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Synthesis of an α-Bromo-β-lactam, 7-Bromo-8-oxo-1-azabicyclo-[4.2.0]octane, by Carbene Insertion*

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For some time we have been searching for methods of synthesizing β-lactams, containing in the α-position an atom or group capable of undergoing transformation under conditions not affecting the β-lactam system. Our attention was directed to the discovery of Soyferth and co-workers, that halomethylphenymercury compounds readily decompose giving phenymercury halides and halocarbene:s, and we have found that on thermal decomposition (N-dibromacetethylpiperidine)phenymercury (I) gives a mixture consisting of two bromo-β-lactams, A and B, and phenymercury bromide.

For the β-lactams we propose the structures 2a and 2b, respectively. These structures would explain the lability of the β-lactams in acidic and alkaline media and are in agreement with their elemental analysis and spectroscopic properties. The NMR spectra indicated that the coupling constant for the C-4a and C-5 protons of the bromo-β-lactam A was larger than that of the isomer B and the resonance of the C-5 proton of A occurs at lower field than that of B. It has been shown that in 2-azetidinones (e.g. 3) the coupling constant is larger for the cis protons (3a) than for the trans protons (3b) and that the C-3 and C-4 protons of the cis isomer absorb at lower field than those of the trans isomer.2+ Hence A must have the cis configuration (2a) and B the trans configuration (2b).

These conclusions were supported by the mass spectra of the bromo-β-lactams. The


relative intensities of the peaks corresponding to loss of bromine and to cleavage of the azetidinone ring were higher for 2a than for 2b which is in accordance with earlier results for similar compounds.\textsuperscript{3,4,6}

In several reports a-haloorganometallic compounds have been assumed to form carbenes on thermal decomposition.\textsuperscript{7,8}

Thus in our case the analogous carbene from the thermal cleavage of I could be the intermediate.

We are now exploring the scope of this novel \(\beta\)-lactam synthesis.

**Experimental.** \(N\)-Dibromoacetylpiriperidine. Dibromoacetic acid (34.0 g) was added to an excess of refluxing thionyl chloride (30 ml) over a period of 1 h. The solution was heated under reflux for an additional 3 h period, the thionyl chloride was removed, and the product distilled at reduced pressure to give dibromoacetyl chloride, b.p. 58°/12 mm (31.5 g, 86%). The acid chloride was slowly added to an ice cooled solution of piperidine (25 g) in ether (500 ml); the precipitated piperidine hydrochloride was filtered off, the ether solution washed, dried, and the ether evaporated. The residue was recrystallised from ether, giving \(N\)-dibromoacetylpiriperidine (28.8 g, 75%), m.p. 70—71\(^\circ\). (Found: C 29.0; H 3.8; Br 58.9. Calc. for \(C_{6}H_{11}Br_{2}NO\): C 29.5; H 3.8; Br 56.1.)

\(N\)-Dibromoacetylpiriperidine (1) is a mixture of \(N\)-dibromoacetylpiriperidine (55.0 g) and phenylmercury chloride (17.2 g) in dry benzene (500 ml), under an atmosphere of purified nitrogen, was stirred with a high speed stirrer and cooled to 0—5\(^\circ\). Freshly sublimed potassium t-butoxide (18.0 g) was added during 1.5 h. After an additional 3 h period, the mixture was poured into ice water (500 ml). After filtration and work up in the usual manner, the product was chromatographed on silica gel (Grace Chemical, Copenhagen, 0.15—0.30 mm) giving (\(N\)-dibromoacetylpiriperidine)phenylmercury (2) (15.0 g, 50%), m.p. 126—128\(^\circ\). (Found: Br 28.2; Hg 35.4. Calc. for \(C_{6}H_{11}Br_{2}HgNO\): Br 28.45; Hg 35.7.) NMR (CDCl\(_3\), \(\delta\)-units relative to TMS as internal standard): 1.65 (s, \(CH_{3}\)), 3.73 (s, N—CH\(_3\)), 7.27 (s, aromatic protons). IR: CO 1605 cm\(^{-1}\), Substantial amounts of \(N\)-dibromoacetylpiriperidine (35.5 g) were recovered.

**Thermal decomposition of (\(N\)-dibromoacetylpiriperidine)phenylmercury.** (\(N\)-Dibromoacetylpiriperidine)phenylmercury (2.05 g) was decomposed by heating for 1.7 h in refluxing bromobenzene (dried over sodium hydride and distilled). The solvent was removed in vacuo, ether was added, and the insoluble phenylmercury bromide (1.27 g, 98%) was filtered off. The other components of the product were then separated by preparative thin layer chromatography on silica (Merck, FF\(_{254}\), using ether as developer) giving the two isomeric \(\beta\)-lactams (2a) and (2b) and a small amount of \(N\)-dibromoacetylpiriperidine (0.10 g, 14%).

\(cis\)-5-Bromo-6-oxoazetidinol(1,2-a)piriperidine (2a, 0.10 g, 14%). (Found: C 42.7; H 5.0; Br 38.0. Calc. for \(C_{6}H_{11}BrNO\): C 41.2; H 4.9; Br 39.2.) NMR: 1.2—2.2 (m, H-2, H-3, and H-4) 2.5—4.0 (m, H-1, H-4a), 4.98 (two d, J 1.4 and 4.4 cps, H-5). IR: CO 1760 cm\(^{-1}\). Mass spectrum: 205, 203 (M, 2), 124 (M—Br, 100), 82 (M—C\(_{6}H_{4}BrO\), 22), and \(trans\)-5-bromo-6-oxoazetidinol(1,2-a)piriperidine (2b, 0.34 g, 47%), m.p. 72—74\(^\circ\). (Found: C 40.9; H 4.9; Br 39.1. Calc. for \(C_{6}H_{11}BrNO\): C 41.2; H 4.9; Br 39.2.) NMR 1.2—2.3 (m, H-2, H-3, and H-4), 2.5—4.0 (m, H-1 and H-4a), 4.4 (d, J 1.3 cps, H-5). IR: CO 1760 cm\(^{-1}\). Mass spectrum: 205, 203 (M, 4), 124 (M—Br, 100), 82 (M—C\(_{6}H_{4}BrO\), 14).

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Some Unusual Flavonoids from *Myrica gale* L.

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A small bush with a strong aromatic scent, *Myrica gale* L. (bog myrtle) which is very common on moist ground and on peat land in this country, has for ages been utilized as a moth repellant and as a hop substitute in the brewing of beer. A number of terpenoids and flavonoids are known to be present in the plant. 1

We now wish to report the isolation of three new aromatic compounds 1, 2, and 3 from an acetone extract of fruits from this bush. 1 was isolated by column and thin-layer chromatography as yellow needles and recrystallized from ether-petroleum ether (m.p. 116 - 117°C) [$\lambda_{max}$ (EtOH) 224 (14 200), 280 (17 400), and 350 (4200) nm; IR: 3600, 1620, 1500, and 1455 cm$^{-1}$]. The molecular composition of this compound was established as $C_{18}H_{24}O_6$ by accurate measurement of the molecular ion peak (calc. 300.1362, found 300.1365). The NMR spectrum shows two aromatic methyl groups (7.92, 6H $s$) and one methoxy methyl group (6.32, 3H $s$). An $A_2B_4$ system ($\delta_A$ 6.60, $\delta_B$ 7.00) and a five proton singlet at 2.80 suggest that the compound might be a dihydrochalcon. Finally a two proton singlet at 0.45 due to two identical hydrogen-bonded hydroxy protons is in good agreement with the constitution 1.

Additional evidence can be found in the mass spectrum where the base peak at $m/e$ 195 ($C_{18}H_{16}O_6$) is due to a favoured cleavage leading to the oxonium ion 4. The relative positions of the methoxy and methyl groups were assigned on the basis of symmetry considerations.

2 was isolated from a more polar fraction from the column and proved to be an isomer of 1 (calc. for $C_{16}H_{15}O_5$, 300.1362, found 300.1365) (m.p. 138 - 139°C) [$\lambda_{max}$ (EtOH) 350 (19 900) nm].

The NMR spectrum in deuteriochloroform solution shows that 3 is a mixture of