tion of α-hydroxy acids and sugars.[2] Lander[3] successfully employed it in the alkylation of amides, phenols, acetoacetic ester, and borneol.

When (+)-phenylmethylcarbinol of 92.8% optical purity was refluxed with ethyl iodide in the presence of silver oxide, the resulting ethyl ether had $[\alpha]^{28}\text{D}$ + 88.0°, or +94.8° for the optically pure ether. The ether prepared from ethyl bromide and the potassium salt of (−)-phenylmethylcarbinol has $[\alpha]\text{D}$ −80.7°,[4] corresponding, therefore, to only 85% optical purity. The methyl ether was also prepared from 92.8% optically pure (+)-phenylmethylcarbinol, methyl iodide and silver oxide, and had $[\alpha]^{28}\text{D}$ +119.1°, or +128.3° for the optically pure ether. The highest rotation reported for this product, prepared from methyl iodide and the sodium salt of (+)-phenylmethylcarbinol, is $[\alpha]\text{D}$ +68°,[5] corresponding, therefore, to only 53% optical purity. The very extensive racemization which accompanied the older preparations of phenylmethylcarbinyl ethers is not surprising, in view of the well-known stereochemical equilibration of alcohols in the presence of alkali alcoholates and traces of oxidizing agents,[6] and the lability of the α-hydrogen in the particular system under investigation. While it seems possible that optically pure ethers might also be prepared by the conventional method under conditions strictly exclusive of oxidants, the silver oxide method has the advantage of great simplicity, no special precautions being needed to avoid the possibility of racemization. Whether or not a very small amount of racemization took place during the silver oxide reaction could not be ascertained conclusively. Although the cleavage of the ethyl ether with anhydrous hydrogen bromide resulted principally in styrene and phenylmethylcarbinyl bromide, and not in phenylmethylcarbinol, the unreacted carbinol isolated from the etherification mixture had retained its original rotation, and the rotation of the ethyl ether remained unchanged when the ether was refluxed with ethyl iodide in the presence of silver oxide. Furthermore, consistent results were obtained on successive alkylations. In view of these results it is highly probable that the optical purity of the ethers is the same as that of the starting carbinol.

Experimental

Ethyl α-Methylbenzyl Ether.—Phenylmethylcarbinol was resolved through its brucine salt.[7] A mixture of 5.5 g. of carbinol, $[\alpha]^{25}\text{D}$ +40.4° (no solvent), 28.2 g. of ethyl iodide and 10.5 g. of freshly precipitated, dry silver oxide was refluxed for one hour. The same quantities of ethyl iodide and silver oxide were then added and refluxing was continued overnight. The mixture was filtered and the excess ethyl iodide was distilled off. The residual oil was heated with phthalic anhydride and pyridine on the steam-bath for two hours, the resulting mixture poured into dilute hydrochloric acid and extracted with ether. The ether layer was washed with dilute, cold sodium hydroxide, dried and distilled to yield 3.6 g. (53%) of the desired product, b.p. 89° (31 mm.), $n^{25}\text{D}$ 1.4846, d^{25}_{4} 0.9187, $[\alpha]^{28}\text{D}$ +88.0° (no solvent). The product was refluxed for one day with the same quantities of ethyl iodide and silver oxide which were employed in its preparation; filtration and distillation afforded the ether with unchanged rotation.

Methyl α-Methylbenzyl Ether.—A mixture of 14.0 g. of phenylmethylcarbinol, $[\alpha]^{25}\text{D}$ +40.4° (no solvent), 65.2 g. of methyl iodide and 26.6 g. of silver oxide was refluxed and worked up as described for the preparation of the ethyl ether, to yield 6.0 g. (38%) of the desired product, b.p. 88° (47 mm.), $n^{25}\text{D}$ 1.4905, d^{25}_{4} 0.9353, $[\alpha]^{28}\text{D}$ +119.1° (no solvent). A mixture of 21.6 g. of phenylmethylcarbinol, $[\alpha]^{25}\text{D}$ −40.2° (no solvent), 100 g. of methyl iodide and 41 g. of silver oxide afforded 7.7 g. (32%) of product, $[\alpha]^{28}\text{D}$ −118.2°. The sodium hydroxide washings from this reaction were heated at 100° for three minutes, the liberated oil extracted with ether and distilled, affording 9.0 g. of phenylmethylcarbinol, $n^{25}\text{D}$ 1.5272, $[\alpha]^{25}\text{D}$ −40.2° (no solvent).

Cleavage of Ethyl α-Methylbenzyl Ether.—A mixture of 7.6 g. (0.05 mole) of (±)-ethyl α-methylbenzyl ether and 4.1 g. (0.05 mole) of anhydrous hydrogen bromide, sealed in a tube, was heated at 100° for one hour. The water which had separated was pipetted off; the organic layer, after neutralization and drying with potassium carbonate, weighed 10.6 g. Fractionation yielded diethyl ether, ethyl bromide, ethanol, styrene and phenylmethylcarbinyl bromide. While the residual dark colored oil might have contained some phenylmethylcarbinol, the amount was too small to make further distillation profitable.

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[2] Purdie, *et al.*, *J. Chem. Soc.*, 157, 485 (1899); *ibid.*, 1021, 1037 (1903); McKenzie, *ibid.*, 754 (1899).

[3] Lander, *ibid.*, 729 (1900); *ibid.*, 690 (1901); *ibid.*, 414 (1903).

[4] Extrapolated from values reported by Kenyon and Phillips, *ibid.*, 1676 (1930).

[5] From values reported by Hughes, Ingold and Scott, *ibid.*, 1201 (1937).

[6] Doering and Aschner, THIS JOURNAL, **71**, 838 (1949).

[7] Downer and Kenyon, *J. Chem. Soc.*, 1156 (1939).

Diphenates. I. Preparation of Diphenic Acid

BY WILLIAM F. O'CONNOR AND EMIL J. MORICONI

Recorded instances of the peroxide oxidation of phenanthrene appear only scattered in the literature. Using 30% hydrogen peroxide, the primary oxidation product, 9,10-phenanthrenequinone, has been obtained in unrecorded yields.[1] Furthermore, the quinone, as a reactant, has been converted to diphenic acid *via* the same oxidizing medium,[2] and by treating its reduction product, 9,10-phenanthrenediol, with sodium peroxide in an alkaline medium.[3]

The one-step oxidation of phenanthrene to diphenic acid has been effected with 30% hydrogen peroxide in 29% yield and accompanied by a considerable proportion of resins.[4] The most recent work, using 20% hydrogen peroxide and an osmium tetroxide catalyst, gave a 16% yield of the quinone and a negligible yield of diphenic acid.[5] Both reactions involve long contact time.

We have found that recently available 50% hydrogen peroxide[6] in glacial acetic acid oxidizes phenanthrene to high-purity diphenic acid with minimum by-product formation, short contact time and in 65–70% yields.

Using the same peroxide/phenanthrene molar ratio and identical reaction conditions, 90% hydrogen peroxide[6] gave lower yields and a more difficultly purified diphenic acid.

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[1] Henderson and Boyd, *J. Chem. Soc.*, **97**, 1661 (1910); Milas, British Patent 508,526.

[2] Perkins, *Proc. Chem. Soc.*, **23**, 166 (1907); Holleman, *Rec. trav. chim.*, **23**, 171 (1924); Charrier and Moggi, *Gazz. chim. ital.*, **54**, 988 (1924); Linstead and Walpole, *J. Chem. Soc.*, 855 (1939).

[3] Williams, U. S. Patent 1,423,980.

[4] Charrier and Moggi, *Gazz. chim. ital.*, **57**, 736 (1927).

[5] Cook and Shoental, *J. Chem. Soc.*, 47 (1950).

[6] Research sample supplied by Buffalo Electro-Chemical Co., Inc., Buffalo 7, N. Y.

Experimental

To a mixture of 9.0 g. (0.506 mole) of phenanthrene in 75 ml. of glacial acetic acid was added 45 ml. of 50% hydrogen peroxide (0.792 mole). On warming slowly, the white paste went into solution. At 60–70°, the exothermic reaction commenced and the deep red solution was kept at a slow reflux for two hours. On refrigeration, 8.0 g. of yellow-white needles crystallized. These were collected and dissolved in warm caustic. After filtering the undissolved quinone, diphenic acid was precipitated as a white powder by acidification of the filtrate with concd. hydrochloric acid. Additional diphenic acid was recovered from the mother liquor by adding it slowly with stirring into warm caustic to decompose the excess peroxide and any peracetic acid formed *in situ*. The solution was treated with charcoal and filtered, and the filtrate was acidified.

The total yield of phenanthrenequinone was 0.5 g. (4%), m.p. 204–206°; of diphenic acid was 8.3 g. (68%), m.p. 229–230°.

A mixed melting point of the latter with a known sample of diphenic acid gave no depression.

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Addition Compound of Boron Tribromide and Trimethylamine

BY ROBERT C. OSTHOFF, CHARLES A. BROWN AND FRANK H. CLARKE

In view of the fact that the trimethylamine addition compounds of boron trifluoride[1] and boron trichloride[2] have been isolated and characterized, it is surprising that the similar ammine of boron tribromide, $Br_3BN(CH_3)_3$, has not been reported previously.

Johnson[3] attempted preparation of $Br_3BN(CH_3)_3$ by the introduction of gaseous trimethylamine into a solution of boron tribromide in carbon tetrachloride, but he was unable to isolate any product which could be characterized. However, Johnson did report the addition compounds of boron tribromide with triethylamine, dimethylaniline and pyridine.

The authors were able to prepare the stable white solid compound of boron tribromide and trimethylamine by direct combination. This compound further illustrates the ability of the boron halides to form stable coördinate covalent bonds with simple tertiary amines.

The following method for the study of the reaction was used. In a typical run tensiometrically pure Eastman Kodak Co. "White Label" trimethylamine (2.106×10^{-3} mole) was introduced into a previously evacuated reaction bulb by means of a compensating gas buret. The pressure of the completely vaporized sample was determined at room temperature and the trimethylamine was "frozen out" with liquid nitrogen. Successive small weighed amounts of boron tribromide[4] (vapor pressure at 23° obsd. 61 mm.; calcd. 62 mm.) were added, the reaction bulb warmed to 25° and the pressure determined following each addition.

The pressures were plotted against mole ratio, $BBr_3/N(CH_3)_3$ giving a straight line (see Fig. 1) which intersected the mole ratio axis at a value of one, corresponding to the formation of $Br_3BN(CH_3)_3$. Continued addition of boron tribromide showed formation of no other compound, and gave only the expected increase in pressure.

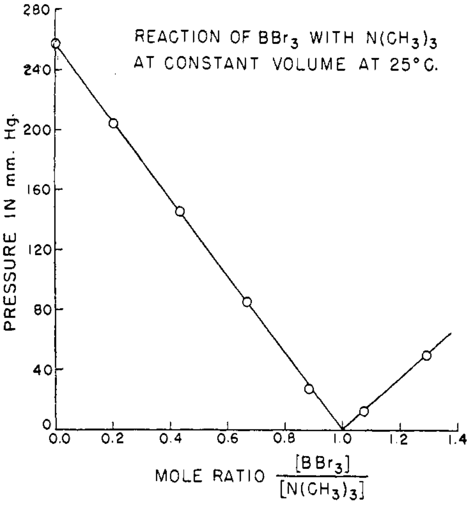

Fig. 1.

The white solid obtained from the reaction was found to be stable in air. It crystallized as long white needles from benzene, melting at 238–240° with some decomposition. The substance was soluble in benzene, chloroform and carbon tetrachloride and insoluble in water at 10°.

Anal. Calcd. for $Br_3BN(CH_3)_3$: C, 11.62; H, 2.90; N, 4.52; Br, 77.55. Found: C, 11.77; H, 2.98; N, 4.79; Br, 78.25.

Cryoscopic measurements in anhydrous benzene gave a molecular weight value of 321 (calcd. for $Br_3BN(CH_3)$ 310).

The infrared spectrum of the compound in chloroform solution was obtained with a Baird spectrophotometer. The principal absorption bands in the range of 2–16 mμ were: 3.19, 6.75, 6.87, 9.00, 10.46 and 12.22 mμ.

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[2] E. Wiberg, *Z. anorg. Chem.*, **202**, 355 (1931).

[3] A. R. Johnson, *J. Phys. Chem.*, **16**, 1 (1912).

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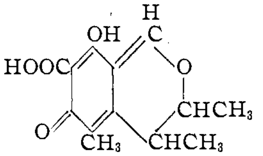
The Preparation of 6-Hydroxyisochroman[1]

BY L. SCHIELER[2] AND R. D. SPRENGER

Recent investigations[3,4,5] have shown that the antibiotic citrinin has the structure (I). Dihydrocitrinin (II) which has been obtained by the catalytic reduction of citrinin may thus be considered a derivative of isochroman (III). The desirability of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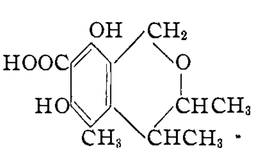
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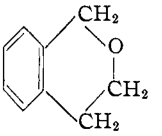
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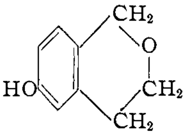
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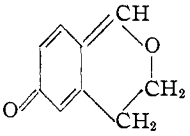
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[1] This work was supported by a grant from the Research Corporation and is a portion of a thesis presented by Leroy Schieler at the College of Puget Sound in partial fulfillment of the requirements for the M.S. degree.

[2] Chemistry Department, University of California, Los Angeles.

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[5] Brown, Robertson, Whalley and Cartwright, *J. Chem. Soc.*, 867 (1949).