

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

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### Chloromethyltriethylammonium Chloride. A Serendipitous Preparation

DAVID A. WRIGHT AND CLAUS A. WULFF\*

Department of Chemistry, The University of Vermont,  
Burlington, Vermont 05401

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In a cryogenic study of the thermodynamics of hydrogen bond formation in the previously described adduct<sup>1</sup> 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 [ $\delta$  (CDCl<sub>3</sub>) 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.<sup>2</sup> 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.<sup>3</sup>

#### Experimental Section

**Materials.**—The Eastman TEA was distilled three times from a slurry with KOH and the Baker MC was triply distilled from CaCl<sub>2</sub> in a dry N<sub>2</sub> 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 [C<sub>7</sub>H<sub>17</sub>NCl]<sup>+</sup>Cl<sup>-</sup>: 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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\* To whom correspondence should be addressed.

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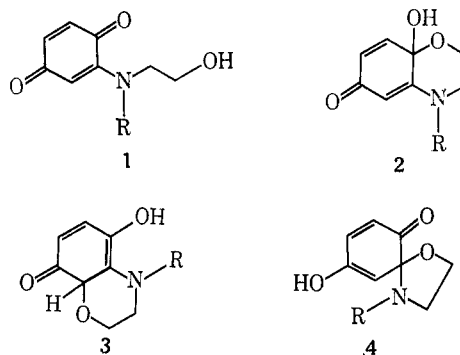
### König's Adducts of *N*-Alkyl(aryl)aminoethanols and Quinones. 3,4-Dihydro-4-alkyl(aryl)-8a-hydroxy-2*H*-1,4-benzoxazin-6(8*aH*)-ones

KENNETH D. McMURTREY AND G. DOYLE DAVES, JR.\*

Oregon Graduate Center, Portland, Oregon 97225

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König<sup>1-3</sup> 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 curve<sup>3-6</sup> very different from those exhibited by quinones.<sup>7</sup> 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<sup>1-6,8,9</sup> 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 discarded<sup>9</sup> 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.<sup>10</sup> Berg and coworkers<sup>8</sup> suggested the correct structure (2) for the adducts; however, they appear not to have con-

\* To whom correspondence should be addressed.

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(10) The transformation 1  $\rightarrow$  3 is inherently unlikely since it requires 1,4 addition of the alcohol moiety to the quinone in a sense opposite to the polarization of the  $\pi$  electron system caused by the presence of the amino function.

sidered structure 4 and present no data which distinguish between these structures.

In principle, 2,4- and 2,5-dienones (*i.e.*, structures 4 and 2, respectively) are distinguishable on the basis of their ultraviolet spectra.<sup>11</sup> In this case, however, the presence of the amino function makes hazardous a structure assignment on this basis.<sup>12</sup> Similarly, study of the infrared, nmr,<sup>9</sup> and mass spectra (see Experimental Section) did not provide unambiguous discrimination between structures 2 and 4. We therefore undertook a study of the chemical properties of a representative adduct in order to provide an unambiguous structure assignment.

Addition of 2-methylaminoethanol to 1,4-benzoquinone in acetone solution yields an adduct<sup>1</sup> with properties which rule out its formulation as the aminoquinone 1 ( $R = CH_3$ ). To ensure that we were studying a single species and not an equilibrating mixture of two or more forms,<sup>6</sup> the initial adduct was treated with methyl iodide and silver oxide. A monomethyl derivative was formed which exhibited an ultraviolet absorption maximum ( $\lambda_{\max}^{\text{MeOH}}$  359 nm) identical with that shown by the initial adduct indicating that no unexpected change had occurred.

Since cyclohexadienes (both 2,4- and 2,5-) are known<sup>13</sup> to rearrange to phenols under reducing conditions, the methylated adduct in ether solution was treated with platinum oxide in a hydrogen atmosphere. A single phenolic compound was obtained (~30% yield) from the resulting reaction mixture which also contained a number of reduction products. The nmr spectrum of the phenolic derivative (see Experimental Section) exhibits signals which indicate that the three ring protons, the *N*-methyl, and the ethylene bridge protons present in the methylated adduct remain. However, no signal owing to methoxy protons is present. Thus, the net change which occurs in formation of the phenolic derivative from the methylated adduct is addition of hydrogen and loss of methanol. This conclusion was confirmed by examination of the mass spectrum of the phenolic derivative (see Experimental Section) which exhibits an intense parent ion at  $m/e$  165. These results require that the methoxy group be at tetrahedral carbon and establishes the structure of the methylated adduct as 3,4-dihydro-4-methyl-8a-methoxy-2*H*-1,4-benzoxazin-6(8a*H*)-one (5); *i.e.*, a deriva-

tive of the hemiketal 2,5-dienone (2) rather than of the spiro-2,4-dienone (4). This assignment was further confirmed by independent synthesis of the phenolic derivative, 3,4-dihydro-4-methyl-2*H*-1,4-benzoxazin-6-ol (6) from 2-[2'-bromoethylmethylamino]-1,4-benzohydroquinone (7).

### Experimental Section

Melting point determinations were made with a Thomas hot-stage. Nmr spectra were obtained using a Varian HA-100 spectrometer, ultraviolet spectra were recorded on a Perkin-Elmer 202, infrared spectra were recorded on a Perkin-Elmer 337, and mass spectra were measured using a CEC 21-110B high resolution mass spectrometer. Analyses were by the Heterocyclic Chemical Corp., Harrisonville, Mo. Thin layer chromatography (tlc) was performed on silica gel G plates.

**3,4-Dihydro-4-methyl-8a-methoxy-2*H*-1,4-benzoxazin-6(8a*H*)-one (5).**—To a solution of 18.1 g of 3,4-dihydro-4-methyl-8a-hydroxy-2*H*-1,4-benzoxazin-6(8a*H*)-one (2)<sup>1</sup> and 42.6 g of methyl iodide in 50 ml of acetone was added 46.4 g of silver oxide. The mixture was stirred at ambient temperature for 8 hr, the solid residue was removed by filtration, and the filtrate was evaporated. The resulting residue was purified by column chromatography (1:1 benzene-acetone on silica gel) to yield 11 g (56%) of 5 as a light yellow oil which crystallized upon standing. The resulting crystals melted at 73–74°: uv  $\lambda_{\max}^{\text{MeOH}}$  359 nm ( $\epsilon$  10,000); ir (KBr) 6.00  $\mu$  (C=O); nmr  $\delta$  2.82 (NCH<sub>3</sub>), 3.14 (OCH<sub>3</sub>), 3.0–4.4 (4 H, complex multiplet), ABX system (3 H),  $\delta_A$  6.22,  $\delta_B$  5.90,  $\delta_X$  5.01 ( $J_{AB} \sim 10$  cps,  $J_{BX} \sim 2$  cps); mass spectrum  $m/e$  (rel intensity) 195 (31), 165 (100), 164 (50), 150 (23), 136 (81), 82 (15).

*Anal.* Calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>3</sub>: C, 61.9; H, 6.70; N, 7.19. Found: C, 61.5; H, 6.71; N, 7.17.

**3,4-Dihydro-4-methyl-2*H*-1,4-benzoxazin-6-ol (6).** **Method A.**—A mixture of 1 g of 3,4-dihydro-4-methyl-8a-methoxy-2*H*-1,4-benzoxazin-6-one (5) and 0.1 g of platinum oxide in 100 ml of ether was shaken in a Parr apparatus under 2 atmospheres of hydrogen for 0.5 hr. The catalyst was removed by filtration and the filtrate was evaporated. The resulting crude product was separated by tlc (benzene-methanol 9:1) to yield 0.25 g (30%) of 3,4-dihydro-4-methyl-2*H*-1,4-benzoxazin-6-ol (6) as a colorless oil which crystallized on standing: mp 77.0–78.5°, uv  $\lambda_{\max}^{\text{MeOH}}$  308 nm ( $\epsilon$  5300); ir (KBr) 3.2 (OH, broad), 3.39, 3.47 (CH), no C=O bond, 6.29 (C=C), 6.60, 8.23 (broad, probably CO), 11.95, 16.10  $\mu$ ; nmr (CDCl<sub>3</sub>)  $\delta$  2.80 (NCH<sub>3</sub>), 3.22 (triplet, -CH<sub>2</sub>N), 4.20 (triplet, -CH<sub>2</sub>O), 6.0–6.7 (3 H aromatic); mass spectrum  $m/e$  (rel intensity) 165 (100), 164 (20), 150 (45), 136 (20), 94 (20), 82 (18).

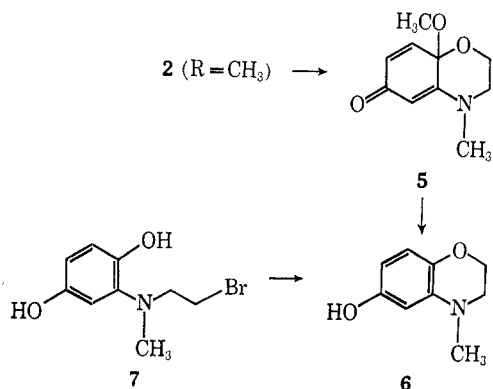
*Anal.* Calcd for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>: C, 65.5; H, 6.67; N, 8.49. Found: C, 65.4; H, 6.81; N, 8.61.

**Method B.**—A solution of 1 g of 2-(2'-bromoethylmethylamino)-1,4-benzoquinone in 100 ml of chloroform was shaken with an aqueous solution containing excess sodium dithionite until the organic layer became colorless. The organic layer was separated and dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed. The colorless, glassy residue was dissolved in 100 ml of dioxane-triethylamine (1:1) and the solution was heated on a steam bath for 12 hr. The residue obtained by evaporation of the solvent was purified as described in method A to yield 0.6 g (89%) of material which exhibited spectral properties indistinguishable from those described above.

**2-(2'-Bromoethylmethylamino)-1,4-benzoquinone.**—To a solution of 30 g of 1,4-benzoquinone and 30 g of 2-bromoethylmethylamine hydrobromide in 2 l. of 50% aqueous methanol at 0° was added 500 ml of 0.2 *N* sodium hydroxide solution dropwise with stirring. After 2 hr the resulting mixture was filtered, and the solid material obtained was washed well with water and then triturated with acetone. The acetone-soluble portion was separated and the solvent was removed to yield 6 g of dark red crystals, mp 140–144°, which exhibited  $\lambda_{\max}^{\text{MeOH}}$  481 nm ( $\epsilon$  2400).

*Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>Br: C, 44.3; H, 4.10; N, 5.74. Found: C, 44.1; H, 4.28; N, 5.86.

**Registry No.**—5, 26438-49-3; 6, 26438-50-6; 2-(2'-bromoethylmethylamino)-1,4-benzoquinone, 26372-67-8.



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