

The product can be further purified either by sublimation at 80–85° (ca. 10^{-3} mm) or by recrystallization from ethyl ether to yield yellow crystals of 1, mp 162–163°. A proton nmr spectrum of 1 in CDCl_3 solution exhibits a single resonance at τ 4.68.

In similar experiments in which the reflux period was 9, 48, 82, and 162 hr, the yields of 1 were 8, 62, 82, and 94%, respectively. In a reaction in which equimolar amounts of hexacarbonylchromium and 2-picoline were heated to reflux in excess benzene for 68 hr, the yield of 1 was only 6%.

Reaction of Benzene, 2-Picoline, and Hexacarbonylmolybdenum. A mixture of 10.56 g (0.04 mol) of hexacarbonylmolybdenum, 100 ml of benzene, and 100 ml of 2-picoline was heated to reflux under nitrogen as described above. When heating was commenced, gas evolution was noted and the reaction mixture turned yellow. After a reflux period of 96 hr, the solution was dark orange and a yellow precipitate had formed. The solid was filtered under nitrogen, washed twice with benzene, and dried overnight at aspirator pressure. There remained 12.2 g (77%) of a powdery yellow solid, tentatively identified as bis(2-picoline)tetracarbonylmolybdenum (5), mp ca. 175° dec (N_2) with darkening from ca. 150°.

Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{MoN}_2\text{O}_4$: C, 48.73; H, 3.58; N, 7.10. Found: C, 48.44; H, 3.58; N, 7.35.

An attempted sublimation of 5 *in vacuo* was not successful. No sublimate could be detected at temperatures up to 80°, and heating above this temperature resulted in considerable darkening of the solid, a metallic mirror, and hexacarbonylmolybdenum being formed.

Reaction of Benzene, 2-Picoline, and Hexacarbonyltungsten. A mixture of 7.04 g (0.02 mol) of hexacarbonyltungsten, 100 ml of benzene, and 100 ml of 2-picoline was heated to reflux under nitrogen as described above. After 70 hr, the dark red reaction mixture containing a brown solid was allowed to cool to room temperature and the solvents were removed using a rotary evaporator and a water bath maintained at 50–60°. The residue which remained was transferred to a vacuum sublimator. Sublimation at 80–100° (10^{-3} mm) over a 24-hr period produced 1.00 g (12%) of yellow crystals of (2-picoline)pentacarbonyltungsten (6), mp 85–86° (N_2).

Anal. Calcd for $\text{C}_{11}\text{H}_7\text{NO}_5\text{W}$: C, 31.68; H, 1.69; N, 3.36; W, 44.09; mol wt, 417. Found: C, 31.45; H, 1.42; N, 2.94; W, 44.4; mol wt, 415, 420 (osmometric in benzene).

Nmr (CDCl_3) τ 7.20 (s, CH_3), 2.67, 2.13, 1.13 (m, ring protons); nmr (CDCl_3) for 2-picoline τ 7.45 (s, CH_3), 2.93, 2.43, 1.47 (m, ring protons).

An ir spectrum of the material collected in the trap during the sublimation indicated it to be essentially pure hexacarbonyltungsten. The black residue which remained after sublimation of 6 is pyrophoric, and should be decomposed under nitrogen.

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Registry No.—1, 12082-08-5; 5, 51270-99-6; 6, 39210-59-8; benzene, 71-43-2; 2-picoline, 109-06-8; hexacarbonylchromium, 13007-92-6; hexacarbonylmolybdenum, 13939-06-5; hexacarbonyltungsten, 14040-11-0.

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- A very small amount of hexacarbonylchromium occasionally sublimes into the condenser during the early stages of the reaction. This can be scraped back into the reaction vessel, if desired.

Kinetics of Oxidation of Aldo Sugars by Cerium(IV) in Aqueous Sulfuric Acid

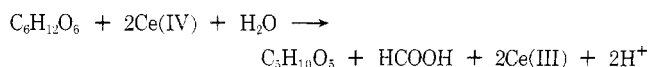
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The metal ion oxidation of aldo sugars, in acid medium, seems to have received very little attention. The oxidation of glucose by chromium(VI)¹ and that of arabinose² by cerium(IV) in sulfate medium are reported, however, in the literature. Since this work had been completed there has appeared a report on the oxidation of glucose by cerium(IV) in perchloric acid.³ Nevertheless, the present study adds a few significant new results besides confirming most of the results of Pottenger and Johnson.³ The inherent interest in starting this work had been to examine whether the oxidation of these sugars involved exclusively its pyranose structure or also the open-chain structure having a free aldehyde group, because it is well known that glucose reduces Fehling's solution and adds hydrocyanic acid but in contrast to the ordinary aldehydes it does not give the Schiff's test.

Products and Stoichiometry. The qualitative analysis of the oxidized reaction mixtures, having excess concentrations of either glucose or mannose, indicated the absence of formaldehyde^{4a} and gluconic and glucuronic acid^{4b} and the presence of arabinose and formic acid.^{4c} The quantitative estimation of formic acid indicated that 2 equiv of cerium(IV) are used per mole of formic acid formed. The stoichiometric equation of the reaction could be written as shown below.



Experimental Section

The method used to follow the progress of the reaction has been described elsewhere.⁵ The reaction has been studied at 25° and it has been followed for more than 2 half-lives. The kinetic runs have been carried out in the presence of a large excess of sugar so that the rate of reduction of cerium(IV) is controlled by the substrate concentration only and not by the concentration of the product which accumulates in the reaction mixture. The first-order rate constant k_1 , with respect to cerium(IV), was calculated as has been described earlier.⁵

Kinetic Results. The rate constant k_1 increased proportionately with the increase in substrate concentration. The plots of rate constant k_1 vs. [substrate] were linear and passed through the origin. The second-order rate constant k_2 (Table I) for each substrate was obtained from the slopes of these plots.

The other results, based on the kinetic data (available as supplementary material, see paragraph at end of paper), are only briefly summarized here. The rate constant k_1 decreased with the increase in (a) bisulfate ion concentration at constant hydrogen ion; (b) ionic strength, which was adjusted with sodium perchlorate; (c) deuterium oxide concentration (v/v consideration). How-

Table I
Second-Order Rate Constant k_2 ($= k_1/[\text{substrate}]$)
for the Oxidation of Various Aldo Sugars and
Other Related Compounds^a

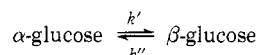
Substrate	$10^3 k_2$, l. mol ⁻¹ sec ⁻¹
D(+)-Galactose	6.0 ± 0.1
D(+)-Mannose	3.0 ± 0.1
D(+)-Glucose	2.4 ± 0.1
L(+)-Rhamnose	2.9 ± 0.1
α-Methyl-(+)-D(+)-glucoside	0.017 ± 0.002
2-Deoxy-D(+)-glucose	1.5 ± 0.1
L(+)-Arabinose	6.5 ± 0.1
D(+)-Xylose	3.5 ± 0.1

^a [cerium(IV)] = 0.0025 M; [sulfuric acid] = 0.5 M; temperature = 25°.

ever, the rate constant k_1 increased with the increase in hydrogen ion at constant bisulfate ion concentration.

Comparative Rates of Oxidation and Mutarotation. Pottenger and Johnson³ have not made any attempt to correlate the rate of mutarotation with the rate of oxidation of glucose, the model compound for the oxidation of other isomeric sugars. This information is needed to show that the oxidation rates of α and β isomers could not be separated by using the pure samples of these anomers.

The rate of mutarotation, k_m , of glucose at 25° has been calculated by an equation given in the literature.⁶ Its value in 0.5 M sulfuric acid is 0.1386 min⁻¹. The value of k' , in the equilibrium given below, is found to be 0.0885 min⁻¹ when the values of the



equilibrium constant K' and k_m are taken as 1.77 and 0.1386 min⁻¹, respectively.

The first-order rate constant k_g , with respect to glucose, calculated by eq i, is 0.00018 min⁻¹, where k_1 is the first-order rate constant with respect to cerium(IV) and n is the number of cerium(IV) equivalents (2) that are used per glucose molecule.

$$k_g = \frac{k_1[\text{Ce(IV)}]}{n[\text{glucose}]} \quad (\text{i})$$

The respective values of k_g and k' indicate that the rate of transformation of α -glucose into β -glucose is many times greater than the rate of glucose oxidation with respect to glucose. The observed rate is therefore the sum total contribution of each of the α and β forms in addition to the possible contribution from the free aldehyde form which is the intermediate form in the dynamic equilibrium between the two anomers. Thus the experimental separation of the oxidation rates of α and β anomers by using the pure samples of these anomers is not possible.

Solvent Isotope Effect. The retardation of the rate in deuterium oxide should not be explained in terms of mutarotation; the mutarotation of glucose proceeds more slowly in deuterium oxide⁷ than in water, because it has been shown that the mutarotation equilibrium is established at a much faster rate than the rate of oxidation of glucose.

The solvent isotope effect, $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.5$ and 1.9 for glucose and galactose, respectively, compares well with the value 1.7 observed in cerium(IV) oxidation of formaldehyde in sulfuric acid.⁵ The magnitude of the solvent isotope effect is too small to allow any exclusive conclusion in favor of O-H fission in the rate-limiting step. However, it does indicate that some O-H bond is being affected in the rate-limiting step and as such it substantiates to some degree the assumption of O-H fission by Pottenger and Johnson³ in cerium(IV) oxidation of glucose in perchlorate medium. It is just possible that both O-H and C-H bonds might be breaking by two competitive pathways in the rate-limiting step.⁸

Mechanism and Discussion

Although a similar system is involved in our study and that reported earlier by Pottenger and Johnson,³ there are a few striking differences in the two results which need mention.

Pottenger and Johnson have reported a fractional order in glucose which helped them to substantiate the formation of cerium(IV)-glucose complex on the basis of kinetic

data. However, our results have indicated a strict first-order dependence on glucose, thus preventing us from substantiating any such complex formation on a similar basis. This behavior is not unexpected because in our system the substrate has to compete against the stronger nucleophilic sulfate ion as a ligand for the cerium(IV) ion.

However, the possibility of the formation of an intermediate complex is indicated by a change in the color of cerium(IV) solution on adding the substrate solution. Such a change in the color of cerium(IV) solution has been previously considered^{9,10} to indicate the formation of a complex of transient nature.

Another striking difference is found in the comparative rates of oxidation of glucose and 2-deoxyglucose. The oxidation of glucose is some 1.6 times faster than that of 2-deoxyglucose in our case as compared to some 29 times in perchloric acid.³ This could only be rationalized by assuming a cyclic transition state involving hydrogen bonding as has been suggested by Young and Trahanovsky¹¹ involving alcohols, glycols, and cerium(IV).

The hydrogen bonding between C-2 hydrogen and hydroxyl group of CeOH³⁺, the reactive cerium(IV) species in perchloric acid,^{12a} is stronger than the hydrogen bonding between C-2 hydrogen and sulfate ion, the ligand attached to cerium(IV) species in sulfuric acid.^{12b} The relative stability of the two cyclic cerium(IV)-2-deoxyglucose complexes explains the more pronounced retardation in the rate of oxidation of 2-deoxyglucose in perchloric acid than in sulfuric acid.

The assumption of the formation of a cyclic complex also explains successfully the changes in the rates of oxidation of glucose, α -methylglucoside, and 2-deoxyglucose. These relative rates of oxidation of glucose and two of its compounds differing in structure by a replaced hydroxyl group at C-1 and C-2, respectively, together with the proven presence of formate ester³ as the intermediate product, indicate that the hydroxyl groups at C-1 and C-2 are involved in the redox reaction.

It is interesting to note that the oxidation rates of various sugars studied are of the same order. This means that these sugars are oxidized by a common mechanism, *i.e.*, cerium(IV) forms a cyclic chelate with C-1 and C-2 hydroxyl groups of the sugar prior to its rate-limiting disproportionation to a free radical. The formation of the free radical is substantiated by the induced polymerization of acrylonitrile.

Although the differences between the individual rates of oxidation of sugars are small, they are definitely there, as evinced by our own results and those of Pottenger and Johnson.³ We are of the opinion that these differences are not due to structural variations in the pyranose structure of the sugars, for almost similar percentages of the α and β forms and an identical orientation of hydrogen atoms at C-1 and C-2 atoms¹³ (Table II), the seat of the reaction, should have not only produced oxidation rates of the same order but also of the same magnitude.

However, in terms of magnitude the experimental results are not in agreement with this expectation. It was, therefore, considered probable that these small differences could be due to the very small but differing concentrations of the free aldehyde sugars, present as intermediates in the dynamic equilibrium of mutarotation in aqueous solution.¹⁴ As a measure of crude approximation this probability could be substantiated if there is a linear correlation between the observed rate and the concentration of the free aldehyde sugar present in the reaction system. Such a correlation is shown in Figure 1, and this could not be termed as fortuitous because a similar correlation has been also established¹⁵ in the oxidation of these sugars by vanadium(V).

Table II
Orientation of the Hydrogen Atom at C-1 and C-2 in the
 α - and β -Pyranose Form and the Percentage of the α and β Forms^a

Sugar	α -Pyranose form			β -Pyranose form		
	Orientation of proton at		%	Orientation of proton at		%
C-1	C-2	C-1		C-2		
D(+)-Glucose	Equatorial	Axial	36	Axial	Axial	64
D(+)-Galactose	Equatorial	Axial	35	Axial	Axial	65
D(+)-Mannose	Equatorial	Equatorial	64	Axial	Equatorial	36
D(+)-Xylose	Equatorial	Axial	29	Axial	Axial	71
L(+)-Arabinose	Axial	Axial	63	Equatorial	Axial	37

^a The α and β anomers of the sugar would form either cis or trans transient complexes depending whether the two hydroxyl groups at C-1 and C-2 are in the cis or trans position.

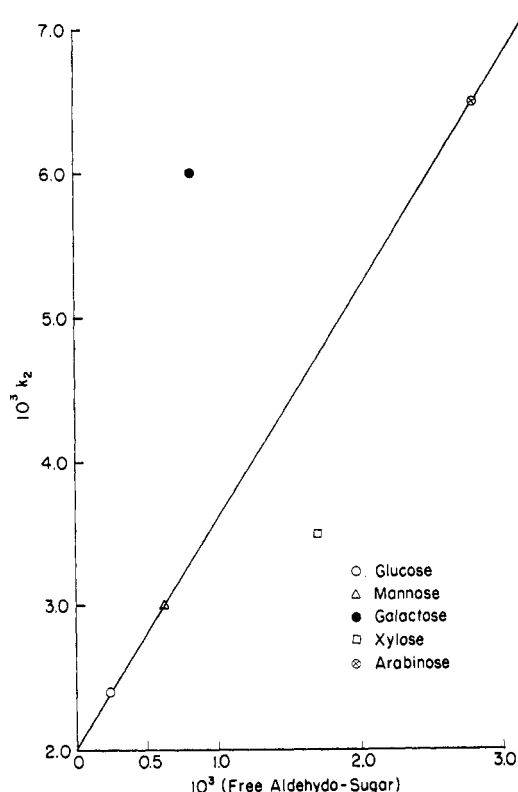
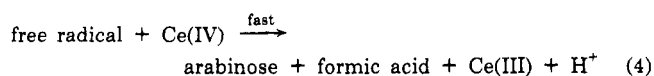
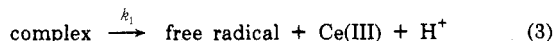
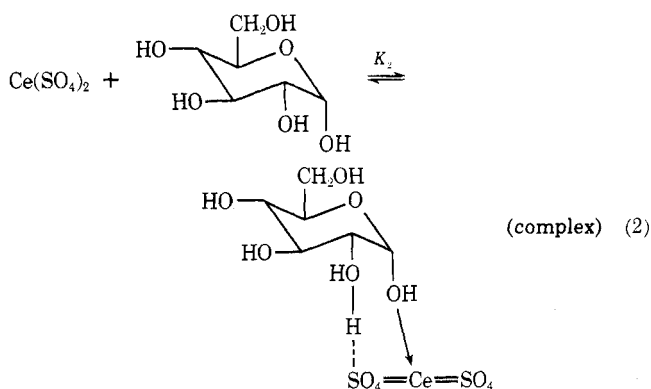


Figure 1. The linear plot of the rate constant k_2 vs. the respective concentrations of the free aldehyde form of the sugar present in aqueous solution.

Mechanism. The reactions 1-4 are supposed to be the possible steps in the mechanism of the oxidation of the



also sugars. The rate law 5 is derived by considering these reactions, where K_1 has a value of 20 at 25° as reported by Hardwick and Robertson.^{12b} Arabinose is thought to be formed through the intermediate formation of formyl ester. The formyl ester is supposed to hydrolyze to arabinose in a fast step³ and is supposed to be an intermediate in periodate and lead tetraacetate oxidations of glucose.¹⁶ The rate of disappearance of cerium(IV) at any time could be expressed by eq 5.

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{2k_1K_2[\text{Ce(IV)}][\text{sugar}]}{1 + K_1[\text{HSO}_4^-][\text{H}^+]^{-1} + K_2[\text{sugar}]} \quad (5)$$

Since the reaction has a strict first-order dependence in [sugar], it is apparent that $K_1[\text{HSO}_4^-][\text{H}^+]^{-1} \gg (1 + K_2[\text{sugar}])$, which is consistent with the high value of K_1 . The rate law (eq 5) is thus reduced to the final rate law (eq 6).

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{2k_1K_2[\text{Ce(IV)}][\text{sugar}]}{K_1[\text{HSO}_4^-]} [\text{H}^+] \quad (6)$$

The rate law eq 6 indicates that the plot of k_1 , the first-order rate constant, against [sugar] or against $[\text{H}^+]$ or $[\text{HSO}_4^-]^{-1}$ at constant concentration of the other should be linear and pass through the origin. (These figures are available as supplementary material; see paragraph at end of paper.)

The decrease in the rate with the increase in ionic strength might be considered to be inconsistent with the proposed mechanism involving neutral molecules as the reactants. In the first place the concentrations used to study the effect of ionic strength were rather high for the Brønsted relation to be strictly applicable. However, the negative salt effect could still be explained by considering the equilibrium (eq 1) governing the formation of the proposed reactive cerium(IV) species.

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Registry No.—Cerium, 7440-45-1; D(+)-galactose, 59-23-4; D(+)-mannose, 3458-28-4; D(+)-glucose, 50-99-7; L(+)-rhamnose, 3615-41-6; α -methyl-(+)-D(+)-glucoside, 97-30-3; 2-deoxy-D(+)-glucose, 154-17-6; L(+)-arabinose, 5328-37-0; D(+)-xylose, 58-86-6.

Supplementary Material Available. The kinetic data involving the variation of bisulfate ion, hydrogen ion (at the constant concentration of each other), and v/v variation in deuterium oxide concentration together with the figures consistent with the rate law (eq 6) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-1788.

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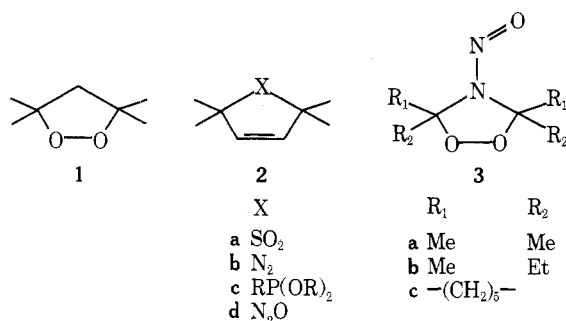
Synthesis and Characterization of *N*-Nitroso-4-aza-1,2-dioxolanes, and Their Thermolysis and Photolysis

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The introduction of the peroxide bond into a five-membered ring, e.g., the 1,2-dioxolane **1**, promotes ring fragmentation by homolysis of the peroxide bond either by thermal¹ or photochemical² activation. Alternatively, scission of the five-membered ring **2** can be induced either by thermal or photochemical extrusion of a small stable fragment, e.g., sulfur dioxide,³ nitrogen,⁴ phosphonites,⁵ and nitrous oxide.³ Usually a double bond is essential to effect such ring fragmentations. Since the thermal stability of the peroxide linkage in **1** is dramatically enhanced as compared to that of *tert*-butyl peroxide (ca. 10⁴ factor),⁶ we decided to investigate the thermal and photochemical behavior of bifunctional peroxides such as **3**. The extru-



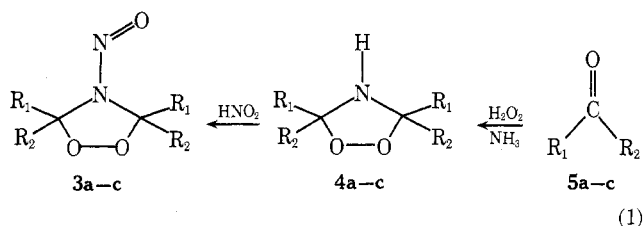
sion reaction could aid peroxide bond homolysis, or vice versa, by providing for more selective conditions of ring fragmentation through such potential symbiosis. Therefore, the hitherto unknown *N*-nitroso-4-aza-1,2-dioxolanes **3a-c** have been prepared and characterized and their thermolysis and photolysis investigated.

The derivatives **3a-c** of these novel bifunctional peroxides are readily prepared in good yields (50–80%) by nitrosation of the respective 4-aza-1,2-dioxolanes **4a-c**. The latter are available from the ketones **5a-c** (eq 1).⁷ The

Table I
Nmr Spectra of 4-Aza-1,2-dioxolanes and *N*-Nitroso-4-aza-1,2-dioxolanes^{a,b}

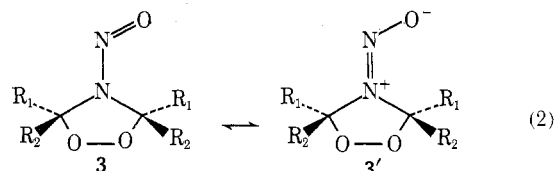
	R ₁	R ₂	3		Δδ	4	Multiplicity
			syn	anti			
a	Me	Me	1.58	1.82	0.24	1.17	Singlet
b	Me	Et	1.50	1.74	0.24	1.20	Singlet
			0.92	1.03	0.11	0.83	Triplet
c	-(CH ₂) ₅ -		2.10	2.10	0.00	1.50	Quartet
			1.62	1.70	0.08	1.49	Multiplet
			2.06	2.10	0.04		Multiplet

^a Values given in δ (parts per million). ^b Syn is the isomer having R₂ and R₁ cis to the oxygen.



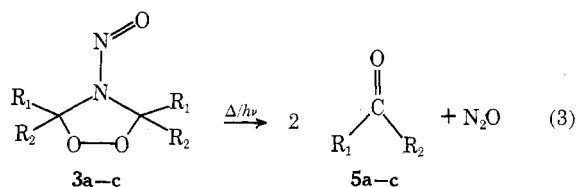
peroxides **3a-c** gave a positive Liebermann test for the nitroso group, which was also identified by infrared analysis in terms of its 6.8-, 7.0-, and 7.8-μ bands, characteristic of dialkyl *N*-nitrosamines.⁸ The assigned structures were further substantiated by elemental analysis and mass spectra. Molecular ions at *m/e* 160, 174, and 240 for **3a-c**, respectively, were obtained in addition to NO, NO₂, O₂, and the corresponding ketone fragments.

Most reassuring were the nuclear magnetic resonance data for **3a-c** (Table I). The spectrum of compound **3a**, for example, indicated two different types of methyl groups present in equal proportion. These results are best explained in terms of the respective syn and anti isomers **3'** (eq 2), since such isomerism is well documented for *N*-



nitrosamines,⁹ and attributed to significant dipolar contributions to the *N*-nitroso group, the barrier for syn-anti interconversion being 23 kcal/mol.^{9c} In the case of **3b**, the present data do not distinguish between the cis and trans arrangement of the ethyl and methyl groups with respect to the ring. A nuclear magnetic resonance spectrum of **3a** taken at 100° was exactly equal to that taken at 35°.

The products of the thermolysis of **3a-c** at 110–120° (25–30 hr) in carbon tetrachloride were characterized as the respective ketones **5** and nitrous oxide by means of infrared and gas-liquid partition chromatography. Comparison of infrared and glpc data with those of authentic materials afforded identical spectra (eq 3). The quantitative



results established by infrared analysis are summarized in Table II. Thus for **3a** and **3b** the formation of ketone was essentially quantitative, while for **3c** a fraction of the product was an unidentified high molecular weight residue. Similarly, the photolysis of **3** at 300 nm (2–6 hr) in