The Light-Catalyzed Oxidation of Starch with Aqueous Chlorine

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Products of relatively high carbonyl content (to 25 mole %) were prepared in good yield by the oxidation of cornstarch with aqueous chlorine in the presence of ultraviolet radiation. The rate of this oxidation is greatly affected by illumination. In certain cases, oxidations which require 5–8 days in the dark can be accomplished in a matter of hours when illuminated. The light-catalyzed oxidation also is affected significantly by pH. Comparative experiments (at both room temperature and ice-bath temperature) indicate that the reaction rate is three times as fast at pH 4 as at pH 0.5. Under comparable conditions of illumination, chloric acid was shown to be unreactive with starch. Product yields (recovered by simple filtration) varied considerably from 97% at pH 0.5 and ice-bath temperature to 30% at pH 4 and room temperature. At pH 4 and low temperature, products of 25 mole % carbonyl content were isolated in 91% yield. In general, about 17 mole % carbonyl is introduced for each equivalent of chlorine consumed. Under certain conditions products are obtained in which more than half of the observed carbonyl content is due to the presence of aldehyde groups.

In earlier publications,[1] we reported that the aqueous chlorine oxidation of cornstarch was strongly catalyzed by light. Although the chemical action of chlorine on starch was recognized as early as 1829,[2] it is surprising that this rather drastic effect of light had not been reported. In the many references to chlorine–water oxidation of carbohydrates,[3] we have found only one mention[4] of the effect of light on the reaction rate. The authors of this work noted that ultraviolet radiation caused fiftyfold increases in the rate of oxidation of D-mannitol (to D-mannose and D-fructose) by aqueous chlorine. Evidently, no additional work has been done to exploit this rather drastic effect of light on aqueous chlorine oxidation.[5]

Perhaps, the well-known fact that chlorine water can be decomposed by light was the reason that most previous investigators performed their experiments in the dark. This light-catalyzed decomposition of chlorine water has been investigated in considerable detail by Allmand[6] and co-workers who have demonstrated that ultraviolet radiation can completely decompose chlorine water to chloric acid, hydrochloric acid, and oxygen. In our work, we noted that the decomposition of chlorine water, under identical conditions of illumination, proceeded many times more slowly than the starch oxidation.

Working with nongelatinized cornstarch to simplify product recovery, we observed that, in the dark, the consumption of one equivalent of chlorine per anhydroglucose unit (A.G.U.) of starch requires about 8 days at room temperature (using approximately 0.1 *N* chlorine water). A similar experiment in a clear glass vessel exposed to indirect sunlight required only 6 hr. for the complete consumption of the chlorine.

Gelatinization of the starch causes a further increase in the reaction rate. In comparative experiments, using nearly identical conditions of illumination, temperature, and reagent concentrations, gelatinized starch is oxidized about four times as fast as nongelatinized starch (Fig. 1).

In the dark, gelatinized starch is oxidized only about 1.7 times as fast as nongelatinized starch (Fig. 2). Therefore, in the illuminated experiments, the predominant reason that the gelatinized starch is more rapidly oxidized is probably the fact that the gelatinized reaction mixture is more transparent. Note that in the illuminated experiments, the oxidation is complete in a matter of hours, not days.

It is well-known that the pH of the chlorine–water solution influences the rate of starch oxidation in the dark. As might be expected, the light-catalyzed oxidation is affected similarly. At room temperature, the oxidation is about three times as fast at pH 4 as at pH 0.5. A similar rate relationship was noted when the experiments were performed at ice-bath temperature (Fig. 3). In these experiments, the starch was not gelatinized, chlorine–starch ratio was 1.5 equivalents/A.G.U., and the products were isolated by filtration. At ice-bath temperature the yields were above 90%, but at room temperature, the yields dropped considerably (Table I).

TABLE I

THE EFFECT OF REACTION pH AND REACTION TEMPERATURE ON YIELD AND PRODUCT COMPOSITION

	pH 4		pH 0.5	
	25°	0°	25°	0°
Yield (%)	30	91	47	97
Carboxylic acid content (mole %)		12.9		4.1
Carbonyl content (mole %)		24.6		13.2
Aldehyde content (mole %)		13.3		4.4

It has been shown[7] that, in aqueous chlorine at pH 4, the species present is almost exclusively hypochlorous acid. Conversely, at pH 0.5 the reagent consists almost entirely of molecular chlorine. Thus, the rate data indicate that both reagents are capable of oxidizing starch and that hypochlorous acid reacts about three times as fast as molecular chlorine. It should be noted, however, that these findings do not

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(1) (a) A. F. Meiners and F. V. Morriss, Abstracts, Thirteenth Annual Kansas City Chemistry Conference, paper 17, published in "The Kansas City Chemist," November, 1961; (b) A. F. Meiners and F. V. Morriss, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, p. 20.

(2) J. Liebig, *Poggendorff's Ann. Phys. Chem.*, **15**, 541 (1829). This publication and other early observations are discussed by J. A. Radley, *Mfg. Chemist*, **13**, 104 (1942).

(3) See, for example, the work on starch oxidation by (a) M. E. McKillican and C. B. Purves, *Can. J. Chem.*, **32**, 312 (1954); (b) C. H. Hullinger and R. L. Whistler, *Cereal Chem.*, **28**, 153 (1951); and (c) R. L. Whistler and R. Schweiger, *J. Am. Chem. Soc.*, **79**, 6460 (1957). (d) See also, a review on the oxidation of glycosides and cellulose by O. Theander, *Svensk Kem. Tidskr.*, **71**, 1 (1959).

(4) R. Bognar and L. Somogyi, *Acta. Chim. Acad. Sci. Hung.*, **14**, 407 (1958).

(5) N. Uchino and R. L. Whistler [*Cereal Chem.*, **39**, 477 (1962)] recently reported that visible light caused a slight acceleration of the reaction of chlorine gas with moist wheat starch.

(6) K. W. Young and A. J. Allmand, *Can. J. Research*, **27B**, 318 (1949).

(7) B. P. Ridge and A. H. Little, *J. Textile Inst. Trans.*, **33**, T33 (1942).

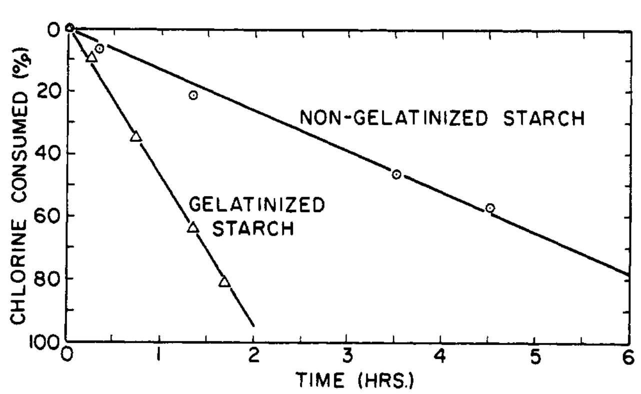

Fig. 1.—The ultraviolet-catalyzed chlorine oxidation of starch (1.5 equiv./A.G.U.).

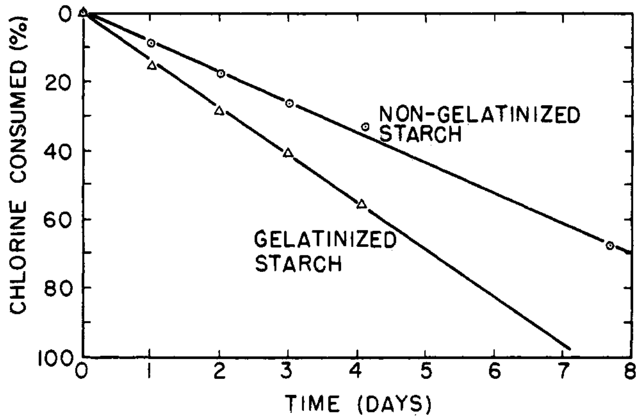

Fig. 2.—The chlorine oxidation of starch in the dark (0.77 equiv./A.G.U.).

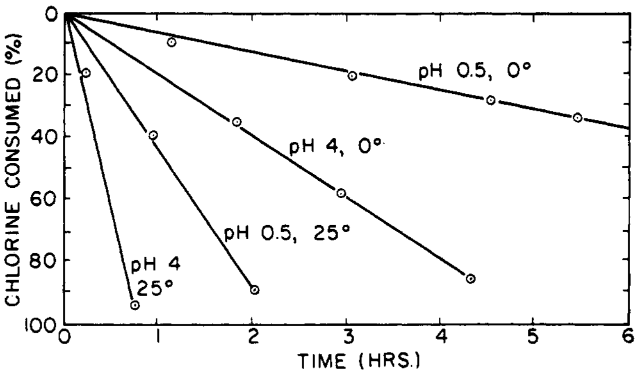

Fig. 3.—The influence of pH and temperature on rate of the ultraviolet-catalyzed chlorine oxidation of nongelatinized starch (1.5 equiv./A.G.U.).

demonstrate that either the chlorine molecule or the hypochlorous acid molecule is the actual reacting species. A comparable relationship between reaction rate and pH was observed in the oxidation of ethanol by bromine[8]; above pH 3, the reaction rate increases markedly with increasing pH. However, subsequent work[9] demonstrated conclusively that bromine and *not* hypobromous acid was the reactive species.

Chloric acid was initially suspected of being an intermediate in the starch oxidation, since chloric acid can be produced in significant quantities by the photolysis of chlorine water.[6] Although it is known that chloric acid will not oxidize aldoses,[10] it was necessary to demonstrate that chloric acid would not oxidize starch in the presence of strong illumination. In a suitable experiment, it was shown that only small amounts of chloric acid were consumed when starch was treated with two equivalents of chloric acid per A.G.U. It also was demonstrated that only relatively small amounts of chloric acid are generated when chlorine water is illuminated similarly. Thus chloric acid cannot be a significant intermediate in the light-catalyzed chlorine–starch oxidation.

A series of oxidized starches was prepared in order to observe the effect of the chlorine–starch ratio on the yields and carbonyl contents of the products (Table II). These experiments were performed at 10–12° using untreated chlorine water, which has a pH of about 2.5. In each case about 17 mole % of carbonyl content was introduced for each equivalent of chlorine consumed. The products were recovered by filtration and again it was observed that the yields decreased as the extent of oxidation increased.

Table II

The Effect of Reactant Ratio

	Reactant ratio (equiv. of Cl_2/A.G.U.)		
	0.33	0.67	1.0
Weight of starch (g.)	250	250	165
Chlorine concentration (*N*)	0.014	0.032	0.032
Reaction time (hr.)	5.0	7.0	7.0
Equiv. of chlorine consumed/A.G.U.	0.25	0.58	0.87
Yield (%)	95	94	85
Carbonyl content of product (mole %)	4.7	10.0	14.8

These oxidized starches were not much different visibly from the starting materials. Microscopic examination showed that the starch granules are intact and are indistinguishable from the original product. All of the products contained some carboxylic acid, but the amounts were fairly low, usually being less than one-third of the observed carbonyl content. The products were 95–99% dispersible in water, but formed dispersions of much lower paste viscosity than ordinary cornstarch. As might be expected, the paste viscosity decreases as the extent of oxidation increases. When heated in mild alkali, for example at pH 9, the oxidized starches evidently decomposed producing dark brown solutions.

Experimental evidence indicates that a significant portion (usually about one-half) of the observed carbonyl content in the oxidized starches consists of aldehyde groups. Also, the results of previous investigators indicate that a majority of the aldehyde groups are located at the 6-position in the anhydroglucose unit. For example, McKillican and Purves,[3a] in a study of the hypochlorous acid oxidation of wheat starch in the dark, concluded that 65 to 80% of the carbonyl groups in their products were aldehyde groups in the 6-position. Also Olof Theander[3d] isolated and identified products from the oxidation of methyl β-glucoside with hypochlorous acid at pH 4. He observed the formation of all four of the theoretically possible oxoglucosides. His results indicated that the product having the alde-

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[8] L. Farkas, B. Perlmutter, and O. Schächter, *J. Am. Chem. Soc.*, **71**, 2829 (1949).

[9] B. Perlmutter-Hayman and Y. Weissman, *ibid.*, **86**, 2323 (1962).

[10] A. Jeanes and H. S. Isbell, *J. Res. Natl. Bur. Std.*, **27**, 131 (1941).

hyde group in the 6-position represents about half of the total yield of carbonyl-containing products.

Aldehyde contents were determined using some analytical methods developed for chlorine-oxidized starch by Ellington and Purves.[11] One method involves determining the carbonyl content of the product before and after treatment with chlorous acid. The observed decrease in carbonyl content represents the aldehyde content, since chlorous acid does not oxidize ketone groups under the conditions prescribed.

Another method is based on the fact that, under certain conditions, alkaline hypoiodite oxidizes aldehyde groups, but not ketone groups. By measuring the uptake of hypoiodite, the aldehyde content can be calculated.

The results of our analytical studies using both methods are in fair agreement. For example, analysis of an oxidized starch prepared by a light-catalyzed oxidation at pH 0.5 (1.5 equivalents of chlorine/A.G.U., 7.25 hr. reaction time, 97% yield, total carbonyl content of 17.7%) showed an aldehyde content of 8.6 mole % according to the chlorous acid procedure and in the range 7.6 to 9.8 mole % according to the hypoiodite procedure.

Experimental

The Oxidation of Starch with Aqueous Chlorine in the Dark.—Ordinary cornstarch[12] (10.0 g., 0.056 A.G.U.) was gelatinized in 250 ml. of water by heating and stirring constantly until the temperature of the water reached 96°. After cooling, the dispersion was diluted to 900 ml. with water and chlorine water so that the final mixture contained 0.044 equiv. of chlorine. In a similar experiment, performed simultaneously, the starch was not gelatinized. The reaction vessels were brown, screw-capped bottles and the mixtures were stirred by means of magnetic stirrers. Insulation was placed between the bottles and the stirrer to minimize heating, and both experiments were placed in a hood so that a constant stream of air at room temperature passed over the bottles and the stirrers. At intervals, 50-ml. aliquots of each reaction mixture were taken and the chlorine concentration determined. Potassium iodide was added to acidified aliquots and the liberated iodine was titrated with 0.1 *N* thiosulfate. Since it required several minutes to remove the iodine color from particles of nongelatinized starch, these end points were difficult to see. Therefore, an excess of thiosulfate was added and, when the iodine color had disappeared, the excess thiosulfate was back-titrated with 0.05 *N* iodine. A plot of % chlorine reacted *vs.* time (Fig. 1) indicates that the rate of oxidation of gelatinized starch is 1.7 times as fast as the rate of oxidation of nongelatinized starch.

The Light-Catalyzed Oxidation. A. The Effect of Gelatinization.—Cornstarch (30 g., 0.167 A.G.U.) was gelatinized as before in 400 ml. of water. The starch gel was cooled in ice, mixed with 2.2 l. of a cold aqueous solution containing 0.237 equiv. of chlorine, and the mixture was diluted to 3.0 l. The reaction mixture was irradiated with a 100-w. mercury flood lamp (General Electric-H4JM) and stirred by means of a magnetic stirrer. An ice bath was used to hold the temperature of the reaction mixture between 10–12° and the progress of the reaction was followed as before. In a second experiment, conditions were duplicated except that the starch was not gelatinized. The gelatinized starch was oxidized 3.6 times as fast as the nongelatinized starch (Fig. 2) and both of the light-catalyzed reactions were many times as fast as comparable oxidations in the dark (note that the time scale in Fig. 2 is in hours, not days).

B. The Effect of pH and Temperature.—Two sets of duplicate experiments were performed in which the incident illumination and the pH of the solutions were accurately controlled. In the low pH experiments, the chlorine water was acidified with concentrated hydrochloric acid (50 ml./l.) to pH 0.5. In the other runs, the pH was adjusted to pH 4.0 with sodium dihydrogen phosphate and sodium hydroxide. During the runs, the pH was observed continuously and additional sodium hydroxide was added at intervals to maintain pH 4.0. The previously described ultraviolet lamp was placed in exactly the same position for each run.

The concentration of cornstarch in the reaction mixtures was 1% by weight, and the chlorine concentration, 0.9 *N*, provided a chlorine–starch ratio of 1.5 equiv./A.G.U.

Two sets of experiments were run, one at room temperature and one at ice-bath temperature. The progress of the reactions was followed as before. A comparison of the rates is presented in Fig. 3. The products were recovered by filtration, washed with methanol, and air-dried. The yields and product compositions are presented in Table I.

C. The Effect of Reactant Ratio.—A series of larger-scale reactions were performed in which the chlorine–starch ratio was varied. The reaction vessel was a 30-l. Pyrex resin kettle illuminated by three ultraviolet lamps. The experiments were performed at 10°, using an efficient stirrer and an ice-bath to maintain this temperature (±1°) during the reaction. Table II summarizes the reaction conditions and typical results. The products were recovered as before.

Functional Group Analyses.—Carbonyl contents were determined using a modification of the procedure described by Gladding and Purves.[13] Starch samples (1–5 g.) were adjusted to pH 5.0, allowed to stir for several hours, and then adjusted back to pH 5.0, if necessary. Reagent grade hydroxylamine hydrochloride solution (5% by weight) was adjusted to pH 5.0 and 100 ml. of the freshly prepared solution was pipeted into the starch suspensions. The mixtures were placed in brown bottles and shaken mechanically overnight. Samples and blanks (usually in duplicate) were then titrated to pH 3.2.

Carboxylic acid determinations were done by the calcium acetate procedure described by Yackel and Kenyon[14] and by the paste titration procedure of Mattisson and Legendre.[15] The products obtained from an acid environment showed little difference between the original and de-ashed samples.

Aldehyde determinations were done using modifications of the methods described by Ellington and Purves.[11]

A. Chlorous Acid Procedure.—In a typical analysis, a starch sample (6–7 g.) was treated with 150 ml. of 4% sodium chlorite (analytical reagent grade) in 30% acetic acid at room temperature for exactly 1 hr. Anhydrous methanol (400 ml.) was added and the mixture was filtered. The product was washed successively with (1) 70% methanol that had been made 0.5 *N* with hydrochloric acid, (2) 70% methanol, and (3) absolute methanol. After vacuum drying at 50° overnight, the product was obtained in yields of 84–89%. A carbonyl analysis of the product was obtained (using the hydroxylamine procedure) and the difference between this figure and the original carbonyl content was taken as the aldehyde content.

B. Hypoiodite Procedure.—In a typical analysis, duplicate samples (1.7–2.6 g.) of oxidized starch were placed in a solution consisting of 50.0 ml. of carbonate–bicarbonate buffer (pH 11.2) and 25.0 ml. of 0.05 *N* iodine. The pH of the resulting mixture was 9.7. Duplicate blank runs were made on the oxidized starch at pH 5.6 by employing identical amounts of buffer and iodine to which 20.0 ml. of 0.33 *N* sulfuric acid was added. The samples were shaken vigorously for 2.5 hr. at room temperature. An identical amount of acid was added to the alkaline samples and a slight excess (15.0 ml.) of 0.1 *N* thiosulfate was added to all four mixtures. Shaking was continued until all of the solutions became colorless and each was titrated to the iodine end point with 0.05 *N* iodine. The aldehyde contents were calculated as the difference in iodine uptake between the alkaline oxidation and the acid oxidation.

The Treatment of Starch with Chloric Acid in the Presence of Ultraviolet Radiation.—Cornstarch (30 g., 0.167 A.G.U.) was added to 3 l. of 0.02 *M* potassium chlorate which had been acidified to pH 1.5 with dilute sulfuric acid. The reaction vessel was identical to the one used in the light-catalyzed oxidation study. The mixture was cooled to 10° and the ultraviolet lamp (the same as used previously) was positioned as before. At intervals, aliquots were withdrawn and analyzed for chlorate.

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[11] A. C. Ellington and C. B. Purves, *Can. J. Chem.*, **31**, 801 (1953).

[12] The cornstarch used in all of the experiments was the variety prepared for domestic use and contained 9.5–10.5% moisture.

[13] E. K. Gladding and C. B. Purves, *Paper Trade J.*, **116**, 26 (1943).

[14] E. C. Yackel and W. O. Kenyon, *J. Am. Chem. Soc.*, **64**, 121 (1942).

[15] M. F. Mattisson and K. A. Legendre, *Anal. Chem.*, **24**, 1942 (1952).

Chlorate analyses were done by the following procedure. An aliquot (20 ml.) was transferred to a beaker containing excess (50 ml.) 0.1 *N* ferrous ammonium sulfate. The mixture was heated to boiling in an atmosphere of carbon dioxide. On cooling, the mixture was titrated with 0.1 *N* permanganate. The end point was determined electrometrically using a Beckman portable pH meter with a silver indicator electrode.

After 4 hr. of illumination, only 5% of the available chloric acid had been consumed. The original concentration of chloric acid (2 equiv./A.G.U.) was considerably greater than the chloric acid concentration that would be generated by comparable illumination of chlorine water (only 0.0034 mole of chloric acid was produced when 3.0 l. of 0.103 *N* chlorine water was illuminated for 5 hr. at pH 1.5 and 10°). These observations indicate that chloric acid is not a significant intermediate in the light-catalyzed chlorine–starch oxidation.

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Acridizinium Ion Chemistry. IV.[1] Oxidation with Nitric Acid

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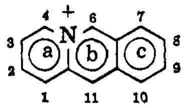
Oxidation of the acridizinium nucleus by nitric acid results in attack at ring b when no strong activating groups are present, yielding 2-(2-carboxy-4-nitrobenzoyl)pyridines. Oxidation with nitric acid of an acridizinium salt containing one or more hydroxyl or methoxyl groups in ring c, results in degradation of ring c, and the formation of a betaine of 2,3-dicarboxyquinolizinium hydroxide.

Although the acridizinium, or benzo[*b*]quinolizinium ion (I) has been known since 1954,[3] little is known about its behavior on oxidation. It has been stated[3] that oxidation of the ion (I) in alkaline permanganate yielded phthalic acid, while more recently Paquette[4] has shown that alkaline ferricyanide solution can convert the acridizinium ion to an amide (II). Since it is known[1,5] that the acridizinium ion in alkaline solution exists almost entirely as the pseudobase, both of the previous oxidation attempts could probably best be described as oxidation of the pseudobase.



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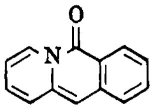
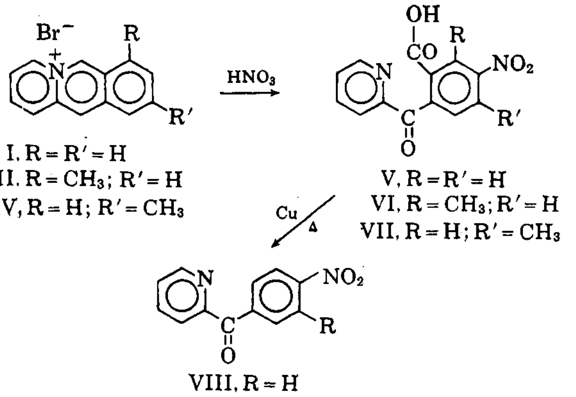


II

It was felt that oxidations carried out in an *acidic* medium might lead to new and interesting results, and in this paper are described our experiments using nitric acid. When acridizinium bromide (I) was heated for 3 hr. at 100° with 12 *M* nitric acid, the product was an acid, the composition of which suggested that nitration as well as oxidation had occurred. Decarboxylation of the acid gave the known 2-(4-nitrobenzoyl)pyridine (VIII) and established the structure of the acid as V.

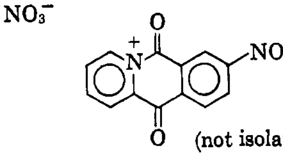


I, R = R' = H
III, R = CH_3; R' = H
IV, R = H; R' = CH_3

V, R = R' = H
VI, R = CH_3; R' = H
VII, R = H; R' = CH_3

VIII, R = H
IX, R = CH_3

The oxidation may be considered to be similar to that of the attack of nitric acid on anthracene to yield anthraquinone. The intermediate acylammonium salt (X) would be expected to hydrolyze rapidly to the keto acid V. The same nitroketo acid was obtained (25% yield) with even quite dilute (3 *M*) nitric acid. It is not certain whether nitration precedes oxidation, but it is perhaps significant that nitration has occurred in what corresponds to position 8, theoretically one of the least electron-deficient of the acridizinium nucleus.[6]



(not isolated)

X

The oxidation of the 7-methyl- (III) and 9-methylacridizinium (IV) salts[3] likewise afforded nitroketo acids which by analogy were assigned structures VI and VII. That the assumption concerning the location of the nitro group was correct was shown by the fact that both acids afforded the same nitro ketone (IX) on decarboxylation.

This demonstration of the vulnerability of ring b to nitric acid oxidation made it of interest to try similar experiments in which ring c would be highly activated, and, hence, more likely to be oxidized. When 7,10-dimethoxyacridizinium picrate[7] (XI) was oxidized with 8 *M* nitric acid a very insoluble product was formed. This new substance had a composition indicating the loss of four carbon atoms, and a neutral equivalent cor-

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[1] For the preceding communication of this series, see C. K. Bradsher and J. H. Jones, *J. Am. Chem. Soc.*, **81**, 1938 (1959).

[2] This research was supported by a research grant NSF-G19901 of the National Science Foundation.

[3] C. K. Bradsher and L. E. Beavers, *Chem. Ind.* (London), 1394 (1954); C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **77**, 4812 (1955).

[4] L. A. Paquette, *Chem. Ind.* (London), 1292 (1962).

[5] J. H. Saylor and J. G. Frost, unpublished spectrographic data.

[6] Position 8 is remote from the charged nitrogen atom and, unlike neighboring positions 7 and 9, cannot (by charge delocalization) become the site of a positive charge.

[7] C. K. Bradsher and M. W. Barker, *J. Org. Chem.*, **29**, 61 (1964).