clear solution was evaporated, under reduced pressure, to about 30 cc. The solution was then acidified with sulfuric acid (congo red). The liquid yielded 0.4 g. of colorless crystals, m. p. 230–233°. They were recrystallized by the procedure given before for the acid obtained by alkaline hydrogen peroxide oxidation of the 233°-melting compound. When pure, the acid melted at 239° and was identical with the acid obtained with hydrogen peroxide (the mixed melting point was not depressed). Titration and carbon and hydrogen determinations gave the following results: C, 57.15; H, 6.72; mol. wt. (titration calcd. as 1 COOH group), 461.

Hydrolysis of the 233°-Melting Compound.—A suspension of 0.5 g. of the 233°-melting compound in 5 cc. of 0.4% hydrochloric acid was boiled for approximately one minute. The suspended material quickly dissolved, and at the same time a new material separated. The mixture was cooled and allowed to crystallize for an hour. The resulting white crystals were separated and the compound was identified as tenulin by its melting point (194–195°), its failure to depress the melting point of an authentic sample of tenulin, and its optical crystallographic properties.

The mother liquors were neutralized and evaporated under reduced pressure to about 1 cc. and then treated by shaking with 0.4 cc. of benzoyl chloride and 10 cc. of 10% sodium hydroxide. The resulting benzoyl derivative was recrystallized from 50% ethanol. It melted at 73° and did not depress the melting point of an authentic sample of dibenzoyl ethylene glycol.

Summary

The compound, m. p. 233°, obtained from a certain lot of *Helenium tenuifolium* and reported as having the composition $C_{16}H_{22}O_5$ has now been shown to have the molecular formula $C_{19}H_{26}O_6$. It is an ether with properties characteristic of an acetal and is formed by a reaction involving the elimination of a molecule of water from ethylene glycol (used as a solvent in its preparation) and tenulin.

The formation of this compound further substantiates the suggestion that tenulin contains a sterically hindered hydroxyl group, and that this group and the acetoxyl group of tenulin are probably adjacent to each other.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

The Bromination of 2-Naphthyl Benzoate

BY STEWART E. HAZLET

In previous studies on esters containing diphenyl groups it has been shown that hydroxy and acetoxy groups direct an entering bromine atom to the same position,[1] but that benzoyloxy[2] or benzenesulfonyloxy[3] groups in place of the smaller ones cause the bromine atom to enter the molecule at a more remote position.

These results suggested that 2-naphthyl benzoate might brominate in the ring not bearing the benzoyloxy group. It was found, however, that bromination of this ester took place in position 1. The product was definitely proved to be 1-bromo-2-naphthyl benzoate by its hydrolysis to 1-bromo-2-naphthol.

Experimental Part

2-Naphthyl Benzoate.[4]—This compound was prepared by the action of benzoyl chloride on 2-naphthol in pyridine as in similar syntheses.[5] After recrystallizations from methanol, the yield of material melting at 105°[4] was 81%.

The Bromination of 2-Naphthyl Benzoate.—Ten grams of 2-naphthyl benzoate was dissolved in 100 ml. of glacial acetic acid with vigorous stirring on a steam-bath. Bromine (3.2 ml., approximately 1.5 molecular proportions) dissolved in glacial acetic acid (10 ml.) was added slowly, and then a trace of iron powder was introduced into the reaction flask. After the vigorous reaction which followed the introduction of the iron had subsided, the stirring and heating were continued for three hours. At the end of this period the reaction mixture was poured into 1000 ml. of water. The product represented only a 40% yield of a monobromo-2-naphthyl benzoate; no other products were recovered. Recrystallizations from methanol resulted in considerable loss, but yielded a product which melted between 98 and 99°.

Anal. Calcd. for $C_{17}H_{11}O_2Br$: Br, 24.41. Found: Br, 24.35, 24.46.

Hydrolysis of the Monobromo-2-naphthyl Benzoate.—One gram of the purified monobromo ester was refluxed gently in a solution which contained 25 ml. of ethanol, 25 ml. of water, and 3 g. of potassium hydroxide. After fourteen hours of refluxing, the ethanol was removed by distillation, more water was added, and the alkaline solution was extracted with ether. Next, carbon dioxide was passed into the aqueous solution. The precipitated phenolic component was extracted with ether and the ethereal solution was dried with anhydrous sodium sulfate in the presence of Norite. The yield of crude bromonaph-

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(1) Hazlet and Kornberg, THIS JOURNAL, **61**, 3037 (1939).

(2) Hazlet, Alliger and Tiede, *ibid.*, **61**, 1447 (1939).

(3) Hazlet, *ibid.*, **59**, 1087 (1937).

(4) Koenigs and Carl, *Ber.*, **24**, 3900 (1891).

(5) Hazlet, THIS JOURNAL, **59**, 287 (1937).

thol was 88%. After recrystallizations from methanol-water (1:1), the compound melted at 83°.

From the aqueous solution which remained after the last ether extraction above, benzoic acid was recovered in 94% yield.

1-Bromo-2-naphthol.[6]—This compound was prepared in almost quantitative yield from equimolecular proportions of bromine and 2-naphthol dissolved in glacial acetic acid. The mixture was heated on a steam-bath for two hours and poured into water. The crude product was distilled at 10 mm. pressure and recrystallized twice from benzene-ligroin (1:3)[7]; m. p. 80–81°.[6] A mixture of this product and that of m. p. 83°, obtained by hydrolysis of the brominated ester, melted without depression.

1-Bromo-2-naphthyl Acetate.[8]—A sample (0.6 g.) of the bromonaphthol described above was refluxed gently for one hour in acetic anhydride (15 ml.) to which had been added anhydrous sodium acetate (1 g.). The reaction mixture was poured into 200 ml. of water and, after thirty hours, excess sodium carbonate was added. The ester was extracted with ether. The oil which was recovered was dissolved in warm ethanol and crystallization was effected by rapid cooling in a carbon dioxide–acetone mixture. After the first recrystallization from ethanol, a 70% yield resulted; the second recrystallization gave a product which melted at 55–56°.[10]

1-Bromo-2-naphthyl Benzoate.—From 0.7 g. of 1-bromo-2-naphthol, 1-bromo-2-naphthyl benzoate was obtained[5] in almost quantitative yield. Recrystallizations from methanol gave a product which melted at 98.5–99.5°. A mixture of this product and that of m. p. 98–99°, obtained by the bromination of 2-naphthyl benzoate, melted without depression.

Summary

The bromination of 2-naphthyl benzoate in glacial acetic acid results in the formation of 1-bromo-2-naphthyl benzoate.

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[6] Smith, *J. Chem. Soc.*, **35**, 789 (1879) ("Beilsteins Handbuch der organischen Chemie," Verlag Julius Springer, Berlin, 4th ed., Vol. VI, 1923, p. 650).

[7] Boiling range of the ligroin, 30–60°.

[8] In order to be certain that the bromonaphthol which was obtained in this work was the 1-bromo compound, it was necessary to convert it to the corresponding acetate, for both 1-bromo-2-naphthol[6] and 3-bromo-2-naphthol[9] melt at almost the same temperatures, *viz.*, 83 or 84°; the m. p. of 1-bromo-2-naphthyl acetate is 56°[10] and that of the 3-bromo isomer is 94°.[9]

[9] Fries and Schimmelschmidt, *Ann.*, **484**, 268 (1930).

[10] Hewitt and Mitchell, *J. Chem. Soc.*, **89**, 1173 (1906).

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF CALIFORNIA]

Sulfophenylarsonic Acids and Certain of their Derivatives. III. *p*-Sulfo- and *p*-Sulfonamidodiphenylarsonic Acids

BY J. F. ONETO AND E. L. WAY

Doak's[1] recent publication called our attention to the alcoholic Bart reaction described by Scheller.[2] When this reaction was applied to sulfanilic acid and phenyldichloroarsine, unreacted sulfanilic acid (64%) and phenylarsonic acid (84%) were recovered from the reaction mixture. We have shown in a separate experiment that nitrous acid in alcoholic solution is capable of oxidizing the trivalent arsenic in phenyldichloroarsine to a pentavalent state. On subsequent steam distillation of the reaction mixture an 86% yield of phenylarsonic acid resulted. *p*-Sulfodiphenylarsonic acid was obtained, however, through the barium salt stage, by first diazotizing the sulfanilic acid in aqueous solution, adding alcohol and then carrying out the Scheller reaction in the usual way.

On application of the Bart reaction to sulfanilic acid and phenyldisodium-arsenite, 70–75% yields of phenylarsonic acid resulted when coupling was carried out in alkaline solution. We were unable to isolate *p*-sulfodiphenylarsonic acid from the reaction products.

p-Sulfonamidophenylarsonic acid was obtained in relatively low yields by application of the Bart reaction and Sakellarios'[3] modification of the Bart reaction to sulfanilamide and phenyldisodium arsenite. Coupling in both instances was carried out in acid solution, the yields of *p*-sulfonamidodiphenylarsonic acid being 11 and 23%, respectively. Sixty to 65% yields of phenylarsonic acid were obtained from the Bart reaction when the order of coupling was reversed. The Scheller reaction gave 29–32% yields of *p*-sulfonamidodiphenylarsonic acid when applied to sulfanilamide and phenyldichloroarsine.

p-(N-Chloro)-sulfonamidodiphenylarsonic acid was obtained on treating the corresponding acid in alkaline solution with sodium hypochlorite. The N-chloro compound precipitates on acidification with sulfuric acid.

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[1] Doak, THIS JOURNAL, **62**, 167 (1940).

[2] Scheller, French Patent 624,028, *Chem. Zentr.*, **98**, II, 229 (1927).

[3] Sakellarios, *Ber.*, **57**, 1514 (1924).