The alkoxycarbonylhydrazones were prepared by the method of Rabjohn[5] and purified either by crystallization from aqueous ethanol; or by preparative thin layer chromatography on silica gel G in chloroform–methanol (95:5); or by high-vacuum fractionation. All compounds ran as a single spot on tlc plates. Methoxycarbonylhydrazine (methyl carbazate) was synthesized according to the method of Diels[15] while ethyl carbazate was generously provided by Dr. O. Halpern of the Syntex Research Center, Palo Alto, Calif. Melting points and analyses of derivatives not previously described are tabulated in Table I.

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(15) O. Diels, *Ber.*, **47**, 2186 (1914).

The Anodic Oxidation of Organic Compounds. I. The Electrochemical Methoxylation of 2,6-Dimethoxypyridine and N-Methylpyrrole

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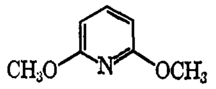
The first examples of nitrogen heterocycles, 2,6-dimethoxypyridine and N-methylpyrrole, have been anodically methoxylated. The dimethoxypyridine afforded a bisketal and a tetramethoxypyridine believed to be 2,3,3,6,6-pentamethoxy-1,4-azacyclohexadiene and 2,3,5,6-tetramethoxypyridine, respectively. N-Methylpyrrole gave 1-methyl-2,2,5,5-tetramethoxypyrroline. The ketal groups of these products were successfully hydrolyzed either partially or totally depending on the concentration of acid. Possible mechanisms for these novel reactions are discussed.

Anodic alkoxylations of organic compounds have been described in the furan,[1] thiophene,[2] benzenoid aromatic,[3] and olefinic series.[4] The products observed in these reactions are usually cyclic acetals, bisquinone ketals, ortho esters, and ethers, which are derived from the over-all addition of at least two alkoxy groups to the reductant. The electrochemical alkoxylation of nitrogen heterocycles has not, to our knowledge, been previously reported.

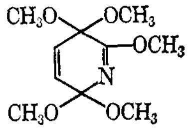
The anodic oxidation of 2,6-dimethoxypyridine I in methanol gave a mixture of at least five components as determined by vpc analysis (Figure 1). The crude electrolysate afforded four fractions on distillation and a considerable quantity of tarry residue. The lowest boiling fraction consisted of starting material (Figure 1, peak A). The second fraction (peak B) could not be isolated in sufficient quantity and purity for a positive identification; however, spectral data (ultraviolet and infrared) indicated that this oil was aromatic.

The third fraction (peak D) was obtained as a colorless oil, possessing no characteristic aromatic absorption, but a very strong ketal region in its infrared spectrum. The elemental analysis and the nmr spectrum showed an over-all addition of three methoxy groups to I. There are two possible structures that may be accommodated by these observations: the *p*-azaquinone ketal II and the *o*-azaquinone ketal III. By spectroscopic comparison with similar compounds it may be demonstrated that the *p*-azaquinone ketal II is the more probable structure. Thus the nmr spectrum[3] of 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (IV) had bands at τ 6.80 and 6.38 and a group of eight peaks (ABX system) extending from 5.12 to 3.93 with $J_{AB} = 10.0$ cps, while the spectrum of the product exhibited peaks at τ 6.75 and 6.25, and a quartet (AB system) extending from τ 4.23 to 3.75 with $J_{AB} = 10.0$ cps. In addition the ultraviolet spectrum of 3,3,6,6-tetramethoxy-1,4-cyclohexadiene (V) with λ_{max} 215 mμ (ϵ 1000) was almost identical with that of the product, with λ_{max} 213 mμ (ϵ 1100).

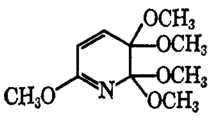
The last fraction obtained from the electrolysate solidified on standing and was identified (peak C) as a tetramethoxypyridine from its nmr spectrum and elemental analysis. Two isomers are possible: the 2,3,5,6- and the 2,3,4,6-tetramethoxypyridine (VI and VII). However, the symmetry of that portion of the nmr spectrum characteristic of methoxy groups (a doublet of equal intensity at τ 6.32 and 6.20) is consistent with structure VI.



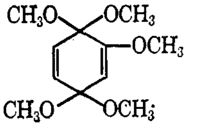
I



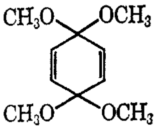
II



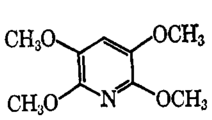
III



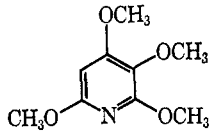
IV



V



VI



VII

The chemistry of the azaquinone ketal II (or III) was briefly explored. Hydrolysis in aqueous acetic acid gave two compounds, dimethyl 4,4-dimethoxyglutaconate (VIII) and 4,4-dimethoxyglutaconimide (IX). The major product in 10 to 25% acetic acid was VIII, while in 0.5% acetic acid, almost pure IX could be isolated. The glutaconate VIII, a mixture of *cis* and *trans* isomers, was converted to dimethyl α-oxoglutarate 2,4-dinitrophenylhydrazone.

The glutaconimide IX had an nmr spectrum with peaks at τ 6.65 and 6.70 (doublet of equal intensity for

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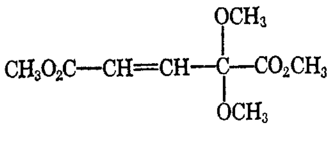
(1) N. Elming in "Advances in Organic Chemistry: Methods and Results," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 67.

(2) K. E. Kolb, Ph.D. Thesis, The Ohio State University, 1953.

(3) N. L. Weinberg and B. Belleau, *J. Am. Chem. Soc.*, **85**, 2525 (1963).

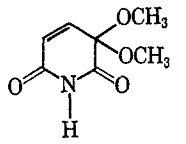
(4) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka, and S. Tsutsumi, *Tetrahedron Letters*, 1409 (1963).

ketal methoxy), a quartet centered at 3.45 with J = 10.5 cps (olefinic hydrogens), and a singlet at 0.90 (NH). The ultraviolet spectrum exhibited λ_{max} 218 mμ (ϵ 6100). The above spectroscopic data is similar to that of 4,4-dimethoxy-2,5-cyclohexadien-1-one (X), obtained by partial hydrolysis of the bisquinone ketal V. Compound X possessed ketal methoxy absorption at τ 6.70, and a vinyl quartet centered at 3.55 (J = 10.5 cps) while the ultraviolet spectrum had λ_{max} 213 mμ (ϵ 9500).[5] Hydrolysis of IX in dilute hydrochloric acid solution gave 2-hydroxyazaquinone (XI).[6]

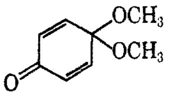


$CH_3O_2C{-}CH{=}CH{-}\overset{OCH_3}{\underset{OCH_3}{C}}{-}CO_2CH_3$

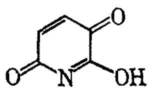
VIII



IX

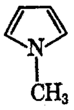


X

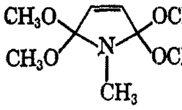


XI

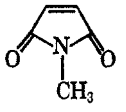
The anodic methoxylation of N-methylpyrrole (XII) (unlike the methoxylation of furans which affords dimethoxydihydrofurans) gave 1-methyl-2,2,5,5-tetramethoxy-3-pyrroline (XIII). The nmr spectrum of this solid exhibited three peaks at τ 7.75 (NCH_3), 6.86 (OCH_3), and 3.87 (olefinic hydrogens). Hydrolysis in dilute hydrochloric acid gave N-methylmaleimide (XIV). In dilute acetic acid solution partial hydrolysis occurred affording 1-methyl-5,5-dimethoxy-3-pyrrolin-2-one (XV).



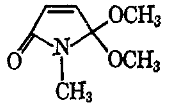
XII



XIII



XIV



XV

Discussion

Mechanisms of anodic oxidation of organic compounds have for the most part been confined to the Kolbe reaction and "side" reactions. For example, Eberson[7] and Salzberg and co-workers[8] have shown that aromatic acetoxylation reactions occur *via* a charge transfer of the aromatic compound at the anode, followed by nucleophilic attack by solvent on the reactive species. Anodic oxidation of the aromatic compound has been observed at a lower potential than that of acetic acid. While cation-radical intermediates have been postulated[9,10] where coupled products are found, dication intermediates have been suggested for numerous examples including the generation of tropylium ion,[11] the pyridination of anthracene,[12] and the acetoxylation of several polymethylbenzenes.[13]

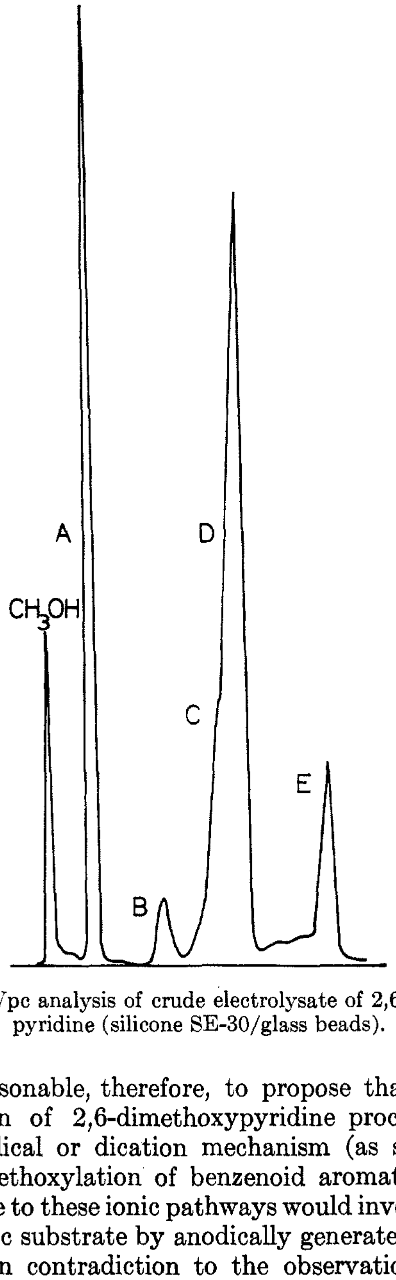


Figure 1.—Vpc analysis of crude electrolysate of 2,6-dimethoxypyridine (silicone SE-30/glass beads).

It is reasonable, therefore, to propose that the methoxylation of 2,6-dimethoxypyridine proceeds *via* a cation radical or dication mechanism (as suggested[14] for the methoxylation of benzenoid aromatics). The alternative to these ionic pathways would involve attack of aromatic substrate by anodically generated methoxy radicals, in contradiction to the observation[15,16] that methanol is oxidized at a significantly higher potential than the aromatic compounds studied.

In the absence of controlled-potential studies and in analogy with other aromatic electrochemical oxidations,[11-13] a two-electron oxidation of 2,6-dimethoxypyridine would give the resonance-stabilized dication XVI. On solvolysis, this would afford 2,3,6-trimethoxypyridine (XVII, Figure 2; suspected[17] as being peak B of Figure 1, but not positively identified). Similarly, a two-electron oxidation of 2,3,6-trimethoxypyridine would yield a second dication which could react with either 1 or 2 equiv of solvent to afford the tetramethoxypyridine VI and the bisketal II (or III).

In the absence of other data the electrolysis of N-methylpyrrole XII (Figure 3) could also be considered as a two-electron oxidation. The dimethoxypyrroline XIX formed by solvolysis of the dication XVIII pre-

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[5] W. Dürckheimer and L. A. Cohen, *Biochemistry*, **3**, 1948 (1964).
[6] J. H. Boyer and S. Kruger, *J. Am. Chem. Soc.*, **79**, 3552 (1957).
[7] L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963).
[8] M. Leung, J. Herz, and H. W. Salzberg, *J. Org. Chem.*, **30**, 310 (1965).
[9] K. E. Friend and W. E. Ohnesorge, *ibid.*, **28**, 2435 (1963).
[10] J. F. K. Wilshire, *Australian J. Chem.*, **16**, 432 (1963).
[11] D. H. Geske, *J. Am. Chem. Soc.*, **81**, 4145 (1959).
[12] H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).
[13] L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).
[14] B. Belleau and N. L. Weinberg, manuscript in preparation.
[15] R. W. Kiser, "Tables of Ionization Potentials," U. S. Atomic Energy Commission, Washington, D. C., 1960.
[16] E. M. Voigt and C. Reid, *J. Am. Chem. Soc.*, **86**, 3930 (1964).
[17] An analogous compound was produced in the electrolysis of 1,3-dimethoxybenzene and was identified as 1,2,4-trimethoxybenzene.

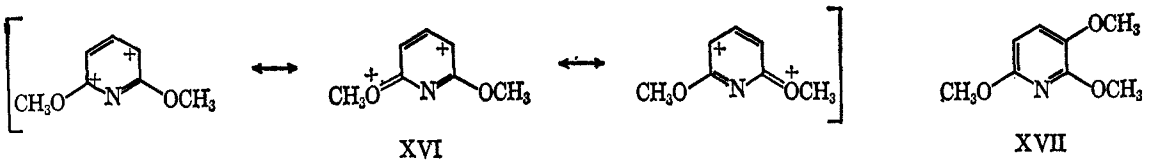


Figure 2.

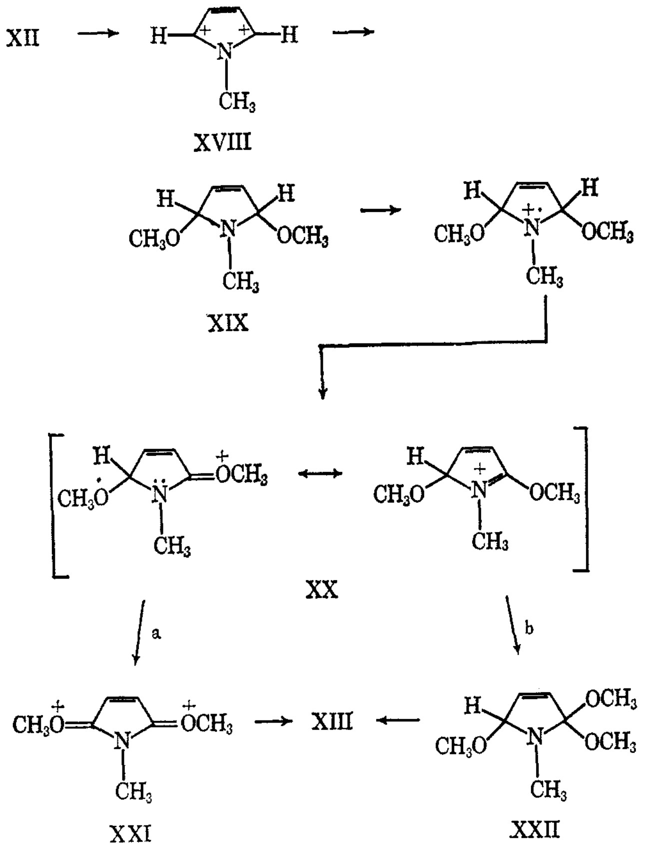


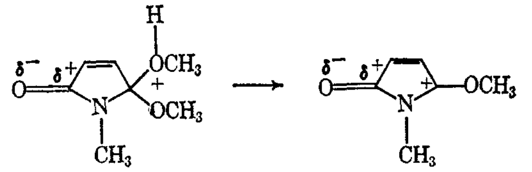
Figure 3.—Anodic methoxylation of N-methylpyrrole.

sumably is the precursor of the observed product XIII (in analogy to furan electrolyses[1]). The dimethoxypyrroline could undergo further anodic oxidation whereas dimethoxydihydrofurans do not, probably because of the lower ionization potential of amines relative to ethers.[15] In addition XIX should have a lower ionization potential than the aromatic N-methylpyrrole. Indeed electrolysis of N-methylpyrrole with less than 2 faradays per mole gave a mixture whose composition (vpc analysis) was 7% starting material, 90% tetramethoxypyrroline, and 3% unidentified materials.

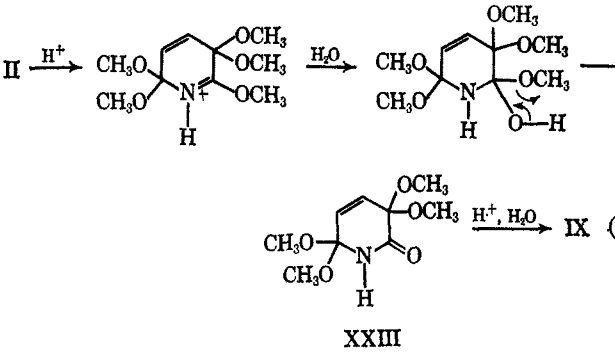
The oxidation of dimethoxypyrroline could be written as a one-electron transfer to give a cation radical which could lose a proton and a second electron to afford the cation XX. The latter could then undergo a second electron and proton loss (path a) to give the dication XXI followed by solvolysis to yield XIII, or alternatively (path b) could react with solvent, giving the trimethoxypyrroline XXII. Again XXII may be oxidized by a cation-radical process to give XIII. While the dimethoxy- and trimethoxypyrrolines could not be isolated, conceivably a controlled-potential electrolysis could provide a means of preparation.

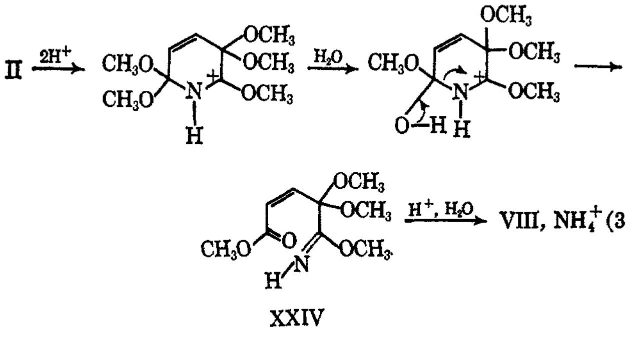
It is of interest to note that chemical oxidation[18] of N-methylpyrrole to N-methylmaleimide (XIV) is analogous to the above electrochemical oxidation.

The partial hydrolysis of ketal groups noted for the bisazaquinone ketal II (or III) and for the tetramethoxypyrroline XIII may be explained in terms of charge–dipole interaction. Thus the partial hydrolysis of XIII to the pyrrolinone XV in dilute acetic acid solution is successful because a strong charge–dipole interaction would exist between the carbonyl group and the developing allylic cation (eq 1). A similar argument also accounts for the stability in dilute acid of ketals VIII and IX. The conversion of 3,3,6,6-tetramethoxy-1,3-cyclohexadiene (V) to the cyclohexadienone X provides a further example of this reaction.

 (1)

The ratio of the two products in the hydrolysis of II (or III) was found to be dependent on acid concentration. The glutaconimide IX was favored in dilute while the glutaconate VIII was favored in more concentrated acetic acid solution. These results may be explained by mono- and diprotonation, respectively, of the bisketal. Assuming that the structure of the bisketal is II (compound III would give identical hydrolysis products), monoprotonation of II (eq 2) followed by hydrolysis of the lactam XXIII would afford the glutaconimide. Diprotonation of II (eq 3) and subsequent hydrolysis of the imino ether XXIV would yield the glutaconate.

 (2)

 (3)

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[18] P. Pratesi and G. Castorina, *Gazz. Chim. Ital.*, **83**, 913 (1953).

Experimental Section

Melting points (Gallenkamp melting point apparatus) are uncorrected. Infrared absorption spectra were recorded on a Perkin-Elmer 237B, ultraviolet spectra (in methanol) were recorded on a Unicam SP 800, and nmr spectra were taken on a Varian A-60 spectrophotometer (tetramethylsilane internal standard, $CDCl_3$ solvent). Gas chromatographic analyses were conducted on an Aerograph Autoprep A-700 using 10% silicone gum rubber on glass beads as column packing. The electrolysis cell and its operation have been described previously.[8]

Electrolysis of 2,6-Dimethoxypyridine in Methanol.—A solution consisting of 112 g (0.80 mole) of 2,6-dimethoxypyridine (Aldrich Chemical Co.), λ_{max} 278 mμ (ε 10,000), 10 g of potassium hydroxide, and 750 ml of methanol was electrolyzed at 5.0 amp at 25°. After 27 hr the electrolysate was concentrated at reduced pressure to a thick paste, the inorganic material was precipitated by the addition of 1 l. of anhydrous ether and filtered, and the filtrate was concentrated. The viscous residue (140 g) had five peaks in its vpc (Figure 1), and was distilled, affording four fractions and a nondistillable tar.

The first fraction [bp 55° (8 mm), 15.5 g] was examined by vpc and found to be pure 2,6-dimethoxypyridine (peak A of Figure 1). The second fraction [bp 72–113° (8 mm), 3.0 g] could not be positively identified. The vpc indicated that at least 30% was starting material. However, the ultraviolet spectrum exhibited relatively strong absorption at 293 mμ not observed in any of the other products.

The largest fraction [bp 113–116° (8 mm), $n^{20}D$ 1.4722, 49.6 g, 26%] was obtained as a colorless liquid. This had no aromatic peaks in its infrared spectrum, but had strong bands at 1675 and 1660 cm^{-1} in addition to characteristic ketal absorption between 1000 and 1200 cm^{-1}. The ultraviolet spectrum had λ_{max} 213 mμ (ε 1100). The nmr spectrum exhibited a doublet at τ 6.75 for ketal methoxy, 6.25 for vinyl methoxy, and a quartet from 4.23 to 3.75 with J = 10.0 cps for olefinic hydrogens. The integrated areas gave a ratio of 12:3:2, respectively. The compound was identified as a pentamethoxyazacyclohexadiene (peak D of Figure 1).

Anal. Calcd for $C_{10}H_{17}NO_5$: C, 51.94; H, 7.41; N, 6.06; OCH_3, 67.5. Found: C, 51.38; H, 7.38; N, 6.02; OCH_3, 70.3.

The last fraction [bp 116–120° (8 mm), 5.0 g, 3%] solidified on standing and was recrystallized from benzene and sublimed at 50° (0.1 mm), giving a colorless solid, mp 73.5–75.5°, λ_{max} 229 mμ (ε 12,000) and 305 mμ (ε 9500). Infrared analysis showed that this material was aromatic (1615 and 1500 cm^{-1}). The nmr spectrum had a doublet with bands of equal intensity at τ 6.32 and 6.20 for aromatic methoxy, in addition to a band at 3.23 for aromatic hydrogen. The integrated area was 12:1, respectively, for 2,3,5,6-tetramethoxypyridine (VI) (peak C of Figure 1).

Anal. Calcd for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.56; H, 6.48; N, 6.94.

Hydrolysis of the Bisazaquinone Ketal. (i) **In 25% Acetic Acid Solution.**—The bisazaquinone ketal (13.7 g, 0.059 mole) in 50 ml of 25% aqueous acetic acid was stirred magnetically at 25° for 36 hr. The solution was neutralized with solid sodium bicarbonate, extracted with methylene chloride, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was concentrated leaving 10.5 g of an oil. Distillation gave 9.0 g (70%) of dimethyl 4,4-dimethoxyglutaconate (VIII), bp 135–140° (15 mm), $n^{20}D$ 1.4539, and 0.8 g of an oily residue which crystallized on standing. The diester had λ_{max} 220 mμ (ε 2200), while its nmr spectrum indicated a mixture of *cis* and *trans* isomers in the ratio of 5:1. The olefinic region had a quartet centered at τ 3.45 with J = 10.5 cps (*trans* olefin) and a singlet at 3.95 (*cis* olefin).

Anal. Calcd for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.87; H, 6.61.

The diester (5.0 g, 0.023 mole) was hydrogenated in methanolic solution over platinum catalyst to yield, after work-up, 4.5 g (90%) of dimethyl 2,2-dimethoxyglutarate, bp 135° (12 mm), $n^{20}D$ 1.4435. The nmr spectrum was consistent with the assigned structure.

Anal. Calcd for $C_9H_{16}O_6$: C, 49.08; H, 7.32. Found: C, 49.29; H, 6.87.

The 2,4-dinitrophenylhydrazone of this material, mp 121–123°, was compared with an authentic sample prepared from dimethyl α-oxoglutarate (lit.[19] mp 122–123°).

(ii) **In 10% Acetic Acid Solution.**—A mixture consisting of 25 g (0.11 mole) of the bisazaquinone ketal in 100 ml of 10% aqueous acetic acid was stirred magnetically at 25° for 24 hr. Distillation of the crude product (21.5 g) isolated as in section i gave two fractions. The lower boiling fraction, bp 135–141° (15 mm), 13.2 g, 55%, was identified as dimethyl 4,4-dimethoxyglutaconate (VIII).

The second fraction had bp 120° (0.5 mm), and crystallized on standing. This material was sublimed at 50° (0.05 mm), giving 5.8 g (31%) of 4,4-dimethoxyglutaconimide (IX), mp 85–86°. The infrared spectrum (Nujol) had bands at 3450 (NH), 1740 (C=O), and 1645 cm^{-1} (C=C), while the ultraviolet spectrum had λ_{max} 218 mμ (ε 6100). The nmr spectrum consisted of a doublet at τ 6.65 and 6.70 for ketal methoxy, a quartet with J = 10.5 cps centered at 3.45 for vinyl hydrogens, and a singlet at 0.90 for the imide hydrogen. The rato of areas was 6:2:1, respectively.

Anal. Calcd for $C_7H_9NO_4$: C, 49.12; H, 5.30; N, 8.18. Found: C, 49.24; H, 5.45; N, 8.09.

Hydrolysis of a sample of this material in 5% aqueous hydrochloric acid solution deposited 2-hydroxy-*p*-azaquinone (XI) decomposing above 300°. This product was identical with that described by Boyer and Kruger.[6]

(iii) **In Dilute Acetic Acid Solution.**—The bisazaquinone ketal (18.2 g, 0.079 mole) in 100 ml of water was stirred magnetically and cooled to 10°. Acetic acid (10 ml of a 5% solution) was added dropwise over 15 min, and the resultant mixture was allowed to come to room temperature over 24 hr. Work-up as before gave 15 g of a viscous oil, which solidified on standing, and was crystallized from diethyl ether, affording 12.5 g (92%) of 4,4-dimethoxyglutaconimide (IX), mp 84–86°.

Partial Hydrolysis of 3,3,6,6-Tetramethoxy-1,4-cyclohexadiene (V).—To a magnetically stirring solution of acetic acid (50 ml, 1%) at 5° was added 5.0 g (0.026 mole) of 3,3,6,6-tetramethoxy-1,4-cyclohexadiene. After 1 hr the mixture was allowed to stand at 5° for 17 hr. It was then neutralized with saturated sodium bicarbonate and gave after work-up 2.5 g (62%) of 4,4-dimethoxycyclohexadien-1-on (X), bp 110° (13 mm), λ_{max} 213 mμ (ε 9500). This material was identical with that described by Dürckheimer and Cohen.[5] The nmr spectrum exhibited an olefinic quartet centered at τ 3.55 with J = 10.5 cps.

Electrolysis of N-Methylpyrrole in Methanol.—The electrolysis of a solution of 21.7 g (0.268 mole) of N-methylpyrrole, 5 g of potassium hydroxide, and 400 ml of methanol was carried out at 6.0 amp and 20°. After 6 hr the product was isolated and distilled at 95–105° (7 mm), affording 31.0 g of 1-methyl-2,2,5,5-tetramethoxy-3-pyrroline (XIII). This slowly crystallized on standing. Sublimation gave mp 52–53°. The nmr spectrum exhibited peaks at τ 7.75 (NCH_3), 6.86 (OCH_3), and 3.87 (olefinic H) in a ratio of 3:12:2).

Anal. Calcd for $C_9H_{17}NO_4$: C, 53.19; H, 8.43. Found: C, 52.96; H, 8.35.

In a second electrolysis, a solution of 40.5 g (0.50 mole) of N-methylpyrrole, 5 g of potassium hydroxide, and 300 ml of methanol was electrolyzed at 3 amp and 20° for 6.5 hr. Solvent was distilled off at atmospheric pressure and inorganic salts were precipitated from the cooled residue with anhydrous diethyl ether. This was filtered and the ether was removed by distillation. Vpc analysis of the residue (39 g) indicated the presence of two materials. These were identified by their retention times as N-methylpyrrole (7%) and tetramethoxypyrroline XIII (90%). In addition there were two peaks (3%) of unknown origin.

N-Methylmaleimide (XIV).—Treatment of 1.0 g (0.0052 mole) of the tetramethoxypyrroline with 10 ml of 3% aqueous hydrochloric acid solution precipitated colorless, crystalline solid within several minutes. This was filtered and dried in air, affording 0.137 g (23%) of N-methylmaleimide XIV, mp 90–92° (lit.[20] mp 96°). The infrared spectrum of this material was identical with that of a sample of authentic N-methylmaleimide.

1-Methyl-5,5-dimethoxy-3-pyrrolin-2-one (XV).—To a cold (5–10°), magnetically stirring solution of 1 l. of 0.05% acetic acid was added 50 g (0.26 mole) of 1-methyl-2,2,5,5-tetramethoxy-3-pyrroline (XIII) in 150 ml of methanol over 10 min. After 1.5 hr the reaction was neutralized with saturated sodium bicarbonate and extracted with diethyl ether. The combined extract was dried over anhydrous magnesium sulfate and filtered, the

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filtrate was concentrated, and the residue was distilled. A heart cut, bp 101–104° (5 mm), solidified on standing and afforded 30 g (73%), mp 43–45°. The infrared spectrum exhibited a strong carbonyl band at 1720 cm^{-1}, while the nmr spectrum had peaks at τ 7.34 (NCH_3), and 6.81 (OCH_3) and a quartet centered at 3.38 (AB system for olefinic H) with J = 6.5 cps. The ratio of integrated areas was 3:6:2, respectively.

Anal. Calcd for $C_7H_{11}NO_3$: C, 53.49; H, 7.05. Found: C, 53.88; H, 7.23.

Acknowledgments.—The authors wish to thank Professor B. Belleau and Professor R. R. Fraser of the University of Ottawa for helpful advice and nmr spectra, respectively.

The Anodic Oxidation of Organic Compounds. II. The Electrochemical Alkoxylation of Tertiary Amines

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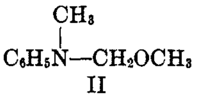
A series of tertiary amines has been anodically methoxylated. N,N-Dimethylaniline gave two products, N-methoxymethyl-N-methylaniline and N,N-bis(methoxymethyl)aniline. The product composition in the electrolysis of three benzylamines showed that alkoxylation takes place preferentially at the alkyl rather than the benzyl position. N-Benzyl-N-methylethanolamine and N-benzyldiethanolamine, in addition to oxazolidines, gave products derived from a dehydroxymethylation reaction. Possible mechanisms are proposed, but one in which a maximally adsorbed cation radical undergoes transfer of an electron to the anode, loss of a proton from a nonadsorbed site, and solvolysis of the resultant cation appears to best account for the observed results.

Anodic acyloxylation reactions of organic compounds have been examined in some detail in recent years.[2–10] It is now generally believed[5] that the mechanism of acetoxylation probably does not involve reaction of organic substrate with anodically generated acetoxy radicals. Rather the organic substrate is oxidized at the anode (at potentials lower than that of acetic acid) and the cation radical or dication thereby produced reacts with solvent to form the final product. Anodic methoxylation reactions have been interpreted in terms of similar ionic mechanisms.[5,11,12] Except for the methoxylation of 2,6-dimethoxypyridine and N-methylpyrrole,[12] there are no reports in the literature concerning anodic methoxylation of amines. In terms of their ionization potentials[13] amines ought to undergo oxidation even more readily than amides. Indeed, an examination of the literature[14–19] shows that there is a variety of methods available for chemical oxidation of amines.

In a continuation of studies of preparative organic electrochemistry we have examined the electrochemical methoxylation of several amines. Anodic oxidation of N,N-dimethylaniline (I) in methanolic solution gave two products in a ratio of 6:1, identified as N-methoxymethyl-N-methylaniline (II) and N,N-bis(methoxymethyl)aniline (III), respectively. The latter could also be derived by methoxylation of II. Lithium aluminum hydride reduction of these products afforded N,N-dimethylaniline quantitatively.

$C_6H_5N(CH_3)_2$

I



$C_6H_5N(CH_3)CH_2OCH_3$

II

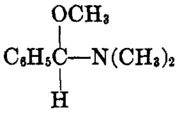
$C_6H_5N(CH_2OCH_3)_2$

III

The reactions of a series of three N-benzylamines were examined to provide an understanding of the scope of this new electrochemical oxidation and perhaps some insight into the mechanism involved. The methoxylation of N,N-dimethylbenzylamine (IV) gave a mixture of two isomeric products, α-methoxy-N,N-dimethylbenzylamine (V) and N-methoxymethyl-N-methylbenzylamine (VI). The ratio of V to VI as determined by vpc, nmr, and hydrolytic studies was 1:4.

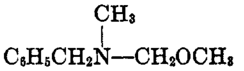
$C_6H_5CH_2N(CH_3)_2$

IV



$C_6H_5CH(OCH_3)N(CH_3)_2$

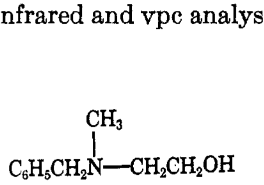
V



$C_6H_5CH_2N(CH_3)CH_2OCH_3$

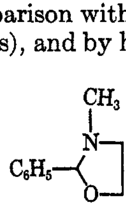
VI

The electrolysis of N-benzyl-N-methylethanolamine (VII) gave a mixture of three products in approximately equal proportion. One of these materials was identified as N-methoxymethyl-N-methylbenzylamine (VI) while the other two were found to be 3-methyl-2-phenyloxazolidine (VIII) and 3-benzyloxazolidine (IX). The structures of the three products were determined by nmr analysis, by comparison with authentic samples (infrared and vpc analyses), and by hydrolytic studies.

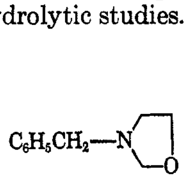


$C_6H_5CH_2N(CH_3)CH_2CH_2OH$

VII



VIII



IX

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