

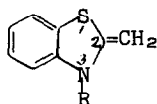
ISOLATION OF MONOMERIC METHYLENE BASES DERIVED
FROM BENZOTHAZOLIUM QUATERNARY SALTS

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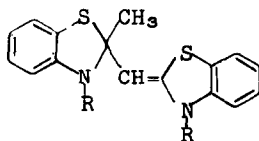
(Received in USA 24 April 1969; received in UK for publication 4 June 1969)

The methylene base derived from 2,3-dimethylbenzothiazolium quaternary salt was first isolated by König and Meier (1), who assigned to it structure I (R=Me). Subsequently, Mumm (2) used cryoscopic measurements to prove that



I R=Me, Et

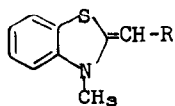
the methylene base isolated by König and Meier was actually dimeric. Larivé and Dennilauler (3) deduced by chemical and physical methods that the correct structure for the dimer was II (R=Et). This was later confirmed (4) by the



II R=Me, Et

use of nmr spectroscopy.

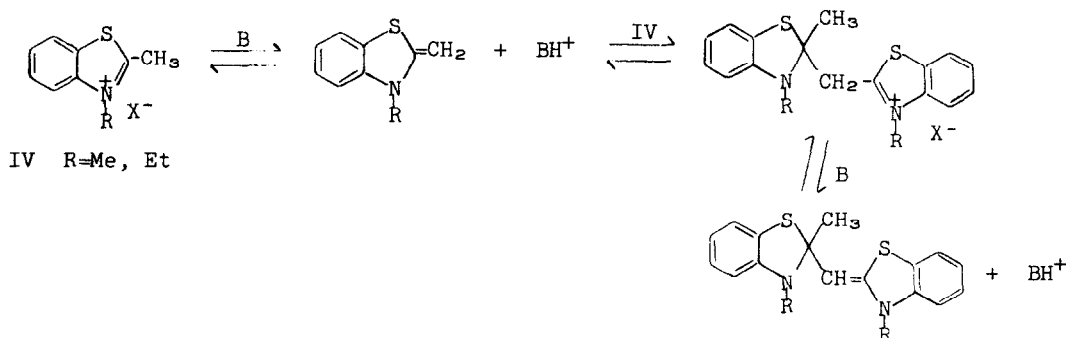
Although the preparation of monomeric methylene bases from benzothiazolium quaternary salts containing groups other than methyl at the 2-position (e.g., III, R=C₆H₅, Et) has been reported (4,5), the isolation of monomeric methylene bases I (R=Me, Et) has never been reported to date. That monomer I (R=Me) is



III

a likely intermediate in certain reactions of the corresponding dimer was shown by Vorsanger (6,7) through crossing experiments using deuterium labeling, and by spectrophotometric determinations in various solvents. The absence of any peak higher than m/e 163 (m.w. of monomer) in the mass spectrum of the dimer, furthermore, suggested that dimer dissociates to monomer in the vapor phase. A similar conclusion was reached from the mass spectrum of II (R=Et), taken independently in these laboratories.

We wish to report the first successful isolation of the monomeric methylene bases I (R=Me, Et) as distillable liquids. The approach used in the preparation of these monomers was based on the mechanism proposed by Larivé (8) for dimerization (Scheme I), which requires as an intermediate step that monomer react with quaternary salt (IV).



According to this scheme, generation of the monomeric methylene base in the absence of quaternary salt would prevent dimerization. This was realized experimentally through the use of a large excess of a strong base (tetramethylguanidine) and by the use of a reaction solvent in which the quaternary salt was sparingly soluble (benzene or ligroin). Sodium hydride was added to remove tetramethylguanidine hydrosalt as it was formed.

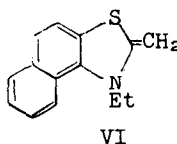
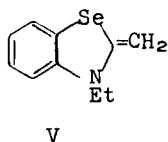
Accordingly, 3-ethyl-2-methylbenzothiazolium *p*-toluenesulfonate (0.04 mol) was added at ice-bath temperature in small portions to a mixture of dry benzene (110 ml) and tetramethylguanidine (40 ml) containing sodium hydride (0.06 mol). The mixture, which was kept under a nitrogen atmosphere, was stirred at ice-bath temperature for 1 hr after addition and then at room temperature an additional 20 hr. The reaction mixture was filtered through

diatomaceous earth, the solvents were removed by vacuum distillation, and the remaining yellow oil was distilled under vacuum to give 5.9 g (83%) of a clear liquid, b.p. 110° (0.05 mm); uv max (99.7% CH₃CN, 0.3% tetramethylguanidine) 294 nm (ϵ 1.13 x 10⁴). The nmr spectrum of the liquid showed the terminal methylene protons as an AB pattern at δ 3.9, as well as the expected methyl and methylene protons of the ethyl group, which appeared as a triplet at δ 0.92 (J = 7 Hz) and a quartet at δ 3.31 (J = 7 Hz), and the aromatic multiplet at δ 7.1-6.2.

The monomer (I, R=Et) was stable at dry-ice temperature for several weeks. On exposure to air at room temperature the liquid rapidly solidified. This material possessed an identical melting point and nmr spectrum to those of the dimer prepared according to the method of Larivé (3).

In a similar manner 3-methyl-2-methylenebenzothiazolium (I, R=Me) was prepared in 72% yield using ligroin as solvent. The distilled liquid (b.p. 90-91° (0.07 mm)) solidified at room temperature, m.p. 23.5-25°. Although the material dimerized too rapidly on exposure to air to obtain an nmr spectrum, the uv spectrum (uv max (96% CH₃CN, 4% tetramethylguanidine) 294 nm (ϵ 1.16 x 10⁴)) was almost identical to that of 3-ethyl-2-methylenebenzothiazoline. The solid was stable at dry-ice temperature under nitrogen but dimerized within 2 hr at 0° under nitrogen. The nmr spectrum of the dimerized material was in agreement with that reported by Larivé (4) for II (R=Me).

Two additional methylene bases, 3-ethyl-2-methylenebenzoselenazoline (V) and 1-ethyl-2-methylenenaphtho[1,2-d]thiazoline (VI) were prepared by this method using ligroin as the solvent. The corresponding dimeric forms have



been reported by Larivé (3). Monomer V was prepared in 59% yield, b.p. 105° (0.025 mm); uv max (99.7% CH₃CN, 0.3% tetramethylguanidine) 295 nm (ϵ 8.43 x 10³). The liquid solidified at room temperature, m.p. 23-25°. The nmr of the melted solid showed the characteristic AB pattern centered at δ 4.2

for the terminal methylene group, as well as the methyl triplet at δ 0.89 ($J = 7$ Hz), the N-methylene quartet at δ 3.28 ($J = 7$ Hz), and the aromatic multiplet at δ 6.1-7.1. The monomer could be kept under nitrogen at 0° for several days without decomposition.

Monomeric methylene base VI was stable only in tetramethylguanidine solution. When the tetramethylguanidine was removed under vacuum at room temperature, a colored viscous material formed. An nmr spectrum of the tetramethylguanidine solution after removal of the solvent, ligroin, indicated that the monomer was the species present. The spectrum showed the terminal methylene group as an AB pattern at δ 4.1, as well as the methyl triplet at δ 1.33 ($J = 7$ Hz), the N-methylene quartet at δ 3.91 ($J = 7$ Hz), and the aromatic multiplet at δ 7.1-8.0. The tetramethylguanidine protons appeared as singlets at δ 2.6 and δ 5.43.

ACKNOWLEDGMENT

The author is indebted to T. H. Regan and R. L. Young for determination of the nmr spectra and to G. P. Happ and D. P. Maier for the determination of the mass spectrum.

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