3. A comparison of these absorption spectra reveals a pronounced similarity in the region of the shorter wave lengths as far as 5.5μ and beyond this point shows increasing dissimilarity as the longer wave lengths are approached.

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THE REACTION BETWEEN ORGANIC PEROXIDES AND ORGANOMAGNESIUM HALIDES

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RECEIVED JULY 20, 1925 PUBLISHED NOVEMBER 5, 1925

In connection with studies on the relationship between chemical constitution and antiseptic action, an investigation has been made of the reaction between some typical organic peroxides and the Grignard reagent. 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.

$$\mathrm{ROOR} + \mathrm{R'MgX} \longrightarrow \mathrm{ROR'} + \mathrm{ROMgX} \qquad (1)$$

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] obtained 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 (1) takes place. When an excess of Grignard 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

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[1] Wuyts [*Bull. soc. chim.*, **35**, 166 (1906)] predicted a like reaction with diselenides and also probably with peroxides.

[2] Oddo and Binaghi, *Gazz. chim. ital.*, [II] **51**, 343 (1921); **54**, 193 (1924); *C. A.*, **18**, 3166 (1924).

[3] Durand and Naves, *Compt. rend.*, **180**, 521 (1925).

[4] Unpublished results of work by Agnes Wood.

[5] Although good yields of tertiary alcohols are obtainable, the reaction merits little consideration from a synthetic viewpoint. Unpublished 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).

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.

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 (1) also took place. Diethyl peroxide is not to be confused with the ether peroxide [$CH_3CH(OOH)(OC_2H_5)$] described by Clover[8] in his work on the auto-oxidation of ether. This peroxide and 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 molecular weight like benzohydryl disulfide [$(C_6H_5)_2CHSSCH(C_6H_5)_2$] and bornyl disulfide.

It has long been known that oxygen produces chemiluminescence 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.

Experimental Part

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 hydrolyzed by dil. hydrochloric acid. The ether-benzene layer was separated, washed with dilute

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[7] The authors wish to express their appreciation to Frederick Stearns and Co. of Detroit for ample supplies of this compound.

[8] Clover. This Journal, **44**, 1107 (1922).

[9] Evans and Dufford, *ibid.*, **45**, 278 (1923). Dufford, Calvert and Nightingale, *ibid.*, **45**, 2058 (1923). Most recently, Dufford, Nightingale and Calvert, *ibid.*, **47**, 95 (1925).

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.

Various conditions were used in the reactions with 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[a]	Compounds formed (yield, %)
Dibenzoyl[b]	0.416	Bromobenzene	0.41	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*-butylphenyl carbinol (72)
Dibenzoyl	.04	Benzyl chloride	.2	Dibenzylphenyl carbinol (73)[f]
Succinic[g]	.2	Bromobenzene	.2	......
Triacetone[h]	.09	Bromobenzene	.8	Dimethylphenyl carbinol (25); phenol (66)
Diethyl	.5	Bromobenzene	.63	Phenetole (34); diphenyl (30)[i]
Triphenylmethyl[j]	.03	Bromobenzene	.05	......

[a] The quantity of RMgX used was approximately that actually present [Gilman and McCracken, THIS JOURNAL, **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 medium was extracted with benzene prior to hydrolysis. Concentration of this benzene solution gave phenyl benzoate. The solid residue after extraction with benzene was practically pure bromomagnesium benzoate ($C_6H_5CO_2MgBr$). This was determined from the weight of benzoic acid obtained on acidification.

[c] Fifty 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 overnight the mixture was refluxed for an hour; 8.5 g. or 80% of benzoic acid was also obtained.

The di-*n*-butylphenyl 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. p., 125–126° (7 mm.); d_4^{21}, 0.9319; n_{D}^{21}, 1.4824. At room temperatures the tertiary alcohol is a thick, colorless oil. The temperatures recorded in this paper are uncorrected.

[f] The dibenzylphenyl 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; m. p., 90–94°. This compound may have been the monophenyl ester of succinic acid. A repetition of this experiment wherein refluxing was carried out for 13 hours in benzene-ether gave no solid product.

The ether was largely replaced by anisole in a third experiment, and after the mixture had been heated 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 that this compound was not α,Δ-dihydroxy-α,α,Δ,Δ-tetraphenylbutane $[(C_6H_5)_2C(OH)CH_2CH_2C(OH)(C_6H_5)_2]$. It is possible that the 199° compound may be a dehydration product of the dihydroxybutane, namely, tetraphenylbutadiene; m. p., 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° and 120°. The time factor in these rapid decompositions is also significant. In some experiments the reaction mixture exploded after being heated for several hours at 100–110°, 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 during 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 0.5 g. 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 mole of peroxide and 0.67 mole of phenylmagnesium bromide were 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° had been continued for five 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 the method of 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.

$$\begin{array}{ccc} \mathrm{H{-}O{-}O{-}H} & \mathrm{H{-}O{\equiv}O{-}H} & \mathrm{O{=}O{=}H_2} \\ \mathrm{A} & \mathrm{B} & \mathrm{C} \end{array}$$

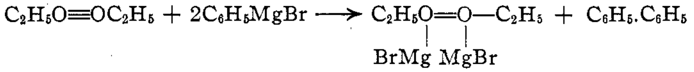
Oddo admits that no decisive answer concerning the constitution of hydrogen peroxide can be made as yet. On the basis of his work he inclines towards Formulas B and C. He postulates with (B) and one molecule of RMgX compound the hypothetical addition compound (MgX)HO=OH(R).

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 unusual quantities of diphenyl formed in the reaction between diethyl peroxide and phenylmagnesium bromide suggested at once that an analogy might truly exist between peroxides and azo compounds.[11] Gilman and Pickens[12] found that the following reaction takes place between azobenzene and phenylmagnesium bromide.

$$C_6H_5N{=}NC_6H_5 + 2C_6H_5MgBr \longrightarrow C_6H_5N(MgBr)N(MgBr)C_6H_5 + C_6H_5.C_6H_5 \qquad (2)$$

If we admit the correctness of Oddo's conjecture that addition of RMgX to hydrogen peroxide may take place, and if we admit also the correctness of the analogy between peroxides and azo compounds made by Gelissen and Hermans, then the following reaction may occur between diethyl peroxide and phenylmagnesium bromide.



$$C_2H_5O{\equiv}OC_2H_5 + 2C_6H_5MgBr \longrightarrow C_2H_5\underset{\displaystyle BrMg}{\underset{|}{O}}{=}\underset{\displaystyle MgBr}{\underset{|}{O}}{-}C_2H_5 + C_6H_5.C_6H_5 \qquad (3)$$

Certain it is that diethyl peroxide behaves differently towards RMgX compounds than the other peroxides. The formation of phenetole shows that some of the splitting reaction of (1) occurs. However, none of the other peroxides gave any more than the usual quantities of diphenyl found in the preparation of phenylmagnesium bromide. Furthermore, the quantity of phenol obtained in the experiments with diethyl peroxide is that found in the customary preparation of phenylmagnesium bromide.[4,11] Dibenzoyl and triacetone peroxides gave significant 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 intermediate 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 oxidation of RMgX compounds (such

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[10] Ref. 6, p. 984. Also, Bigiavi [*Gazz. chim. ital.*, [II] **51**, 324 (1921)] studied the action of RMgX compounds on peroxides of some nitrogen compounds such as glyoximes.

[11] Porter and Steel [THIS JOURNAL, **42**, 2650 (1920)] found that the quantity of diphenyl present in the preparation of phenylmagnesium bromide is not altered by passing oxygen through the ether solution.

[12] Gilman and Pickens, *ibid.*, **47**, 2406 (1925).

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: $ROOR + R'MgX \longrightarrow ROR' + ROMgX$. 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.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF EDGEWOOD ARSENAL, UNITED STATES CHEMICAL WARFARE SERVICE,[1] AND JOHNS HOPKINS UNIVERSITY]

REACTIONS OF β,β'-DICHLORO-ETHYL SULFIDE WITH AMINO COMPOUNDS

BY WALTER E. LAWSON[2] AND E. EMMET REID

RECEIVED JULY 20, 1925 PUBLISHED NOVEMBER 5, 1925

Four theories have been advanced to explain the remarkable vesicant action of β,β'-dichloro-ethyl sulfide. Each of these fits certain facts but none is entirely satisfactory. The present investigation was undertaken to obtain more information about the reactions of this compound with substances containing the amino group, since amino compounds are important constituents of living tissue. It was hoped to prepare derivatives from the more complicated amino acids but it seemed best to begin with a more thorough study of reactions with simpler amino compounds.

The present investigation comprises the following. (1) A further study of the thiazanes, $S<(CH_2CH_2)_2>NR$, from primary amines. (2) Investigation of the new thiazane-1-oxides, $OS<(CH_2CH_2)_2>NR$. (3) Extension of the preparation of thiazane-1-dioxides, $O_2S<(CH_2CH_2)_2>NR$, to aliphatic amines. (4) A study of the reactions of β,β'-dichloro-ethyl sulfide, sulfoxide and sulfone with secondary aliphatic amines to form $S(CH_2CH_2NR_2)_2$, $OS(CH_2CH_2NR_2)_2$ and $O_2S(CH_2CH_2NR_2)_2$. Among these, the sulfide derivative from dimethylamine lost one amine grouping in a surprising way to form the unsaturated compound $(CH_3)_2NCH_2CH_2SCH{:}CH_2$. (5) The preparation of salts of quaternary bases, $S(CH_2CH_2NR_3Cl)_2$, $OS(CH_2CH_2NR_3Cl)_2$ and $O_2S(CH_2CH_2NR_3Cl)_2$. (6) A study of the reactions of β,β'-dichloro-ethyl sulfone with free amino acids instead of their esters, to form such compounds as $O_2S<(CH_2CH_2)_2>NCH(COOH)CH_2C_6H_5$.

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[13] It is probable that an aid to the solution of this problem will be found in some studies now in progress on the reaction between sulfenic esters (R—S—O—R) and the Grignard reagent.

[1] Published by permission of the Chief of the Chemical Warfare Service.

[2] From the dissertation of W. E. Lawson, Johns Hopkins University, 1925.