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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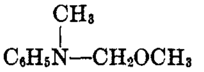
A series of tertiary amines has been anodically methoxylated. N,N-Dimethylaniline gave two products, N-methoxymethyl-N-methylaniline and N,N-bis(methoxymethyl)aniline. The product composition in the electrolysis of three benzylamines showed that alkoxylation takes place preferentially at the alkyl rather 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

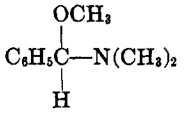
$C_6H_5N(CH_2OCH_3)_2$

III

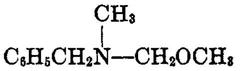
The reactions of a series of three N-benzylamines were examined to provide an understanding of the scope of this new electrochemical oxidation and perhaps some insight into the mechanism involved. The methoxylation of N,N-dimethylbenzylamine (IV) gave a mixture of two isomeric products, α-methoxy-N,N-dimethylbenzylamine (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

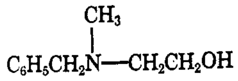

$C_6H_5CH(OCH_3)-N(CH_3)_2$

V

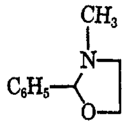

$C_6H_5CH_2N(CH_3)-CH_2OCH_3$

VI

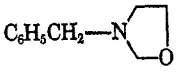
The electrolysis of N-benzyl-N-methylethanolamine (VII) gave a mixture of three products in approximately equal proportion. One of these materials was identified as N-methoxymethyl-N-methylbenzylamine (VI) while the other two were found to be 3-methyl-2-phenyloxazolidine (VIII) and 3-benzyloxazolidine (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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(1) American Cyanamide Co., Stamford Conn.

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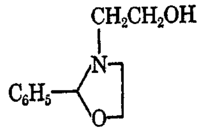
The oxidation of N-benzyldiethanolamine (X) gave at least four products (vpc analysis) of which two materials were readily identified. These were 3-benzyloxazolidine (IX) and 3-(β-hydroxyethyl)-2-phenyloxazolidine (XI). The former comprised about 45% of the crude mixture. Hydrolysis of a sample of the crude mixture gave a 30% yield of benzaldehyde.

$C_6H_5CH_2N(CH_2CH_2OH)_2$

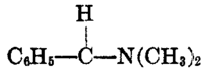
X



XI

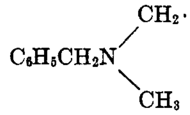
Discussion

There are at least four mechanisms which could account for the electrochemical methoxylation of N,N-dimethylbenzylamine (IV). A simple radical-abstraction mechanism involving anodically generated methoxy radicals would afford the benzyl radical XII and the primary alkyl radical XIII. Because of resonance stabilization the benzyl radical would be expected to have a higher ionization potential[13] than the primary alkyl radical. Hence anodic oxidation of the radicals XII and XIII to the corresponding cations XIV and XV should favor the formation of N-methoxymethyl-N-methylbenzylamine (VI) on solvolysis. There are, however, several serious drawbacks to this proposal. It is well established[20] that radical abstraction of hydrogen is preferred in the order tertiary > secondary > primary (the same order as carbonium ion stability). Furthermore, Dunstan and Henbest[19] have demonstrated that N,N-dimethylbenzylamine is oxidized by N-bromosuccinimide or benzoyl peroxide at the benzyl group to give benzaldehyde in about 65% yield.

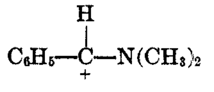


$C_6H_5\overset{H}{\dot{C}}N(CH_3)_2$

XII

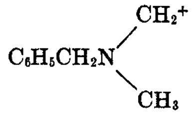


XIII



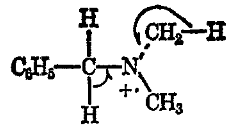
$C_6H_5\underset{+}{\overset{H}{C}}N(CH_3)_2$

XIV



XV

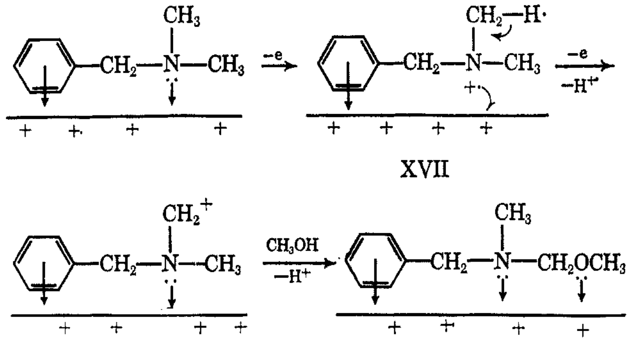
A second mechanism which may be considered involves loss of a hydrogen radical from the anodically generated cation radical XVI. The manner of this elimination is predictable from a study of mass spectra of similar compounds. For example, it has been established[21] that when a choice exists between loss of a primary (CH_3) or secondary (CH_2) hydrogen, the latter is always favored. By such a pathway the benzylic cation XIV would predominate over the primary cation XV and on solvolysis would afford the incorrect ratio of substitution products (V > VI).



XVI

A third process in which a proton would be lost from the cation radical XVI, followed by anodic oxidation of the radical and solvolysis of the resultant cation, again suffers from the fact that benzylic cations are in general more stable than primary alkyl cations.

Several groups[9,22-26] have shown the importance of adsorption of substrate on the electrode. We suggest likewise that adsorption of substrate on the anode determines the nature of the final products for the anodic oxidation of tertiary amines. Thus formation of the product-forming cation XVIII (eq 1) from the adsorbed cation radical XVII would occur *via* loss of a proton from the methyl rather than the benzyl group. The primary cation XVIII would thereby be generated as remotely from the plane of the anode as possible. The alternative deprotonation at the benzyl group would entail the unfavorable formation of a positive charge at the surface of the anode and adjacent to an already positively polarized aromatic ring.

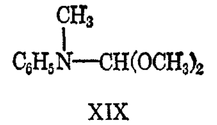


XVII

XVIII

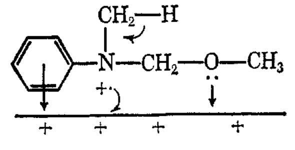
(1)

Similar reasoning would account for the formation of N-methoxymethyl-N-methylaniline (II), and N,N-bis(methoxymethyl)aniline (III), and the absence of any N-dimethoxy-N-methylaniline (XIX). The latter would certainly be expected in a reaction in solution in view of the mode of chemical oxidation of amines.[14-19] However, the maximally adsorbed cation radical XX would conceivably undergo concerted transfer of an electron to the anode and loss of a proton from the methyl rather than the methoxymethyl group.



$C_6H_5\overset{CH_3}{N}CH(OCH_3)_2$

XIX



XX

McLafferty[27] has recently stated that mass spectral mechanisms should parallel those of organic solution chemistry. It may be added that mass spectral mechanisms at least in their initial pathways do appear analogous to anodic oxidations. Generation of cationic

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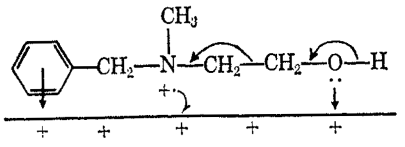
species are well cataloged in mass spectral studies.[28] The dehydroxymethylations of the benzylethanolamines are excellent examples of the parallelism which exists between the two fields. Thus the transfer of an electron to the anode from the cation radical of N-benzyl-N-methylethanolamine (XXI) could result in loss of the elements of formaldehyde and a proton to form the cation XVIII.



XXI

It should be noted, in conclusion, that anodic adsorption probably accounts for the stereochemistry of products observed in other electrochemical alkoxylation reactions.[29–32] Indeed, examination of molecular models of these examples in reference to a hypothetical anode surface allows prediction of the favored stereochemistry in product formation.

Experimental Section

Melting points (Gallenkamp melting apparatus) are uncorrected. Infrared absorption spectra were recorded on a Perkin-Elmer 237B, and nmr spectra were obtained on a Varian A-60 spectrophotometer (tetramethylsilane internal standard, $CDCl_3$ solvent). Gas chromatographic analyses were conducted on an Aerograph Autoprep A-700 using silicone SE-30 on glass beads as column packing. The electrolysis cell and its operation have been described previously.[33]

Electrolysis of N,N-Dimethylaniline in Methanol.—A solution consisting of 53.7 g (0.45 mole) of N,N-dimethylaniline and 10 g of potassium hydroxide in 500 ml of methanol was electrolyzed at 5.5 amp at 25°. After 6 hr the electrolysate was concentrated to a thick paste, the inorganic material was precipitated by the addition of 1 l. of anhydrous ether and filtered, and the filtrate was evaporated, leaving 63.2 g of crude product. Vpc analysis of this oil showed three peaks in a ratio of 1:24:4. The first peak was identified as unreacted amine by comparison of retention times with starting material.

This oil was distilled (spinning-band column) to give two fractions: fraction 1, bp 103–106° (10 mm), 46 g, n^{20}_D 1.5448; fraction 2, bp 123–126° (10 mm), 2.5 g, n^{20}_D 1.5338. The nmr spectrum of the first fraction exhibited the following characteristic bands: τ 7.18 (NCH_3), 6.92 (OCH_3), 5.51 (OCH_2N), 2.7–3.4 (aromatic H). The ratio of their respective areas was 3:3:2:5 in agreement for N-methoxymethyl-N-methylaniline.

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.84; H, 8.67; N, 9.40.

A sample of this fraction (10 g, 0.066 mole) was reduced with lithium aluminum hydride (1.26 g, 0.033 mole) in 100 ml of 1,2-dimethoxyethane to N,N-dimethylaniline (7.9 g, 100%) which was identical (infrared) with an authentic sample of this amine.

The nmr spectrum of the higher boiling fraction had τ 6.92 (OCH_3), 5.43 (OCH_2N), 2.7–3.4 (aromatic H). The ratio of areas (6:4:5, respectively) agreed with the assignment, N,N-bis(methoxymethyl)aniline.

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.37; H, 8.59; N, 8.40.

Reduction of this oil with excess lithium aluminum hydride in ether afforded N,N-dimethylaniline quantitatively.

Electrolysis of N-Methoxymethyl-N-methylaniline in Methanol.—A solution of 3.0 g (0.020 mole) of N-methoxymethyl-N-methylaniline, 2 g of potassium hydroxide, and 200 ml of methanol was electrolyzed at 2.0 amp and 20°. After 16 min the reaction was processed as before giving 2.5 g of crude product. Vpc analysis demonstrated that N-methoxymethyl-N-methylaniline and N,N-bis(methoxymethyl)aniline were present in approximately equal proportions.

Electrolysis of N,N-Dimethylbenzylamine in Methanol.—A solution consisting of 27 g (0.20 mole) of N,N-dimethylbenzylamine, 5 g of potassium hydroxide, and 300 ml of methanol was electrolyzed at 5.0 amp and 20°. After 1.5 hr the electrolysate was concentrated and worked up as before to afford 27 g of oil. The vpc of this material indicated three peaks with unreacted amine comprising about 40% of the mixture. The other two peaks were in a 1:4 ratio.

The product was distilled at 15 mm to give the following fractions: fraction 1, bp 75–80°, 10.0 g (37%) of N,N-dimethylbenzylamine; fraction 2, bp 80–88°, 2.5 g; fraction 3, bp 88–98°, 8.4 g; pot residue 3.5 g. The vpc analysis of fraction 3 indicated a mixture of two compounds in a 3:7 ratio. The nmr spectrum indicated a similar ratio and was consistent for a mixture of α-methoxy-N,N-dimethylbenzylamine [τ 7.82 (NCH_3), 6.75 (OCH_3), 5.37 (ArCH)], and N-methoxymethyl-N-methylbenzylamine [τ 7.71 (NCH_3), 6.87 (OCH_3), 6.37 (NCH_2O), 6.10 ($ArCH_2$)]. The latter was the major component of the mixture of isomers. No attempt was made to isolate these compounds.

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.22; H, 9.18; N, 8.51.

Hydrolysis of fraction 3 (2.75 g, 0.0167 mole) in 25 ml of 10% aqueous hydrochloric acid at 25° for 0.5 hr gave on work-up 0.456 g (26%) of benzaldehyde. After neutralization of the aqueous layer, N-methylbenzylamine was isolated and characterized as the hydrochloride (1.20 g, 0.010 mole, 60%), mp 178–180°. A mixture melting point with an authentic sample was undepressed.

Electrolysis of N-Benzyl-N-methylethanolamine in Methanol.—A solution of 106 g (0.65 mole) of N-benzyl-N-methylethanolamine, 20 g of potassium hydroxide, and 800 ml of methanol was electrolyzed at 5.0 amp and 15°. After 7.5 hr, removal of solvent and inorganic salts yielded 115 g of crude product. Analysis by vpc indicated three peaks of approximately equal area. The oil was distilled (spinning-band column) at 7 mm giving the following fractions: fraction 1, bp 80–87°, 5.0 g; fraction 2, bp 95–100°, 3.5 g, n^{20}_D 1.5262; fraction 3, bp 100–105°, 28.0 g; fraction 4, bp 105–120°, 12.5 g; pot residue was tarry.

(a) The nmr spectrum of fraction 2 had a ratio of benzylic H (τ 5.48) to NCH_3 (τ 7.85) of 1:3. Comparison of the infrared spectra of this material and that of an authentic sample of 3-methyl-2-phenyloxazolidine[34] showed that these were identical.

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.97; H, 8.37; N, 7.72.

Hydrolysis of this fraction (2.2 g) in 25 ml of 10% aqueous hydrochloric acid yielded 1.1 g (73%) of benzaldehyde.

(b) Fraction 3 was redistilled (spinning-band column) at 30 mm to give 10.5 g of oil, bp 135°, n^{20}_D 1.5330. The vpc of this material showed less than 10% contamination by 3-methyl-2-phenyloxazolidine. The nmr spectrum had characteristic peaks at τ 5.88 ($ArCH_2$), 6.48 (NCH_2O), and an A_2X_2 sextet from 6.28 to 7.39 with $J = 7.2$ cps (NCH_2CH_2O). The ratio of areas of these peaks (1:1:2) agreed with the assignment of structure as 3-benzyloxazolidine. The infrared spectra of the product and an authentic sample[35] were identical.

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.36; H, 8.19; N, 8.09.

A sample of this fraction (2.0 g, 0.012 mole) was hydrolyzed in aqueous acid, affording 0.03 g of benzaldehyde. On neutralization 1.7 g (90%) of N-benzylethanolamine was obtained (identical infrared spectrum with that of authentic material).

(c) The vpc of fraction 1 consisted of two components in the ratio 2:3. The smaller peak was identified by retention time as 3-methyl-2-phenyloxazolidine, while the larger peak was N-methoxymethyl-N-methylbenzylamine. No attempt was made to

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isolate these components. The mixture (2.82 g, 0.0172 mole) was hydrolyzed in aqueous hydrochloric acid as before, and gave 1.08 g (59%) of benzaldehyde. Neutralization and treatment in ether with dry hydrogen chloride afforded N-methylbenzylamine hydrochloride (0.88 g, 43%).

Electrolysis of N-Benzyldiethanolamine in Methanol.—N-Benzyldiethanolamine (100 g, 0.5 mole) in 400 ml of methanol containing 10 g of potassium hydroxide was electrolyzed at 5.5 amp and 20° for 5.5 hr. After removal of solvent and inorganic salts there remained 125 g of viscous oil. Vpc analysis indicated at least four components existing as three distinct peaks in the ratio of 9:1:10. (One constituent of the mixture was a shoulder on the largest peak.)

The oil (52 g) was distilled and gave the following fractions: fraction 1, bp 90–95° (1.5 mm), 4.5 g, fraction 2, bp 110–115° (1.5 mm), 8.6 g; fraction 3, bp 125° (1 mm), 16 g; pot residue, 20 g (tarry). Fraction 1, the second largest of the components by vpc, was identified as 3-benzyloxazolidine by comparison of the nmr and infrared spectra of this oil with that of authentic material. Fractions 2 and 3 were redistilled (spinning-band column). A fraction, bp 110–120° (0.25 mm), 6.5 g, n^{20}_{D} 1.5471, was obtained which was pure according to vpc analysis. The infrared spectrum had strong, broad absorption for hydroxyl at 3300–3400 cm^{-1}, while the nmr spectrum exhibited a characteristic ArCHO band at τ 5.21. The integrated ratio of areas for aromatic H to ArCHO to all others was 5:1:8 in agreement with the structural assignment for this material as 3-(β-hydroxyethyl)-2-phenyloxazolidine.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.63; H, 7.94; N, 7.21.

A solution of 3.2 g (0.017 mole) of this fraction in dilute, aqueous hydrochloric acid afforded 1.7 g (94%) of benzaldehyde while neutralization gave 0.75 g (42%) of diethanolamine (compared with authentic material by infrared).

A mixture of 11 g of the crude electrolysate in 50 ml of 10% hydrochloric acid was kept at 25° for 0.5 hr. Ether extraction provided 1.5 g (30%) of benzaldehyde and on neutralization 5.7 g of a mixture of amino alcohols.

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

Competitive Carbonium Ion Processes. Catalysis of Acylation and Acetoxylation Reactions by Polyphosphoric Acid

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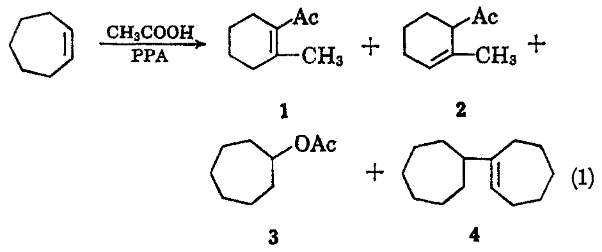
The reaction of simple cycloalkenes with acetic acid in polyphosphoric acid (PPA) is shown to give rise to the acetylation product, 1-acetylcycloalkene, and to the cycloalkyl acetate as well as minor products. Evidence is presented to indicate that an increase in the ratio of the yields of ester to ketone is a function of an increase in the stability of the carbonium ion resulting from protonation of the olefin. Cyclopentene, cyclohexene, and cyclooctene each leads to ketonic and ester mixtures, whereas norbornene, α-pinene, and β-pinene each gives predominantly esters. In a series of styrenes, higher relative yields of ketones are obtained the more sterically hindered the vinyl group. In certain instances, higher reaction temperatures increase the yield of ketone, as does a higher equivalent of P_4O_{10} in the PPA.

The acetylation of olefins with carboxylic acids, using polyphosphoric acid (PPA) as the catalyst, is not an uncommon procedure.[2] In appropriately structured molecules, the PPA also serves to induce cyclization, aromatization, dehydration, and carbonium ion rearrangements. It was surprising, however, to find[3] that the attempted acylation of cycloheptene with acetic acid in PPA gave the products shown in eq 1, but no 1-acetylcycloheptene. One of the major products, 1-acetyl-2-methylcyclohexene (1), reflects rearrangement, as does the unconjugated ketone (2) which was produced in smaller yield. In contrast, the other main and minor products, cycloheptyl acetate (3) and the hydrocarbon, 1-cycloheptylcycloheptene (4), respectively, did not suffer rearrangement.

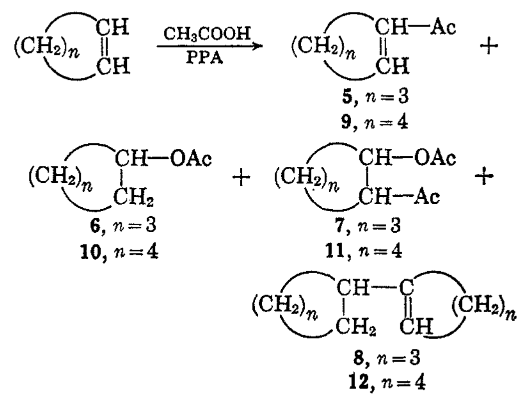


(1)

In view of the unexpected products obtained with cycloheptene, it was considered worthwhile to ascertain whether other cyclic olefins also gave rise to similar complex mixtures, and to determine more fully the catalytic behavior of PPA.

Discussion of Results

Reaction of cyclopentene with acetic acid in PPA gave two major products, 1-acetylcyclopentene (5) and cyclopentyl acetate (6). In addition, 2-acetylcyclopentyl acetate (7) and 1-cyclopentylcyclopentene (8) were obtained as minor products. Similarly, reaction



(2)

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[1] Taken from the Ph.D. Dissertation of R. J. Dolinski, University of Detroit, Detroit, Mich., 1966.

[2] (a) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958); (b) F. Uhlig and H. R. Snyder, *Advan. Org. Chem.*, **1**, 35 (1960).

[3] L. Rand and R. J. Dolinski, *J. Org. Chem.*, **31**, 3063 (1966).

[4] Similar products were proposed from the reaction of cyclohexene with acetyl chloride and silver perchlorate or with acetic anhydride and perchloric acid: H. Burton and P. F. G. Praill, *Chem. Ind.* (London), 75 (1954).