The methods of preparation are illustrated by the following examples.

4-(*p*-Methylphenacyl)-morpholine Hydrobromide.—Heat was evolved when 3.5 g. of morpholine and 5.4 g. *p*-methylphenacyl bromide were mixed without any solvent. The reddish-brown sticky paste recrystallized from ethanol yielded 5.35 g. (45%) of white crystals, m.p. 200–202°.

4-Methyl-4-(5,6,7,8-tetrahydro-β-naphthacyl)-morpholinium Iodide.—5,6,7,8-Tetrahydro-β-naphthacyl bromide was prepared in 43% yield by dropwise addition of a mixture of 204 g. of bromoacetyl bromide (1.01 moles) and 120 g. of tetralin (0.91 mole) in 600 ml. of carbon disulfide to 150 g. of aluminum chloride (1.13 moles) in 1200 ml. of carbon disulfide at 0–10°, stirring 2 hours, and decomposing with ice and dilute hydrochloric acid, m.p. 69° after recrystallization from isopropyl alcohol to constant melting point. This product was also obtained in approximately the same yield by bromination of 5,6,7,8-tetrahydro-2-acetonaphthone in acetic acid. Thirty grams of the bromide dissolved in 150 ml. of acetone, mixed with 25 g. of sodium iodide, the sodium bromide filtered off, the acetone solution evaporated and the residue recrystallized from hot methanol yielded 18 g. (49%) of 5,6,7,8-tetrahydro-β-naphthacyl iodide, m.p. 58–59°. A mixture of 7.80 g. of this iodide (0.026 mole) and 2.36 g. of 4-methylmorpholine (0.026 mole) in 50 ml. of chloroform produced a large quantity of white crystals within 36 hours. After standing several days the salt was filtered off and purified by repeatedly dissolving in hot methanol and adding ether until a constant melting point of 192–193° was reached; yield of pure product 2.38 g. (23%).

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Oximes of β-Naphthacyl Halides and their Pyridinium Salts[1]

BY CARL T. BAHNER, PAUL T. SCOTT, CAROLYN CATE, BETTY GAY WALDEN AND H. DAVID BALDRIDGE, JR.

An oxime of β-naphthacylpyridinium iodide has been reported to damage sarcoma cells *in vivo*,[2] but the configuration of the oxime was not specified. In order to settle this point we have prepared the antiform of the oximes of β-naphthacyl bromide and iodide and their pyridinium salts and have submitted samples of the salts to the National Cancer Institute for screening. The 3-bromopyridinium salt has been reported in another article.[3]

Experimental

Anti-β-naphthacyl Bromide Oxime (I).—A saturated solution of 13.95 g. of hydroxylamine hydrochloride in water was added to 50 g. of β-naphthacyl bromide in 1800 ml. of methanol at room temperature, the mixture allowed to stand 6 hours at room temperature, a part of the methanol removed by vacuum distillation, the liquid cooled and filtered to recover one crop of crystals, the removal of solvent and chilling repeated to obtain a second and a third crop of crystals which were then subjected to systematic fractional crystallization from methanol. There were obtained 15.4 g. of crystals melting at 172.5°, 9.30 g. melting at 170° and 8.0 g. melting at 169°. Repeated recrystallization produced a fraction melting at 174°. A sample of the less soluble, high melting crystals was subjected to Beckmann rearrangement followed by hydrolysis and a 61% yield of β-naphthylamine was isolated, but no β-naphthoic acid could be detected.

Anti-β-naphthacylpyridinium Bromide Oxime.—The pyridinium salt, white crystals, m.p. 245°, was obtained in 83% yield by reaction of I with pyridine in alcohol. It was purified by recrystallization from ethanol and water.

Anal. Calcd. for $C_{17}H_{15}BrN_2O$: Br, 23.25. Found: Br, 23.21, 23.31.

Anti-β-naphthacyl Iodide Oxime (II).—A solution of 0.92 g. of I dissolved in a minimum volume of acetone was mixed with 1.42 g. (excess) of sodium iodide in 10 ml. of acetone, the sodium bromide removed after several hours by filtration and the oxime obtained in crystalline form by cooling the solution in an ice-bath and filtering. After repeated recrystallization from ethanol the product melted at 148°. Beckmann rearrangement, followed by hydrolysis, gave a 71% yield of β-naphthylamine, m.p. 105–107°. A portion of this compound was treated with acetic anhydride to give the N-acetyl derivative, m.p. 134–135°. No β-naphthoic acid was isolated.

The oximes appeared to be stable for several days at room temperature, but after several weeks most of the samples had turned brown and showed other indications of decomposition.

Anti-β-naphthacylpyridinium Iodide Oxime.—A mixture of 2.5 g. of II (0.008 mole) and 0.63 g. of pyridine (0.008 mole) in a little acetone seemed to react completely within a few minutes. After several hours 2.6 g. of white crystals were removed by filtration and washed with chloroform; m.p. 222–223° (dec.) after recrystallization from methanol.

Anal. Calcd. for $C_{17}H_{15}IN_2O$: C, 52.34; H, 3.88. Found: C, 51.94; H, 4.02.

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DEPARTMENT OF CHEMISTRY
CARSON-NEWMAN COLLEGE
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Investigations in the Acetylene Series. I. The Reactions of 3-Methyl-1-butyn-3-ol with Phosphorus Trichloride and of 3-Methyl-3-buten-1-yne with Hydrochloric Acid

BY ERNST D. BERGMANN AND D. HERRMAN

Hennion, Sheehan and Maloney[1] have recently reported on the reaction of 3-methyl-1-butyn-3-ol (I) with hydrochloric acid under various conditions. The present note supplements their conclusions.

In the reaction of 3-methyl-1-butyn-3-ol (I) with phosphorus trichloride, the corresponding *t*-chloride (II) and 3-methyl-1-chloro-1,3-butadiene (V) were obtained; they were identified by their reactions. When hydrochloric acid reacted upon (I), 3-methyl-1-chloro-1,2-butadiene (VII), isolated by Hennion and co-workers[1] in their experiments,

(1) This investigation was supported in part by a research grant from the National Cancer Institute of the National Institutes of Health, Public Health Service, for which we are grateful.

(2) Albert J. Dalton, in "Approaches to Cancer Chemotherapy," American Association for the Advancement of Science, F. R. Moulton, Editor, Washington, D. C., 1947, p. 246; *cf.* J. L. Hartwell and S. R. L. Kornberg, THIS JOURNAL, **68**, 1131 (1946).

(3) Carl T. Bahner, Wm. K. Easley, Madge D. Pickens, Harold D. Lyons, Lilburn L. Norton, Betty Gay Walden and George E. Biggerstaff, THIS JOURNAL, **73**, 3499 (1951).

(1) Hennion, Sheehan and Maloney, THIS JOURNAL, **72**, 3542 (1950).