of ether with 47.7 g. (0.3 mole) of *n*-butyl *N*,*N*-diethylaminomethyl ether[18] in 200 ml. of dry ether. After 1 hr. the reaction mixture was decomposed with water, and the two layers were separated. The ether layer was dried over magnesium sulfate and the solvent removed. The residue was distilled *in vacuo*, the fraction boiling at 140–165° at 8 mm. being collected. Redistillation of this fraction gave 32.4 g. (43%) of amine IV, b.p. 171–171.5° at 10 mm.

Anal. Calcd. for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.54. Found: C, 85.53; H, 9.17; N, 5.35.

Samples of amine (IV) obtained by each method were converted to the picrate which, after recrystallization from ethanol, melted at 192–193°; a mixture melting point was the same.

(*D*) *With sodium diphenylmethide.* To a stirred solution of 0.03 mole of sodium diphenylmethide in 300 ml. of liquid ammonia[12] was added 10 g. (0.0285 mole) of tosylate (II). After 3 hr. (red color of reagent discharged), the ammonia was evaporated as an equal volume of ether was added. The resulting suspension was shaken with water, and the two layers were separated. The ether layer was dried over Drierite, and the solvent was partly removed to precipitate unchanged tosylate (II), which was removed by filtration (3 g. of II, m.p. 116°, after recrystallization from acetone). The ether filtrate was evaporated almost to dryness, and petroleum ether (b.p. 30–60°) was added. The resulting mixture was cooled in a Dry Ice–acetone bath to precipitate hydrocarbon (V), which was removed by filtration (1.2 g. of V, m.p. 80–81° after recrystallization from ethanol; its infrared spectrum was identical with that of an authentic sample of V[12]). The filtrate was distilled to give 2.75 g. of olefin (III), b.p. 137–140° at 11 mm. (see note a of Table I), contaminated with about 15% of diphenylmethane as estimated from the infrared absorption spectrum.

(*E*) *With piperidine.* A solution of 3.0 g. of tosylate (II) in 50 ml. of piperidine was heated on the steam bath for 6 hr. Excess amine was removed under reduced pressure, and the residue was taken up in ether. After washing with water, the ether solution was dried over Drierite, and the solvent removed. The residue was dissolved in 50 ml. of ethanol, and the solution treated with 50 ml. of saturated picric acid solution diluted with 80 ml. of ethanol. Overnight standing afforded large yellow crystals, which were recrystallized from ethanol to give 2.9 g. (59%) of the picrate of *N*-(2,2-diphenylethyl)piperidine (VI), m.p. 186°.

Anal. Calcd. for $C_{25}H_{26}N_4O$: C, 60.72; H, 5.30; N, 11.33. Found: C, 61.11; H, 5.50; N, 11.23.

Independent synthesis of VI was effected[19] by treating 0.15 mole of benzohydrylmagnesium bromide[11] in 300 ml. of ether with 20.5 g. (0.12 mole) of *N*-*n*-butoxymethylpiperidine[18] (b.p. 72–73.5° at 3.5–4 mm., $n^{23.5}_{D}$ 1.4454, yield 66%) in 100 ml. of ether. After 16 hr. at room temperature, the reaction mixture was decomposed with hydrochloric acid and the resulting two phases made basic with ammonium hydroxide. The layers were separated. The solvent was removed from the ether layer, and the residue distilled to give 16.3 g. (51%) of amine (VI), b.p. 118–120° at 0.12 mm., n_D^{24} 1.5663 (lit. b.p. 167–170° at 1 mm.).[20] The picrate melted at 184–185; this melting point was not depressed on admixture with a sample of the picrate obtained as described above.

(*F*) *With morpholine.* A solution of 3.0 g. of tosylate II in 50 ml. of morpholine was heated on the steam bath for 4 hr., and then allowed to stand overnight at room temperature. The reaction mixture was worked up as described above for that with piperidine. There was obtained 3.2 g. (65%) of the picrate of *N*-(2,2-diphenylethyl)morpholine (VII), m.p. 206–207° after recrystallization from ethanol.

Independent synthesis of amine (VII) was effected[19] from benzohydrylmagnesium bromide and *N*-*n*-butoxymethylmorpholine (b.p. 75–76° at 2.4 mm., n^{25}_{D} 1.4442, yield 54%) essentially as described above for the amine (VI). There was obtained 17.1 g. (53%) of amine (VII), m.p. 50–51° (recrystallized from ligroin, b.p. 60–90°).

Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 81.21; H, 8.05; N, 5.20.

The picrate melted at 205–207°, which was not depressed on admixture with a sample of the picrate obtained as described above.

DURHAM, N. C.

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(18) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 536 (1923).

(19) We are indebted to Dr. G. F. Morris for performing this experiment.

(20) O. Exner, J. Pliml, and M. Protiva, *Chem. Listy*, 48, 65 (1954).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SOUTH DAKOTA STATE COLLEGE]

Decomposition of Ditriphenylmethyl Peroxide in Concentrated Sulfuric Acid

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Gomberg's early work on the decomposition of ditriphenylmethyl peroxide in concentrated sulfuric acid has been repeated and confirmed. Evidence is presented for the mechanism whereby the major product is triphenylcarbinol. The base soluble products are shown to result from the oxidation of triphenylcarbonium ion by Caro's acid.

In several of Gomberg's early papers on triphenylmethyl[1,2] it was reported that on diluting ditriphenylmethyl peroxide dissolved in cold concentrated sulfuric acid with water an 80% yield of triphenylcarbinol was obtained. This observation was found to be disturbing for several reasons. First of all it appeared on first glance to be a reduction taking place in concentrated sulfuric acid. Secondly, a likely mechanism which involved the protonation of one of the peroxide oxygens followed by a heterolytic oxygen–oxygen cleavage should have given rise to triphenylcarbinol and a triphenylmethoxy cation. The triphenylmethoxy cation would be expected to undergo a 1,2-rearrangement whereby a phenyl group migrates to the oxygen atom with the open sextet. Such rearrangements have been postulated for the Baeyer-Villiger

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(1) M. Gomberg, *Chem. Ber.*, 33, 3157 (1900).

(2) M. Gomberg, *J. Am. Chem. Soc.*, 22, 765 (1900).

rearrangement of benzophenone[3] and shown for the acid-catalyzed decomposition of *p*-nitrotriphenylmethyl hydroperoxide.[4] This type of mechanism would imply the formation of a mole of triphenylcarbinol, a mole of phenol, and a mole of benzophenone from a mole of ditriphenylmethyl peroxide. The yield of triphenylcarbinol should therefore have been less than 50% rather than the 80% reported by Gomberg.

In order to clarify this seeming anomaly, Gomberg's experiment was repeated. Ditriphenylmethyl peroxide was dissolved in concentrated sulfuric acid and quenched on ice. For two separate runs, the neutral ether extract yielded 91% and 92% triphenylcarbinol assuming a theoretical yield of two moles of triphenylcarbinol per mole of ditriphenylmethyl peroxide. These samples checked with authentic triphenylcarbinol both with respect to melting point and infrared spectrum. Benzophenone could not be isolated. Its absence was further indicated by a lack of the carbonyl frequency at 1670 cm.$^{-1}$ in the infrared. In order to make certain, the infrared extinction coefficient was determined for benzophenone in carbon tetrachloride solution. The neutral fraction when quantitatively analyzed showed that benzophenone, if present, occurred in amounts less than 0.9% of the weight of the total neutral fraction. The acidic fraction, which was a dark reddish brown tar, decolorized bromine in carbon tetrachloride, giving off hydrogen bromide. The infrared spectrum indicated a hydrogen-bonded OH stretching frequency. However, no phenol could be sublimed from the mixture. Using the same conditions, small quantities of phenol could easily be detected in artificial mixtures.

It was discovered that the aqueous mixture formed by pouring a solution of ditriphenylmethyl peroxide in concentrated sulfuric acid on ice readily liberated iodine from potassium iodide. Efforts were made to assay for this peroxygen content. Sulfatoceric methods were developed for small amounts of peroxides in the presence of large amounts of sulfuric acid.[5] However, the water-soluble organic substances were slowly oxidized by the sulfatoceric ion leading to indefinite end points. Since the iodometric determinations in concentrated acid solutions are more prone to errors due to air oxidation[6,7] and to induced decomposition of the thiosulfate,[8,9] titrations were carried out using the same techniques as those used in analyzing the reaction mixture. The results shown in Fig. 1 indicated that in the acid concentrations used, the error was probably no greater than about ten parts per thousand. Using this iodometric technique it was shown that the peroxide molar concentration varies from 73% to a trace of approximately 0.1% depending on the length of time the trityl peroxide is allowed to stand in contact with the concentrated sulfuric acid. The highest peroxide value was obtained by quenching the reaction mixture on ice after about fifteen minutes. Shorter times were not attempted because it takes approximately the above length of time before all the organic peroxide is dissolved. The trace value was obtained by analyzing a mixture which had been allowed to stand for forty-eight hours.

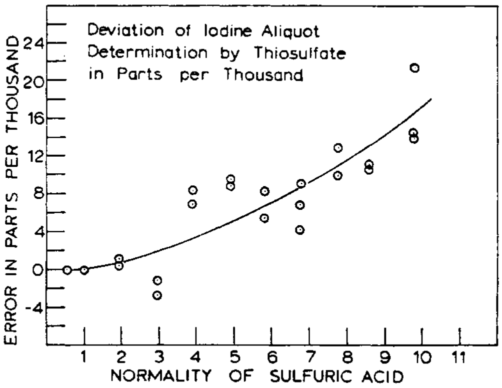

Figure 1

Because the secondary reactions of the peroxygen species with the organic substrate complicated the use of the peroxide analysis as a means of demonstrating the reaction pathway, ultraviolet absorption spectra were studied. The ditriphenylmethyl peroxide in concentrated sulfuric acid produced the same absorption characteristics as that found for triphenylcarbinol in sulfuric acid with the exception that the molar extinction coefficient for the peroxide was twice that of the alcohol. The strong bands for the triphenylcarbinol in sulfuric acid agreed with those reported for triphenyl carbonium ion by Hantzsch[10] and Gold and Hawes.[11] This indicated that the common species produced from the ditriphenylmethyl peroxide and triphenylcarbinol was the triphenyl carbonium ion.

Finally, clear evidence was obtained that Caro's acid was the peroxygen species that rapidly reacted with the triphenyl carbonium ion in sulfuric acid. Triphenylcarbinol was dissolved in concentrated sulfuric acid and mixed with a solution of potassium persulfate in concentrated sulfuric acid. This mixture gave rise to an acidic fraction which gave the same infrared spectrum as the acidic fraction obtained from the solution of ditriphenylmethyl

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[3] G. W. Wheland, *Advanced Organic Chemistry*, 3rd ed., John Wiley and Sons, Inc., N.Y., 1960, p. 568.

[4] P. D. Bartlett and J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **72**, 3095 (1950).

[5] J. Tanaka, *Proc. S. Dakota Acad. Sci.*, **38**, 181 (1959).

[6] W. C. Vosburgh, *J. Am. Chem. Soc.*, **44**, 2120 (1922).

[7] K. Bottger and W. Bottger, *Z. Anal. Chem.*, **70**, 209 (1927).

[8] E. Puxeddu, *Gazz. Chim. Ital.*, **59**, 687 (1929).

[9] V. L. LaMer and A. S. Kenyon, *J. Colloid Sci.*, **2**, 257 (1947).

[10] A. Hantzsch, *Chem. Ber.*, **54B**, 2573 (1921).

[11] V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

peroxide in sulfuric acid. The amount of the acid fraction recovered did not seem to indicate a dependency on the reaction time. Eight runs were made varying in time from fifteen minutes to five days. The sodium hydroxide soluble fraction varied from about 12 to 16% of the total products recovered. This fraction was further separated into the bicarbonate-soluble and insoluble fractions. The bicarbonate-insoluble portion ran about three to five times the amount of the bicarbonate soluble portion for the various runs.

The formation of the large yield of triphenylcarbinol on dilution of a solution of ditriphenylmethyl peroxide now seems clear. The peroxide is diprotonated in a manner reminiscent of the benzidine rearrangement.[12] This diprotonated peroxide is then cleaved at the carbon-oxygen bond giving rise to triphenyl carbonium ions and hydrogen peroxide which in concentrated sulfuric acid is Caro's acid. The peroxide preferentially cleaves at the carbon-oxygen bond because of the stability of the carbonium ion formed. The Caro's acid formed in the cleavage rapidly reacts with some of the triphenylcarbonium ions forming various oxidation products. On dilution with water, the remaining carbonium ions solvate to form triphenylcarbinol. That there must have been an initial hydroxylation of the ring was indicated by the phenolic character of the oxidation products in terms of acidity, reaction with bromine, and the prescence of the OH stretching frequency in the infrared. That this was further oxidized was indicated by the strong acid characteristics and the presence of a band at 1900 cm.$^{-1}$ in the infrared. The infrared did not show the presence of a sulfonic acid group which might have formed by an aromatic sulfonation process. This is not surprising in view of the relative insolubility of sulfonic acids in ether. It is unlikely that a substantial amount of the compound was sulfonated and lost in the aqueous phase because of the generally close correspondence in weight of the materials recovered to the weight of the peroxide used.

EXPERIMENTAL

Ditriphenylmethyl peroxide. Triphenylmethyl was prepared by stirring 20 g. of mercury, 6 g. of triphenylmethyl chloride, and 50 ml. of benzene under nitrogen for 7 to 8 hr. The mixture was filtered through sintered glass and the filtrate exposed to the air. The precipitate which formed was washed with acetone to remove traces of triphenylcarbinol and triphenylmethane. The approximate solubility of the peroxide in acetone at 26° obtained by equilibrating solid peroxide in acetone in a constant temperature bath for 24 hr. was 0.013 g. per 100 ml. of acetone, whereas the likely impurities were found to be readily soluble in acetone. The washed peroxide was then recrystallized from dioxane. Undue heating was avoided by saturating boiling dioxane with peroxide, which was about 0.6 g. of peroxide per 100 ml. of dioxane, and allowing to cool. The melting point (uncorrected in a capillary) was 184.5–186°.

Anal. Calcd. for $C_{38}H_{30}O_2$: C, 88.0; H, 6.17. Found: C, 87.36, 87.33; H, 5.67, 5.74.

The infrared in a Nujol mull did not show an OH stretching frequency. Strong bands were located at 975, 776, 758, and 700 cm.$^{-1}$ Medium bands were found at 1218, 1038, 918, 908, and 900 cm.$^{-1}$ Weak bands were found at 1950, 1810, 1600, 1185, 1155, 1080, 1000, 945, 932, 822, 720, 645, and 630 cm.$^{-1}$

The extent of agreement of the elemental analysis was somewhat disturbing. That there was a trace of impurity left after recrystallization was indicated by observations under an ultraviolet light. The precipitate collected after exposure of the trityl radical in benzene solution to the air showed a brilliant fluorescence. This observation is in line with Lichtin's work[13] indicating the nonquantitative nature of this reaction. On recrystallization from dioxane there was only an occasional spot of fluorescence still visible. This amount would not account for the discrepancy in the analysis. The explanation for this discrepancy, if not in an analytical error, might lie in a contamination by a dioxane peroxide to the extent of several per cent.

That the compound was essentially ditriphenylmethyl peroxide was assumed on the basis of agreement with the following observations. A characteristic of ditriphenylmethyl peroxide is its insolubility in a wide range of solvents as noted by Gomberg.[1] The melting point also agreed well with that reported by Gomberg.[1] These criteria have been used by a number of modern workers.[13–15] Furthermore, the method of preparation is a standard one.[16] Several workers have identified their products by comparing with an authentic sample prepared in this way.[17,18]

An immediately obvious alternate method of testing for purity has not presented itself. A peroxygen analysis using lithium aluminum hydride has been found not to be applicable.[15] Because of the insolubility, the iodometric method is not satisfactorily quantitative.[19] Molecular weight determinations as well as NMR determinations are also made difficult by the insolubility of the compound.

Triphenylcarbinol from ditriphenylmethyl peroxide. Ditrityl peroxide (1.5798 g.) was dissolved in 25 ml. of concd. sulfuric acid. After about 0.5 hr., the solution was poured on ice. The aqueous mixture was extracted with several portions of ether. The combined ether extract was then extracted with several portions of potassium hydroxide solution. The ether residue was dried with calcium chloride and reduced in volume to approximately 50 ml. To this about 20 ml. of petroleum ether (b.p. 60–68°) was added. No precipitate formed, so the solution was allowed to stand for 2 days. On further evaporation of the ether, 0.7076 g. of triphenylcarbinol crystals formed as the first crop. The melting point on a Fisher-Johns melting point apparatus was 160–161°. The second crop melted at 157–159°, the third crop at 150–154° and the fourth crop started softening at 127° and finished melting at 150°. All, however, gave almost identical infrared spectra. The combined yield was 1.4620 g., which amounts to a 92% yield.

Isolation of acidic fractions. The potassium hydroxide extracts were acidified and extracted again with ether.

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[12] G. S. Hammond and H. J. Shine, *J. Am. Chem. Soc.*, **72**, 220 (1950).

[13] N. N. Lichtin and G. R. Thomas, *J. Am. Chem. Soc.*, **76**, 3020 (1954).

[14] M. F. Hawthorne, *J. Org. Chem.*, **21**, 363 (1956).

[15] G. A. Russell, *J. Am. Chem. Soc.*, **75**, 5011 (1953).

[16] L. Gattermann and H. Wieland, *Laboratory Methods of Organic Chemistry*, The Macmillan Company, New York, 1937, p. 352.

[17] D. Y. Curtin and W. R. Proops, *J. Am. Chem. Soc.*, **76**, 494 (1954).

[18] A. J. Betterton and W. A. Waters, *J. Chem. Soc.*, 329 (1953).

[19] G. S. Hammond and W. Overhults, unpublished results.

On evaporation of the ether, a dark reddish brown tar resulted. This tar reacted with bromine in carbon tetrachloride with formation of hydrogen bromide. On sublimation, no phenol could be separated. The infrared was determined on a film placed on a salt plate by painting the salt plate warmed on a hot plate with an acetone or ether solution of the tar.

Search for benzophenone. Pilot runs were conducted with synthetic mixtures of triphenylcarbinol and benzophenone. Chromatography using petroleum ether (b.p. 60–68°) as solvent and alumina as a support was not satisfactory. An infrared extinction coefficient was determined for a carbon tetrachloride solution of benzophenone by drawing an arbitrary base line connecting the start and end of the ketone peak. When the neutral fraction was analyzed in the same way, there was found to be no more than 0.0136 g. of benzophenone. Because of the method of drawing the base line, this is an upper limit rather than an indication of the presence of benzophenone.

Thiosulfate titration of iodine solutions. An iodine–potassium iodide solution was prepared to approximately 0.1N. An approximately 0.1N solution of sodium thiosulfate was prepared and standardized against potassium iodate. The iodine-iodide was then determined by the standard thiosulfate solution. A solution of approximately 1N sodium hydroxide was prepared and standardized against potassium acid phthalate. Solutions of sulfuric acid ranging from 1N to 18N were prepared and determined by the standard base. The acidic iodine solutions were then prepared on the most part by mixing a precooled 25-ml. aliquot of the iodine-iodide and a precooled 25-ml. aliquot of the acid. The amount of the acid aliquot was changed slightly for several of the runs in order to obtain a range of acidities. The acidic iodine solution was then titrated in the usual manner with thiosulfate.

Caro's acid reaction with triphenylcarbinol. Caro's acid was prepared by dissolving 5 g. of potassium peroxydisulfate in 20 ml. of concd. sulfuric acid and allowing to stand for 1 hr. Five grams of triphenylcarbinol was dissolved in 25 ml. of concd. sulfuric acid and poured into the Caro's acid. After an appropriate period of time the reaction was quenched by pouring on ice. The quench mixture was then extracted in a separatory funnel by a number of portions of ether until the ether no longer became colored. At this point there was still a distinct brown color in the aqueous layer. The combined ether extract was then extracted several times with 3N sodium hydroxide. The color was extracted by the base leaving a clear ether solution. This ether solution after evaporation produced triphenylcarbinol contaminated by a slight amount of a light tan impurity. The base portions on acidification with 6N sulfuric acid turned from a dark brown color to a light brown color. On extraction of the acidified portions with ether, a colored ether layer resulted. The combined ether extracts on evaporation gave rise to a reddish brown tar. In some runs, the ether extract of the acidified base extract was extracted further with a 5% sodium bicarbonate solution.

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Some Facets of the Grignard Reagent–Cobaltous Halide Reaction

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The reactions of several Grignard reagents with stoichiometric equivalents or an excess of cobaltous bromide have been examined. Arylmagnesium halides react principally to give coupling products, while alkylmagnesium halides give disproportionation or hydrogen abstraction products. When mixtures of alkyl and aryl Grignard reagents are treated with cobaltous bromide very little cross coupling occurs. Changes in the ratios of unsaturated to saturated products in these mixed reactions indicate some modification of the course of the reaction compared to the reactions of the individual reagents.

The reactions of Grignard reagents with cobaltous halides and other metallic halides have for many years been a subject of considerable interest.[1] In most of the "abnormal" reactions of Grignard reagents the cobalt salt was used in small over-all amount, and the reaction proceeded in the presence of some third compound such as an aryl or alkyl halide. Surprisingly, there seem to be only a few cases available where the Grignard reagents alone were treated with anything approaching the required stoichiometric amount of cobalt salt.

Gilman and Lichtenwalter[2] have reported that the treatment of a cold ether solution of 0.03 mole of phenylmagnesium iodide with 0.01 mole of cobaltous chloride produced a 98% yield of biphenyl, while Kharasch and Fields[3] reported that the phenylmagnesium bromide (0.11 moles)–cobaltous chloride (0.03 mole) reaction gave only a 64% yield of biphenyl. Smith[4] has reported that treatment of n-butyl bromide with magnesium and cobaltous bromide in ether produced a quantitative yield of mixed butanes and butenes. It has been observed also that the treatment of 1-bromo-2-phenylethane with magnesium and cobaltous bromide gives a 44% yield of ethylbenzene and

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(1) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, Chap. V.

(2) H. Gilman and M. Lichtenwalter, *J. Am. Chem. Soc.*, **61**, 957 (1939).

(3) M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

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