(O)Cl$_2$ in H$_2$O/C$_6$H$_6$: mp 164 °C (lit.[51] mp 164-166 °C); too insoluble in CDCl$_3$ to record the ^{31}P NMR signal; ^{31}P NMR (CD$_3$CN, 85% H$_3$PO$_4$) δ = 20.2 ppm, broad (lit.,[52] acetone, 85% H$_3$PO$_4$, δ = 17.5 ± 1). Phenylphosphonic acid phenyl ester, PhO(Ph)P(O)OH, was prepared by reflux of PhO(Ph)P(O)Cl in H$_2$O/C$_6$H$_6$: mp 70 °C (lit.[53] mp 70-72 °C); ^{31}P NMR (CDCl$_3$, 85% H$_3$PO$_4$) δ = 12.3 ppm.

Acetonitrile and CHCl$_3$ (Aldrich, gold label)[3] were passed over neutral alumina and deoxygenated by flushing with dry nitrogen prior to use. The substrates used in the LFP and EPR experiments were purified by standard methods.

LFP Measurements. The experimental procedure has been described.[3]

EPR Spectroscopic Measurements. Degassed samples in 4-mm quartz tubes were placed in the cavity of a Varian E 104 EPR spectrometer and irradiated with the light from a 1-kW Hg/Xe lamp. In a typical spin-trapping experiment, we would employ 1 mL of a ca. 2 × 10^{-2} M solution of 1 in CHCl$_3$ or CH$_3$CN and 0.1 mL (or 0.1 g) of the trapping agent.

Product Studies. The thermal and photochemical decompositions of 4.6 × 10^{-2} M solutions of 1 in CDCl$_3$ and 2.0 × 10^{-3} M solutions of 1 in CD$_3$CN were performed in quartz tubes under nitrogen. The kinetics of the thermal decomposition was followed by monitoring the peroxide's UV absorption at 308 nm. For the photolytic decomposition, a 1-kW Hg/Xe lamp with a 260-nm filter was employed. The ^{31}P NMR spectra were recorded on a Varian XL-200 instrument using 85% phosphoric acid as an external standard. ^{1}H NMR spectra were recorded on a Varian EM-60 spectrometer with TMS as an internal standard.

Acknowledgment. We thank Miss P. Lommes for experimental assistance, H. Bandmann for recording the ^{31}P NMR spectra, Professor T. T. Tidwell (Toronto) for the sample of 1,1-di-*tert*-butylethene, Dr. J. C. Scaiano for a generous allotment of time on his LFP instrument, and an anonymous referee for several very helpful suggestions.

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(51) Lecher, H. Z.; Greenwood, R. A.; Whitehouse, K. C.; Chao, T. H. *J. Am. Chem. Soc.* **1956**, *78*, 5018-5022.

(52) Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 5715-5726.

(53) Burger, A.; Anderson, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 3575-3579.

NMR and Ultraviolet Spectral Characterization of Dihydrobenzene Intermediates in the Displacement of Hydrogen by Intramolecular Nucleophilic Aromatic Photosubstitution

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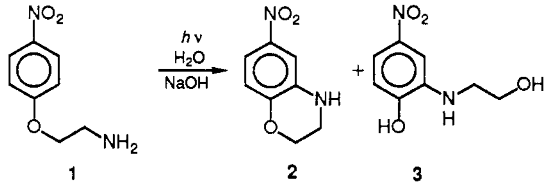
Direct ^{1}H NMR observation of reaction mixtures reveals that photolysis of 4-O$_2$NC$_6$H$_4$OCH$_2$CH$_2$ND$_2$ in NaOD/D$_2$O generates a long-lived, oxygen-stable dihydrobenzene intermediate (**11**) resulting from formal intramolecular addition of an N-D bond across the C$_2$-C$_1$ double bond of the nitrophenyl ether. This species (UV λ_{max} at 321 and 260 nm) is proposed to rearrange thermally by a 1,5-sigmatropic hydrogen shift to a dihydrobenzene (**9**) that adds $^-$OD (to give **16**) and further rearranges to an open-chain structure (**17**). These intermediates exist in equilibrium in solution, are not oxidized by oxygen or 1,4-benzoquinone, but are oxidized thermally by 3,5-dinitrobenzoate ion. The aromatized photoproducts (**2** and **3**) reported earlier (ref 11) are generated from the array of intermediates by thermal reaction with 3,5-dinitrobenzoate ion or by prolonged photolysis.

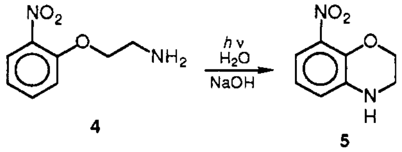
Nucleophilic aromatic photosubstitution involving displacement of hydrogen has been observed in photoreactions of nitrobenzene derivatives with ammonia,[1] cyanide ion,[2] and cyanate ion,[3] imidazoles with cyanide ion,[4] methoxyaromatics with cyanide ion,[5] aromatic hydrocarbons with cyanide ion,[6] and aminoanthraquinones with amines.[7,8] In several of these cases, rather stable UV-absorbing intermediates of unclear structure are observed,[1,2,7] and the presence of oxygen or another oxidant increases the photochemical efficiency or product yield.[1-3,5-8] Lack of knowledge of the structures and stabilities of these intermediates has hindered understanding of which photoproducts are formed and, in flash photolysis studies,[5,9,10] which transient absorptions are to be expected for the several possible σ-complexes.

We reported recently[11] that the intramolecular formal photodisplacements of hydride ion in β-(nitrophenoxy)-ethylamines in aqueous alkali—giving **2** and **3** from the para isomer **1** (eq 1), and **5** from the ortho isomer **4** (eq 2)—were accompanied by long-lived UV absorptions at 323



(1)

1 2 3



(2)

4 5

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(1) van Vliet, A.; Kronenberg, M. E.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1970**, *26*, 1061-67.

(2) Letsinger, R. L.; McCain, J. H. *J. Am. Chem. Soc.* **1966**, *88*, 2884-5; **1969**, *91*, 6425-31.

(3) Hartsuiker, J.; deVries, S.; Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 611-13.

(4) Oldenhof, C.; Cornelisse, J. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 35-38.

(5) Cornelisse, J.; Lodder, G.; Havinga, E. *Rev. Chem. Intermed.* **1979**, *2*, 231-65.

(6) Vink, J. A. J.; Verheydt, P. L.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1972**, *28*, 5081.

(7) Griffiths, J.; Hawkins, C. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2283-87.

(8) (a) Yoshida, K.; Okugawa, T.; Nagamatsu, E.; Yamashita, Y.; Matsuoka, M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 529-33. (b) Yoshida, K.; Hikasa, M.; Ishii, K.; Kadota, H.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 758.

(9) van Eijk, A. M. J.; Huizer, A. H.; Varma, C. A. G. O.; Marquet, J. *J. Am. Chem. Soc.* **1989**, *111*, 88-95.

(10) Wubbels, G. G.; van Zeyl, P. H. M.; Varma, C. A. G. O. *Abstracts of Papers*; 185th National ACS Meeting, Seattle, March 1983; ORGN-50.

(11) Wubbels, G. G.; Halverson, A. M.; Oxman, J. D.; DeBruyn, V. H. *J. Org. Chem.* **1985**, *50*, 4499-4504.

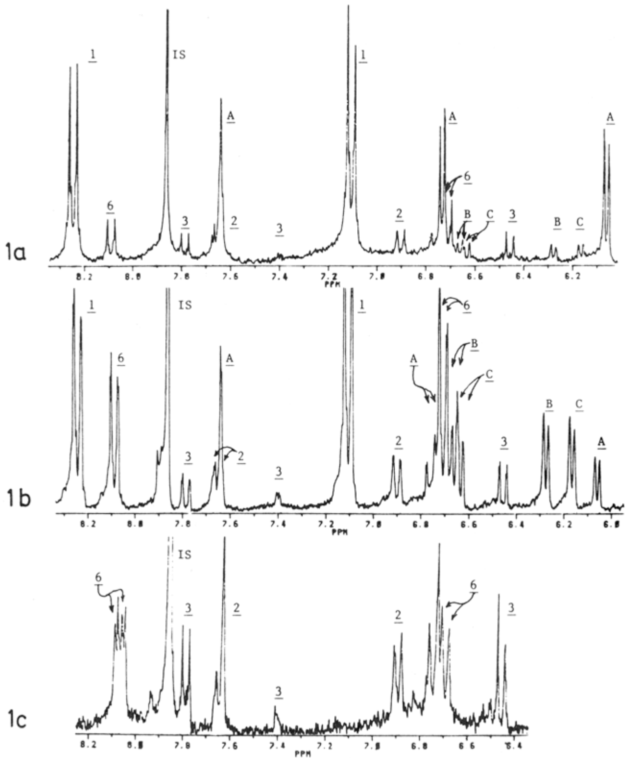

Figure 1. (a) NMR spectrum of **1** (0.015 M) irradiated for 25 min at 0 °C in 0.076 M NaOD/D_2O. (b) Same solution as above after 8 h at 25 °C in the dark. (c) Same solution as above irradiated for 4 days. IS denotes internal standard (terephthalate dianion).

and 287 nm, respectively. We report herein that these absorptions correspond to stable dihydrobenzene intermediates that oxidize to aromatized photoproducts only via a second photoreaction.

Results

Irradiation of **1** (0.015 M) at 350 nm in D_2O containing 0.076 M NaOD at 0 °C (to suppress thermal Smiles rearrangement) for 25 min caused about 75% of **1** to disappear. New NMR signals (see Figure 1a) appeared in the range of δ 6.0–8.3 that we associate with intermediate species A: δ 6.06, doublet (J = 5.8 Hz); δ 6.73, doublet (J = 5.8 Hz); and δ 7.64, singlet. When this solution was kept in the dark for 8 h at room temperature, the signals of A decreased to 20% of their original intensities, and signals for two new intermediate species (B and C) appeared (see Figure 1b): for B, a doublet (J = 6.1 Hz) at δ 6.27 and a doublet (J = 6.1 Hz) at δ 6.66, and for C, a doublet (J = 5.8 Hz) at δ 6.17 and a doublet (J = 5.8 Hz) at δ 6.64. A modest amount (10–20%) of Smiles rearrangement product, 4-$O_2NC_6H_4NHCH_2CH_2OH$ (**6**), is observed in each spectrum (doublets at δ 8.09 and 6.71) that we attribute to thermal reaction.[11] Extensive irradiation (~4 days) was required to convert these intermediates to the isolable photoproducts, **2** and **3**,[11] that are evidenced by their NMR signals in Figure 1c. Also evident in Figure 1c are doublets (δ 8.07 and 6.75) just upfield and downfield, respectively, from the doublets of **6** at δ 8.09 and 6.71. The intensities of these peaks depended on the NaOD concentration and the time of irradiation; we attribute them to the dealkylated Smiles product, 4-nitroaniline. Hydroxide-catalyzed photodealkylation of nitroanilines is a known photoreaction[12] that probably accounts for this product. Flushing the original solution with nitrogen gas had no effect on the photochemistry.

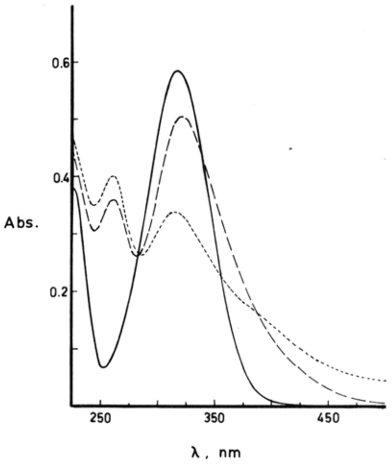

Figure 2. Electronic spectra of **1** (1.0 × 10^{-4} M) in 0.1 M aqueous NaOH (—); of above solution after 6 min of irradiation at 0 °C (– –); of irradiated solution after 23 h in dark at 25 °C (- - -).

A significant deviation from the spectra of authentic **2** and **3** occurred in the intensity of the peak for **3** at δ 7.40, which was only 15–25% of the expected intensity. We attribute the low intensity to exchange of deuterium for hydrogen at that position. No other significant deuterium exchange in the photoproducts was evident from the NMR spectrum, and the exchange in **3** was not dependent upon the extent of its exposure to light.

When the thermally equilbrated mixture of A, B, and C stood at room temperature in the dark for 10 days, no change occurred as indicated by the NMR spectrum. When the mixture (A:B:C = 1:2:2) was heated in the dark at 90 °C for 2.5 h, the proportions of A:B:C changed to 1:1:1, but the mixture returned spontaneously to the original concentrations upon standing at room temperature in the dark for 12 h. Adding 1,4-benzoquinone or oxygen to the mixture had no effect, but adding 3,5-dinitrobenzoic acid caused A, B, and C to disappear slowly in the dark as **2** and **3** appeared.

The rate of the thermal conversion of A to B and C, and the proportions of A to B to C at equilibrium were independent of the NaOD concentration. The chemical shifts of the doublets of B and C varied, however, with the NaOD concentration. The doublet of B at δ 6.21 in 0.02 M NaOD shifted to δ 6.48 in 1 M NaOD while the doublet at δ 6.65 did not shift. The resonances of C at δ 6.22 and 6.63 in 0.02 M NaOD shifted to δ 6.07 and 6.57 in 1 M NaOD. These small shifts were immediately reversed by reduction of the NaOD concentration (achieved by dilution), and the shifts also occurred, but to a smaller extent, when NaCl was added.

The ratio of final products, **2** and **3**, stayed roughly constant at about 1.5:1 (**2**:**3**) as the NaOD concentration was varied. Also, the ratio of **2** to **3** did not differ appreciably for a solution irradiated continuously at 0 °C for 4 days versus a solution irradiated for 30 min at 0 °C, thermally equilibrated (to give A:B:C = 1:2:2), and then irradiated for 4 days.

Photolysis of a dilute solution of **1** (1.0 × 10^{-4} M) in 0.1 M aqueous NaOH in a cuvette for a period (6 min) just sufficient to generate the first intermediate completely showed that it had λ_{max} at 321 (A = 0.50) and 260 nm (A = 0.36) (see Figure 2). We associate these absorptions with intermediate A. This solution, after standing at room temperature in the dark for 23 h, showed maxima at 315 (A = 0.34) and 260 nm (A = 0.40) that did not undergo

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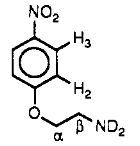
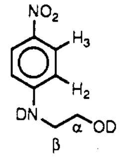
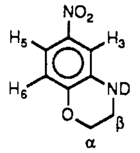
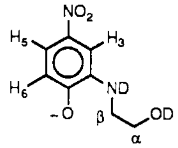
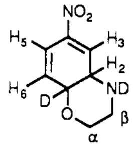
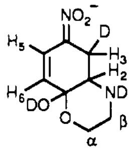
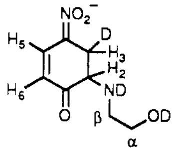
[12] Doepp, D.; Gerding, B. IX IUPAC Symposium on Photochemistry, Pau, France, July 1982; paper no. 52.

Table I. Proton NMR Chemical Shift Assignments of Reactant, Products, and Intermediates[a]

		chemical shifts (δ) in 0.076 M NaOD/D_2O					
symbol	structure	H_2	H_3	H_5	H_6	H_α	H_β
1		7.11	8.25			4.17	3.03
6		6.70	8.09			3.78	3.42
2			7.63	7.65	6.89	4.35	3.39
3			7.40	7.79	6.47	3.84	3.29
A		3.97	7.64	6.73	6.06	3.93	3.55
B		3.63	2.84	6.66	6.27	4.36	3.05 3.20
C		3.79	2.94	6.64	6.17	3.68	2.75 2.88

[a] 4-Nitrophenol, 4-nitroaniline, and 2-aminoethanol under these conditions show resonances at δ 8.06 and 6.52, 8.07 and 6.75, and 3.58 and 2.71, respectively.

further changes. We attribute these absorptions to B and C.

Discussion

In assigning structures to A, B, and C, we have relied on the extensive literature on anionic σ-complexes[13] and nitronate salts.[14] We should note at the outset, however, an important difference between the ground-state chemistry[13] and that reported here, namely, that the first σ-complex produced photochemically forms by nucleophilic attack meta to the nitro group, whereas those formed in the ground state involve attack ortho or para to the nitro group. The former σ-complex, unlike the latter, is not stabilized by delocalization of the negative charge onto the nitro group, and this difference alters the chemistry profoundly.

That the primary photochemical process is indeed nucleophilic attack at C-2 of triplet 1 by the side-chain amino group is indicated by: (1) precedent for efficient formation of the triplet on photoexcitation of a nitrophenyl ether;[15] (2) the regiochemical prediction of the "energy gap law" for related photosubstitutions;[16] (3) the presence of nitrogen covalently bound to C-2 in the isolable photoproducts, 2 and 3;[11] and (4) the near certainty that nucleophilic attack at C-1 would lead efficiently to Smiles rearrangement, an outcome we observe to be minor.

We have assigned structures and chemical shifts to the reactant, products, and intermediates involved as shown in Table I. Assignments for the numbered structures are based on spectra of authentic samples; those for A, B, and C are based on considerations discussed below. Spectra are shown only for the region δ 8.3–6.0, but we also assigned the resonances (not shown) in the region δ 4.4–2.7 as indicated in the table. Because the signals in the latter region are complex and overlapping, the assignments there are less certain than those in the lower field region.

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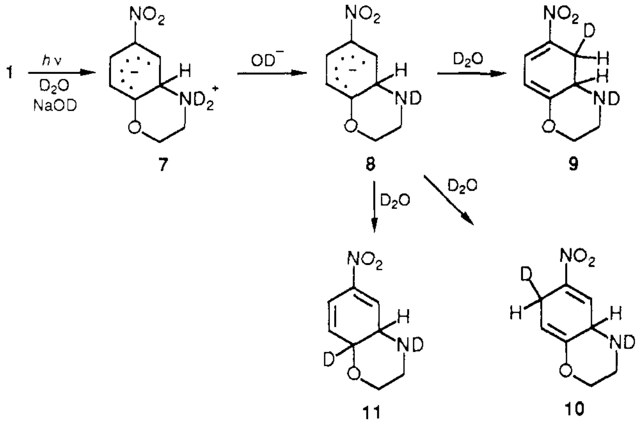
[13] Buncel, E.; Crampton, M. R.; Strauss, M. J.; Terrier, F. *Electron Deficient Aromatic- and Heteroaromatic-Base Interactions*; Elsevier: New York, 1984.

[14] Torssell, K. B. G. *Nitrile Oxides, Nitrones, and Nitronates in Organic Synthesis*; VCH Publishers: New York, 1988.

[15] For a discussion, see: Wubbels, G. G.; Susens, D. P.; Coughlin, E. B. *J. Am. Chem. Soc.* **1988**, *110*, 2538–42.

[16] van Riel, H. C. H. A.; Lodder, G.; Havinga, E. *J. Am. Chem. Soc.* **1981**, *103*, 7257–62.

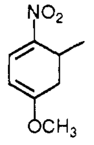
Scheme I



If the first σ-complex is **7**, as shown in Scheme I, we expect it to lose deuterium ion from nitrogen to OD^- at the rate of diffusion[17] to give **8**. Strongly basic **8**, having no adequate nucleofuge, will accept deuterium on carbon from D_2O to give **9**, **10**, or **11**, all of which, given their expected stabilities, are prospects for intermediate A.

It is obvious by inspection that, of these three, only **11** has three vinyl hydrogens as seen in the NMR spectrum of A. The only other prospect for a shift $\geq \delta$ 6 is the allylic hydrogen α to nitrogen, but shifts to similar hydrogens in σ-complexes suggest that its shift would be less than δ 5.5.[18] In fact, we find a likely signal for this proton at δ 3.97.

A close model of **9**, namely **12**, has been isolated and characterized.[19] This substance shows λ_{max} in $CHCl_3$ at 362 nm that is not reconcilable with the observed λ_{max} of A (in H_2O) at 321 nm. Moreover, **12** shows NMR signals ($DCCl_3$) at 7.56 and 5.15 (J = 6.8 Hz) that do not resemble the observed NMR signals of A.



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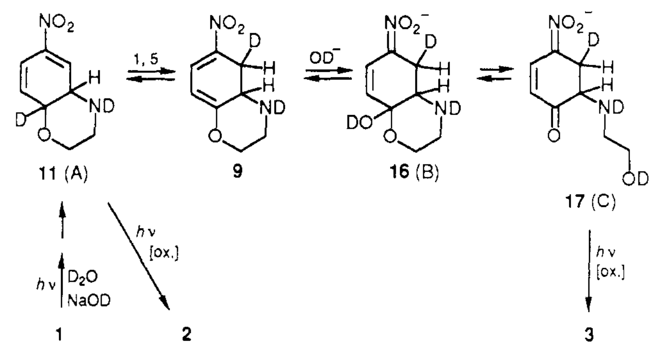
Similarly, **10** is inconsistent with the properties of A. The long-wavelength UV maximum of **10** would be expected at about 258 nm, the maximum for 1-nitrocyclohexene in ethanol–water,[20] but the maximum of A is observed at 321 nm. The NMR spectrum of **10** would show but two signals in the observed region (at ca. δ 7.6 and 5.0), an unacceptable correspondence to the spectrum of A.

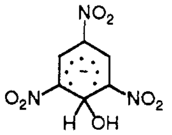
Scheme II



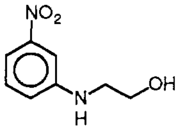
The properties of A correspond well to those expected for **11**. The shift of H-3 at δ 7.64 corresponds to the shifts of analogous protons in the model compounds **12** (δ 7.56), 1-nitro-1,3-butadiene (δ 7.6),[21] and 1-nitropropene (δ 7.00).[22] The expected small couplings of H-3 by H-5 and H-2 are not resolved under our conditions. Protons H-5 and H-6 are coupled (J = 5.8 Hz) to the expected extent,[23] and their observed shifts are reasonable. For example, $O_2NCH_2CH{=}CH_2$ shows the C-2 vinyl proton at δ 6.20 and the C-1 *trans*-vinyl proton at δ 5.58.[22] The ether oxygen of **11**, and its nitro group that is cross-conjugated with the diene, exert a somewhat larger electron withdrawal on the C_5–C_6 vinyl group of **11** than does the nitromethyl substituent on the vinyl moiety of $O_2NCH_2CH{=}CH_2$, and accordingly, the vinyl protons are shifted further downfield (δ 6.73 and 6.06 for H-5 and H-6). The UV absorption of A at 260 nm can be attributed to the 1-nitrocyclohexene chromophore (λ_{max} 258 nm)[20] of cross-conjugated **11**. We attribute the long-wavelength absorption of A at 321 nm to a 1,3-cyclohexadiene absorption (264 nm) that is shifted bathochromically by the nitro auxochrome.

We notice that the site of protonation of the initial σ-complex **8** cannot be predicted by preference for the thermodynamically most stable adduct, which would be **9**,[24] nor by the theoretically justified prediction that protonation will occur across the ring from the initially quaternized carbon,[24] which would give **10**.

It is surprising that **11** does not exist in the alkaline solution as its conjugate base, since H-2 appears likely to ionize with a pK_a near 11 by the model of 1-nitrocyclohexene.[20] The evidence that it does not ionize, however, is persuasive. Anionic σ-complexes with leaving groups as good as OR^- located on a tetrahedral carbon atom ortho or para to a nitro group are quite labile. For example, expulsion of OH^- from **13** in water occurs with k = 10 s^{-1}.[25] Applying the estimate[26] that removing one conjugating ortho nitro group accelerates the expulsion of OR^- by 4 × 10^4, the loss of two nitro groups would give the putative anion of **11** a rate constant for ring opening of around 10^{10} s^{-1}. In fact, not even minor amounts of the ring-opened product, **14**, can be detected. The best explanation evident to us for the absence of ionization of **11** is that the bicyclic structure may position H-2 in a geometry unfavorable for delocalization of the carbanion into the nitrovinyl π-orbitals. One geometry that would accomplish this is shown by **15**. It is interesting that, without a special effect that prevents nitronate anion formation, long-lived dihydrobenzene intermediates from nitrophenyl ethers would be unobservable in strongly basic solution when protonation



13



14

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[17] Wubbels, G. G.; Celander, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7669–70.

[18] (a) Crampton, M. R.; Gold, V. *J. Chem. Soc. B* **1967**, 23. (b) Foster, R.; Fyfe, C. A. *Rev. Pure Appl. Chem.* **1966**, *16*, 61–82.

[19] Bartoli, G.; Bosco, M.; Melandri, A.; Boicelli, A. C. *J. Org. Chem.* **1979**, *44*, 2087–92.

[20] Nielsen, A. T. *J. Org. Chem.* **1962**, *27*, 2001–06.

[21] Bloom, A. J.; Mellor, J. M. *Tetrahedron Lett.* **1986**, *27*, 873–6.

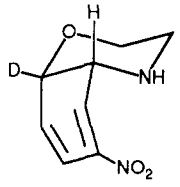
[22] Baskov, Yu. V.; Urbanski, T.; Witanowski, M.; Stefaniak, L. *Tetrahedron* **1964**, *20*, 1519.

[23] *Applications of NMR Spectroscopy in Organic Chemistry*, 2nd ed.; Jackman, L. M., Sternhell, S.; Pergamon: Oxford, 1969; p 304.

[24] Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 284–9.

[25] Terrier, F. *Chem. Rev.* **1982**, *82*, 78–152.

[26] Bernasconi, C. F. *Acc. Chem. Res.* **1978**, *11*, 147–52.



15

of the initial anion (e.g. 8) occurs on the ring carbon bearing the alkoxide substituent.

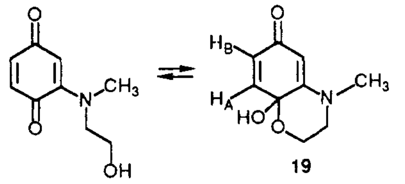
The overall chemistry of this system is summarized in Scheme II in which we identify B with **16** and C with **17**. Since the NMR signals labeled B and C are so similar in the region δ 8.3–6.0 and the species responsible appear simultaneously in equal proportions, we cannot tell whether the signals of B and C in this region are caused by **16** and **17** or by **17** and **16**, respectively. The directions of the ionic strength induced shifts, however, are consistent with the assignment we have made. The reversibility of A $\rightleftharpoons$ C was shown by experiments described in Results, and is accommodated by the scheme.

We attribute the conversion of A to B to a 1,5-sigmatropic rearrangement of deuterium (**11** $\rightleftharpoons$ **9**) followed by nucleophilic conjugate addition of OD^- to give anion **16**. On the basis of the argument advanced above concerning the putative anion of **11**, we expect **16** (or B) to be labile, losing OD^- or OR^- rapidly to give **9** or **17**. Since we see discrete NMR signals for **16** and **17** at frequency differences as small as 6 Hz, the lifetimes of **16** and **17** must be longer than the NMR coalescence lifetime of 0.04 s. That this rate of alkoxide expulsion is so much slower than those of the planar σ-complexes[25] may be due to distortion of the cyclohexene rings of **16** and **17** from planarity. This conclusion is also suggested by the H_5–H_6 coupling constants of **16** and **17** (6 Hz) that are smaller than the vicinal couplings in σ-complexes (about 10 Hz).[18b]

Scheme II accommodates several experimental observations. That the rate of conversion of A to B and C is independent of the NaOD concentration can be attributed to rate-determining sigmatropic rearrangement followed by fast attack by OD^-. The independence of [NaOD] of the ratio of [B] to [C] ([**16**]:[**17**]) is accommodated by the absence of stoichiometric involvement of OD^- in that equilibrium. That the ratio of [A] to [B] + [C] also is independent of [NaOD] can be understood if the equilibrium constant [**16**]/([**9**][OD^-]) is large; in this case the proportion [A]/([B] + [C]) would be controlled mainly by the equilibrium constant for the sigmatropic rearrangement.

A possible prototropic tautomerization of **11** to **9** can be excluded on two grounds. The C-1 deuterium of **11** should be negligibly acidic at pD 13 because anion **8** has little resonance stabilization. Moreover, as noted above, the rate of the conversion is independent of [NaOD]. The proposed 1,5-sigmatropic hydrogen shift at room temperature finds precedent in reactions of 1,3-cyclopentadienes.[27] 1,3-Cyclohexadienes that contain only carbon and hydrogen require temperatures in the range of 200–300 °C.[27] A system having an allenic function at the migration terminus rearranges in benzene at 110 °C.[28] It seems likely that resonance electron withdrawal by the nitro group activates **11** and **9** for the observed 1,5-shifts, but the 1,5-shift of hydrogen from C-2 is not similarly activated and is not observed.

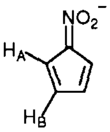
The proposed ring-chain tautomerism of **16** and **17** finds close precedent in that observed for **18** and **19**.[29] The



18 **19**

chemical shifts of H_A and H_B in **19** (in DMSO-d_6) are δ 6.46 and 5.85, respectively,[29b] which are not far different from the observed shifts for B (or **16**) of δ 6.66 and 6.27.

That the observed chemical shifts are reasonable for the structures proposed for B and C can be inferred from shifts of some nitronate anions. The nitrocyclopentadienyl anion **20** in D_2O shows H_A and H_B at δ 6.54 and 6.28, respectively.[30] Anion **21** in 3:2 DMSO-$MeNO_2$ shows H_A and



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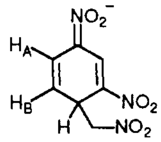
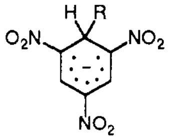


21

H_B at δ 6.59 and 5.38, respectively.[31] Given the structural differences of these species from **16** and **17**, we regard these observations as adequate justification for the proposed structures. We ascribe the effect of NaOD and NaCl concentrations on the chemical shifts of anions **16** and **17** to a salt effect that tends to concentrate charge on the nitro and keto oxygens of these species.

We have no evidence concerning which structure, **16** or **17** or both, gives rise to which UV absorption (observed at 315 and 260 nm for B and C). That the maxima are not unreasonable for the proposed structures can be inferred from those observed for the 1-nitrocyclohexene anion in 85% EtOH/H_2O at 285 and 241 nm.[20] Substituents and solvents, moreover, play a large role in determining the UV maxima for these highly polarizable species. For example, the long wavelength maximum of **22** in DMSO varies from 485 to 580 nm as the substituent R is changed from OH to NR_2 to SR,[32] and the Janovsky complex **23** varies in λ_{max} from 536 to 587 nm as the solvent is changed from MeOH to DMSO.[32]



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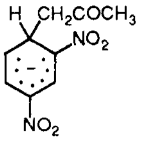

23

The observation of deuterium incorporation specifically at C-3 of photoproduct **3** strongly supports Scheme II. When **11** is photooxidized to **2**, the deuterium at C-1 must be lost in order to aromatize the ring. However when open-chain **17** is photooxidized to **3**, deuterium or protium will be retained at C-3. A normal primary kinetic isotope effect of $k_H/k_D = 3$ in the photooxidation would rationalize the observed 75–85% of deuterium at C-3 of **3**. Photooxidations of a great variety of substrates by nitro compounds have been widely reported,[33] and no doubt account

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[27] Mironov, V. A.; Fedorovich, A. D.; Akhrem, A. A. *Russian Chem. Rev.* **1981**, *50*, 666–81.

[28] Palenzuela, J. A.; Elnagar, H. Y.; Okamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1770–73.

[29] (a) Rettig, H.-P.; Berg, H. *Z. Phys. Chem. (Leipzig)* **1963**, *222*, 193. (b) Day, J. H.; Joachim, A. *J. Org. Chem.* **1965**, *30*, 4107–11. (c) McMurtrey, K. D.; Daves, G. D., Jr. *J. Org. Chem.* **1970**, *35*, 4252–53.

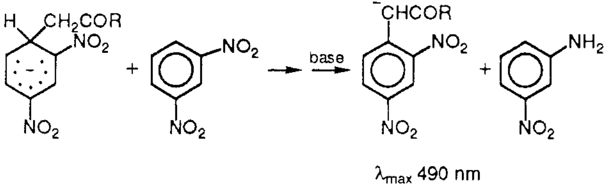
[30] Kerber, R. C.; Chick, M. J. *J. Org. Chem.* **1967**, *32*, 4329.

[31] Fyfe, C. A. *Can. J. Chem.* **1968**, *44*, 3047–54.

[32] Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667–712.

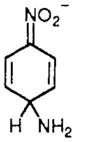
for the photooxidations of **11**, **16**, and **17**. These species are NADH analogues,[34] and a kinetic isotope effect (k_H/k_D) of 5 has been reported[35] for a thermal oxidation of one such species.

These findings shed light on several mysteries of nucleophilic aromatic photosubstitutions involving the displacement of hydrogen. The stability of neutral **11** and anionic **16** and **17** toward oxygen is surprising in view of the frequent observation[1-3,5-8] that oxygen must be present in order to form aromatized products. Structural differences may account for this difference. Moreover, at the high concentrations of preparative photoreactions,[1-3,5-8] oxygen may participate in radical chain reactions that are photoinitiated; such reactions may not occur efficiently at the lower substrate concentration we have used. Our observation that 3,5-dinitrobenzoate ion is a sufficiently strong acceptor to oxidize **11**, **16**, and **17** can be correlated with the known success of the Zimmermann reaction, a color test for enolizable ketones that depends on the thermal oxidation of a Janovsky complex by a dinitrobenzene (eq 3).[36]



(3)

On the basis of our findings for **16** and **17**, we suggest that the oxygen-stable intermediate (λ_{max} 335 nm) observed when nitrobenzene is photolyzed in liquid ammonia[1] is **24** rather than the proposed structure **25**. Anion **24** in a polar protic solvent could well absorb at 335 nm whereas **25** would be little different in its UV spectrum from anilinium ion (λ_{max} 254 nm).[37]



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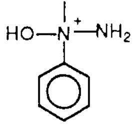

25

Experimental Section

D_2O and 30% NaOD in D_2O were 99.8% deuterium from Aldrich. **1** was available from a previous study.[11] NMR spectra were obtained with an IBM/Bruker NR/300 spectrometer with samples in 5-mm tubes at 25 °C. Proposed couplings were all verified by spin decoupling experiments. UV spectra were obtained with a Beckman 5260 spectrophotometer with samples in 1.00-cm quartz cuvettes.

Samples were prepared in volumetric flasks at 0 °C by weighing and quantitative transfer with syringes. Irradiations were carried out at 0 °C in a Rayonet RPR-208 reactor with 350-nm lamps. NMR sample tubes were suspended in the reactor in an Ace Glass jacketed quartz well maintained at 0 °C by circulating ethanol–water coolant. Terephthalic acid (as its dianion, δ 7.86) was used as an internal standard for the NMR spectra.

Acknowledgment is made to the National Science Foundation (Grant CHE-8605343) for support of this work.

Registry No. 1, 60814-16-6; 1-*N,N*-d_2, 123934-49-6; **2**-*N*-*d*, 123934-50-9; **3**-*N,O*-d_2·Na, 123934-51-0; **6**-*N,O*-d_2, 123934-52-1; A, 123962-98-1; B·Na, 123962-99-2; C·Na, 123934-53-2.

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(33) Doepp, D. *Top. Curr. Chem.* **1975**, *55*, 49–85.

(34) (a) Ohno, A.; Ohara, M.; Oka, S. *J. Am. Chem. Soc.* **1986**, *108*, 6438–40. (b) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305–16. (c) Tanner, D. D.; Kharrat, A. *J. Am. Chem. Soc.* **1988**, *110*, 2968–70.

(35) Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *J. Am. Chem. Soc.* **1989**, *111*, 1497–99.

(36) Hall, T. N.; Poranski, C. F., Jr. In *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H., Ed.; Wiley: New York, 1970; Part 2, p 361.

(37) Doub, L.; Vandenbelt, J. M. *J. Am. Chem. Soc.* **1947**, *69*, 2714.

Electronic Structure of [*n*.1.1]Propellanes. PE Spectroscopic Investigations

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The PE spectra of five [*n*.1.1]propellanes have been recorded. The first four PE bands have been assigned by comparison with bicyclobutane derivatives and by comparison with the results of MINDO/3 and ab initio (STO-3G) calculations. We find that the energy of the first band depends very strongly on *n*. For $n = 1$ the ionization energy is located around 9 eV, for $n = 3$ and 4 it is recorded above 8 eV. This difference is ascribed to two effects, the inductive effect of the methylene groups and the lower s character for $n = 3$ and 4 as compared to $n = 1$.

Among the [*m.n.o*]propellanes[1] the most interesting examples are the ones that are highly strained [$m, n, o < 3$). The recent synthesis of [1.1.1]propellane **1**[2] and several of its congeners[3-5] provided the motivation of our study concerning the electronic structure of strained propellanes. In 1972 two groups investigated the electronic structure of **1**[6,7] using the extended Hückel method and a Hartree–

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(1) Ginsburg, D. *Propellanes*; Verlag Chemie: Weinheim, Germany, 1975. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975.

(2) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A. D. *Chem. Ber.* **1989**, *122*, 397.

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