Decomposition of Quaternary Hydroxides. (a) α-dl-Methadol.—To a solution of 5 g. of α-dl-methadol methiodide in aqueous ethanol was added 3 g. of silver oxide. The mixture was stirred vigorously until the presence of iodide ion could no longer be detected. The mixture was filtered and the precipitate was washed with ethanol and water. The filtrate and washings were combined and concentrated at reduced pressure. The residue was transferred to a Claisen flask (using a minimum amount of ethanol) and the material was pyrolyzed under 15–20 mm. pressure. The distillate was dissolved in ethanol and cooled. The crystals which separated were recrystallized from ethanol; m.p. 88–89°.

(b) α-d-Isomethadol.—This was run as above using 10 g. of α-d-isomethadol methiodide. The yield was 3.9 g. of material melting at 63–64.5°.

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Bromohydrins from Olefins and N-Bromosuccinimide in Water

BY CYRUS O. GUSS[1] AND RUDOLPH ROSENTHAL

The reaction of olefins with N-bromoacetamide in water to form bromohydrins has been known and used for many years.[2,3] It might be assumed that N-bromosuccinimide would behave similarly. Results have verified this assumption; for several years we have employed the latter reagent for the preparation of bromohydrins, and thence, olefin oxides. The availability and stability of this reagent, the ease of reaction and the yields obtained make this method superior, in many instances, to alternative methods. Some of the results that illustrate the scope of this method are summarized in Table I to supplement those already reported.[4]

Experimental

The general procedure used can be illustrated by the reaction of styrene (26.0 g., 0.25 mole), NBS (47 g., 95% purity, 0.25 mole) and water (100 ml.). These were stirred together vigorously at room temperature until the solid NBS disappeared (35 minutes). In all experiments, the disappearance of the NBS was a good criterion of the progress of the reaction. The styrene bromohydrin layer was separated and the aqueous layer extracted with benzene. Distillation of the combined product gave 41.0 g. (81.6%) of styrene bromohydrin, b.p. 120–123° (5 mm.), n^{19}D 1.5785; lit.[5] b.p. 109–110° (2 mm.), n^{17}D 1.5800.

In a similar run the styrene bromohydrin was taken up in ether and, after removal of the ether, was converted to styrene oxide by stirring for one-half hour with sodium hydroxide (15 g.) in water (75 ml.) at 60°. Extraction with ether and distillation gave 25.6 g. (85.3%) of styrene oxide, b.p. 65° (5 mm.), n^{20}D 1.5340; lit.[6] b.p. 87–88° (23 mm.), n^{20}D 1.5331. α-Methylstyrene gave equally good results.

The aqueous solution of succinimide from the separation of the bromohydrin was treated with sodium hydroxide (10 g.), cooled to 0°, and then bromine (13.6 ml.) was added. The mixture was shaken for two minutes, and the NBS filtered off, washed with cold water and dried to give 23.5 g. (50% recovery by reconversion) of NBS of 95% purity.

It was found that the bromohydrin could often be converted to the oxide by adding sufficient aqueous sodium hydroxide without separating the bromohydrin from the NBS–olefin mixture.

Tetrachloroethylene, crotonaldehyde, cinnamaldehyde

(1) Department of Chemistry, Colorado A. and M. College, Fort Collins, Colorado.

(2) E. Schmidt, W. Knilling and A. Ascherl, Ber., 59, 1279 (1926).

(3) (a) S. Winstein and H. J. Lucas, THIS JOURNAL, 61, 1576 (1939); (b) S. Winstein, ibid., 64, 2780 (1942).

(4) S. Winstein and L. L. Ingraham, ibid., 74, 1160 (1952).

(5) J. Read and W. Reid, J. Chem. Soc., 133, 1487 (1928).

(6) C. Golumbic and D. L. Cottle, THIS JOURNAL, 61, 996 (1939).

and benzalacetophenone were used in this reaction without success.

BROMOHYDRINS FROM OLEFINS AND NBS IN WATER

Olefin	Time	Yield.[a] % Bromohydrin	Oxide
Cyclohexene[b]	10 min.	79.3[c]	81.2[d]
Trimethylethylene[b]	25 min.	76.5[e]	78.2[f]
Allylbenzene[g]	48 hr.[h]		56.3[i]
1,4-Dihydronaphthalene[g]	12 hr.	30.0[j]	
Indene[k]	3 hr.	59.1[l]	
Mesityl oxide[g]	15 min.		56.1[m]
Fumaric acid[g] (Na salt)	48 hr.		60.6[n]
Cinnamic acid[g,o] (K salt)	2 hr.	35.0[p]	

[a] The oxides usually were obtained by taking the bromohydrins up in ether and then converting the crude material directly to the oxide. [b] 0.25 mole of olefin, 0.25 mole of NBS and 100 ml. of water. [c] B.p. 73–75° (5 mm.), n^{20}D 1.5180; lit.[3b] b.p. 86.6–88.4° (10 mm.), n^{25}D 1.5184. [d] B.p. 129–130°, n^{20}D 1.4528; "Organic Syntheses," Coll. Vol. 1, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 185, gives b.p. 129–134°. [e] B.p. 49–51° (10 mm.), n^{20}D 1.4723; lit.[4] b.p. 48–51° (10 mm.), n^{25}D 1.4712. Comparable results were obtained by Winstein and Ingraham[4] in this same reaction. [f] B.p. 72–74°, n^{18}D 1.3885; lit.[4] b.p. 73–73.3°, n^{25}D 1.3822. [g] 0.125 mole of olefin in 100 ml. of ether stirred with 0.125 mole of NBS in 100 ml. of water. [h] A 50% yield of the oxide was obtained when the ether was omitted and a 4-hour reaction time used. [i] B.p. 72–75° (3 mm.); E. Fourneau and M. Tiffeneau, Compt. rend., 140, 1596 (1905), report b.p. 94–98° (15 mm.). [j] M.p. 106–106.5°; E. Bamberger and W. Lodter, Ber., 26, 1833 (1893), report the same value. [k] 0.063 mole of olefin, 0.063 mole of NBS and 50 ml. of water. [l] M.p. 130–131°, lit.[2] m.p. 131–132°. [m] B.p. 61–63° (20 mm.), n^{17}D 1.4290; E. Weitz and A. Scheffer, ibid., 54, 2327 (1921), report b.p. 44–48° (15 mm.). [n] M.p. 212–213°; W. Lossen, Ann., 348, 299 (1906), reported m.p. 203° and R. Kempf, J. prakt. Chem., 83, 388 (1911), reported m.p. 215°. These references describe the isolation method used. [o] 200 ml. of water used and reaction flask cooled in ice-bath during reaction. [p] M.p. 124–125°; E. Erlenmeyer, Ber., 39, 788 (1906), reported m.p. 125°.

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The Oxygenation of the Tri-(p-nitrophenyl)-methide Ion. A Novel Oxidation–Reduction Reaction[1]

BY M. F. HAWTHORNE[2] AND GEORGE S. HAMMOND

Tri-(p-nitrophenyl)-methane (I) is a pseudo-acid probably having a pK_a near 13[3] and its solution in alcoholic alkali exhibits the deep purple color of the highly resonance stabilized anion II.

Previously, it was reported that the air oxidation of the anion II in alcoholic alkali gave high yields of tri-(p-nitrophenyl)-carbinol (III) as well as traces of p-nitrophenol and 4,4'-dinitrobenzophenone.[4] This nearly exclusive production of carbinol III seemed anomalous to us in view of the ease of

(1) Presented at the 125th National Meeting of the American Chemical Society, Kansas City, Missouri, 1954.

(2) Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Ala.

(3) G. W. Wheland and A. A. Danish, THIS JOURNAL, 62, 1125 (1940).

(4) O. Fischer and G. Schmidt, Chem. Zentr., 75, I, 460 (1904).
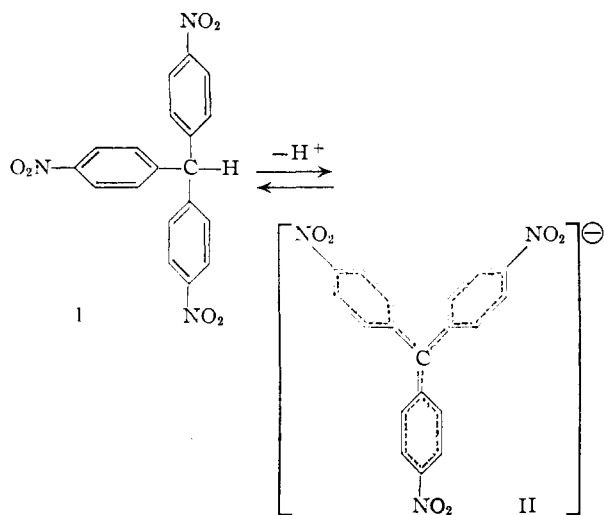
oxygenation of stable carbanions[5] to hydroperoxides and prompted a reinvestigation of the reaction.

Results and Discussion

The hydrocarbon I was found to be totally inert toward oxygen when dissolved in chlorobenzene at 140°. Addition of azo-bis-butyronitrile did not initiate an oxidation reaction at the same temperature. Further evidence showing the inertness of hydrocarbon I toward radical attack is based on the observation[6] that the air oxidation of cumene is not inhibited by the addition of I to the reaction mixture.

The anion II, in alcoholic alkali at room temperature, reacts easily with oxygen to give a 59% yield of a new compound, tri-(p-nitrophenyl)-methyl hydroperoxide (IV). The remainder of the reaction product was chiefly carbinol III and traces of p-nitrophenol. A quantitative determination of oxygen consumption by the anion II indicated that more than one mole of oxygen is absorbed per mole of anion. It must be pointed out that this result is not reliable since the ethanol used as solvent could have quite easily suffered oxidation as well as the anion II.

The structure of the hydroperoxide IV was proved by its quantitative cleavage to carbinol III with acidic potassium iodide in alcohol, carbon and hydrogen analysis and the presence of an O–O stretching band at 11.7 μ in the infrared absorption spectrum.

It was found that the hydroperoxide IV decomposed very slowly in ethanolic alkali to give carbinol III and a small amount of p-nitrophenol. An explanation of this observation cannot be offered at this time. However, it was clear that this slow decomposition of hydroperoxide IV would not account for the large amount of carbinol found in the crude oxidation product mixture and that another process was operating to give carbinol III.

This other process was shown to be the one-electron transfer oxidation–reduction reaction

$$R_3C:\ominus + R_3COOH \longrightarrow R_3C\cdot + R_3CO\cdot + OH\ominus$$
$$R = p\text{-}NO_2 \text{ phenyl}$$
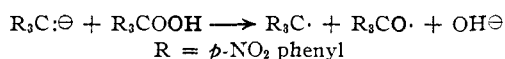
(5) For example, the oxidation of Grignard reagents reported by C. Walling and S. A. Buckler. This Journal, **75**, 4372 (1953).

(6) G. S. Hammond and C. E. Boozer. unpublished results.

since the anion II reacted with the hydroperoxide IV in ethanolic alkali at room temperature and in the absence of oxygen to give high conversion to the free tri-(p-nitrophenyl)-methyl radical and the carbinol III. The latter material undoubtedly was produced from the corresponding alkoxy radical by hydrogen abstraction from the solvent.

It is interesting to note that the driving force of this novel reaction is probably the unusual stability of the free tri-(p-nitrophenyl)-methyl radical.[7a,b] Furthermore, the oxidation–reduction system employed may be unique in that the hydrocarbon I probably is a stronger acid than the hydroperoxide IV and this situation allows free hydroperoxide and the anion II to exist simultaneously in ethanolic alkali.[8]

The formation of hydroperoxide IV and carbinol III during the oxygenation of the anion II is thus explained on the basis of the direct oxidation of anion II to hydroperoxide IV which in turn may undergo a one-electron transfer reaction with anion II to yield carbinol III (*via* the corresponding alkoxy radical) and the free tri-(p-nitrophenyl)-methyl radical. The fate of the tri-(p-nitrophenyl)-methyl radical and the source of the p-nitrophenol produced have not been elucidated.

Experimental

Tri-(p-nitrophenyl)-methane was prepared by mixed acid nitration of triphenylmethane,[9] m.p. 214–215° after three recrystallizations from chloroform–ether. When this material was placed on an alumina chromatographic column and eluted with benzene, only one red-violet band appeared which proved to be pure hydrocarbon, m.p. 214–215°.

Attempted Air Oxidation of Tri-(p-nitrophenyl)-methane. —Six hundred thirty mg. of pure hydrocarbon and 5 ml. of freshly distilled chlorobenzene were placed in a tube having a reflux condenser and a sintered glass bottom through which oxygen was admitted. The whole was immersed in a metal-bath at 140 ± 10° and gas admitted for nine hours. A small sample was removed, cooled, filtered and washed with pentane to give a melting point identical with that of hydrocarbon.

Fifty mg. of azo-bis-isobutyronitrile was then added and oxygen admitted for another 36 hours at 140°. The solution was then cooled, the solid removed by filtration, and washed with pentane, m.p. 214°.

The inertness of the pure hydrocarbon toward radical attack was further shown by its failure to inhibit the air oxidation of cumene.[6]

Quantitative Air Oxidation of Tri-(p-nitrophenyl)-methide Ion. A. Oxygen Consumption.—Two hundred twenty-nine mg. of pure hydrocarbon, 0.5 g. of potassium hydroxide and 40 ml. of absolute ethanol were placed in a thermostated reaction cell and stirred magnetically while connected to a gas buret filled with oxygen and thermostated at 25.00 ± 0.05°. The blue solution absorbed 66% of theoretical amount of oxygen in one hour (calculated for one mole of oxygen per mole of hydrocarbon). After 12 more hours 150% of the theoretical amount of oxygen had been absorbed. This high value was no doubt due to oxidation of solvent or secondary oxidation of the products of the anion oxidation.

B. Products.—Three and two-tenths grams of hydrocarbon, 3.5 g. of potassium hydroxide and 200 ml. of absolute ethanol were stirred in a slow stream of oxygen for nine hours. To the resulting yellow solution was added 600 ml.

(7) (a) K. Ziegler and E. Boye. *Ann.*, **458**, 248 (1927), report that this radical reacts slowly with air at room temperature; (b) F. S. Allen and S. Sugden. *J. Chem. Soc.*, 440 (1936), have found the radical to crystallize as such by magnetic susceptibility measurements.

(8) This appears to be a reasonable assumption since hydrocarbon I is known to have a pK_a near 14 ± 2 while hydroperoxides are only slightly more acidic than their corresponding alcohols of pK_a near 17.

(9) J. B. Shoesmith, C. E. Sosson and A. C. Hetherington. *J. Chem. Soc.*, 2227 (1927).

of water and the precipitated material was extracted with 200 ml. of ether in three portions. The combined ether extracts were dried over magnesium sulfate and the solvent was evaporated on the steam-bath; crude yield 2.80 g., m.p. 156–170° dec. This material was shown to be 74% hydroperoxide, using iodometric assay in ethanol,[10] or to represent a yield of 59%.

Two recrystallizations of this crude material gave 2.10 g. of white leaflets from ethanol–water, m.p. 190–191° dec.

Fifty mg. of the material from alcohol–water was dissolved in benzene and put on a 14-cm. alumina column and eluted with one liter of benzene. At this point, a small band which was visible only under ultraviolet light and which had the purple fluorescence characteristic of authentic tri-(p-nitrophenyl)-carbinol had moved about 5 cm. A very minute yellow band remained at the very top of the column. Chloroform was then passed through the column and the carbinol band was removed to give ca. 5 mg. of material melting at 157–160°. Following this material there appeared the hydroperoxide which was invisible under both ultraviolet and white light and which melted at 186.5–187.5 dec. The small yellow band remained at the top of the column. *Anal.* Calcd.: C, 55.55; H, 3.19. Found: C, 55.80; H, 3.28.

The material melting at 190–191° gave infrared absorption peaks characteristic of O–H stretching (2.95 μ) and O–O stretching[11] (shoulder at 11.7 μ) in a Nujol mull. No carbonyl absorption was indicated.

C. Hydrogen Iodide Cleavage.—Excess sodium iodide was added to 179.7 mg. of hydroperoxide dissolved in 20 ml. of absolute ethanol and the solution heated to incipient boiling, cooled, excess thiosulfate added and the solution flooded with water. The solution was warmed and allowed to cool slowly giving 150.7 mg. (87%) of tri-(p-nitrophenyl)-carbinol, m.p. 190–191°.[12] The infrared spectrum of a Nujol mull showed absorption peaks characteristic of O–H stretching (2.90 μ) and tertiary carbon–oxygen stretching (7.10 μ) were observed. No absorption was observed at the carbonyl and peroxide wave lengths.

Oxidation of this material with excess chromic acid in boiling acetic acid gave a 10% yield of long white needles which melted at 189–190°,[13] and depressed the melting point of the starting material, indicating that this product is 4,4'-dinitrobenzobenzophenone.

The Reaction of Tri-(p-nitrophenyl)-methide Ion with Tri-(nitrophenyl)-methyl Hydroperoxide.—In a one-liter flask closed with a stopper bearing a stopcock was placed 249 mg. of hydroperoxide, 218 mg. of hydrocarbon and 1.0 g. of potassium hydroxide. The flask was flushed with nitrogen, 100 ml. of absolute ethanol was added and the flask stoppered. The flask outlet was opened to a vacuum line and the solvent briskly boiled to expel residual oxygen and the stopcock was then closed. The blue solution then was shaken occasionally and allowed to stand at room temperature for ten hours. Crystals were noted on the bottom and sides of the flask. These were separated by decantation, washed with alcohol and the mother liquor and washings combined and quickly flooded with water. The crystals were triturated with alcohol–water and removed by filtration. The crystals were bright green and decolorized rapidly in air to give a yellow solution. The crystals appeared to be dark brown, but when scratched appeared green. Solution of the crystals in ethyl acetate resulted in rapid decolorization.[14]

Evaporation of the ethyl acetate followed by the addition of pentane precipitated long yellow needles melting at 155–157°. Continued recrystallization lowered and broadened the melting point range. The crude yield of this unidentified material was estimated at 50 mg.

The original mother liquor was extracted with ethyl acetate, separated, dried and the solvent removed in an air jet. The yield of crude material was 201 mg. This material was recrystallized three times from ethanol–water to give 110

(10) V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941).

(11) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 282 (1951).

(12) M. Gomberg, *Ber.*, **37**, 1639.

(13) W. Staedel and E. Haase, *ibid.*, **23**, 2578 (1890), report a melting point of 189–190° for 4,4-dinitrobenzophenone.

(14) K. Ziegler and E. Boye (ref. 5a) report an identical description of the tri-(p-nitrophenyl)-methyl radical.

mg. of material melting at 165–170°. The mother liquor from the first recrystallization deposited leaflets of hydroperoxide. The material melting at 165–170° was chromatographed on a small alumina column using benzene to develop the chromatogram. Three bands were observed: a small yellow band at the top of the column, a fast purple-red band (hydrocarbon) and a slower moving band invisible in white light but purple under ultraviolet radiation. This band was collected separately by elution with chloroform and recrystallized from ethanol water to give ca. 100 mg. of short white needles melting at 189–189.5°, and showing no depression when mixed with carbinol obtained from cleavage of the hydroperoxide.

The Reaction of Tri-(p-nitrophenyl)-methyl Hydroperoxide with Ethanolic Hydroxide Ion.—A solution of 118.9 mg. of tri-(p-nitrophenyl) hydroperoxide melting at 190–191° was made up of 25.00 ml. at 43.2 ± 0.1° in 0.0870 N potassium hydroxide in absolute ethanol. The rate of appearance of p-nitrophenol was followed by periodically observing the optical density of the solution at 460 mμ with a Beckman model DU spectrophotometer. It was found that a maximum of 12% reaction had occurred after 11 hours at 43.2°. After standing at this temperature for three weeks 15 ml. of the solution was flooded with water and extracted with ether. Recrystallization of the residue obtained on evaporation of the ether gave 35 mg. of material melting at 180–191° without decomposition and giving no hydroperoxide test. One more recrystallization from ethanol–water raised the melting point to 192°. A mixed melting point with hydroperoxide was depressed at 175° and the compound gave an infrared absorption spectrum in a Nujol mull identical with authentic carbinol.

A control experiment which contained no base was carried out simultaneously. After three weeks the presence of hydroperoxide was detected easily with potassium iodide. Treatment of a small sample with solid potassium carbonate produced an immediate yellow coloration which was discharged on the addition of acid.

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Galactosyl Glycerol from *Gelidium pristoides* and *Gracilaria confervoides*

BY JOHN R. NUNN AND MAVIS M. VON HOLDT

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The recently reported work of Putman and Hassid[1] on the structure of α-D-galactopyranosyl-2-glycerol from the red alga, *Irideae laminaroides*, has prompted us briefly to record similar work which was in progress in this Laboratory at the time of the appearance of the above report.

Methanolic extraction of *Gelidium pristoides* and subsequent deionization (using Amberlite IR 120 and IR 4B resins) of the product yielded a sirup, which was chromatographed on a charcoal–Celite column.[2] The main fraction (1% of dried seaweed) crystallized in colorless needles, m.p. 127–127.5°, $[\alpha]^{19}D$ 172° (c 0.70, water) (Found: C, 42.8; H, 7.2. Calcd. for $C_9H_{18}O_8$: C, 42.5; H, 7.2). It was nonreducing to Fehling solution. This substance was hydrolyzed (N sulfuric acid for 4 hours), and the products, which were separated by paper chromatography, were shown to be glycerol (tri-p-nitrobenzoate, mixed m.p. 191–193°), and galactose (mucic acid, mixed m.p. 215°). A quantitative estima-

(1) E. W. Putman and W. Z. Hassid, THIS JOURNAL, **76**, 2221 (1954).

(2) R. L. Whistler and D. F. Durso, *ibid.*, **72**, 677 (1950).