

26142-41-6; β -chloro-*N*-ethenylcarbazole, 23787-95-3; 4 (polymer), 25067-59-8.

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Chloromethyltriethylammonium Chloride. A Serendipitous Preparation

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In a cryogenic study of the thermodynamics of hydrogen bond formation in the previously described adduct¹ of triethylamine (TEA) and methylene chloride (MC), we encountered an unexpected reaction at room temperature that yielded chloromethyltriethylammonium chloride (1). This salt crystallized in analytically pure form from a solution of the components containing excess amine. The nmr spectrum [δ (CDCl₃) 1.50 (t, 9, J = 8 Hz), 3.72 (q, 6, J = 8 Hz), and 5.68 ppm (s, 2)] was consistent for structure 1.

The analogous reaction of triethylphosphine and MC was described over 100 years ago.² An alkylation product from MC and a tertiary amine has apparently not been isolated, although formation of polymers from diamines and methylene chloride at 40° has been observed.³

Experimental Section

Materials.—The Eastman TEA was distilled three times from a slurry with KOH and the Baker MC was triply distilled from CaCl₂ in a dry N₂ atmosphere. The minimal purities of these reagents, as determined by subsequent fractional fusion, were: TEA, 99.9%; MC, 99.8%.

Product.—Compound 1 was formed in ca. 1% yield by allowing a TEA-rich mixture of the two reagents to stand undisturbed, at room temperature, for three days. It was noted that product formation was inhibited at lower temperatures, and we were unable to prepare it at -80°. The compound crystallized in fine white needles. X-ray powder photographs indicated a noncubic structure. The d spacings corresponding to the three most prominent lines were 3.62 Å, 3.33 Å, and 5.47 Å. The compound melted at 186°.

Anal. Calcd for [C₇H₁₇NCl]⁺Cl⁻: C, 45.1; H, 9.12; N, 7.5; replaceable Cl, 19.0. Found: C, 44.8; H, 9.5; N, 7.2; replaceable Cl, 18.7.

Registry No.—1, 26157-53-9.

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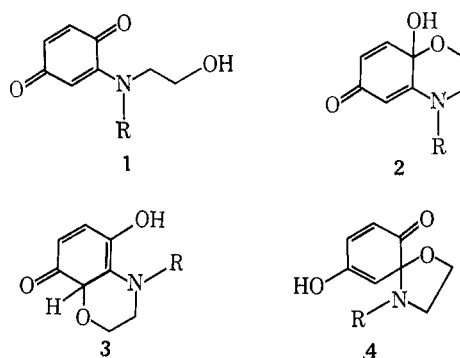
König's Adducts of *N*-Alkyl(aryl)aminoethanols and Quinones. 3,4-Dihydro-4-alkyl(aryl)-8a-hydroxy-2*H*-1,4-benzoxazin-6(8*aH*)-ones

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König¹⁻³ discovered that adducts of *p*-benzoquinones and 2-alkyl(aryl)aminoethanols (1) are in equilibrium with a second, usually predominant species which (a) is nearly colorless in crystalline form and in nonpolar solvents, (b) is soluble in base, and (c) exhibits a double polarographic reduction curve³⁻⁶ very different from those exhibited by quinones.⁷ Three structures (2-4) can be considered for the bicyclic form of the adduct. We have studied some aspects of the chemistry of these interesting compounds and have established that the correct structure is 3,4-dihydro-4-alkyl(aryl)-8a-hydroxy-2*H*-1,4-benzoxazin-6(8*aH*)-one (2).



Previous workers^{1-6,8,9} have focused on the thermochromic, solvatochromic, and unusual electrochemical properties of the quinone-aminoethanol adducts. Surprisingly, no detailed study of the structure of the adducts has been reported. Structure 3 has been considered and discarded⁹ since the adducts, formed under equilibrating conditions, exhibit properties (*e.g.*, ABX systems in the aromatic/olefinic region of the nmr spectra) inconsistent with their formulation as the thermodynamically more stable hydroquinone tautomer of 3.¹⁰ Berg and coworkers⁸ suggested the correct structure (2) for the adducts; however, they appear not to have con-

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