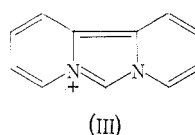
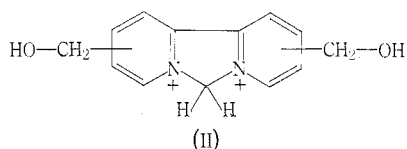
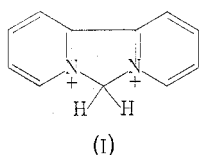


THE FORMATION OF THE 6,8-DIHYDRODIPYRIDO[1,2-*c*:2',1'-*e*][1,3,6]OXADIAZEPIDI-INIUM CATION IN THE REACTION OF 2,2'-BIPYRIDYL WITH METHYLENE SULPHATE*

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During work which was aimed at the synthesis of the 6*H*-dipyrido[1,2-*c*:2',1'-*e*]-imidazolidi-inium cation (I), Homer and Tomlinson¹ examined the reaction of 2,2'-bipyridyl with methylene sulphate in nitrobenzene. After removal of the solvent and addition of water and sodium iodide these authors obtained a compound C₁₃H₁₄N₂O₂I₂, which crystallized in red needles, melted at 280°C with decomposition, and had λ_{max}^{H₂O} at 295 mμ (ε 18,800). On the basis of these data Homer and Tomlinson assigned the structure (II) to this product without defining the positions of the nuclear hydroxymethyl groups.



The properties disclosed by Homer and Tomlinson for the product of the reaction of 2,2'-bipyridyl with methylene sulphate are not compatible with those of a derivative of the 6*H*-dipyrido[1,2-*c*:2',1'-*e*]imidazolidi-inium cation (I). Thus, (I) is a strong acid owing to the aromatic character of its conjugate base(III) (only one resonance structure is shown), and the ultraviolet spectrum of (I) is characterized by two intense bands at 311 and 323 mμ (ε 15,500 and 18,000, respectively).² These discrepancies prompted a reexamination of the reaction of 2,2'-bipyridyl with methylene sulphate, the results of which are now reported.

Following the directions given by Homer and Tomlinson, a red crystalline material was obtained which melted at 276–277°C with decomposition. Elementary analyses carried out on two different samples agreed with each other within experimental error and corresponded to the empirical formula C₁₂H₁₂N₂OI₂. The ultraviolet spectrum of this compound exhibited a broad maximum at 295 mμ (ε 16,000). This absorption resembles that of a bridged 2,2'-bipyridyl containing either two or three bridge atoms. (cf. Homer and Tomlinson).¹ In the infrared spectrum of this product two intense bands occurred at 1136 and 1140 cm⁻¹; strong absorption was

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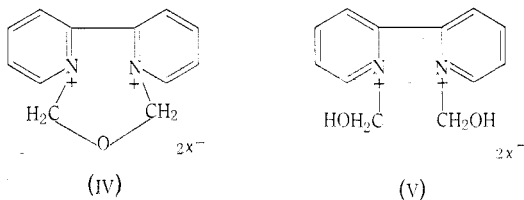
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¹ Homer, R. F., and Tomlinson, T. E. (1960).—*J. Chem. Soc.* **1960**: 2498.

² Calder, I. C., Spotswood, T. M., and Sasse, W. H. F. (1962).—*Tetrahedron Letters* **1962**: (in press).

lacking between 1620 and 2780 cm^{-1} , and no absorption was detected at frequencies above 3030 cm^{-1} . This suggested the presence of the grouping C—O—C in the compound $\text{C}_{12}\text{H}_{12}\text{N}_2\text{OI}_2$. The proton magnetic resonance spectrum of this compound showed five groups of signals (measured at 60 Mc/s in deuterium oxide with water as internal standard; τ approximately 5.2). A singlet (four protons) occurred at -95 c/s, two doublets (two protons each) were centered at -247 and -289 c/s, and two triplets (two protons each) were centered at -235 and -264 c/s. This spectrum shows that the aliphatic protons are equivalent, and that none of nuclear positions in 2,2'-bipyridyl have been substituted.

The evidence presented in the present paper is consistent with the structure (IV; X = I) for the product of the reaction of 2,2'-bipyridyl with methylene sulphate. This structure was proved by an independent synthesis of the 6,8-dihydrodipyrido[1,2-c:2',1'-e][1,3,6]oxadiazepidi-inium di-iodide (IV; X = I) which involved quaternization of 2,2'-bipyridyl with *sym.*-chloromethyl ether to give the chloride of (IV; X = Cl), followed by conversion to the iodide.



The formation of the seven-membered ring in (IV) must be preceded by the quaternization of both nitrogen atoms in 2,2'-bipyridyl to form a sulphate ester of 1,1'-di(hydroxymethyl)-2,2'-bipyridyl (V). Several possibilities exist for this intermediate (*inter alia* a cyclic nine-membered ester) and in fact, a mixture of esters may be formed. However, each of these esters should undergo hydrolysis during the working up of the reaction mixture to yield either monosulphate esters of (V), or (V) itself. These species should undergo intramolecular cyclization even more readily than the corresponding biphenyl derivatives.³

Experimental

General.—The microanalyses were performed by the Australian Microanalytical Service, Melbourne. The ultraviolet spectra were measured with an Optica CF4 recording spectrophotometer, and with a Hilger Uvispek spectrophotometer. The infrared spectra were determined with a Perkin-Elmer Infracord 137 spectrophotometer. The proton magnetic resonance spectra were measured with a Varian DP60 n.m.r. spectrometer. Melting points are uncorrected. Paper chromatograms were run on Whatman No. 1 paper with n-butanol-concentrated hydrochloric acid-water, 8:2:6.

Reaction of 2,2'-Bipyridyl with Methylene Sulphate.—This was carried out according to Homer and Tomlinson with freshly prepared methylene sulphate, m.p. 154–155°C (lit. m.p. 155°C).⁴ The resulting mixture was worked up following the directions of Homer and Tomlinson¹ to give red needles, m.p. 276–277°C (decomp.), of 6,8-dihydrodipyrido[1,2-c:2',1'-e][1,3,6]oxadiazepidi-inium di-iodide (IV; R = I) (Found: (a) C, 31.5; H, 2.8; N, 6.0; I, 55.5%; (b) C, 32.0;

³ Wittig, G., Davis, P., and Koenig, G. (1951).—*Chem. Ber.* **84**: 627.

⁴ Baker, W. (1931).—*J. Chem. Soc.* **1931**: 1767.

H, 2.7; N, 6.3; I, 55.3%. $C_{12}H_{12}N_2OI_2$ requires C, 31.6; H, 3.1; N, 6.1; I, 55.6%. $C_{13}H_{14}N_2O_2I_2$ requires C, 32.2; H, 2.7; N, 5.8; I, 52.5%. It had R_F 0.08 and 0.9 (iodide), $\lambda_{\text{max}}^{\text{MeOH}}$ at 295 m μ (ϵ 16,000), and ν_{max} at 1136 and 1140 cm^{-1} (Nujol).

Preparation of 6,8-Dihydrodipyrido[1,2-c:2',1'-e][1,3,6]oxadiazepidi-inium Di-iodide from 2,2'-Bipyridyl and sym.-Chloromethyl Ether.—A mixture of 2,2'-bipyridyl (5 g) and *sym.*-chloromethyl ether (5 g) was heated at 80°C for 24 hr. The solid which had formed was filtered off and washed with ether. It was crystallized first from ethanol-water (1:1) (charcoal), and then from methanol-benzene(2:1). The resulting product was dissolved in water and treated with a saturated aqueous solution of sodium iodide to yield a red precipitate. This was recrystallized from aqueous ethanol to form red needles, m.p. 276–277°C (decomp.), of 6,8-dihydrodipyrido[1,2-c:2',1'-e][1,3,6]oxadiazepidi-inium di-iodide (IV; X = I) (10% yield), which was identical in all respects with the iodide isolated from the reaction of 2,2'-bipyridyl with methylene sulphate.