drogen peroxide during an experiment, V is the volume of the "light reaction" vessel, N is Avogadro's number, $I_{\text{abs.}}$ is the average intensity of the absorbed light expressed as galvanometer deflection in centimeters, $h\nu$ is the energy of a photon of λ 5300 Å., and S is the sensitivity of the galvanometer thermopile system in ergs per minute per cm. deflection. This expression will give the true value of the quantum yield only if it is directly proportional to the concentration of the hydrogen peroxide.[7] However, if the quantum yield were independent of the concentration of hydrogen peroxide, the error introduced by the use of this approximate relation would be less than the average error of the experimental determination of the quantum yield. The average value of the quantum yield (so computed) is 0.4.[8] It is noteworthy that this value is less than unity, and is therefore not in agreement with any chain mechanism of the reaction. More exact measurements of the effect of light on the steady-state rate and function (preferably at a lower temperature and at lower concentrations of peroxide) must be available before a detailed discussion of the mechanism of the photochemical process will be justifiable.

Summary

1. The steady-rate of the decomposition of hydrogen peroxide in bromine–bromide solutions has been measured in the dark and in the light, under otherwise comparable conditions. Although light increases the absolute rate of the reaction, within the limits of experimental error the rate for either the dark or light reaction may be represented by the equation $V = K(H_2O_2)(H^+)(Br^-)$. The increase in the absolute rate is satisfactorily accounted for by the increase in the steady-state concentration of hydrobromic acid.

2. The quantum yield for the bromo sensitized decomposition of hydrogen peroxide has been computed (with the aid of certain simplifying assumptions), and has been shown to have an average value less than unity.

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[7] Even for this case the method is an approximate one, since $k_d(H_2O_2)$ does not properly represent the rate of the thermal reaction which is taking place in the illuminated solution. Although this quantity may be readily corrected for the differences in the steady-state concentrations of H^+, Br^- and Br_2 in the "light" and "dark" reacting mixtures, the corrected values of the quantum yield do not differ greatly from the approximate values given in Table I. Therefore, for the sake of simplicity and brevity only the approximate method is presented here.

[8] The value of M/Q for experiment 14 appears to be out of the range of the random distribution of errors and has been excluded from the average.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

The Action of Magnesium on Homonuclear Dibromodiphenyls

BY FRANCIS H. CASE

The study of the action of magnesium on homonuclear dibromo aromatic hydrocarbons has thus far been confined to the compounds *m*- and *p*-dibromobenzene,[1] 3,4-dibromotoluene, *sym*-tribromotoluene, 1,3-dimethyl-4,6-dibromobenzene,[2] and 1,2 and 1,4-dibromonaphthalenes.[3] In the case of *p*-dibromobenzene, which has been rather extensively investigated, it was first believed that in the presence of two atoms of magnesium[4] only one atom of bromine is capable of reacting. Later investigations, however, showed that in an inert atmosphere a part of the second atom[5] of magnesium will react to form a di-Grignard, but this reaction never reaches completion. Thus it has been found that with both *p*- and *m*-dibromobenzene, 87% of the original two atoms of magnesium enters the reaction; 3,4-dibromotoluene, 83%; 1,3-dimethyl-4,6-dibromobenzene, 49.6% of the total bromine; *sym*-tribromotoluene, no reaction; 1,4-dibromonaphthalene, 72% magnesium; 1,2-dibromonaphthalene, 75.5% magnesium. It is worthy of note that in the few cases where unsymmetrical dibromides have been investigated, in only one instance (1,2-dibromonaphthalene) have results been obtained that would indicate which of the bromine atoms is more readily attacked by the magnesium.

The object of the present investigation has been to determine the extent to which certain homonuclear dibromodiphenyls react with two atoms of magnesium, and in the case of unsymmetrical de-

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[1] Salkind and Rogovina, *J. Russ. Phys.-Chem. Soc.*, **59**, 1013 (1927).

[2] Salkind, *J. Gen. Chem.* (U. S. S. R.), **1**, 193 (1931).

[3] Salkind, *Ber.*, **67**, 1031 (1934).

[4] Pink, *J. Chem. Soc.*, **123**, 3418 (1923).

[5] (a) Quelet, *Bull. soc. chim.*, **41**, 933 (1927); (b) Gilman, Beaber and Jones, *Rec. trav. chim.*, **48**, 597 (1929).

rivatives, which bromine atom is preferentially attacked. The compounds chosen for this study were 2,5, 3,5, 2,4 and 3,4-dibromodiphenyls. The preparation of the first three of these dibromides was according to the directions of Scarborough.[6] It should be noted however that 2,4-dibromodiphenyl, which was not obtained in a state of purity by this author, has now been isolated. The preparation of the 3,4-isomer is described in another paper from this Laboratory.[7]

In the experiments to be described, the amount of di-Grignard formation in each case was estimated by weighing the amount of diphenyl solidifying in the receiver after fractional distillation of the hydrolytic products. This method cannot be regarded as strictly accurate as the diphenyl obtained in this way is not entirely pure, yet it gives a better idea of the amount of di-Grignard formation than if the diphenyl obtained were recrystallized, since losses involved in crystallization are large. The nature of the mono-Grignard reagent simultaneously formed was established by oxidizing the monobromodiphenyl resulting from hydrolysis and identifying the corresponding bromobenzoic acid. The unused magnesium was determined by measuring the hydrogen evolved on treatment of the mixture after completion of the reaction with dilute sulfuric acid. The bromine going into water solution was determined gravimetrically.

The results of the experiments in which each of the four isomeric dibromodiphenyls mentioned above was treated with two atoms of magnesium show that the isomers, arranged in the order of decreasing extent of reaction with magnesium, are 2,4, 2,5, 3,5, 3,4. In fact the last-mentioned compound could not be made to react when treated with the activated copper–magnesium alloy of Gilman.[8] From the hydrolytic products of the reactions involving the 2,4- and 2,5-isomers, liquids were obtained which both yielded on oxidation with chromic anhydride, *o*-bromobenzoic acid, thus indicating that in each case the bromine in 2-position was the one less readily attacked. A similar process yielded in the case of 3,5-dibromodiphenyl, *m*-bromobenzoic acid. The close check between the amount of magnesium consumed and the amount of bromine in water solution (indicating a ratio of one atom of each) and the small amount of high boiling residue obtained indicate the absence of any considerable amount of coupling.

The activated copper–magnesium alloy was also used with each of the isomeric dibromodiphenyls, increasing the yield of di-Grignard in the cases of those which reacted with ordinary magnesium.

By treating the 2,5 and 3,5-isomers, respectively, with one atom of magnesium, followed by carbon dioxide, the acids 2-bromodiphenyl-5-carboxylic acid, prepared by Cook and Cook[9] by the oxidation of 2-bromo-5-methyldiphenyl, and 3-bromodiphenyl-5-carboxylic acid, heretofore unknown, were obtained.

In only one case (the 2,5-isomer) was the dicarboxylic acid resulting from the action of carbon dioxide on the di-Grignard formed by the action of 2 atoms of copper–magnesium alloy on the corresponding dibromide, isolated in a state of purity. The 3,5-isomer yielded an acid which could not be freed entirely from bromine even by repeated crystallization. This recalls the difficulties experienced by Gilman[5b] in attempts to obtain pure terephthalic acid from *p*-dibromobenzene. In the case of the 2,4-dibromide, no dicarboxylic acid was found. In the cases of the 2,5, 3,5, and 2,4-isomers, relatively large amounts of monobromocarboxylic acid were isolated. One must therefore conclude that although, as shown by previous experiments, the di-Grignard is formed to a large extent, yet on treatment with carbon dioxide it is partly unaffected as shown by the presence of a certain amount of diphenyl after hydrolysis, and is subject to side reactions leading to the formation of acidic resins obtained as by-products.

Experimental

Preparation of Dibromodiphenyls.—These compounds were tested for absence of nitrogen, and gave a correct bromine analysis.

Preparation of 2,4-Dibromodiphenyl.—By the hydrolysis of 78.5 g. of 4,6-dibromo-3-acetaminodiphenyl with alcoholic hydrobromic acid was obtained 69.2 g. of crude base. The base, dissolved in alcohol, and treated with excess of 1–1 sulfuric acid, was deaminized by means of sodium nitrite. In order to remove from the final product all traces of nitrogenous matter, it was dissolved in absolute ether and filtered from a white precipitate which formed, then washed successively with aqueous hydrobromic acid, and sodium bicarbonate solution. On redistillation, 28 g. was obtained, b. p. 174–176° (7 mm.).

Anal. Calcd. for $C_{12}H_8Br_2$: Br, 51.25. Found: Br, 51.11.

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(6) Scarborough, *J. Chem. Soc.*, 557 (1926); **89**, 3000 (1927).

(7) Case, THIS JOURNAL, **58**, 1249 (1936).

(8) Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

(9) Cook and Cook, THIS JOURNAL, **55**, 1217 (1933).

Action of Dibromodiphenyls on Two Atoms of Magnesium.—Fifteen and six-tenths grams (0.05 mol) of dibromodiphenyl dissolved in absolute ether was refluxed not less than fifteen hours with 2.4 g. of magnesium in the presence of a trace of iodine. With the 3,5 and 2,5 isomers and plain magnesium, an atmosphere of nitrogen was maintained, but in all other experiments hydrogen was the inert gas used. On completion of the reactions, hydrolysis was effected by dilute sulfuric acid, the evolved hydrogen being collected over water. Ether vapors were removed by absorption in concentrated sulfuric acid. The ether layer was carefully separated from the water layer, the latter being analyzed for bromine, after removal of the iodine by means of sodium nitrite. The ether layer was evaporated, and the residue fractionated in a vacuum, the amount of solid collecting in the receiver being weighed as diphenyl. The higher boiling liquid was oxidized by means of chromic anhydride in glacial acetic acid, and the resulting bromobenzoic acid identified by a mixed melting point with an authentic specimen. The results are shown in Table I.

Table I

Action of Dibromodiphenyls on Two Atoms of Magnesium

Isomer (0.05 mole)		3,5	2,5	2,4
Mg unused, g.		0.83	0.83	0.73
Bromine in solution	g.	4.86	5.29	5.59
	%	61	66	70
Diphenyl	g.	2.0	3.0	4.3
	%	26	39	56
Mono-Br-diphenyl, g.		7	4.5	3.9
Benzoic acid from oxidation of mono-Br-diphenyl		*m*-Br-	*o*-Br-	*o*-Br-

Action of the Dibromodiphenyls on Two Atoms of Copper-Magnesium Alloy.—Fifteen and six-tenths grams of dibromodiphenyl, dissolved in absolute ether, was refluxed for not less than fifteen hours with approximately 3 g. of activated copper–magnesium alloy prepared according to the directions of Gilman, Peterson and Schulze.[8] The results are shown in Table II.

Table II

Action of Dibromodiphenyls on Two Atoms of Cu-Mg Alloy

Isomer (0.05 mole)		3,5	2,5	2,4	3,4
Bromine reacting	g.	5.57	6.44	6.56	No reaction
	%	69.6	80.5	82.0	
Yield of diphenyl, g.		2.7	5.3	6.0	....
Diphenyl, %		35.1	68.8	77.9	....

The 3,4-dibromodiphenyl would not react even though a small amount of the activated magnesium of Gilman and Kirby was added to the reaction mixture.[10]

Action of 3,5-Dibromodiphenyl on 1 Atom of Mg + CO_2.—One-twentieth mole of 3,5-dibromodiphenyl was treated with 1.2 g. of magnesium as before. After complete solution of the magnesium, carbon dioxide was passed into the mixture, cooled by ice and salt, for two hours. Decomposition was then effected by dilute hydrochloric acid. The ether solution was washed with alkali, the acid reprecipitated with concd. hydrochloric acid and extracted with ether. After removal of the ether the acid was crystallized from benzene and petroleum ether; yield 3.5 g.; m. p. 177–178°.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 29.21.

Action of 2,5-Dibromodiphenyl on 1 Atom of Mg + CO_2.—The procedure was the same as with the 3,5-isomer. Two grams of a monobromodiphenyl carboxylic acid was obtained, m. p. 247–248°. The 2-bromodiphenyl-5-carboxylic acid of Cook and Cook melted at 242–243°. The identity of the acid obtained above was further confirmed by the fact that the mono-Grignard reagent on hydrolysis yields only *o*-bromodiphenyl.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 28.72.

Action of the Dibromodiphenyls on 2 Atoms of Cu–Mg alloy + CO_2.—The quantities used were the same as when the Grignard was directly hydrolyzed. The results are shown in Table III.

Table III

Action of Carbon Dioxide on Diphenyl Di-Grignard Reagents

Dibromodiphenyl (15.6 g. used)		3,5	2,5	2,4
Yield of bromocarboxylic acid	g.	5.7	1.9	2.0
	%	41	14	15
Yield of dicarboxylic acid	g.	1.3	2.2	0
	%	11	18	0
Diphenyl isolated, g.		0.2	1.0	0.6

Action of 3,5-Dibromodiphenyl.—After the decomposition of the carbon dioxide–Grignard complex with hydrochloric acid, the precipitated acids were extracted with ether, and removed from the ether by extraction with potassium hydroxide. After reprecipitation with concd. hydrochloric acid, 10 g. of crude acid was obtained. This was separated by means of hot benzene into a soluble fraction which on recrystallization from a methyl alcohol–water mixture yielded 5.7 g. of crude 3-bromodiphenyl-5-carboxylic acid, m. p. 168–170°. The benzene-insoluble portion, weighing 1.9 g. was recrystallized four times from glacial acetic acid, yielding 0.6 g. of an acid melting at 330–334° but still containing 1.19% bromine. Equivalent weight: calcd. for $C_{14}H_{10}O_4$: 121. Found: 126.

Action of 2,5-Dibromodiphenyl.—The mixed acids (12.5 g.) obtained by adding hydrochloric acid to the alkaline extract of the original ether solution, and again extracting with ether, were extracted with hot benzene, yielding 4.5 g. of benzene insoluble material, which after repeated crystallization from a benzene–ether mixture yielded 0.5 g. of pure diphenyl-2,5-dicarboxylic acid, m. p. 274–275°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.40; H, 4.16. Found: C, 69.62; H, 4.35.

The benzene soluble portion of the above extraction, after several crystallizations from a benzene–petroleum ether mixture, yielded 1.9 g. of 2-bromodiphenyl-5-carboxylic acid, m. p. 247–248°, previously described. The original ether solution, after extraction with sodium hydroxide solution, yielded after evaporation 1 g. of diphenyl.

Action of 2,4-Dibromodiphenyl.—The original ether solution, after extraction with sodium hydroxide solution, acidification of the alkaline solution with hydrochloric

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(10) Gilman and Kirby, *Rec. trav. chim.*, **54**, 577 (1935).

acid, and extraction with ether yielded 10 g. of crude acid, which dissolved in hot benzene. After several crystallizations from methyl alcohol, 2 g. of an acid was obtained, melting at 213–214°, yielding finally an acid of m. p. 218–219°, which melted unchanged with 2-bromodiphenyl-4-carboxylic acid, prepared from 4-methyl-2-bromoaniline by the method of Gomberg and Pernert.[11]

The original ether solution, after extraction with sodium hydroxide, yielded 0.6 g. of diphenyl.

The author acknowledges the assistance of Mr. Henry Sloviter in connection with a portion of the analytical work in this paper.

Summary

1. A study has been made of the extent of the reaction of 3,5, 2,5, 2,4 and 3,4-dibromodiphenyls, respectively, with (a) one and two atoms of magnesium; (b) two atomic proportions of activated copper–magnesium alloy.

2. The nature of the resulting products has been determined when the Grignard reagent is (a) directly hydrolyzed; (b) first treated with carbon dioxide and then hydrolyzed.

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[11] Gomberg and Pernert, THIS JOURNAL, **48**, 1372 (1926).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

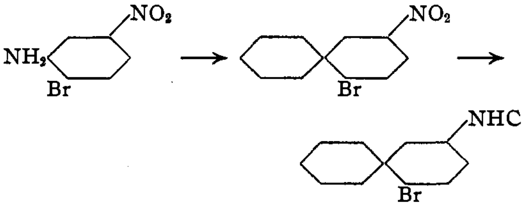
The Preparation of 3,4-Dibromodiphenyl

BY FRANCIS H. CASE

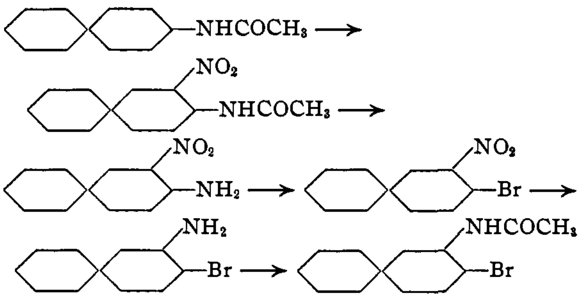
The preparation of 3,4-dibromodiphenyl has previously been reported by Scarborough,[1] who stated that it could be obtained by the replacement by bromine of the amino group in the bromo amine resulting from the hydrolysis of what he believed to be 4-bromo-3-acetaminodiphenyl. Scarborough's evidence for the structure of the dibromodiphenyl is based on its oxidation by chromic anhydride to 3,4-dibromobenzoic acid. Reasoning back he therefore concluded that on monobromination 3-acetaminodiphenyl is substituted in the 4-position rather than in the more to be expected 6-position.

In a study of the action of magnesium on various homonuclear dibromodiphenyls,[2] the so-called 3,4-dibromodiphenyl of Scarborough was subjected to the action of two atoms of magnesium–copper alloy, followed by carbon dioxide. The two acids resulting were identified as 2-bromodiphenyl-5-carboxylic acid, and diphenyl-2,5-dicarboxylic acid. This suggested the possibility that Scarborough's dibromodiphenyl was derived from 2-bromo-5-acetaminodiphenyl, the normal bromination product. On repeating the oxidation of the dibromodiphenyl, however, a small amount of 3,4-dibromobenzoic acid was obtained, in addition to the expected 2,5-dibromobenzoic acid (also in small quantity). The amounts of the two dibromo acids isolated after oxidation do not, however, give a satisfactory idea of the amounts of dibromides present in the original mixture, as experiments with the pure dibromides indicate that the 2,5-isomer is much more easily destroyed by oxidation than the 3,4.

2-Bromo-5-acetaminodiphenyl was next synthesized by the reaction of Gomberg and Pernert,[3] as follows:



4-Bromo-3-acetaminodiphenyl was prepared by the following series of reactions



This latter product melted at 127°, whereas 2-bromo-5-acetaminodiphenyl prepared by Gomberg's method melts at 162–163°, and Scarborough's bromo-3-acetaminodiphenyl at 163–164°. The latter two products when mixed showed no change in melting point. Since the dibromodiphenyl obtained from Scarborough's

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[1] Scarborough, *J. Chem. Soc.*, 3000 (1927).

[2] Case, THIS JOURNAL, **58**, 1246 (1936).

[3] Gomberg and Pernert, *ibid.*, **48**, 1372 (1926).