the yields of the other products.

The pathway shown in Sheme I seems to account for the results of these experiments.

Use in Synthesis

The procedure outlined in this paper provides a useful one-step method for oxidation of meta-substituted toluenes. Thus, **1e** was oxidized to a combined yield of the benzaldehyde **2e** and the benzyl ester **4e** of 43% when propionic acid was used as solvent. Addition of anisole to the reaction can also suppress the formation of ring-brominated byproducts in AcOH solution. Use of KMnO$_4$ obviates the need for preparation of Mn^{III} salts as well as reducing the amount of manganese required.

Experimental Section

Microanalyses were performed by the CNRS. The UV spectra were recorded on a Perkin-Elmer 137UV, IR spectra on a Beckman IR 4210, ^{1}H NMR spectra on an Hitachi Perkin-Elmer 24-B, and ^{13}C NMR spectra on a Brucker WP 60 with shifts given in δ and Me$_4$Si used as a reference. Mass spectra were recorded on a Girdel VPC-coupled quadrupole Riber Mag spectrometer. VPC analyses were performed on a Girdel 30 instrument using glass columns containing 5% OV$_1$ (silicone rubber) on Chromosorb W (Interchim supplier).

Manganic acetate and propionate were prepared according to the literature.[14]

3-(Phenoxy-d_5)toluene was prepared by Ullman reaction of bromobenzene-d_5 with *m*-cresol and was converted to **2-bromo-5-(phenoxy-d_5)toluene** by bromination with CuBr$_2$ in AcOH following the general oxidation procedure.

General Oxidation Procedure. A mixture of 0.1 mol of **1a–f**, 0.2 mol of the halide, 90 mL of the carboxylic acid, and 10 mL of the corresponding acid anhydride was heated to reflux temperature. KMnO$_4$ (10 g, 0.063 mol) was then added in 1-g portions, the color being allowed to disappear before each new addition. The reaction mixture was cooled and poured into 100 mL of water, acidified wit HCl, and extracted continuously for 16 h with ether. The solvents were evaporated, and the residue was distilled in one fraction. Yields were determined by CPV analysis using authentic samples as internal standards. Products were isolated by fractional distillation.

5-Subtituted 2-Bromotoluenes (3). These compounds were prepared by a modification of the preceding procedure with AcOH as the solvent and 0.065 mol of CuBr$_2$ or 0.075 mol of MnBr$_2$ as the halide.

Product Data. The reaction products were identified by mass spectra which were compared to the spectra of authentic samples[15] when possible. Data are reported below for compounds (**3d**, **3e**, and **4e** for R = C$_2$H$_5$ or C$_3$H$_7$) which were not found in the literature.

2-Bromo-5-ethoxytoluene (3d): bp 129 °C (10 mm); n_D^{20} 1.5461; ^{1}H NMR δ 1.25 (t, 3 H), 2.20 (s, 3 H), 3.76 (q, 2 H), 6.10–7.30, (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 138.8 (C^1), 115.3 (C^2), 132.9 (C^3), 113.6 (C^4), 158.4 (C^5), 117.3 (C^6), 23.0, 14.8, 63.5 (values in agreement with those calculated by using increments[16]); mass spectrum, *m/e* (relative intensity) 216 (75), 214 (74), 188 (100), 186 (98), 107 (83), 78 (56), 77 (76). Anal. Calcd for C$_9$H$_{11}$BrO: C, 50.26; H, 5.15; Br, 37.15; 0, 7.44. Found: C, 50.02; H, 5.18; Br, 37.17; 0, 7.43.

2-Bromo-5-phenoxytoluene (3e): bp 114–116 °C (0.15 mm); n_D^{20} 1.6022; ^{1}H NMR (CCl$_4$) δ 2.35 (s, 3 H), 6.40–7.50 (m, 8 H); ^{13}C NMR [on 2-bromo-5-(phenoxy-d_5)toluene in order to check the position of Br on the ring] δ 140.2 (C^1), 119.2 (C^2), 134.1 (C^3), 118.7 (C^4), 157.5 (C^5), 122.1 (C^6) (values in agreement with those calculated using increments[17]); mass spectrum *m/e* (relative intensity), 264 (95), 262 (100), 89 (70), 77 (95), 51 (54). for 2-bromo-5-(phenoxy-d_5)toluene, *m/e* (relative intensity) 269 (96), 267 (100), 94 (30), 93 (37), 90 (29), 89 (56), 82 (62), 78 (35), 77 (25), 54 (42). Anal. Calcd for C$_{13}$H$_{11}$BrO: C, 59.34; H, 4.21; Br, 30.37; O, 6.08. Found: C, 58.72; H, 4.20; Br, 30.49; 0, 6.74.

3-Phenoxybenzyl Propionate and Butyrate (4e). Propionate (4e, R = C$_2$H$_5$): bp 123 °C (0.02 mm); n_D^{20} 1.5463; IR 1735 (C=O), 1180 cm^{-1} (CO); ^{1}H NMR (CCl$_4$) δ 1.08 (t, 3 H), 2.30 (q, 2 H), 4.88 (s, 2 H), 6.60–7.40 (m, 9 H); mass spectrum, *m/e* (relative intensity) 256 (14, 200 (100), 149 (32), 89 (41), 77 (41), 57 (40). Anal. Calcd for C$_{16}$H$_{16}$O$_3$: C, 74.98; H, 6.29; O, 18.73. Found; C, 74.82; H, 6.50; O, 18.98.

Butyrate (4e, R = C$_3$H$_7$): bp 141 °C (0.3 mm); n_D^{20} 1.5439; IR 1735 (C=O), 1175 cm^{-1} (CO); ^{1}H NMR (CCl$_4$) δ 0.89 (t, 3 H), 1.16–1.97 (m, 2 H), 2.20 (t, 2 H), 4.86 (s, 2 H), 6.60–7.40 (m, 9 H); mass spectrum, *m/e* (relative intensity) 270 (10), 200 (100), 183 (18), 89 (27), 77 (31), 71 (21). Anal. Calcd for C$_{17}$H$_{18}$O$_3$: C, 75.53; H, 6.71; O, 17.76. Found; C, 75.57; H, 6.75; O, 17.26.

Solvolysis of 6e. Compound **6e** was prepared by following a reported procedure[3]. A solution of **6e** (20 mmol) in 20 mL of propionic acid and 2 mL of propionic anhydride was heated to reflux, and 6 % of the **6e** was hydrolyzed in 2.5 h. When 60 mmol of NaOAc was added to **6e** AcOH, and Ac$_2$O in the same proportions and under conditions as above, **4e** (85%) was obtained in a few minutes, and NaBr precipitated.

"Trapping" of Br$_2$ with Anisole. A mixture of 20 mmol **1e** and 10 mmol of anisole was oxidized as described in the general procedure (AcOH/Ac$_2$O/KBr) by using 2 g of KMnO$_4$. Analysis of the reaction products gave 59% recovered **1e**, 8% **3e**, and 32% **4e**. 4-Bromoanisole was also formed.

Registry No. 1a, 591-17-3; **1b**, 108-41-8; **1c**, 100-84-5; **1d**, 621-32-9; **1e**, 3586-14-9; **1f**, 122-46-3; **2a**, 3132-99-8; **2b**, 587-04-2; **2c**, 591-31-1; **2d**, 22924-15-8; **2e**, 39515-51-0; **3a**, 615-59-8; **3b**, 14495-51-3; **3c**, 27060-75-9; **3d**, 68155-69-1; **3e**, 77317-53-4; **3f**, 22012-59-5; **4e** (R = C$_2$H$_5$), 78514-43-9; **4e** (R = C$_3$H$_7$), 78514-44-0; **4e** (R = CH$_3$), 50789-44-1; **5e**, 52322-81-3; **6e**, 51632-16-7; KMnO$_4$, 7722-64-7; 2-bromo-5-(phenoxy-d_5)toluene, 78514-45-1.

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(14) a. Chrêtien and G. Varga, *Bull. Soc. Chim. Fr.*, [5] **3**, 2387 (1936).

(15) **2ac, e** and alcohols corresonding to **4a–c,e,f** were obtained from Aldrich Chemical Co. **2d**: C. A. Henrick, U. S. Patent 3 882 157; *Chem. Abstr.*, **83**, 27947 (1975). **3a**: R. Pajeau and J. Lecomte, *Bull. Soc. Chim. Fr.*, [5] **13**, 540 (1946). **3b**: E. D. Bergman and R. Barshai, *J. Am. Chem. Soc.*, 81, 5641 (1959). **3c**: G. I. Feutril and R. N. Mirrington, *Tetrahedron Lett.*, 1327 (1970). **3f**: H. G. Noesler, H. Schnegelberger, andd H. Bellinger, *German (West) Patent* 1 287 257; *Chem. Abstr.*, **70**, 86570 (1969). **4d**: W. J. Koehl, Jr., U. S. Patent 3 649 675; *Chem. Abstr.*, **76**, 126602 (1972).

(16) E. Breitmaier and W. Voelter, "^{13}C NMR Spectroscpy", Verlag Chemie, Weinheim/Bergstr., West Germany, 1974.

(17) P. Lazzeretti and F. Taddei, *Org. Magn. Reson.*, **3**, 283 (1971).

Unusual Photochemical Rearrangement of a Carbonyl Compound

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Received April 14, 1981

As a part of a study of the photochemical oxidation of carbohydrates and nucleosides, we reported several years ago[1] that an effective method for conversion of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) to 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-3-hexulofuranose (**2**) consisted of the synthesis and photolysis of the pyruvate ester **3** (Scheme I). Although compound **2** was obtained in 74% yield from reaction of **1**, irradiation of **3** beyond that required to consume this pyruvate ester (**3**) caused a gradual decrease in the isolated yield of **2**. Recently, we became interested in investigating the photochemical reactivity of **2** to determine whether it was a suitable starting material for synthesis of branched-chain sugars. This study has led to the finding, described below, that **2** experiences exten-

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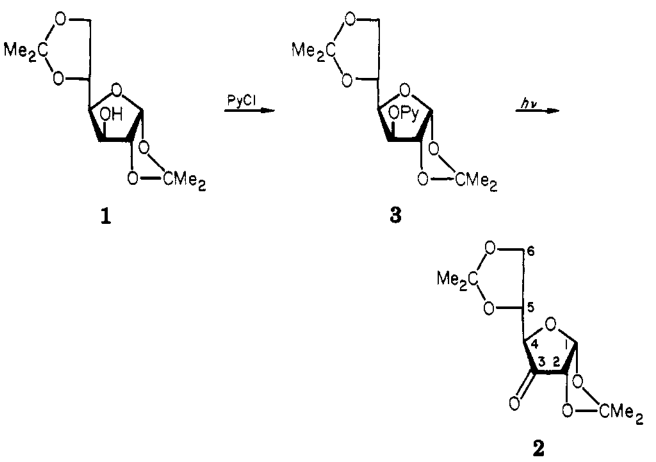
(1) (a) Binkley, R. W. *Carbohydr. Res.* **1976**, *48*, C1. (b) Binkley, R. W. *J. Org. Chem.* **1977**, *42*, 1216.

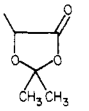
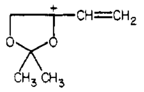
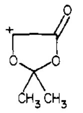
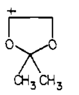
0022-3263/81/1946-4564$01.25/0

Scheme I[a]



[a] Py = $-C(O)C(O)CH_3$.

Table I. Significant Peaks from the CI Mass Spectrum of Compound A (6)

m/e	rel intens	assignment
257	2	P − 1
229	39	P + 1 − H_2CO
201	93	P + 1 − $CH_3C(O)CH_3$
143	50	P + 1 − 
127	47	
115	41	
101	100	

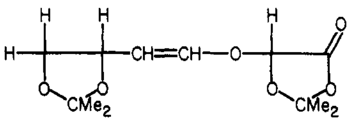
sive molecular rearrangement as a result of photolysis.

Results and Discussion

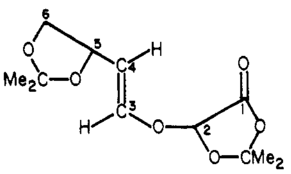
Irradiation of 350 mL of a 0.012 M solution of 2 in benzene for 35 h resulted in considerable darkening of the reaction mixture and complete disappearance of the starting material (2). Chromatography of the reaction mixture on silica gel resulted in isolation of a material (designated compound A) which appeared as a single peak during UV analysis of the column effluent. Considerable dark-colored material remained at the top of the chromatography column even after elution with polar solvent.

The parent peak in the mass spectrum of A (Table I) indicated that it was isomeric with the starting material (2), and the ^{13}C NMR spectrum of A (Table II) confirmed the presence of 12 carbons in the molecule. Six of these carbons were accounted for by the two isopropylidene groups. Among the six remaining carbons, one produced an absorption (δ 166.0) in the region of the spectrum characteristic of an ester or lactone carbonyl carbon. Also, the absorptions at δ 146.3 and 94.4, each derived from a carbon with a single proton attached, corresponded to those expected from enol ether carbons (δ 146.8 and 90.2).[2] Finally, among the three remaining carbons, one (δ 69.7) had two protons bonded to it while the other two (δ 73.9 and 94.4) each had only one. With these structural requirements placed upon A, the basic structure of 4 (stereochemistry undetermined at this point) emerged as the most probably candidate.

The 300-MHz ^1H NMR spectrum of A (Table III) permitted first-order analysis and supported the basic structure 4 for A, and from the $J_{3,4}$ coupling constant (13 Hz) it was determined that the hydrogens attached to the enol ether carbons were trans related[3] (structure 5).



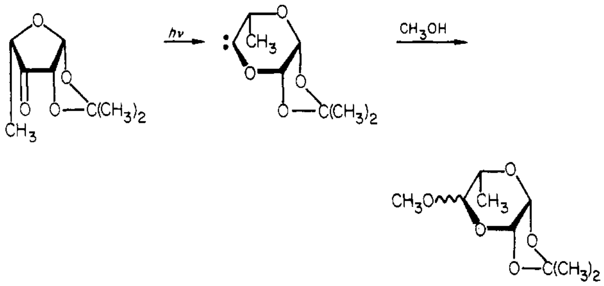
4



5

In order to complete the structural assignment to the photoproduct, it was necessary to assign stereochemistry to C_2 and C_5. Since no bond breaking involving C_5 was required for the photochemical reaction, the absolute configuration at C_5 in the product (A) was assumed to be the same as in the starting material. Assigning the stereochemistry at C_2 in the photoproduct was a different problem because the C_2–C_3 bond definitely was broken during reaction. Due to the lack of formation of a mixture of diastereomers from photolysis of 2, the absolute configuration at C_2 in the photoproduct was either completely inverted or completely retained; however, on the basis of the data available, the stereochemistry at C_2 had to be considered uncertain. Mechanistic considerations (described below) did favor structure 6, that is, retention of configuration.

Two possible mechanisms for the observed rearrangement are shown in Scheme II. The first of these (path A, Scheme II) begins with a photochemical α cleavage of the C_2–C_3 bond to produce the diradical 7, an intermediate which can ring close to the oxacarbene 8. (Formation of oxacarbenes from photolysis of similar carbohydrate derivatives has been proposed (eq 1).[4] Reaction via path A is completed by ring opening and a hydrogen shift to transform 8 into 6. Several aspects of this mechanism deserve further comment.



(1)

First, a photochemical α cleavage in 2 could result in fragmentation of either the C_2–C_3 or C_3–C_4 bond, since the diradicals (7 and 9) produced by these cleavages appear to be comparable in stability. The preferred C_2–C_3 bond fragmentation in excited 2 can be attributed to the relative stabilization of the diradicals 7 and 9 in the early stages of their formation. Stabilization of the radical center developing on C_2 by a nonbonding orbital on the oxygen

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[2] Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectrometry"; Wiley: New York, 1980; p 83.

[3] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1974; pp 216, 218.

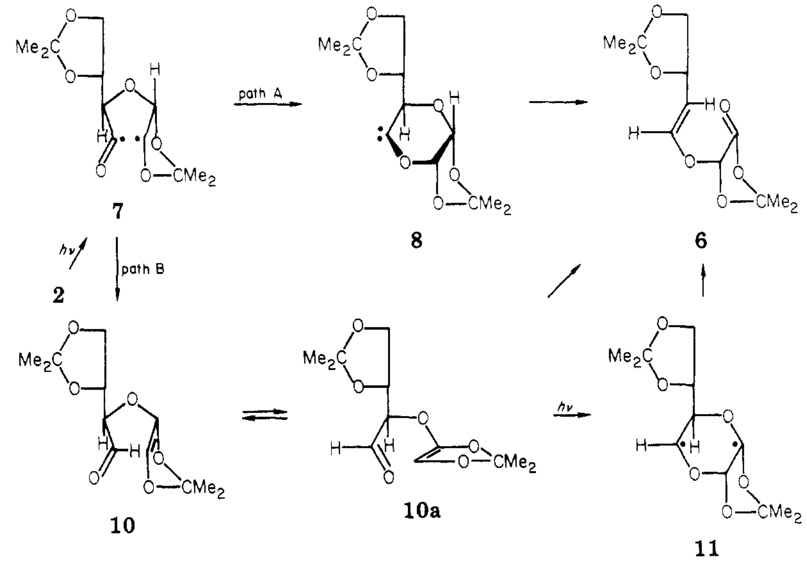
[4] Collins, P. M.; Oparaeche, N. N.; Whitton, B. R. *J. Chem. Soc., Chem. Commun.* 1974, 292.

Table II. ^{13}C NMR Spectral Data for Compounds 2 and A (6)

2			A (6)		
chemical shift^c	mult^{a,b}	assignment	chemical shift^c	mult^{a,b}	assignment
25.4, 26.0, 27.2, 27.6	q	methyl carbon	25.9, 26.7, 27.0, 28.1	q	methyl carbon
103.4	s	ketal carbon	109.2	s	ketal carbon
114.1	s	ketal carbon	113.2	s	ketal carbon
64.4	t	C_6	69.7	t	C_6
76.7	d	C_2, C_4, C_5	73.9	d	C_5
77.4	d		94.4	d	C_4
79.1	d		108.0	d	C_2
103.4	d	C_1	146.3	d	C_3
193.1	s	C_3	166.0	s	C_1

^{a} From gyrogated spectrum. ^{b} s = singlet, d = doublet, t = triplet, and q = quartet. ^{c} Chemical shifts are in parts per million from Me_4Si.

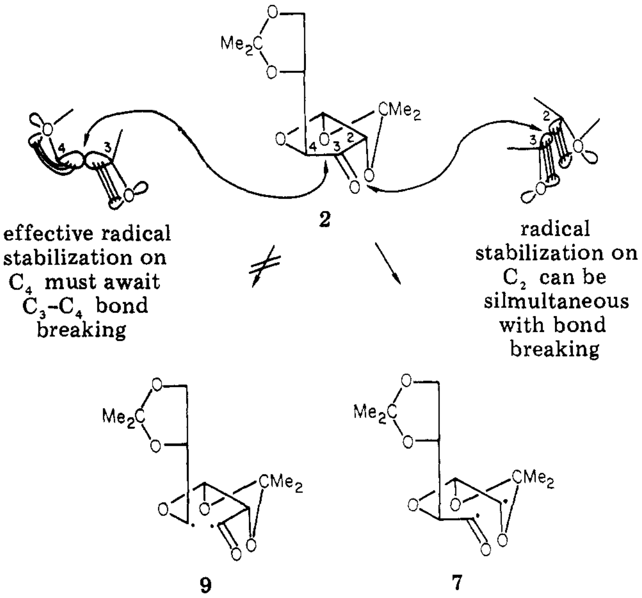
Scheme II



atom attached to C_2 can occur simultaneously with bond breaking since proper orbital alignment exists (Scheme III). In contrast, stabilization of a developing radical center on C_4 by a hybrid orbital on the attached oxygen cannot become significant until sufficient bond breaking has occurred to allow proper orbital alignment; consequently, the C_2–C_3 bond should be broken preferentially.

Formation of oxacarbenes, similar to that proposed in Scheme II, has been reported from photolysis of a number of carbonyl compounds.[5] Typical evidence for the intermediacy of a carbene has been its reaction with the alcohol used as the photolysis solvent. This approach to trapping the proposed oxacarbene 8 had to be used with caution because compound 2 rapidly and quantitatively formed a mixture of stable hemiketals upon dissolving it in methanol. (Heating the hemiketals at 100 °C under vacuum was necessary to regenerate 2). Compound 2 did dissolve in the *tert*-butyl alcohol without appreciable hemiketal formation; however, irradiation in this solvent gave the same photoproduct as obtained from photolysis in benzene. No adducts involving *tert*-butyl alcohol were formed; thus, either the oxacarbene 8 did not form or it rearranged intramolecularly before it could react with the solvent.

Scheme III



A second possible mechanism for reaction of compound 2 involves the intermediate formation of the aldehyde 10 (Scheme II). Compound 10 would result from an intramolecular hydrogen transfer between C_1 and C_3 in the diradical 7. This aldehyde (10) could be transformed into the observed photoproduct either by a thermal reaction or by a second photochemical process. The photochemical process presumably would involve formation of a new diradical (11) capable of rearranging to the photoproduct. The thermal reaction would be a Claisen rearrangement with a quite low energy of activation. Thermal rear-

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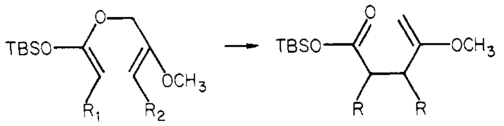
[5] For an excellent review see: Yates, P.; Loutfy, R. O. *Acc. Chem. Res.* 1975, *8*, 209.

Table III. ^{1}H NMR Spectral Data for Compound A (6)

chemical shift[a]	mult[b]	coupling constant, Hz	assignment
1.37, 1.41, 1.63, 1.66	s		CH_3
3.57	t	$J_{6,6'} = J_{5,6} = 8$	$H_{6'}$
4.06	dd	$J_{5,6} = 6$	H_6
4.46	dt	$J_{4,5} = 8$	H_5
5.17	dd	$J_{3,4} = 13$	H_4
5.49	s		H_2
6.54	d		H_3

[a] Chemical shifts are in parts per million from Me_4Si. [b] s = singlet, d = doublet, t = triplet, dd = doublet of doublets, and dt = doublet of triplets.

rangement of **10** would seem to be an unlikely possibility except that some Claisen rearrangements are known to occur readily at room temperature (eq 2).[6]



(2)

$TBS = t\text{-}Bu(CH_3)_2Si$, $R_1 = (CH_2)_2CH_3$, $R_2 = (CH_2)_5CH_3$

The photochemical reaction mixture was analyzed at various stages of conversion to determine if the aldehyde **10** was being formed; however, no indication of this intermediate was obtained. This finding did not exclude the presence of **10** since it is possible that it reacts sufficiently rapidly (either photochemically or thermally) that it fails to accumulate in the reaction mixture.

Although it is not possible to rigorously exclude the intermediacy of the aldehyde **10**, one piece of information, the formation of a single product from photolysis of **2**, does argue against it. The carbonyl oxygen in **10a** should react with C_2 essentially equally well from either side of the unsaturated five-membered ring; that is, **10a** should react to give a mixture of diastereomers. In contrast, the oxacarbene **8** could yield a single product if the diradical **7** cyclized to **8** more rapidly than it assumed a conformation which would allow bonding of the carbonyl oxygen with C_2 in such a manner to invert the C_2 configuration. Thus, the explanation which seems in best accord with all the information is that the configuration at C_2 in the photoproduct **6** is the same as the starting material (**2**) and that the rapidly reacting oxacarbene **8** is an intermediate in the reaction.

Experimental Section

General Procedures. ^{1}H NMR spectra were run on a Varian T-60 spectrometer and a Varian HR-300 spectrometer. ^{13}C NMR spectra were obtained from a Varian XL-100 spectrometer. All NMR spectra were run in deuteriochloroform. IR spectra were measured in carbon tetrachloride on a Beckman Acculab I spectrophotometer. Chemical-ionization mass spectra were obtained from a Finnigan 1015-D mass spectrometer at 150 eV with methane as the reagent gas.

Photolysis of 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-3-hexulofuranose (2). 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-3-hexulofuranose[1] (**2**; 0.99 g, 3.8 mmol) in 350 mL of benzene was purged with nitrogen for 2 h and then irradiated through a Pyrex filter for 35 h with a Hanovia 450-W, medium-pressure, mercury lamp. The solvent was removed under reduced pressure, and the dark-brown residue was chromatographed on a 2.5 × 20 cm column of 200–325-mesh silica gel slurry packed in 1:9 ether–pentane. The effluent from the column was monitored with an ISCO-UA2 ultraviolet analyzer. The only significant amount of material (0.37 g, compound A) eluted from the column came through in the first 400 mL of solvent (1:9 ether–pentane). Increasing the percentage of ether in the solvent and eluting the column with more polar solvents did not result in the isolation of significant amounts of any other material. Compound A was a colorless syrup which was homogeneous by TLC (silica gel) and GC (OV-17) analyses.

The mass, ^{13}C NMR, and ^{1}H NMR spectra are given in Tables I–III, respectively. The IR spectrum of A contained a sharp absorption at 1810 cm^{-1}, characteristic of a lactone, and a doublet at 1675 and 1660 cm^{-1}, characteristic of an enol ether.[7] The use of this spectral information to assign structure **6** to compound A is described in detail in the Results and Discussion.

Photolysis of **2** also was conducted with *tert*-butyl alcohol as the solvent. The result was the same as when benzene was the irradiation solvent.

Acknowledgment. Appreciation is expressed to Professor J. Houser of the University of Akron for his generous assistance in obtaining the 300-MHz ^{1}H NMR spectrum of compound **6**.

Registry No. **1**, 582-52-5; **2**, 2847-00-9; **6**, 78549-99-2.

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[6] Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

[7] Nakanishi, K. "Infrared Absorption Spectroscopy"; Holden-Day: San Francisco, 1962.

Does the 2-Pyridyl Cation Behave Like an Aryne?[1]

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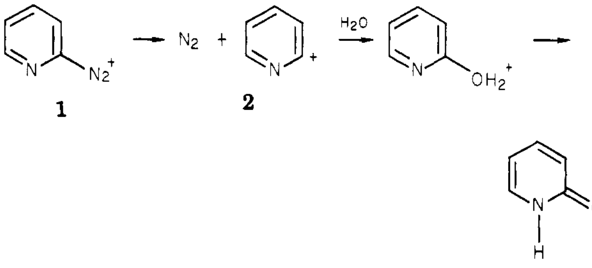
University of California, Santa Cruz, California 95064

Received April 22, 1981

2-Pyridinediazonium ion (**1**) is known to undergo replacement of its diazonio group by nucleophiles with great ease.[3] Although the replacement reaction might be thought to occur by the S_NAr mechanism, with activation by the ring nitrogen atom,[3] both analogy with corresponding reactions in the benzene series[4] and the fact that the diazonio group of 2-pyridinediazonium ion is replaced very rapidly even by such weak nucleophiles as water[5] at pH 2 and fluoride ion in HF solution[6] suggest the S_N1 mechanism of eq 1.



1 2 3

(1)

If this representation is correct, the high rate of the dinitrogen-detachment step is perhaps associated with resonance stabilization, **2a** ↔ **2b**, within the 2-pyridyl

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[1] Research supported in part by the National Science Foundation.

[2] On research leave from Panjab University, Chandigarh, India, 1980–81.

[3] Smith, D. M. In "Rodd's Chemistry of Carbon Compounds", 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1976; Vol. IV, Part F, p 124.

[4] Zollinger, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 141.

[5] Kalatzis, E. *J. Chem. Soc. B* **1967**, 273.

0022-3263/81/1946-4567$01.25/0