0.42 for 66.6% acid (H_0 −5.1). Since in aqueous sulfuric acid the extinctions at 470 mμ of free and ionized *o*-quinone and ionized *p*-quinone are roughly the same, and that of uncharged *p*-quinone is 7.5% of the foregoing, the measured ratio

$$r = \frac{[\alpha](1 - 0.075)}{[\mathrm{H}\beta^+]\left[1 + \frac{1}{K'} + (1 + 0.075\,K)\,\frac{[\beta]}{[\mathrm{H}\beta^+]}\right]} \cong$$

$$\frac{[\alpha]}{[\mathrm{H}\beta^+]}\,\frac{0.925}{1.03 + 2.9\,\frac{h_0}{K_\beta}} \sim \frac{0.8[\alpha]}{[\mathrm{H}\beta^+]}$$

in the original solution. Hence $K = h_0\,[\alpha]/K_\beta[\mathrm{H}\beta^+] = 1.25\,(rh_0/K_\beta) = 26$ (62% acid) and 24 (66.6% acid).

Dehydrolapachone in Sulfuric Acid.—A solution of 15 mg. of dehydro-α-lapachone (XXI) in 1 cc. of concentrated sulfuric acid was allowed to stand for ten minutes, during which its initially green color changed to purple,[21] dropped into 80 cc. of ice-cold 5% sodium carbonate, and the purple suspension extracted immediately with 35 cc. of ether. The orange–red ether solution was washed with water, dried, and evaporated in vacuum. The residue, a purple solid, m. p. 102–107°, imparted an instantaneous purple color to sulfuric acid, dissolved in alcoholic sodium bisulfite to a yellow solution, and was converted by warm alcoholic hydrochloric acid to an orange substance, apparently dehydro-α-lapachone. These observations accord with the hypothesis that the purple substance is dehydro-β-lapachone (XXVII).

Summary

The interconversion of the lapachones in acid is explained from measurements of spectra and ionization in sulfuric acid. The discussion is extended to oxidation–reduction potentials and rates and mechanisms of hydroxyquinone cyclizations.

CAMBRIDGE 38, MASSACHUSETTS

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[21] Hooker, *J. Chem. Soc.*, **69**, 1355 (1896).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY]

Migration Aptitude as a Criterion of Ionic Mechanism in the Rearrangement of Mono-*p*-nitrotriphenylmethyl Hydroperoxide[1,2]

BY PAUL D. BARTLETT AND JOHN D. COTMAN, JR.

Introduction.—The use of numerous acyl peroxides as initiators of polymerization is one of the most familiar pieces of evidence that these peroxides commonly undergo thermal decomposition by a mechanism involving free radicals. The same is true of hydrogen peroxide[3] and its monosubstitution products such as tetralin hydroperoxide.[4] It is now clear, however, that free radical mechanisms are not invariably operative in the decomposition of acyl peroxides and alkyl hydroperoxides. Decomposition of the peroxide of phenylacetic acid,[5] for example, is subject to general acid catalysis. *p*-Methoxy-*p*′-nitrobenzoyl peroxide[6] is capable of decomposition by either a free radical or a polar mechanism according to the conditions. 9-Decalyl hydroperoxide[7] yields a benzoate which decomposes only by way of a rearrangement favored by ionizing solvents. Other examples of duality of mechanism in the decomposition of peroxides have been given by Kharasch.[8] Criegee[7] and Leffler[9] have suggested that polar mechanisms for the rearrangement and decomposition of peroxidic substances are rather general and are particularly clearly indicated in such processes as the reaction of Caro's acid with ketones, the Dakin reaction, certain transformations of autoxidation products such as those of cyclohexene, and the rearrangement of primary into normal ozonides. A polar mechanism for the reaction of perbenzoic acid with ketones has been written by Friess.[10]

Migration Aptitudes as a Criterion of Mechanism.—The existing evidence for polar mechanisms in reactions of peroxides includes the different courses taken by polar and free radical decompositions,[6,7,8,9] susceptibility to general acid catalysis[5,6] and to ionizing media and reagents.[7,8] One of the general characteristics of polar rearrangements such as the Wagner–Meerwein and pinacol rearrangements is the order of migration aptitudes of the organic groups which migrate competitively during the rearrangement. Among aromatic groups the order of migration aptitudes in symmetrical pinacols is similar to the order of reactivity of the corresponding benzenes toward aromatic substitution.[11] This is a consequence of the fact that in both the Wagner–Meerwein rearrangement and aromatic substitution the transition state involves the attachment of an electrophilic reagent to the benzene ring before the old attachment (to carbon or hydrogen) is severed. One of the best criteria for a cationic mechanism in the rearrangement of a peroxide should be the observation that the relative migra-

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[1] From a thesis presented by J. D. Cotman, Jr., for the degree of Doctor of Philosophy at Harvard University, 1949.

[2] Support of this work by a contract with the Office of Naval Research is gratefully acknowledged by the authors and the University.

[3] J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

[4] S. Medvedev, E. Chilikina and V. Klimenkov, *Acta Physicochim. U. R. S. S.*, **11**, 741 (1939).

[5] P. D. Bartlett and J. E. Leffler, THIS JOURNAL, **72**, 3030 (1950).

[6] J. E. Leffler, *ibid.*, **72**, 67 (1950).

[7] R. Criegee, *Ann.*, **560**, 127 (1948).

[8] M. S. Kharasch, 11th National Organic Symposium, Madison, Wis., June 20–22, 1949.

[9] J. E. Leffler, Thesis, Harvard University, 1948; *Chem. Revs.*, **45**, 385 (1949).

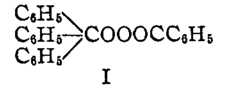
[10] S. L. Friess, THIS JOURNAL, **71**, 2571 (1949).

[11] W. E. Bachmann and F. H. Moser, *ibid.*, **54**, 1124 (1932).

tion aptitudes of groups were those characteristic of the Wagner–Meerwein, pinacol and similar rearrangements and were different from those prevailing in a reaction of known free-radical type.

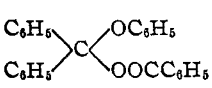
Of the migration aptitudes of groups in a free radical rearrangement comparatively little is known, although the existence of rearrangements analogous to the Wagner–Meerwein proceeding by way of free radicals has been established.[12a,b] One gains the impression,[13] however, that both *o,p*-directing substituents and *m*-directing substituents enhance the susceptibility of the benzene ring to substitution by free radicals. Therefore if a rearrangement proceeded through a free radical mechanism the relative migration aptitudes of the phenyl and anisyl groups or the phenyl and tolyl groups would probably be the same as in a cationic mechanism. It is a reasonable expectation, however, that a competition between the phenyl group and the *p*-nitrophenyl group should distinguish clearly between the two types of mechanism, for nitrobenzene is activated toward free radical attack in comparison with benzene whereas toward cationic attack it is deactivated. It is therefore to be anticipated that in a rearrangement proceeding by way of free radicals the *p*-nitrophenyl group will migrate in preference to the phenyl while the opposite will be true in a rearrangement proceeding by a cationic mechanism.

Some evidence regarding migration aptitudes in a peroxide decomposition exists among substituted triphenylmethyl hydroperoxides. It was observed by Wieland and Maier[14] that the reaction of triphenylmethyl hydroperoxide with benzoyl chloride yielded not the expected triphenylmethyl perbenzoate (I) but an isomeric compound shown by its hydrolysis to be the benzoate of the phenyl hemiacetal of benzophenone (II).

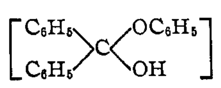


$(C_6H_5)_3COOOCC_6H_5$

I



II

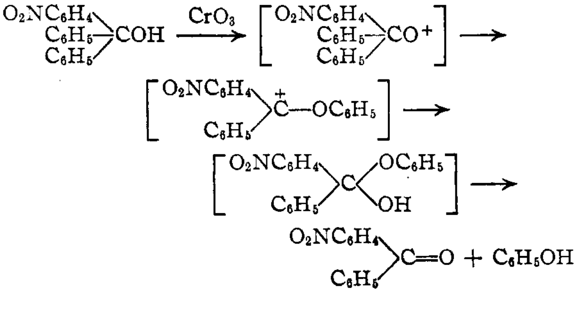


III

Treatment of the hydroperoxide with any strong acid yields directly benzophenone and phenol, presumably by way of the hemiacetal III. Dilthey, Quint and Dierichs[15] surmised that triarylmethyl hydroperoxides were intermediates in the general degradation of triaryl carbinols by means of hydrogen peroxide and perchloric acid. This method of degradation, applied to mono-*p*-methoxytriphenylcarbinol, yielded benzophenone and *p*-methoxyphenol, while from mono-*p*-nitrotriphenylcarbinol it gave phenol and *p*-nitrobenzophenone. This work clearly placed the migration aptitudes of groups in the same order in the peroxide degradation of the triaryl carbinols as in the pinacol rearrangement. It remains to exclude the free radical mechanism for this rearrangement by showing that in a free radical the order of migration aptitudes is different from that found by Dilthey, Quint and Dierichs. In the present work we have isolated mono-*p*-nitrotriphenylmethyl hydroperoxide and shown that the relative migration aptitudes of the phenyl and *p*-nitrophenyl groups are different in the thermal and acid-catalyzed decompositions. The ionic view of the mechanism of the rearrangement also throws light upon the oxidation of the methane and the carbinol.

Synthesis of Mono-*p*-nitrotriphenylmethyl Hydroperoxide.—An attempt was made to prepare *p*-nitrotriphenylcarbinol by the oxidation of the readily available *p*-nitrotriphenylmethane.[16] Like Baeyer and Villiger[17] we were able to isolate only *p*-nitrobenzophenone from this oxidation although chromic acid of various strengths was used. In the light of our later findings this appears to be an example of the easy oxidation of a tertiary alcohol by the mechanism proposed by Mosher.[18] We confirmed that under the conditions of the oxidation of *p*-nitrotriphenylmethane the oxidation of the carbinol is also complete.

According to the schematic mechanism



the high yield of *p*-nitrobenzophenone and the absence of benzophenone foreshadows the result later obtained with the hydroperoxide that the phenyl group migrates to the exclusion of the *p*-nitrophenyl.

The carbinol was actually prepared by the method of Baeyer and Villiger which consists of the hydrolysis of the corresponding chloride formed by the reaction of *p*-nitrobenzophenone dichloride with benzene and aluminum chloride. As a means of hydrolyzing *p*-nitrotriphenylmethyl chloride, which is less reactive than triphenylmethyl chloride in solvolysis by about two

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[12] (a) W. H. Urry and M. S. Kharasch, THIS JOURNAL, **66**, 1438 (1944); (b) S. Winstein and F. H. Seubold, Jr., *ibid.*, **69**, 2916 (1947).

[13] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[14] H. Wieland and J. Maier, *Ber.*, **64**, 1205 (1931).

[15] W. Dilthey, F. Quint and H. Dierichs, *J. prakt. Chem.*, [2] **151**, 25 (1938).

[16] A. Baeyer and R. Lohr, *Ber.*, **23**, 1622 (1890).

[17] A. Baeyer and V. Villiger, *ibid.*, **37**, 604 (1904).

[18] W. A. Mosher and F. C. Whitmore, THIS JOURNAL, **70**, 2544 (1948); W. A. Mosher and E. O. Langerak, *ibid.*, **71**, 286 (1949).

orders of magnitude,[19] we found the formation of the halochromic perchlorate in glacial acetic acid and its hydrolysis by dilution with water a preferable procedure to warming with aqueous alkali as used by Baeyer and Villiger.

To form the hydroperoxide from the relatively unreactive *p*-nitrotriphenylmethyl chloride required more vigorous conditions than those of Wieland and Maier. The conditions eventually adopted avoided on the one hand alkaline solutions which permitted competing hydrolysis and on the other hand acid solutions which tended to decompose the hydroperoxide. The reaction between the chloride dissolved in ether and 90% hydrogen peroxide was catalyzed by stannic chloride, which has the advantage of promoting the ionization of the organic chloride without being a catalyst for the decomposition of hydrogen peroxide.[20] The hydroperoxide was obtained by crystallization from alcohol–water as white needles of the monohydrate melting at 99–101° and decomposing with evolution of gas at 135–140°. Ether solutions of the hydroperoxide oxidized aqueous potassium iodide on shaking, and a solution of the hydroperoxide in acetone–water oxidized ferrous ion to ferric.

The green *p*-nitrotriphenylmethyl free radical can be demonstrated in a convenient test-tube reaction. On addition of potassium iodide to a solution of *p*-nitrotriphenylmethyl chloride in acetone a green coloration is noted which, on shaking in air, fades leaving only the yellow color of the iodine. The cycle can be repeated with the addition of more potassium iodide until all of the chloride is consumed. As the oxygen uptake proceeds, a pale yellow solid precipitates from the solution. This solid was not purified sufficiently to establish its identity as *sym-p*-nitrotriphenylmethyl peroxide or a rearrangement product.

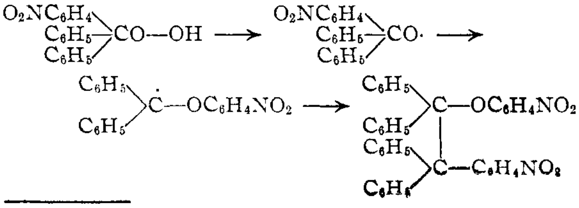
The Acid-Catalyzed Decomposition of *p*-Nitrotriphenylmethyl Hydroperoxide.—The addition of either sulfuric acid or perchloric acid to a cold ether solution of *p*-nitrotriphenylmethyl hydroperoxide produces at first a yellow color which fades. Addition of water, separation of layers, and evaporation of the ether yields a white solid melting at 136–138° alone and when mixed with *p*-nitrobenzophenone. The aqueous solution of perchloric acid had a strong odor of phenol and yielded, on addition of bromine water, tribromophenol, m. p. 92–93°. The best yields obtained in these experiments were 94% of *p*-nitrobenzophenone and 81% of phenol isolated as the tribromo compound. It is clear, therefore, that in the acid-catalyzed decomposition of *p*-nitrotriphenylmethyl hydroperoxide the phenyl group migrates to the exclusion of the *p*-nitrophenyl group.

The Thermal Decomposition of *p*-Nitrotriphenylmethyl Hydroperoxide.—For a study of the products of *thermal* decomposition of the hydroperoxide 0.6 g. was dissolved in benzene, the solution flushed with nitrogen and placed in a sealed tube in an oven at 115–128° for four hours. The product was separated into an alkali-soluble and a non-alkali-soluble fraction and the components of the latter were separated by chromatographic adsorption on alumina. By a combination of purification and weighing of solids with infrared analysis of non-crystalline fractions, the following amounts of material were identified among the products

Compound	Weight, g.	% of the maximum
Phenol	. . .	8–10
p-Nitrophenol	. . .	32
p-Nitrobenzophenone	0.062	14
p-Nitrotriphenylcarbinol	0.129	23
Benzophenone	None	0

Biphenyl (0.011 g.) was isolated and identified by melting point. The presence of this hydrocarbon, a coupling product of radicals from the solvent, is supporting evidence of the radical nature of the reaction.

From these results several conclusions are obvious. First, the over-all course of the thermal decomposition is more complex than that of the acid-catalyzed reaction. The formation of *p*-nitrotriphenylcarbinol in 23% yield indicates that the *p*-nitrotriphenylmethoxy free radical must take a hydrogen atom directly from the solvent as well as being capable of intramolecular rearrangement. This is consistent also with the free radical rearrangements previously cited[11,12] where rearranged and unrearranged products occurred together. Phenol and *p*-nitrophenol were formed in the ratio of about 1:3 or 1:4 but they were not, as in the acid decomposition, accompanied by corresponding amounts of the ketones containing the remainder of the original molecule. The origin of the phenol and *p*-nitrobenzophenone is uncertain; they might result from a small fraction of decomposition by the same mechanism as in the acid-catalyzed process. However, the 32% of *p*-nitrophenol is unaccompanied by any benzophenone and therefore cannot result by the formation of the *p*-nitrophenyl hemiacetal of benzophenone. Wieland[21] observed that triphenylmethyl peroxide on heating in solution rearranged into the diphenyl ether of benzpinacol. The corresponding reaction



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(19) A. C. Nixon and G. E. K. Branch, THIS JOURNAL, **58**, 492 (1936).

(20) W. Machu, "Das Wasserstoffperoxyd," J. Springer, Vienna, 1937, p. 62.

(21) H. Wieland, *Ber.*, **44**, 2550 (1911).

would account for the isolation of *p*-nitrophenol without benzophenone but would not explain the failure to isolate benzpinacol or benzpinacolone from the hydrolysis. The known instability of the free radicals containing the nitro group[22] suggests that these radicals may unite in still other ways, possibly through oxygen to yield unstable nitronic esters.

An attempt was made to prepare β-*p*-nitrophenyl-β,β-diphenylpropionaldehyde in order to induce a rearrangement in the free radical of the neopentyl type produced by the method of Winstein and Seubold.[12] Synthetic difficulties caused the abandoment of this part of the program.

Discussion.—In the experiments just described *p*-nitrotriphenylmethyl hydroperoxide has been decomposed under two different sets of conditions to two quite different sets of products. Under the conditions of an acid catalysis the reaction shows no sign of free radical character and the migration aptitude of the phenyl group is immeasurably greater than that of the *p*-nitrophenyl, as it should be for a cationic mechanism. Although the course of the free radical decomposition has not been fully explained, the phenol and *p*-nitrophenol found as products must have arisen from migrations of the phenyl and *p*-nitrophenyl groups, respectively, in the course of the decomposition. The fact that from three to four times as much *p*-nitrophenol as phenol is found indicates that under this mechanism of decomposition the migration aptitudes of the phenyl and nitrophenyl groups are reversed in comparison to the acid decomposition. In this instance, then, relative migration aptitudes may be used as a criterion of mechanism.

The extent to which the postulated oxygen cation is free, or whether it represents a dip or minimum in the curve of potential energy *vs.* reaction coördinate, is no less difficult a problem here than in rearrangements involving electron-deficient carbon atoms. The study of these oxygen-cationic rearrangements is now in an early stage, where it has been demonstrated only that they are apparently completely analogous to the Wagner–Meerwein rearrangement.

Experimental

***p*-Nitrotriphenylmethane.**—This hydrocarbon was synthesized by the method of Baeyer and Lohr.[16] Yields of 50–60% of a product melting at 91–92° were obtained.

Oxidations of *p*-Nitrotriphenylmethane with Chromic Acid.—A solution of 5 g. of *p*-nitrotriphenylmethane in 50 cc. of glacial acetic acid was warmed on a steam-bath and 8 g. of chromic anhydride added in small portions. The oxidation was vigorous, the color of chromic anhydride fading almost instantaneously to the deep green of chromic ion. After complete addition of the oxidant, the solution was warmed for an hour on the steam-bath. Cooling was followed by addition of water which precipitated the product as an insoluble oil, then ether extraction, washing with water and sodium bicarbonate solution. The ether solution was then dried over calcium chloride.

After evaporation of the ether, the product was dissolved in alcohol and the solution was decolorized with carbon and cooled. A yield of less than one gram of white crystals was obtained, melting from 118 to 125°. Repeated crystallization gave material melting at 136–138°. This synthesis was repeated three times and the products isolated by crystallization from a number of solvents and vacuum sublimation. In every case the crystalline product melted at 136–138°, alone and when mixed with *p*-nitrobenzophenone. The 2,4-dinitrophenylhydrazone of the product melted with decomposition at 230°. *p*-Nitrobenzophenone 2,4-dinitrophenylhydrazone melts at 230–235°, the exact melting point (with decomposition) depending upon the rate of heating. The mixture of the two derivatives melted at 228–232°.

In 70–80% acetic acid the oxidation was not successful and the unreacted hydrocarbon was recovered in almost quantitative amount.

A single attempt at chromatographic separation of the product mixture yielded *p*-nitrobenzophenone in low yield, unchanged *p*-nitrotriphenylmethane and impure *p*-nitrotriphenylcarbinol in low yield.

Oxidation of *p*-Nitrotriphenylmethane with Lead Tetraacetate.—Dimroth and Schweizer[23] oxidized both diphenylmethane and triphenylmethane to the corresponding carbinyl acetates with lead tetraacetate in glacial acetic acid.

p-Nitrotriphenylmethane (1.0 g.) and 1.5 g. of lead tetraacetate were dissolved in 20 cc. of glacial acetic acid. The solution was heated at 100° for one hour. At the end of this time, the addition of water resulted in the formation of a white precipitate indicating that all of the lead tetraacetate had been consumed. The aqueous suspension was treated with solid sodium bicarbonate to neutralize the the acid and the ethereal extract from the neutralized solution was dried over calcium chloride, filtered, and the solvent removed by evaporation. The residue was a brown semi-solid paste. Repeated crystallization, first from alcohol and then from ligroin gave a product melting at 91–92°. The melting point of this solid was undepressed by mixture with *p*-nitrotriphenylmethane. The oxidation product was a sticky oil that resisted all attempts at crystallization.

The Synthesis and Purification of *p*-Nitrotriphenylmethyl Chloride.—*p*-Nitrotriphenylmethyl chloride has been synthesized by the method of Baeyer and Villiger.[17] Yields of purified chloride ranging from 15 to 60% have been obtained. During the treatment of the aluminum chloride complex with ice and hydrochloric acid varying amounts of the chloride undergo hydrolysis to the carbinol. It has been possible to increase the yields of chloride by conversion of some of this carbinol back into the chloride by thionyl chloride. After crystallization of the chloride from ligroin, the carbinol may be obtained by evaporation of the mother liquor followed by crystallization from 90–120° ligroin. The crude carbinol is dissolved in excess thionyl chloride, heated for one-half hour on the steam-bath and the excess thionyl chloride evaporated by heating in a jet of dry air. Solution in 60–90° ligroin followed by decolorization with carbon and cooling has yielded 60–80% of *p*-nitrotriphenylmethyl chloride, m. p. 92–93°, based on the weight of the recovered carbinol.

***p*-Nitrotriphenylcarbinol.**—Baeyer and Villiger converted *p*-nitrotriphenylmethyl chloride to *p*-nitrotriphenylcarbinol by warming the chloride with aqueous sodium hydroxide. A more satisfactory procedure is the following: 10 g. of *p*-nitrotriphenylmethylchloride was dissolved in 50 cc. of glacial acetic acid. Addition of 40 cc. of perchloric acid resulted in the immediate color of *p*-nitrotriphenylcarbonium perchlorate. The solution was poured into a large excess of water and the carbinol precipitated as a white cheesy solid. The precipitate was filtered, washed free of acids and air-dried. Crystallization from 90–120° ligroin yielded 7.3 g. (78%) of *p*-nitrotriphenylcarbinol as gleaming pale yellow plates, m. p. 97–98°.

Chromic Acid Oxidation of *p*-Nitrotriphenylcarbinol.—0.50 g. of *p*-nitrotriphenylcarbinol was dissolved in 10 cc.

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[22] K. Ziegler and W. Mathes, *Ann.*, **479**, 113 (1930).

[23] O. Dimroth and R. Schweizer, *Ber.*, **56**, 1384 (1923).

of glacial acetic acid. The solution was heated on the steam-bath and 1.6 g. of chromic acid was added in two portions. Heating was then continued for an additional hour. The solution was poured into a large volume of water and the precipitated product extracted into ether. The ether solution was washed with sodium bicarbonate and then with water. Evaporation of the ether left a pale yellow solid which crystallized as glistening needles from aqueous ethyl alcohol, m. p. 136–137°. The product weighed 0.24 g., a 65% yield of *p*-nitrobenzophenone.

***p*-Nitrotriphenylmethylhydroperoxide.**—One gram of *p*-nitrotriphenylmethyl chloride was dissolved in 15 cc. of anhydrous ether and cooled to 0° with ice-water. Two cc. of 90% hydrogen peroxide was added to the cold solution and the total contents of the flask recooled. After five minutes in the ice-bath, 0.5 cc. of stannic chloride was added drop by drop with stirring. After two or more hours in the ice-bath, the ether solution was extracted three times with ice-water, once with a saturated ice-cold solution of ferrous ammonium sulfate, and finally with ice-water to remove the ferrous ion. The purpose of the wash with the reducing agent was to aid in the removal of hydrogen peroxide which has been found to decompose the hydroperoxide. The hydroperoxide is so insoluble in water and the ferrous salt so insoluble in ether that there is very little loss of hydroperoxide in this washing. After drying over anhydrous sodium sulfate the ether was evaporated and the residue crystallized from alcohol–water. The hydroperoxide formed granular crystals of a monohydrate melting at 99–101° with loss of water. The yields varied from 61–80% of the crystalline product.

Anal. Calcd. for $C_{19}H_{15}NO_4 \cdot H_2O$: C, 67.25; H, 5.02; N, 4.15. Found: C, 67.20; H, 5.20; N, 4.33.

The Acid-Catalyzed Decomposition of *p*-Nitrotriphenylmethylhydroperoxide.—The addition of 70% perchloric acid or 98% sulfuric acid to a solution of *p*-nitrotriphenylmethylhydroperoxide in acetic acid or ether resulted in a yellow color which was discharged by water. In acetic acid dilution of the acid precipitated *p*-nitrobenzophenone. In ether, evaporation of the solvent left the crystalline *p*-nitrobenzophenone suspended in the water. Crystallization of the solid from alcohol–water gave white needles, m. p. 136–137°.

Addition of bromine water to the diluted aqueous acid precipitated tribromophenol, m. p. 90–91°. After recrystallization from alcohol–water the derivative melted at 92–93°.

p-Nitrotriphenylmethylhydroperoxide (0.422 g.) was dissolved in 5 cc. of glacial acetic acid. The addition of 8 cc. of perchloric acid (with cooling) produced a brilliant yellow persistent color. Addition of water precipitated *p*-nitrobenzophenone. The ketone was filtered, washed and dried in a vacuum desiccator over calcium chloride. The product, m. p. 136–137°, weighed 0.268 g., a yield of 94%. The addition of bromine water to the aqueous acid precipitated tribromophenol. The precipitate was filtered, washed with sodium bisulfite, water, then distilled water, and recrystallized from alcohol–water. The yield of 2,4,6-tribromophenol, m. p. 92–93.5°, was 0.331 g. (81%).

The Thermal Decomposition of *p*-Nitrotriphenylmethylhydroperoxide.—To estimate the amounts of *p*-nitrobenzophenone, *p*-nitrotriphenylcarbinol and biphenyl in the various fractions, a combination of analytical techniques was employed. Wherever possible, the purified components were weighed. In other cases, particularly with *p*-nitrotriphenylcarbinol which could not be isolated quantitatively as a crystalline solid, the amount was estimated from the infrared spectrum in carbon tetrachloride.

There is a sharp carbonyl band at 5.95 μ shown by *p*-nitrobenzophenone alone of the components of this mixture. (The corresponding band for benzophenone is at 6.00 μ.) *p*-Nitrotriphenylcarbinol has a band unique among these products at 9.80 μ, as well as a band at 6.70 μ, which overlaps an absorption of the aromatic ether of Fraction 5, and a band at 7.38 μ which is common to the several aromatic nitro compounds. The optical densities at these four points, as determined with a Baird Associates infrared spectrograph, for *p*-nitrobenzophenone, *p*-nitrotriphenylcarbinol and five fractions from the chromatographic separation, are recorded in Table I.

TABLE I

INFRARED ANALYSIS OF FRACTIONS OF THERMAL DECOMPOSITION PRODUCTS OF *p*-NITROTRIPHENYLMETHYL HYDROPEROXIDE

Chromatographic fraction	Optical density at			
	5.95 mμ	6.70 mμ	7.38 mμ	9.80 mμ
p-Nitrobenzophenone 1%	0.852	....	0.872	....
p-Nitrotriphenylcarbinol 1%	...	0.220[a]	...	0.340[a]
1	0.082	....	0.123	....
2	.365	....	0.310	....
3	.204	0.125	...	0.218
4	.060	0.117	...	.152
5	...	...	...	.170

[a] Optical density corrected for 100% transmission at 91%.

From the data in the Table I and the density of carbon tetrachloride the weight of each of the two components in the chromatographic fractions has been computed.

Wt. *p*-nitrobenzophenone:

$$0.0077 + 0.031 + 0.019 + 0.0040 = 0.062 \text{ g.}$$

The percentage yield of *p*-nitrobenzophenone is 14%

Wt. *p*-nitrotriphenylcarbinol:

$$0.048 + 0.038 + 0.043 = 0.129 \text{ g.}$$

The percentage yield of *p*-nitrotriphenylcarbinol is 23%.

As a check on the amount of *p*-nitrobenzophenone in a fraction, 4.5 cc. of fraction 2 was freed of solvent and the total residue weighed. The weight found was 0.0422 g., equivalent to 0.0469 g. in the total 5 cc. of solution.

The residue was steam distilled and from the steam distillate 0.011 g. of biphenyl was recovered by ether extraction (m. p. 67–69°). The non-steam volatile material weighed 0.027 g. (equivalent to 0.030 g. in 5 cc. of the carbon tetrachloride solution). The ketone melted at 135–137° without recrystallization.

Summary

Mono-*p*-nitrotriphenylmethyl hydroperoxide is decomposed by sulfuric or perchloric acid into high yields of *p*-nitrobenzophenone and phenol; by analogy with previous work by Wieland and Maier and by Criegee this reaction is recognized as a rearrangement in which, as is normal for reactions of cationic type, the phenyl group migrates to the exclusion of the *p*-nitrophenyl group. The oxidation by chromic acid of mono-*p*-nitrotriphenylmethane and of mono-*p*-nitrotriphenylcarbinol also yields *p*-nitrobenzophenone. Thermal decomposition of mono-*p*-nitrotriphenylmethyl hydroperoxide, however, yields a mixture of products including *p*-nitrobenzophenone, phenol, *p*-nitrophenol, *p*-nitrotriphenylcarbinol and, with benzene as the reaction solvent, biphenyl. The relative amounts of these products indicate that the mechanism of thermal decomposition is such that the *p*-nitrophenyl group has a greater migration aptitude than the phenyl group. In this case the relative migration aptitudes of the phenyl and *p*-nitrophenyl groups serve as a means of distinguishing ionic from free-radical mechanisms.

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