structure and mechanism of reaction so far proposed, have not been too convincing because no real evidence of intermediate compound formation has been obtained.

In 1893 Armstrong (31) suggested the structure,

$$R - N \underset{\diagdown N>}{\overset{\diagup N}{\parallel}}$$
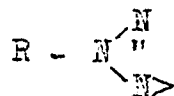
for azoimides, although he advanced no particular evidence
in support of it. This suggests another possible formula
for aliphatic diazo compounds, since they have much in com-
mon with azoimides.

$$\underset{R}{\overset{R}{\diagdown}} C \underset{\diagdown N>}{\overset{\diagup N}{\parallel}}$$
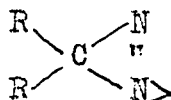
This research was undertaken with the aim to throw
more light on the nature of the intermediate compounds
formed in the reactions of aliphatic diazo compounds, and
if possible to decide between the different structures
that have been proposed.

The reaction with the Grignard reagent was selected as
being the one which might yield the most positive results
necessary for such a proof of structure. The action of
the Grignard reagent in general is one of addition and
is undoubtedly such with aliphatic diazo compounds. If
we knew how the addition actually takes place we would
be in a better position to make more definite conclusions
concerning the structure of aliphatic diazo compounds than
has been possible with the evidence so far accumulated.

31. Armstrong, Chem. News, 67, 153 (1893)

The difficulty in interpreting the reaction heretofore
has been that the -MgX group which, from its behavior in
other compounds does not generally rearrange (32), is re-
placed on hydrolysis by a hydrogen atom which rearranges
easily. That fact has made the products of hydrolysis of
very limited value in determining how the addition of
RMgX occurs.

The -MgX group attached to nitrogen, carbon or sul-
fur is readily replaced before hydrolysis by the ethyl
group using diethyl sulfate (33) and by the benzoyl group
using benzoyl chloride. Such groups do not rearrange
readily and the position of the substituted group in the
compound obtained after hydrolysis establishes the position.

32. The reaction between benzylmagnesium chloride and
trioxymethylene results in the formation of p-tolyl
carbinol instead of the expected benzyl alcohol.
(Tiffeneau and Delange, Compt. Rend., 137, 573 (1903)
The mechanism of this reaction is not well under-
stood, but a rearrangement of the -MgX group may occur.
A rearrangement of -MgX may also take place with
triphenylmethylmagnesium chloride in certain reactions.
(Schmidlin. Ber., 41, 426 (1908)
33. Gilman and Foyle, J. Amer. Chem. Soc., 44, 2261 (1922)
J. E. Kirby, working in this laboratory, has shown
that the -MgX group in benzylmagnesium chloride, which
may rearrange, is replaced normally with various re-
placing reagents. He has indications that the same is
true with triphenylmethylmagnesium chloride, but to-
date the investigation has not been completed.

of the -MgX group and thus the manner in which addition took place.

The procedure was to treat some aliphatic diazo compound with the Grignard reagent, and treat the addition compound formed with different reagents capable of replacing -MgX; hydrolyse, isolate the compound formed and determine the position of the group substituted.

In addition to the replacing reagents mentioned above, diphenylcarbamine chloride, and phenyl isocyanate were found to be very satisfactory compounds for reactions of that type.

The diazo compound selected for study was diphenyldiazomethane. It was chosen because it contains no other reactive group, no easily rearrangeable hydrogen, also because of the relative ease of preparation; and because it has been used in many studies as a typical aliphatic diazo compound.

Discussion of Results.

Diphenyldiazomethane was treated with an equimolecular amount of phenylmagnesium bromide, and hydrolysed, benzophenonephenylhydrazone being obtained as was expected from the work of Zerner (23) and Forster and Cardwell (22) on other aliphatic diazo compounds.

$$\begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!\!> CN_2 \; + \; C_6H_5MgBr \; = \; \begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!\!> C=N-N\!\!\!<\begin{array}{c} C_6H_5 \\ MgBr \end{array}$$

$$\begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!\!> C=N-N\!\!\!<\begin{array}{c} C_6H_5 \\ MgBr \end{array} \; + \; H_2O \; = \; \begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!\!> C=N-N\!\!\!<\begin{array}{c} C_6H_5 \\ H \end{array} \; + $$

$$Mg(OH)Br.$$
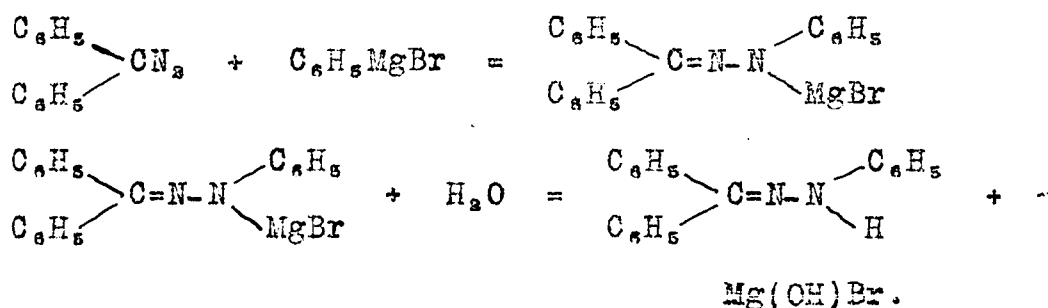
The reaction was then repeated except that diphenylcarbamine chloride was added to the reaction mixture of the phenylmagnesium bromide and diphenyldiazomethane before hydrolysis. The reaction flask was kept in an ice bath during both the addition of the Grignard reagent to the diazo compound and the addition of diphenylcarbamine chloride, in order to have the least favorable conditions for any rearrangement. On hydrolysis in the cold a yellow crystalline compound was obtained. It was thought that the reaction might have taken place in this manner:

$$\underset{C_6H_5}{\overset{C_6H_5}{>}}CN_2 \;+\; C_6H_5MgBr \;=\; \underset{C_6H_5}{\overset{C_6H_5}{>}}C=N-N\underset{MgBr}{\overset{C_6H_5}{<}}$$

$$\underset{C_6H_5}{\overset{C_6H_5}{>}}C=N-N\underset{MgBr}{\overset{C_6H_5}{<}} \;+\; \underset{C_6H_5}{\overset{C_6H_5}{>}}N-CO-Cl \;=\;$$

$$\underset{C_6H_5}{\overset{C_6H_5}{>}}C=N-\underset{C_6H_5}{N}-CO-N\underset{C_6H_6}{\overset{C_6H_5}{<}} \;+\; MgBrCl$$
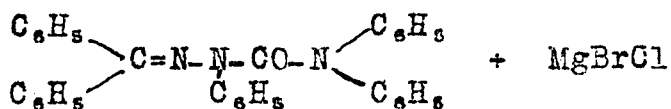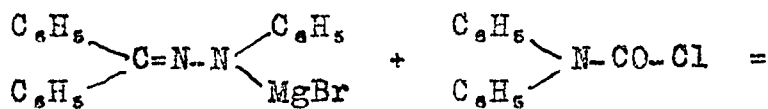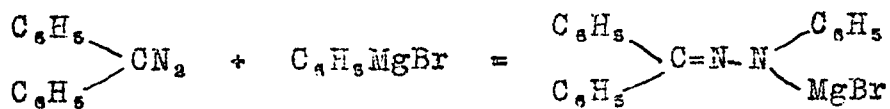
If that mechanism is the correct one the intermediate
compound, $(C_6H_5)_2C=N-N(MgBr)C_6H_5$, should be the same as
that formed when benzophenonephenylhydrazone is treated
with phenylmagnesium bromide, for the hydrazone contains an
active hydrogen which would be replaced by -MgX, as follows:

$$\underset{C_6H_5}{\overset{C_6H_5}{>}}C=N-N\underset{H}{\overset{C_6H_5}{<}} \;+\; C_6H_5MgBr \;=\; \underset{C_6H_5}{\overset{C_6H_5}{>}}C=N-N\underset{MgBr}{\overset{C_6H_5}{<}} \;+\; C_6H_6.$$
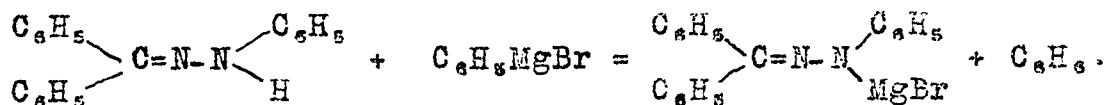
This intermediate compound should give the same final
product when treated with diphenylcarbamine chloride. This
was found to be the case, the compounds were identical.
That the compound obtained in both reactions was benzophe-
none-2,4,4'-triphenylsemicarbazone was further established
by an analysis and by hydrolysis to benzophenone and 2,4,4'-
triphenylsemicarbazide. The identity of the triphenylsemi-
carbazide, which was also unknown, was proven by analysis,
and its ease of formation of a semicarbazone with

benzaldehyde. The identity of the benzophenone-2,4,4'-triphenylsemicarbazone was further established by synthesis in a different manner. Benzophenonephenylhydrazone was treated with sodamide forming the sodium derivative, which on treatment with diphenylcarbamine chloride gave benzophenone-2,4,4'-triphenylsemicarbazone.

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} C=N-NHC_6H_5 \quad + \quad NaNH_2 \quad = \quad (C_6H_5)_2C=N-N \begin{matrix} C_6H_5 \\ Na \end{matrix}$$

$$(C_6H_5)_2C=N-N \begin{matrix} C_6H_5 \\ Na \end{matrix} \quad + \quad (C_6H_5)_2N-CO-Cl \quad =$$

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} C=N-N \begin{matrix} C_6H_5 \\ CO-N \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \end{matrix} \quad + \quad NaCl.$$
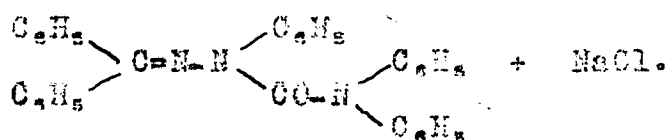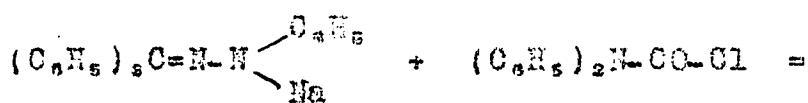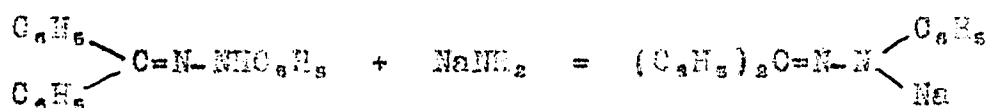
Diphenyldiazomethane was next treated with benzylmagnesium chloride to see if addition took place in the same manner with a different type of Grignard reagent. The reaction product was treated with diphenylcarbamine chloride before hydrolysis, under the same conditions as when the phenylmagnesium bromide was used. A well defined crystalline compound was obtained. If the reaction proceeded in the same way as when phenylmagnesium bromide was used the compound should be the 2-benzyl-4,4-diphenylsemicarbazone of benzophenone.

$$(C_6H_5)_2C=N_2 + C_6H_5CH_2MgCl = (C_6H_5)_2C=N-\underset{MgCl}{\overset{CH_2C_6H_5}{N}}$$

$$(C_6H_5)_2C=N-\underset{MgCl}{\overset{CH_2C_6H_5}{N}} + (C_6H_5)_2NCOCl = (C_6H_5)_2C=N-\underset{CO-N(C_6H_5)_2}{\overset{CH_2C_6H_5}{N}}$$
$$+ MgCl_2.$$

Benzophenone-2-benzyl-4,4'-diphenylsemicarbazone was synthesized from the known compound, benzophenone-4,4'-diphenylsemicarbazone (34), by replacing the active hydrogen by -MgX and treating that compound with benzyl bromide.

$$\underset{C_6H_5}{\overset{C_6H_5}{\Big\rangle}}C=N-N-\underset{H\ \ O}{\overset{}{C}}-N\underset{C_6H_5}{\overset{C_6H_5}{\Big\langle}} + C_6H_5MgBr = \underset{C_6H_5}{\overset{C_6H_5}{\Big\rangle}}C=N-N-\underset{MgBr\ \ O}{\overset{}{C}}-N\underset{C_6H_5}{\overset{C_6H_5}{\Big\langle}}$$

$$\underset{C_6H_5}{\overset{C_6H_5}{\Big\rangle}}C=N-N-CO-N\underset{C_6H_5}{\overset{C_6H_5}{\Big\langle}}\ \underset{MgBr}{} + C_6H_5CH_2Br = \underset{C_6H_5}{\overset{C_6H_5}{\Big\rangle}}C=N-N-CO-N\underset{C_6H_5}{\overset{C_6H_5}{\Big\langle}}\ \underset{CH_2C_6H_5}{}$$

A mixed melting point of the two compounds showed them to be the same. Benzophenone-2-benzyl-4,4'-diphenylsemicarbazone is not described in the literature, so its identity was established by an analysis, and by hydrolysis to benzophenone and 2-benzyl-4,4'-diphenylsemicarbazide. The identity of the 2-benzyl-4,4'-diphenylsemicarbazide was established by an analysis and the formation of a semicarbazone with benzaldehyde.

The evidence just given shows that RMgX adds to one nitrogen only, unless we make the very improbable assumption

34. Toschi and Angliolani, Gazz. chim. ital., (1), 45, 205 (1915); C. A., 9, 2388 (1915)

that the entering $(C_6H_5)_2N-CO-$ group has rearranged. Heavy groups of that nature do not rearrange easily which would have to be the case under the conditions in which the reactions were carried out. However, to further substantiate the belief that no rearrangement took place, the RMgX addition compound was treated with other reagents, capable of replacing $-MgX$. If the different groups substituted should show the same positions in the several compounds obtained it should be very strong evidence in favor of no rearrangement.

When diphenyldiazomethane was treated with phenylmagnesium bromide, and the resulting addition compound acted on by phenyl isocyanate as the replacing reagent, the reaction proceeded analogously to that when diphenylcarbamine chloride was used, benzophenone-2,4-diphenylsemicarbazone being formed.

$$\begin{array}{ll}
\dfrac{C_6H_5}{C_6H_5} \Big\rangle C=N_2 + C_6H_5MgBr = \dfrac{C_6H_5}{C_6H_5} \Big\rangle C=N-N \Big\langle \dfrac{C_6H_5}{MgBr}
\end{array}$$

$$\dfrac{C_6H_5}{C_6H_5} \Big\rangle C=N-N \Big\langle \dfrac{C_6H_5}{MgBr} + C_6H_5N=C=O = \dfrac{C_6H_5}{C_6H_5} \Big\rangle C=N-N-\overset{C_6H_5}{\underset{OMgX}{C}}=NC_6H_5$$

$$\dfrac{C_6H_5}{C_6H_5} \Big\rangle C=N-N-\overset{C_6H_5}{\underset{OMgX}{C}}=N-C_6H_5 + H_2O = \dfrac{C_6H_5}{C_6H_5} \Big\rangle C=N-N-CO-NHC_6H_5$$
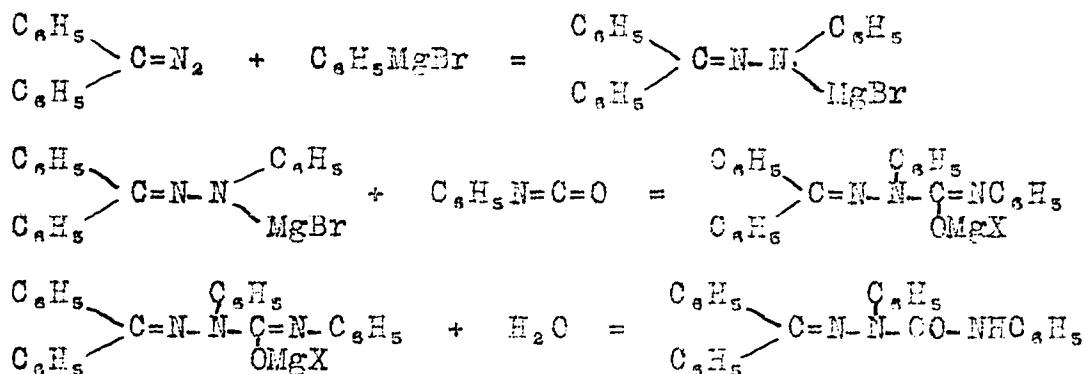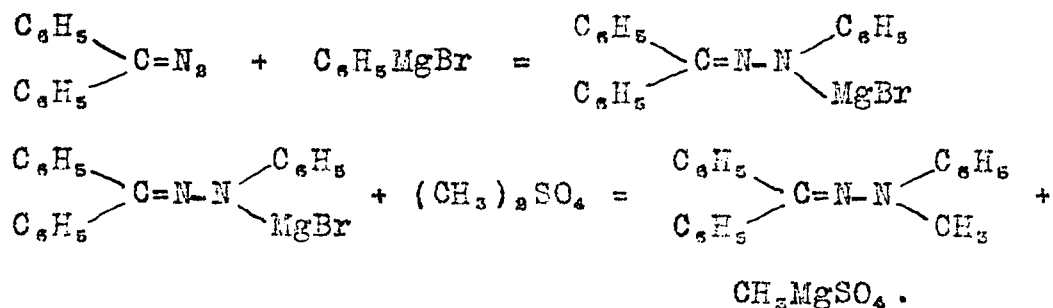
Benzoyl chloride did not prove to be as good a replacing reagent for -MgX in this work as diphenylcarbamine chloride and phenyl isocyanate, oily by-products being formed. However, replacement did take place, showing the same position for -MgX as did the other replacing reagents described above. From the reaction mixture of diphenyldiazomethane, phenylmagnesium bromide and benzoyl chloride there was obtained benzophenonephenylbenzoylhydrazone, together with some benzoylphenylhydrazine hydrobromide.

$$\begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!>\!\!C=N_2 \;+\; C_6H_5MgBr \;=\; \begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!>\!\!C=N\!-\!N\!\!<\!\!\begin{array}{c} C_6H_5 \\ MgBr \end{array}$$

$$\begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!>\!\!C=N\!-\!N\!\!<\!\!\begin{array}{c} C_6H_5 \\ MgBr \end{array} \;+\; C_6H_5\overset{}{\underset{O}{C}}\!-\!Cl \;=\; \begin{array}{c} C_6H_5 \\ C_6H_5 \end{array}\!\!>\!\!C=N\!-\!N\!\!<\!\!\begin{array}{c} C_6H_5 \\ \underset{O}{C}\!-\!C_6H_5 \end{array}$$
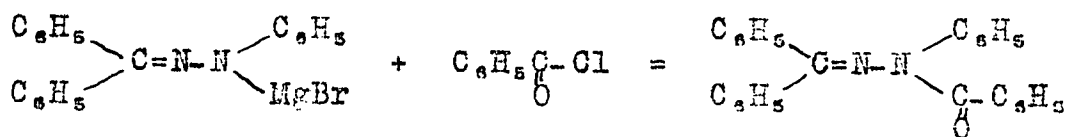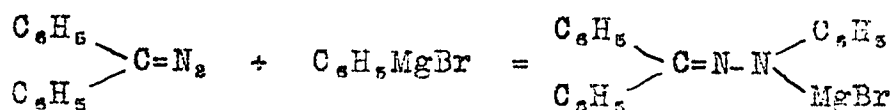
The formation of the benzoylphenylhydrazine hydrobromide was undoubtedly due to hydrolysis in working up the reaction mixture. Benzophenonebenzoylphenylhydrazone was not known, so it was identified by preparing benzoylphenylhydrazine and condensing it with benzophenone. The two compounds were shown to be the same by a mixed melting point.

The last types of replacing reagents used were dimethyl and diethyl sulphates. In the beginning of this

part of the work dimethyl sulphate was selected in combination with phenylmagnesium bromide because it ought to give as a final product the known methylphenylhydrazone of benzophenone, as follows:

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \end{array}\!\!\!C=N_2 \;+\; C_6H_5MgBr \;=\; \begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \end{array}\!\!\!C=N-N\!\!\!\begin{array}{c} C_6H_5 \\ \diagup \\ MgBr \end{array}$$

$$\begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \end{array}\!\!\!C=N-N\!\!\!\begin{array}{c} C_6H_5 \\ \diagup \\ MgBr \end{array} \;+\; (CH_3)_2SO_4 \;=\; \begin{array}{c} C_6H_5 \\ \diagdown \\ C_6H_5 \end{array}\!\!\!C=N-N\!\!\!\begin{array}{c} C_6H_5 \\ \diagup \\ CH_3 \end{array} \;+$$

$$CH_3MgSO_4 .$$

The reaction product was an oil from which no crystalline benzophenonemethylphenylhydrazone separated even after long standing in the cold. Efforts were made to get some crystals for seed to start crystallization, by condensing benzophenone and methylphenylhydrazine, but wihtout success. The condensation was tried under various conditions but always an oil resulted.

The oily reaction product from the diphenyldiazomethane, phenylmagnesium bromide and dimethyl sulfate was then distilled under vacuum in an attempt to isolate the methyl phenylhydrazone of benzophenone. At 160-180° at 4 mm. triphenylmethane distilled over. The presence of triphenylmethane might seem to indicate the addition of the phenyl group of phenylmagnesium bromide to the methylene carbon of

diphenyldiazomethane. It is believed that such a conclusion is not justified since the formation of triphenylmethane was undoubtedly due to decomposition during the distillation. At such a high temperature rearrangement might take place very easily.

After meeting with no success with dimethyl sulfate as the replacing reagent, diethyl sulfate was used instead. It proved to be no better, for only a non-crystallizable oil was obtained. In order to get something definite from the reaction product, it was decided to hydrolyse the oil obtained, and identify the benzophenone and ethylphenylhydrazine as the products of hydrolysis which should be formed if the ethylphenylhydrazone of benzophenone was present. When the oil was treated with 50% sulfuric acid, it either reacted with the acid to form a compound or compounds, other than those looked for, or else a rearrangement of some sort occurred, for no ethylphenylhydrazine cr benzophenone was found.

Believing that the reaction observed with the sulfuric acid was probably due to the influence of the phenyl group attached to nitrogen, the use of phenylmagnesium bromide in conjunction with diethyl sulfate was abandoned. Instead ethylmagnesium bromide was selected as the Grignard reagent,

and diethyl sulfate as the -MgX replacing reagent. The
diethyl hydrazone of benzophenone which should be obtained
as the product of reaction was unknown, but the plan was
to hydrolyse the reaction product and identify the known
diethyl hydrazine, and benzophenone. This would show
whether or not the -MgX was in the same position as demon-
strated by the other replacing reagents used. This was done,
the hydrolysis with 50% sulfuric acid taking place very
smoothly, to the formation of benzophenone and diethylhydra-
zine. The diethylhydrazine was identified in water solution
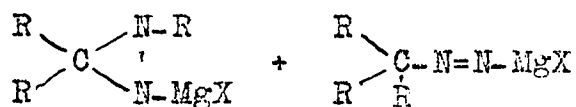by preparing its derivative 1,1'diethylsemicarbazide (35).

The color of the solutions of the addition products of
the Grignard reagents and diphenyldiazomethane were rather
interesting. When phenylmagnesium bromide was added to di-
phenyldiazomethane, the solution changed from a purple red
to a deep blood red. With benzylmagnesium chloride and
ethylmagnesium bromide the solutions obtained were yellow.

Just what significance, if any, the color of these
solutions has on the problem has not been definitely deter-
mined. It is believed that the difference in color is due
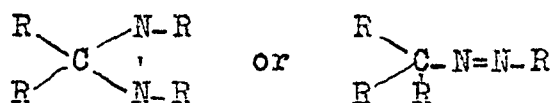to the nature of the R groups of the Grignard reagents,

35. Fischer, Ann. 199, 312 (1879)

rather than to a difference of position in the addition compound.

The results obtained in this work throw out the Curtius cyclic formula entirely, for there are only two ways in which addition may take place and neither satisfies the products obtained. These two possible addition products,

$$R{\diagdown}C{\diagup}{\overset{N-R}{\underset{N-MgX}{|}}} \quad + \quad R{\diagdown}{\underset{R}{C}}-N=N-MgX$$

should give:

$$R{\diagdown}C{\diagup}{\overset{N-R}{\underset{N-R}{|}}} \quad or \quad R{\diagdown}{\underset{R}{C}}-N=N-R$$

depending upon which mode of addition took place. Both the hydrazi (36) and the azo types of compounds are known and it is reasonable to believe that they would have been stable enough for identification under the conditions of experiment, if formed.

The most logical mechanism of reaction from the Angeli-Thiele formula would involve addition at the ultimate-penultimate or the antepenultimate-ultimate positions. Such a mechanism is untenable for addition and must take place at

36. Cornelius, Ber., 20, Register 49 (1887)
    Cornelius and Homolka, ibid., 19, 2239 (1886)
    Rassow and Burmeister, J. prakt. chem. 84, 249 (1911)

one nitrogen only. Addition may be represented as taking

place at the end nitrogen using that structure, as suggest-

ed by Staudinger,

$$\overset{R}{\underset{R}{>}}C=N\equiv N \quad + \quad RMgX \quad = \quad \overset{R}{\underset{R}{>}}C=N\equiv N\overset{R}{\underset{MgX}{<}}$$
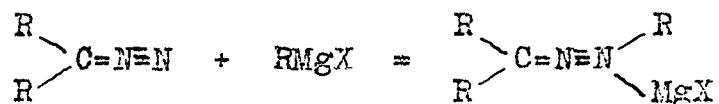
but in that case the nitrogen would have to increase its

valence from three to five (37). That is not in accord with

the facts for the final product after replacing the -MgX

group is a compound in which both nitrogens are trivalent.

The Zerner formula explains the facts more rationally in

our opinion.

$$\overset{R}{\underset{R}{>}}C=N-N< \quad + \quad RMgX \quad = \quad \overset{R}{\underset{R}{>}}C=N-N\overset{R}{\underset{MgX}{<}}$$
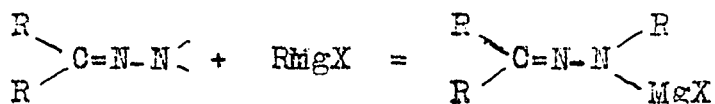
Addition takes place at the end unsaturated monovalent ni-

trogen increasing its valence to three, which is in perfect

accord with the facts obtained.

To be sure the Armstrong formula satisfies the ad-

dition of the Grignard to one nitrogen as well as that of

37. When pyridine and quinoline are treated with phenyl-
     magnesium bromide, the phenyl and -MgBr groups add to
     the ring nitrogen increasing their valence from three
     to five. Oddo, Atti. accad. Lincei (5), 16, I, 538
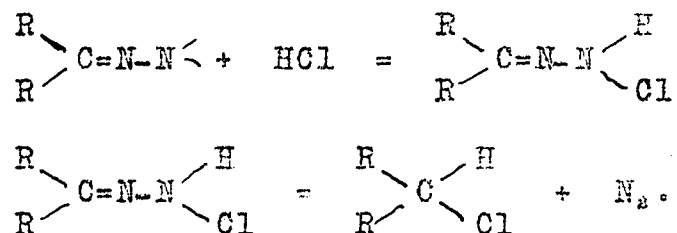   (1907); J. Chem. Soc. Abs. 92, 549 (1907)

Zerner, but it is rejected because a rearrangement is necessary to give the hydrazone.

The question might be raised, however, about the probable stability of such an arrangement as the Zerner structure demands. Highly unstable intermediate compounds in which nitrogen is monovalent have been postulated in certain chemical reactions, but to-date they have not been isolated (38). That monovalent nitrogen is too reactive to be isolated in the free state, is the view held by most workers in this field. A similar view was also held concerning the valence of carbon before the existence of divalent and trivalent carbon was demonstrated. It is believed that the facts obtained warrant the abandonment of the conception that monovalent nitrogen cannot exist in a stable compound.

38. Stieglitz, Amer. Chem. J., 18, 751 (1896)
Stieglitz and Stagner, J. Amer. Chem. Soc., 38, 2046 (1916)
Wieland, Ber., 42, 4207 (1909)
L. W. Jones, Amer. Chem. J., 48, 1 (1912); 50, 440 (1913)
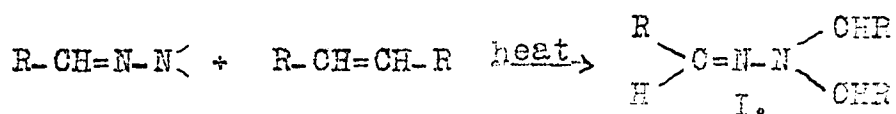
Interpretation of Other Reactions.

The reactions of acids, water, amines and alcohols with aliphatic diazo compounds are explained by the Werner formula as follows, using hydrochloric acid as a type reagent:
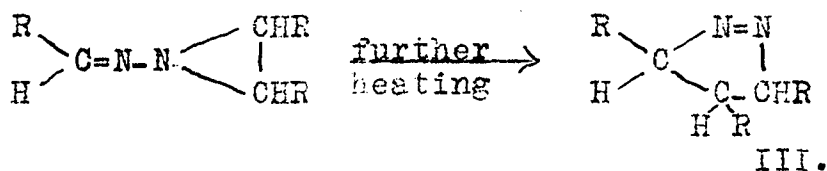
$$\begin{matrix} R \\ R \end{matrix} C=N-N< \;+\; HCl \;=\; \begin{matrix} R \\ R \end{matrix} C=N-N \begin{matrix} H \\ Cl \end{matrix}$$

$$\begin{matrix} R \\ R \end{matrix} C=N-N \begin{matrix} H \\ Cl \end{matrix} \;=\; \begin{matrix} R \\ R \end{matrix} C \begin{matrix} H \\ Cl \end{matrix} \;+\; N_2.$$

In cases of reduction, the end nitrogen adds hydrogen increasing its valence from one to three.

$$\begin{matrix} R \\ R \end{matrix} C=N-N< \;+\; 2H \;=\; \begin{matrix} R \\ R \end{matrix} C=N-NH_2.$$
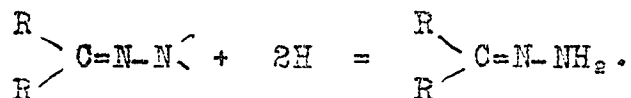
The mechanism of reaction of aliphatic diazo compounds with unsaturated linkages, does not appear to be so easily interpreted at first sight because we start with two straight chain compounds, and obtain one which is considered to contain a five membered ring. The mechanism proposed is this, using an ethylenic compound as a type,

$$R-CH=N-N< \;+\; R-CH=CH-R \xrightarrow{\text{heat}} \begin{matrix} R \\ H \end{matrix} C=N-N \begin{matrix} CHR \\ CHR \end{matrix}$$
$$I.$$

$$R \diagdown C=N-N \diagup CHR \diagdown CHR \quad \xrightarrow{\text{further heating}} \quad R \diagdown C \diagup N=N \diagdown C-CHR \diagdown H \diagup R$$

III.

$$R \diagdown C \diagup N=N \diagdown C-CHR \diagdown H \diagup R \quad \xrightarrow{\text{rearr}} \quad R-C \diagup N-NH \diagdown C-CHR \diagdown H \diagup R$$

IV.

The Zerner configuration predicts the formation of (I) rather than (IV). The isolation of (IV) instead of (I) as the final product is explained by the ketazine-like structure of (I) and the temperature at which the reaction is carried out. Curtius and Foersterling (39) have shown that dimethylketazine rearranges readily into 3-methyl-5-dimethyl-pyrazoline. Certain unsaturated hydrazones also rearrange to form pyrazolines (40). With these very pertinent facts, the Zerner formula explains pyrazolines and pyrazoles from ethylenic and acetylenic compounds very satisfactorily. The suggestion has been made that the so-called pyrazolines obtained are not pyrazolines at all but compounds with the structure (I) (41). However, that view has received little
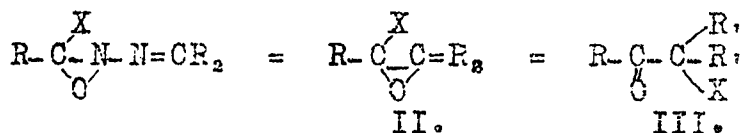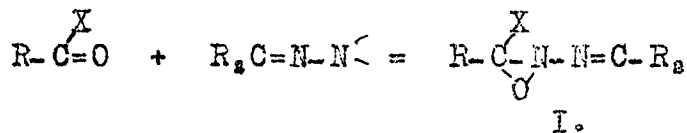
39. Curtius and Foersterling, Ber., 27, 770 (1894)
40. Bauer and Dieterle, ibid., 44, 2697 (1911)
41. Bulow, ibid., 44, 3710 (1911); 45, 528 (1912);
    45, 3349 (1912)

if any, support.

The reactions of diazo compounds with aldehydes and acid halides may be looked upon as proceeding in this manner, (X = H, or Halogen).

$$R-\overset{X}{\underset{}{C}}=O \quad + \quad R_2C=N-N< \quad = \quad R-\overset{X}{\underset{O}{C}}-N-N=C-R_2$$

$$I.$$

$$R-\overset{X}{\underset{O}{C}}-N-N=CR_2 \quad = \quad R-\overset{X}{\underset{O}{C}}-C=R_2 \quad = \quad R-\overset{}{\underset{O}{C}}-\overset{R'}{\underset{X}{C}}R'$$

$$II. \qquad\qquad III.$$

The aldehyde and diazo compound react first to give (I) (42), which is unstable and loses nitrogen to form the methylene oxide derivative (II). Compound (II) by ring splitting goes over the ketone (III) (43).

---

42. This configuration resembles the one, $C_6H_5N-CHC_6H_5$ over O, which has been ascribed to the reaction product of benzaldehyde and phenylhydroxylamine. By analogy it would be expected that formula I ought to be a rather stable arrangement. However, there seems to be some question concerning the structure of the hydroxylamine derivative. Instead of the cyclic formula, the following structure has been suggested by some investigators: $C_6H_5N=CHC_6H_5$ over O
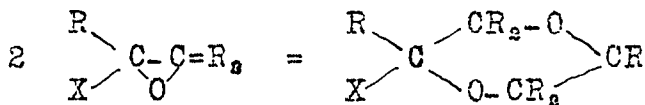
Auwers, Ber., 22, 720 (1889); Forster and Holmes, J. Chem. Soc., 93, 244 (1908); Staudinger and Miescher, Helvetica Chim. Acta, 2, 554 (1919)

43. Fourneau and Tiffeneau, Compt. rend., 141, 662 (1905), have shown that, $ROC_6H_4CH-CHCH_3$ over O, rearranges to

$ROC_6H_4-CH_2-CO-CH_3$ by heating at 200-250°.

In a recent publication Lewis, Nierenstein and Rich
(44) proposed a mechanism for the reaction with acid hal-
ides to explain the formation of 1,4-dioxane derivatives
which are produced along with the ketones. The mechanism
outlined by them is similar to the one given here except
the first intermediate compound (I), which they consider
to be,

$$
\begin{array}{c}
X \\
\diagdown C{-}O{-}N \\
R \diagup \diagdown C{-}N \\
R\ R
\end{array}
$$
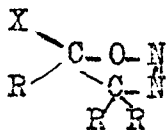
The compound (II) by fission may either form the di-
oxane by the union of two residues,

$$
2\;
\begin{array}{c}
R \\
\diagdown C{-}C{=}R_2 \\
X \diagup O
\end{array}
\;=\;
\begin{array}{c}
R CR_2{-}O \\
\diagdown C \diagup \diagdown CR \\
X \diagup \diagdown O{-}CR_2 \diagup
\end{array}
$$

or go over to the ketone III.

44. Lewis, Nierenstein, and Rich, J. Amer. Chem. Soc.,
    47, 1728 (1925)

Experimental Part

For the preparation of the diphenyldiazomethane used
in this investigation a modification of the method worked
out by Staudinger (45) was adopted. Mechanical stirring
instead of shaking during the oxidation of the benzophe-
nonehydrazone was found to be more convenient. The yields
obtained were a little lower (75-85%) than those recorded
by Staudinger (85-98%) but the reaction time was shorter,
making possible the preparation and use of the diazo com-
pound the same day. With shaking the time for complete oxi-
dation was 6-9 hours. With efficient stirring 3-4 hours
was found to be sufficient.

For all experiments, the diphenyldiazomethane was pre-
pared as described above, in low boiling (30-40°) petroleum
ether. At the completion of the oxidation, the solution
was filtered from the mercury sludge; dried by shaking with
anhydrous sodium sulfate; and the petroleum ether distilled
under a vacuum in a weighed three necked flask.

The residual solid obtained was considered to be 100%
diphenyldiazomethane and the weight recorded as such, although

45. Staudinger, Anthes, and Pfenninger, Ber., 49, 1928 (1916)

it may have been slightly impure. If any unchanged benzo-
phenonehydrazone remained after the oxidation with mercuric
oxide, the amount going through in the filtrate with the di-
azo compound would be very small due to its slight solubili-
ty in petroleum ether. Diphenylketazine which is formed as
a by-product of the oxidation, is also insoluble in petro-
leum ether and would be filtered out along with the mercury
sludge. On standing at room temperature diphenyldiazometh-
ane goes over slowly to diphenylketazine. After filtration
from the mercury residue, the solution was kept cold while
being dried, and also during the evaporation of the solvent
under vacuum. After weighing up the solid diazo compound,
the flask was kept in an ice bath until ready to be used.
Low temperature is very unfavorable for ketazine formation.

To the solid diphenyldiazomethane was added dry ether,
previously cooled in an ice bath and the reaction with the
particular Grignard reagent being used carried out in the
same flask.

The Grignard reagents were always added very slowly by
means of a dropping funnel, and the reaction flask kept at
0° to -5° in order to be sure that no decomposition of the
diazo compound took place due to the heat of reaction. Ef-

ficient mechanical stirring was also used.

' standard solution of phenylmagnesium bromide (about 2 moles per liter) was prepared (46) and the desired amount pipetted out for each experiment. This was found to be as accurate as individual preparations of phenylmagnesium bromide for each experiment, provided the bottle was kept tightly stoppered when not in use. The other Grignard reagents described were prepared just previous to their use.

The Action of Phenylmagnesium Bromide on Diphenyldiazomethane. 28 gr. (.14 moles) of diphenyldiazomethane was treated with 25.5 gr. (.14 moles) of phenylmagnesium bromide. After complete addition of the Grignard reagent, the stirring was continued for one half hour, and then hydrolysed with ammoniacal ammonium chloride solution. ' yellow crystalline solid insoluble in ether and water was formed. This was filtered off, dried, and weighed. It melted at 124-126°, and a mixed melting point with benzophenone phenylhydrazone showed no depression.

The ether layer was washed well with water, dried over anhydrous sodium sulfate and evaporated down on a steam plate until nearly all of the ether had been driven off. On cooling

46. Gilman and Meyers, Ind. Eng. Chem., 15, 61 (1923)
Gilman, Wilkinson, Fischel, and Meyers, J. Amer.
Chem. Soc., 41, 150 (1923)

more benzophenonephenylhydrazone separated. The mother
liquor was not further investigated. The total yield of ben-
zophenonephenylhydrazone was 27 gr. (70%).

The Action of Diphenylcarbamine Chloride on the Addition
Product of Diphenyldiazomethane and Phenylmagnesium Bromide.
13 gr. (.07 moles) of diphenyldiazomethane in 50cc. of dry
ether was treated with 12 gr. (.07 moles) of phenylmagnesium
bromide. Stirring was continued for one half hour after com-
plete addition, and then 16 gr. (.07 moles) of diphenylcarba-
mine chloride in 75 cc of ether was slowly added. A dark pre-
cipitate began to form at once and continued to increase in
amount during the addition. The reaction mixture was allowed
to stand at room temperature for two hours, and was then hydro-
lysed with dilute hydrochloric acid in the cold. A yellow
solid, 2,4,4'-triphenylsemicarbazone of benzophenone precipi-
tated. It was filtered, dried, and weighed; weight 13 gr.
After two recrystallizations from alcohol the compound melted
at 160-161°.

The ether layer was washed with water, dried over anhydrous
sodium sulfate, and the ether distilled off, leaving an oil as
a residue. On standing over night the residue changed to an
oily crystalline mass. The solid was filtered off and proved
to be more benzophenone-2,4,4'-triphenylsemicarbazone; weight

1 gr. The total yield of benzophenone-2,4,4'-triphenyl-semicarbazone was 14 gr. (44%). The compound is slightly soluble in ether, and cold alcohol; more soluble in hot alcohol; and soluble in benzene.

Anal. Calc. for $C_{32}H_{25}ON_3$: N, 8.99. Found: 9.40.

The Preparation of Benzophenone-2,4,4'-triphenylsemi-carbazone from Benzophenonephenylhydrazone, Phenylmagnesium Bromide, and Diphenylcarbamine Chloride. 5 gr. (.018 moles) of benzophenonephenylhydrazone in ether was treated with 3.4 gr. (.018 moles) of phenylmagnesium bromide, to replace the hydrogen by the -MgBr group. To this was added an ether solution of 4.2 gr. (.018 moles) of diphenylcarbamine chlor-ide, producing a heavy precipitate on the sides of the flask. The reaction mixture was hydrolysed with dilute hydrochloric acid, causing a light yellow precipitate to come down, which on recrystallization from alcohol melted at 160°, and by mixed melting point proved to be identical with the benzophe-none-2,4,4'-triphenylsemicarbazone obtained in the previous experiment. The yield was 4 gr. (47%).

The Synthesis of Benzophenone-2,4,4'-triphenylsemicar-bazone from the Sodium Derivative of Benzophenonephenyl-hydrazone. 15 gr. (.055 moles) of benzophenonephenylhydra-zone and 3 gr. (.07 moles) of sodamide were intimately

mixed by grinding quickly in a mortar. The mixture was transferred to a 150 cc. distilling flask and heated gently in a stream of dry hydrogen. Only enough heat was applied to keep up a slow evolution of ammonia, which was driven off in about one hour. On cooling, the sodiumbenzophenone-phenylhydrazone solidified to a hard red mass. The flask was then broken under dry ether in a mortar, ground up quickly, and transferred to a 500 cc. three necked flask with enough ether to make a volume of about 150 cc. To this mixture, under vigorous stirring, was added 15 gr. (.064 moles) of diphenylcarbamine chloride in small portions. In a short time the solution began to warm up, and a yellow precipitate began to form which increased in quantity until all of the diphenylcarbamine chloride had been added. The reaction mixture was stirred for one half hour longer, and then 10^0 cc of water added to dissolve the sodium chloride formed. The yellow solid was filtered off and recrystallized from alcohol; weight 8 gr. The melting point was 156-158°, and a mixed melting point with the benzophenone-2,4,4'-triphenyl-semicarbazone obtained in the two previous experiments showed it to be the same compound.

2 gr. more of the compound was obtained from the ether layer. The total yield was 10 gr. (39%).

Hydrolysis of Benzophenone-2,4,4'-triphenylsemicarbazone. 2.5 gr. (.005 moles) of benzophenonetriphenylsemicarbazone was refluxed with stirring in 85 gr. of 20% hydrochloric acid for one half hour. The solution was cooled; extracted with ether; and the dried ether layer was evaporated to an oil on a steam bath. When seeded with a crystal of benzophenone it solidified to a crystalline mass, which was shown to be benzophenone by mixed melting point; weight .8 gr. (88%).

The acid water layer was made alkaline with sodium hydroxide, extracted with ether, the dried ether layer evaporated down until the ether was driven off, and 10 cc of alcohol added. On cooling, the white crystalline-2,4,4'-triphenylsemicarbazide separated. The crystals were filtered and washed three times with small portions of alcohol; weight .5 gr. (33%). It melted at 124-125°. The compound is slightly soluble in ether and cold alcohol, and very soluble in hot alcohol.

The hydrolysis was repeated using a larger quantity of benzophenone-2,4,4'-triphenylsemicarbazone (.034 moles). A 70% yield of the 2,4,4'-triphenylsemicarbazide was obtained.

Anal. Calc. for $C_{19}H_{17}ON_3$; N, 13.86. Found: 14.27.

When warmed on a steam bath for five minutes in alcohol 2,4,4'-triphenylsemicarbazide condenses with benzaldehyde to form a crystalline compound, probably the benzaldehyde-2,4, 4'-triphenylsemicarbazone. After recrystallizing twice from alcohol, it melted sharply at 158-159°.

The Action of Diphenylcarbamine Chloride on the Addition Product of Benzylmagnesium Chloride and Diphenyldiazomethane. 8 gr. (.041 moles) of diphenyldiazomethane was treated with 6.4 gr. (.042 moles) of benzylmagnesium chloride. To the reaction mixture was added 8.8 gr. (.04 moles) of diphenylcarbamine chloride, causing a precipitate to form.

The reaction mixture was hydrolysed with ammonium chloride solution, and the yellow benzophenone-2-benzyl-4,4'-phenylsemicarbazone which formed, was filtered off, dried, and weighed; weight 8 gr. The melting point was 118-125°. After two recrystallizations from alcohol it melted at 137-139°.

The ether layer from the filtrate was evaporated down to a red oil, 15 cc. of alcohol added, and the solution allowed to stand in the cold. A crop of crystals came down: weight 1 gr. After recrystallizing from alcohol they melted at 160°. A mixed melting point with diphenylketazine showed it to be the same compound.

The mother liquor from the diphenylketazine was evaporated down further, yielding 1.5 gr. more of benzophenone-

2-benzyl-4,4'-diphenylsemicarbazone and making a total
yield of 9.5 gr. (49%).

Anal. Calc. for $C_{33}H_{27}ON_3$: N, 8.75. Found: 9.07.

Analysis by A. Wheeler Ralston.

Synthesis of Benzophenone-2-benzyl-4,4-diphenylsemi-
carbazone from Benzophenone-4,4-diphenylsemicarbazone. 4 gr.
(.01 moles) of benzophenone-4,4-diphenylsemicarbazone, pre-
pared according to the method given by Toschi (34), was
treated with 3.4 gr. (.018 moles) of phenylmagnesium bromide
in 25 cc. of dry ether to replace the active hydrogen with
-MgBr. To the resulting reaction mixture was added 6 gr.
(.047 moles) of benzyl chloride. 25 cc. of dry benzene was
then added and the ether distilled off. The solution was re-
fluxed for one hour, cooled, and hydrolysed with dilute hydro-
chloric acid. The benzene layer was washed with water, dried
over anhydrous sodium sulfate, and evaporated to a small vol-
ume. Absolute alcohol was then added, and the solution evap-
orated down again to remove the remaining benzene. On stand-
ing in the cold a small crop of crystals came out; m.p.125-
130°. After two recrystallizations from alcohol they melted
at 136-137°. A mixed melting point with the benzophenone-2-
benzyl-4,4'-diphenylsemicarbazone obtained in the preceding
experiment showed them to be identical. The yield was .5 gr.
(10%).

Hydrolysis of Benzophenone-2-benzyl-4,4'-diphenyl-
semicarbazone. 5 gr. (.01 moles) of benzophenone-2-benzyl-
4,4'-diphenylsemicarbazone was refluxed for one hour with
80 gr. of 20% hydrochloric acid. The cold solution was ex-
tracted with ether, and the washed and dried ether solution
evaporated down to an oil, which on standing solidified to
crystalline benzophenone. The acid water layer was made
alkaline with sodium hydroxide, and again extracted with
ether. The washed and dried ether solution was evaporated
until nearly all of the ether had been driven off. 10 cc.
of alcohol were added and the solution cooled, causing
2-benzyl-4,4'-diphenylsemicarbazide to separate.

The crystals were washed twice with small portions
of alcohol; m.p. 109-110°. The yield was 1.5 gr. (50%).
The compound is slightly soluble in ether and cold alcohol,
and more soluble in hot alcohol.

Anal. Calc. for $C_{20}H_{19}ON_3$: N, 13.7. Found: 14.00.

When warmed with benzaldehyde in alcohol for five min-
utes, the cold solution yields fine white needles of benz-
aldehyde-2-benzyl-4,4'-diphenylsemicarbazone; m.p. 167-168°.

The Action of Phenyl Isocyanate on the Addition Compound
of Diphenyldiazomethane and Phenylmagnesium Bromide. From
14 gr. (.072 moles) of diphenyldiazomethane, 17 gr. (.094
moles) of phenylmagnesium bromide and 13 gr. (.11 moles)

of phenyl isocyanate was obtained 18 gr. of crude benzo-
phenone-2,4-diphenylsemicarbazone. A fractional crystal-
lization of the crude material yielded some benzanilide
and a small amount of a white alcohol insoluble compound
melting at 180°, which was not identified, as well as the
benzophenone-2,4-diphenylsemicarbazone. The pure benzo-
phenone-2,4-diphenylsemicarbazone melts at 166-167°. It
forms fine pale yellow needles, insoluble in cold alcohol,
more easily in hot, and slightly soluble in ether. The
total yield was 9.4 gr. (36%).

Anal. Calc. for $C_{26}H_{21}ON_3$: N, 10.74. Found: 11.24.

The Replacement of -MgBr in the Reaction Product of
Diphenyldiazomethane and Phenylmagnesium Bromide by Benzoyl
Chloride. 11.5 gr. (.063 moles) of phenylmagnesium bromide
was slowly added to 12 gr. (.061 moles) of diphenyldiazo-
methane in 100 cc of ether, the reaction mixture being well
stirred, and cooled in an ice bath. The benzoyl chloride
was added slowly, the reaction flask still being kept cold,
and after complete addition allowed to come to room temper-
ature and then stand for two hours. The reaction mixture
was then cooled again in an ice bath, hydrolysed with am-
monium chloride solution, the ether layer washed, dried over
anhydrous sodium sulfate, and evaporated to a small volume.

To this residue was added 10 cc of alcohol and the solution
was heated until all of the ether was driven off. After
cooling and standing for several hours a crop of crystals
separated. These were filtered, washed with several small
portions of ether; m.p. 188-190° with gas evolution. A
mixed melting point with benzoylphenylhydrazine hydrobromide
(47) showed it to be the same compound.

The mother liquor from the benzoylphenylhydrazine hydro-
bromide on further standing threw down another crop of crys-
tals; weight .5 gr. (2.2% yield). After recrystallizing from
alcohol the melting point was 143-144°. This compound proved
to be benzophenone benzoylphenylhydrazone, by a mixed melting
point. This hydrazone which is not described in the litera-
ture was made by heating the known benzoylphenylhydrazine with
benzophenone in glacial acetic acid. It was found to crystal-
lize with some difficulty, requiring about 24 hours standing
in the cold.

Attempts to Replace the -MgBr Group of the Reaction
Product of Diphenyldiazomethane and Phenylmagnesium Bromide
with Benzyl Chloride and Benzyl Bromide. 7.5 gr. (.038 moles)
of diphenyldiazomethane was treated with 6.9 gr. (.038 moles)

47. Michaelis and Schmidt, Ber., 20, 43 (1887)

or phenylmagnesium bromide and 5 gr. (.03 moles) of benzyl chloride in ether added. The reaction mixture was then refluxed for four hours. No reaction appeared to take place, so the ether was replaced by dry benzene, and refluxed again for five hours. More ether was then added, and the solution hydrolysed with dilute hydrochloric acid. The washed and dried ether benzene layer was then evaporated to a small volume, and enough alcohol added to make the volume about 25 cc. The solution was seeded with a crystal of benzophenonebenzylphenylhydrazone and allowed to stand in the cold over night but no crystals appeared. It was then evaporated to as small a volume as possible on a steam plate, leaving a dark oil as a residue. This was left in the cold for several weeks but still no solid appeared. It was then treated with more alcohol boiled with bone black, filtered, and the filtrate allowed to stand for several weeks longer, but still no benzophenonebenzylphenylhydrazone appeared.

Other runs were made with benzyl bromide instead of benzyl chloride, and under the same conditions but no benzophenonephenylbenzylhydrazone could be isolated, only noncrystallizable oils being obtained.

The Action of Dimethyl Sulphate on the Addition
Product of Diphenyldiazomethane and Phenylmagnesium Bro-
mide. 19.5 gr. (.1 moles) of diphenyldiazomethane was
treated with 23.8 gr. (.13 moles) of phenylmagnesium bro-
mide. To this solution was added 20 gr. (.16 moles) of
dimethyl sulfate, and the resulting reaction product
allowed to warm up to room temperature. It was stirred
continuously for two hours and then hydrolysed with dilute
hydrochloric acid in the cold. The ether layer was sepa-
rated, washed with water, ammonium hydroxide, with water
again, dried over anhydrous sodium sulfate and evaporated
down to a thick red-brown oil. On standing a crop of crys-
tals came down which proved to be benzophenonephenylhydra-
zone by mixed melting point. The oily mother liquor stood
for two months, but no further crystallization took place.
An attempt was then made to purify the oil by distillation
under reduced pressure. During the distillation decompo-
sition appeared to take place. At 160-180° at 4 mm. a
small amount of distillate came over. About one gram was
collected when the distillation was stopped on account of
solid clogging the side arm of the distillation flask. The
distillate obtained was recrystallized from alcohol, giving
fine white needles; m.p. 91-92°. A mixed melting point

showed it to be triphenylmethane. The tarry residue left in the flask was not further distilled.

The Action of Diethyl Sulfate on the Addition Product of Diphenyldiazomethane and Phenylmagnesium Bromide. 15 gr. (.077 moles) of diphenyldiazomethane was treated with 18 gr. (.1 moles) of phenylmagnesium bromide, and 20 gr. (.12 moles) of diethyl sulfate in ether added slowly and with stirring to the reaction mixture. The solution was stirred at room temperature for two hours and then hydrolysed with ammonium chloride solution. The light yellow ether layer was washed well with water, dried over anhydrous sodium sulfate, and evaporated down until the temperature of the solution was about 50°. On standing a small quantity of a crystalline solid separated out. This was filtered off, and washed three times with small portions of alcohol; m.p. 165-167°. The weight was less than .5 gr. Its identity was not determined.

The mother liquor was heated to 50° under vacuum to drive off the last portion of the solvent, and allowed to stand over night. No solid phase appeared. It was then steam distilled, yielding a small amount of oily distillate, probably a mixture of ethyl benzene and biphenyl. There was no decomposition during the distillation as far as could be determined. The residue in the distillation

flask was taken up with ether, dried, and evaporated down
to a small volume on a steam plate. When cool the residue
became a thick yellow oil.

An attempt was then made to hydrolyse the oil by re-
fluxing it in 60 gr. of 50% sulfuric acid (48) for one and
one half hours. As soon as the acid was added to the oil
a reaction of some kind began to take place, the solution
turning almost black. The cooled reaction mixture was ex-
tracted with ether again. Both acid and basic ether ex-
tracts were washed, dried, and evaporated to as small vol-
umes as possible on a steam plate. The alkaline extract
gave a trace of dark brown oil. This was taken up in ether
again and dry hydrochloric acid gas passed in, giving a
chocolate colored precipitate. This was filtered, dissolved
in a little alcohol, and reprecipitated with ether, the
solid being still dark in color, and when filtered was ob-
tained as a sticky mass. The residue from the acid extract
was dark red in color, and appeared to be of nearly equal
weight to that of the original oil treated with the sul-
furic acid. That seemed to indicate, along with the slight
amount of residue from the alkaline extract, that little

48. Krauz, Chemicke Listy, 5, 12, 54; C. A. 5, 1594 (1911)

if any hydrolysis had taken place.

The experiment was then repeated with the same quantities of starting materials, and the characteristic yellow oil was again obtained after hydrolysis and the evaporation of the ether layer. An attempt was then made to hydrolyse the oil with 150 cc. of concentrated hydro-chloric acid instead of 50% sulfuric acid. As before, the solution turned dark in color. The mixture was refluxed for three hours, and worked up in the same way as when 50% sulfuric acid was used, with the same results. There was only a trace of acid soluble material, from which no ethyl-phenylhydrazine could be isolated (49). The acid ether extract as before, yielded a dark red oil. This oil was taken up with 150 cc. of alcohol and boiled for three hours with bone black to get rid of any tarry material present. The solution was then filtered while hot, the filtrate coming through a dark red.

The filtrate was stirred for twelve hours with 20 gr. of zinc dust and 40 gr. of acetic acid, and filtered again,

49. A dry ether solution with dry hydrogen chloride gave a gummy mass, from which no ethylphenylhydrazine hydrochloride could be obtained. Attempts to form the ethylphenylhydrazone of benzaldehyde by refluxing the residue with benzaldehyde in alcohol also gave negative results.

yielding a light filtrate. This filtrate was set on a hot plate to evaporate, but rapidly turned a dark red again as soon as it became warm, so the zinc and acetic acid treatment was then repeated for five hours more changing the color of the solution back to yellow. The solution was filtered and the filtrate poured into water yielding an oily light yellow precipitate. This was extracted with ether, the ether layer separated, washed several times with water, dried over calcium chloride, and evaporated down on a steam plate.

As the evaporation proceeded, the solution gradually darkened in color again, being very dark red when nearly all of the ether had been driven off. A little more than an equal volume of alcohol was then added, and the solution allowed to boil down again. As the evaporation proceeded the red color gradually faded until the solution was yellow. When nearly all of the alcohol had evaporated off the solution was allowed to stand over night, yielding a crop of needle-like crystals. After two recrystallizations from alcohol, the solid melted sharply at 175-176°. The identity of the compound was not determined.

The mother liquors from the two recrystallizations were evaporated down, yielding another crop of crystals

which on two more crystallizations melted at 175-176°.
The combined mother liquors of the second crop of 175-
176° melting compound was further evaporated down until
nearly all of the alcohol was driven off. A mass of
yellow crystals formed on cooling. These were filtered,
and recrystallized three times from as small amounts of
alcohol as possible; m.p. 90-92°. A mixed melting point
with triphenylmethane showed no depression. The mother
liquor was not further investigated.

The Action of Diethyl Sulphate on the Reaction
Product of Diphenyldiazomethane and Ethylmagnesium Bro-
mide. Ethylmagnesium bromide made from 4.5 gr. (.19
moles) of magnesium and 18 gr. (.16 moles) of ethyl bro-
mide was added to an ether solution of 15 gr. (.077 moles)
of diphenyldiazomethane.

During the addition of the Grignard reagent the pur-
ple red color of the solution gradually changed to yellow.
In that respect the reaction mixture was different than
when phenylmagnesium bromide was used, for it gave a deep
blood-red solution.

26 gr. (.16 moles) of diethyl sulfate was then added
in the cold but no reaction appeared to take place. The
ice bath was removed and in about five minutes a white

or a light yellow precipitate began to form, and the solution warmed up enough to start the ether refluxing. The reaction flask was cooled down enough to stop the refluxing and then stirred at room temperature for three and a half hours. The reaction mixture was hydrolysed with ammonium chloride in the cold, the light yellow ether layer separated, washed well with water, dried over calcium chloride, and evaporated down until the temperature of the solution was 50-55°. The residue was a bright yellow oil.

On standing over night, no solid phase appeared. No attempt was made to isolate the unknown benzophenonediethylhydrazone, but instead the oil was hydrolysed by refluxing four hours with 120 gr. of 50% sulfuric acid. The resulting solution was treated with more water after cooling and extracted with ether. The acid layer was then made alkaline with sodium hydroxide and steam distilled until the volume of the distillate was 500 cc. The distillate was made acid with hydrochloric acid and evaporated down to a thick, almost colorless oil on a steam plate.

The oil obtained was shown to be diethylhydrazine hydrochloride by preparing its known derivative 1,1-diethylsemicarbazide by boiling an alkaline solution of it with potassium cyanate, according to the method of Fischer.

(35). Fine white needles were obtained; m.p. 146-148°.
A mixed melting point with 1,1-diethylsomicarbazide (35)
made from known diethylhydrazine showed no depression.

SUMMARY

1. It has been proven that the Grignard reagent adds
to a single nitrogen atom in diphenyldiazomethane,
which supports the Zerner formula for the general struc-
ture of aliphatic diazo compounds.

2. Interpretations of other reactions of aliphatic
diazo compounds on the basis of the Zerner structure,
have been proposed.

3. A new method for the synthesis of substituted semi-
carbazides has been described.

PART III.

ATTEMPTS TO PREPARE LEAD TETRA-ALLYL
AND LEAD TETRABENZYL

Introduction.

Midgley (1) has shown that lead tetraethyl exerts a
very marked antiknock action in internal combustion engines.
This discovery by Midgley is of special importance in con-
nection with the development of high compression automobile
engines.

This work was undertaken to obtain the unknown lead
tetra-allyl and lead tetrabenzyl and to discover whether or
not they possessed any antiknock properties.

Lead tetra-allyl was selected for preparation, because
it would contain unsaturated linkages in addition to an atom
of lead. Gasolines which have a high percentage of unsatur-
ated compounds do not have as great a tendency to "knock"
as those which contain a smaller quantity. On that ground
it was thought that lead tetra-allyl might show antiknock
action superior to lead tetraethyl.

1. Midgley, J. Eng. Chem., 14, 589, 849, 894 (1922)

Discussion of Results.

Allylmagnesium bromide and benzylmagnesium chloride
were treated under various conditions with lead chloride
(2). In no case was any definite compound isolated.

The results obtained from the attempts to prepare
lead tetra-allyl were so discouraging that it was decided
to consult the literature concerning the allyl compounds
of other metals which may have a valence of four. It was
found that no allyl compound analogous to lead tetra-allyl
was known. On account of the negative results obtained,
and the fact that no other analogous metallic compounds
were known, it was decided as highly probable that the lead
tetra-allyl, if formed, was unstable.

No explanation has been found for the failure to ob-
tain lead tetrabenzyl. It may be that the particular con-
ditions necessary for its formation were not applied, though
that seems improbable.

2. The general method followed was that described for
   the preparation of lead tetraphenyl by Pfeiffer and
   Truskier, Ber., 37, 1125 (1904)

Experimental.

<u>Attempts to Prepare Lead Tetra-allyl</u>. 60.5 gr. (.5 moles) of allyl bromide in dry ether was slowly dropped into a suspension of 12 gr. (.5 moles) of magnesium, and 48 gr. (.17 moles) of lead chloride in dry ether. Vigorous mechanical stirring was used during the addition. A very vigorous reaction took place. After the completion of the addition of the allyl bromide, the mixture was stirred for fifteen minutes longer, the reaction flask cooled in an ice bath, and then hydrolysed with dilute hydrochloric acid.

There was a dark mass of insoluble material in the flask, after decanting the ether and water layers. This residue was washed several times with benzene, and the washings added to the ether layer. The resulting ether-benzene solution was washed with water, dried over anhydrous sodium sulfate, and heated to dryness on a steam plate. No residue remained, showing the absence of any organic lead compound in the solution.

The experiment was then repeated, using the same molecular quantities but having the reaction flask immersed in a freezing bath at -10°. When all of the allyl bromide had been added, the freezing bath was removed, and the reaction mixture refluxed for twenty minutes.

The mixture was hydrolysed with dilute hydrochloric acid, and the washed and dried ether layer distilled. Two fractions were collected, 35-40° and 40-50°. A very small amount of liquid, in which was suspended a slight, yellow precipitate remained in the distillation flask. The liquid burned completely, leaving no residue, when ignited. The dried yellow precipitate would not burn.

The residue from the reaction flask was then dried, and extracted with benzene for several hours, using a Soxhlet extractor. No residue remained after evaporating of the benzene.

Another run was made using the same molecular quantities, but instead of ether as a solvent, 200 cc. of dry toluene and 25 cc. of dry ether were used. The addition of the allyl bromide was very slow, taking about four hours for completion. The reaction flask was kept at 90-95°.

Attempts to Prepare Lead Tetrabenzyl. Benzylmagnesium chloride was prepared in the usual manner, with stirring, from 85 gr. (.67 moles) of benzyl chloride and 18 gr. (.75 moles) of magnesium. To this solution with rapid stirring was added 70 gr. (.25 moles) of lead chloride in small portions. With the addition of the first bit of lead chloride the solution turned dark and considerable heat was

evolved. After the addition of all of the lead chloride, 250 cc of benzene were added, and the ether distilled off. The resulting benzene solution was then refluxed for five hours, cooled, and hydrolysed with dilute hydrochloric acid. A residue remained in the bottom of the flask which appeared to be metallic lead.

The benzene layer was separated, washed with water, dried, and evaporated to a small volume. This residue was steam distilled until all of the benzene and dibenzyl were driven over. Some yellow amorphous appearing material was left behind . The amount was very small, less than .5 gr. On ignition the dry residue burned to a metallic looking residue, which might have been lead.

Another run was made under the same conditions, except that an equal quantity of toluene was added with the benzene in replacing the ether as the solvent. It was hoped that this attempt would yield more of a yellow material, which might be lead tetrabenzyl. To that end the reaction mixture was refluxed twice as long (8 hrs.), and then worked up in the same way as before. The result was the same, only a trace of the yellow material being obtained.

SUMMARY

Unsuccessful attempts have been made to prepare lead tetra-allyl and lead tetrabenzyl. Their possible use as antiknock compounds for automobile engines has been discussed.