Novel Intramolecular Photorearrangement of Nitronate Anions

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The photochemistry of alkanenitronate anions is described. Irradiation of the alkanenitronate anions leads to hydroxamic acids by oxygen photorearrangement via π–π^* triplet excited states. The stoichiometry of reaction, anion structure and selectivity of migration, the nature of the excited state, the quantum yield of reaction, rehybridization on excitation, and the base dependency are discussed. From the results of a detailed structural study of 19 products it was found that this photorearrangement is a highly regio- and stereospecific reaction.

Introduction

The photochemistry of aliphatic nitro compounds has been widely investigated, and its reaction mechanisms have been studied in detail.[1] However, the photochemical behavior of alkanenitronate anions in basic solution has not been studied.

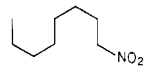
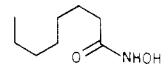
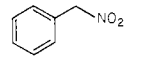
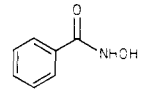
Recently we investigated a novel and stereospecific photorearrangement of alkanenitronate anions.[2] The rearrangement of nitronate anions was found to provide an interesting synthetic method for introducing hydroxamic acid functions,[2] which possess a wide range of biological activities.[3] The present paper will describe the photorearrangement of nitronate anion, including the stoichiometry of reaction, anion structure and selectivity of migration, the nature of the excited state, the quantum yield of reaction, rehybridization on excitation, and the base dependency of the reaction.

Results and Discussion

Stoichiometry. Deprotonation of 1-nitrooctane (**1**, Table I) in EtOH–H_2O–NaOH leads to octanenitronate anion, which shows a strong UV absorption at 233 nm (ϵ 10200). This anion was transformed to caprylohydroxamic acid (**2**) by irradiation with a low-pressure mercury lamp. The color of the photoproduct **2** exhibited a reddish purple color with ferric chloride test and was identical with the spectra of an authentic sample.[4] The yield of the hydroxamic acid was very low, however, and the stoichiometry of this reaction is not easily recognized. The inability to determine the stoichiometry was caused by the fact that hydroxamic acids and their salts are very soluble in water and are not easily extracted with organic solvents. Many isolation methods for hydroxamic acids were tried such as Cu-complex formation,[5] use of ion-exchange resins,[6] and Mo-complex formation,[7] in addition to the usual isolation procedures. A variety of bases were also examined to produce the alkanenitronate anion. Methylamine was especially useful for the reaction of primary nitroalkanes such as **1** and phenylnitromethane (**3**), which appeared to be almost quantitatively.

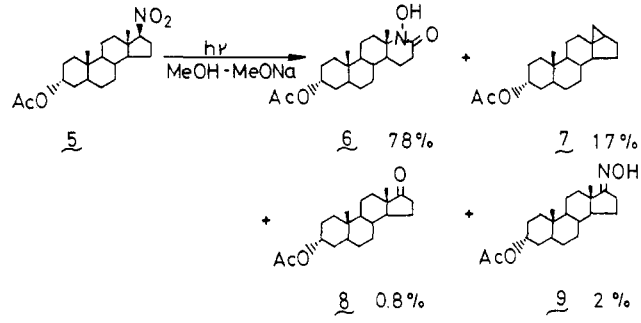
Irradiation of the nitronate anion of 3α-acetoxy-17β-nitro-5α-androstane (**5**) in MeOH–MeONa was carried out, and the solution was neutralized with AcOH–EtOH and concentrated, followed by extraction with chloroform. The extracted reaction mixture was separated by column chromatography into the hydroxamic acid (**6**, Scheme I), which exhibited a reddish purple color with ferric chloride. In addition, components 7–9 were isolated. From the spectral data, which consisted of a NMR signal at δ 5.01, a MS spectrum fragmentation pattern, and a specific rotation $[\alpha]^{20}_D$ −2°, the structure of **6**, 17a-aza-3α,17α-dihydroxy-D-homo-5α-androstan-17-one 3-acetate, was identical with that of the photolysis product obtained from 5α-androstane-3α,17β-diol 3-acetate 17-nitrite (**10**) by the method of Nakazaki and co-workers.[8,9] The NMR spectra indicated that the byproduct **7** contained a cyclopropane ring that is fused with the D ring. In 1968, Misiti and co-workers[10] reported that the signals of the protons C-17H, C-18H and C-18′H appeared at δ 0.8 to −0.2 in the spectra of 3β-acetoxy-17,18-cycloandrost-5-ene (**11**). In

Table I. Comparison of Yields by EtONa and $MeNH_2$

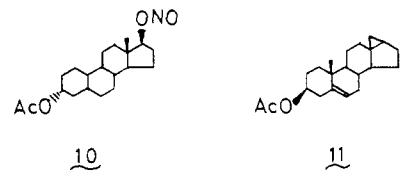
nitroalkane	hydroxamic acid	yield, %[a] EtONa	yield, %[a] $MeNH_2$
 **1**	 **2**	30	85
 **3**	 **4**	27	91

[a] Isolated yields.

Scheme I



5 **6** 78% **7** 17% **8** 0.8% **9** 2%



10 **11**

(1) Morrison, H. A. "The Chemistry of the Nitro and Nitroso Groups"; Patai, S., Ed.; Interscience: New York, 1969; Part 1, pp 165–213.
(2) Yamada, K.; Kanekiyo, T.; Tanaka, S.; Naruchi, K.; Yamamoto, M. *J. Am. Chem. Soc.* **1981**, *103*, 7003.
(3) Kumaki, K.; Tomioka, S.; Kobayashi, K.; Hase, J. *Chem. Pharm. Bull.* **1972**, *20*, 1600.
(4) Lewis, A. H. *Biochem. J.* **1927**, *20*, 1358.
(5) Hoffmann, C. *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 2856.
(6) Wise, W. M.; Brandt, W. W. *J. Am. Chem. Soc.* **1955**, *77*, 1058.
(7) Matlin, S. A.; Sammes, P. G.; Upton, R. M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2481.
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(9) Robinson, C. H.; Gnoj, O.; Mitchell, A.; Wayne, R.; Kabasakalian, F.; Oliveto, E. F. *J. Am. Chem. Soc.* **1961**, *83*, 1771.
(10) Misiti, D.; Rosini, G.; Caglioti, L. *Gazz. Chim. Ital.* **1968**, *98*, 1284.

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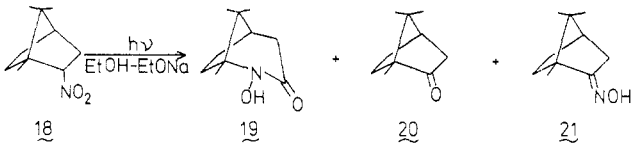
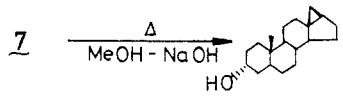
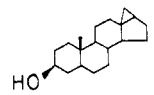
Scheme II



addition, the half-height width of C-3H ($W_{1/2}$ = 7 Hz), according to Hassner[11] suggested that this proton was located in an equatorial position. Hydrolysis of **7** in



NaOH–MeOH afforded **12** (mp 130–132 °C, $[\alpha]^{20}_D$ +12°), which has lost the acetyl methyl proton signal with the appearance of a hydroxy proton at δ 5.5–6.0. Cyclopropanoid ring protons were retained in the spectra of **12**. Cyclosteroid **12** is a new compound, but 3β-hydroxy-17,18-cyclo-5α-androstane (**13**)[12] was reported to melt at



153–155 °C, ($[\alpha]^{20}_D$ −12°). Because the half-height width of C-3H proton of **12** is 9 Hz, cyclopropanoid **12** was considered to be the epimer of **13**. Accordingly, product **7** was characterized as 3α-acetoxy-17,18-cyclo-5α-androstane, which occurs with retention of the conformation of C-3H.

Product **8** could be eluted with 6:1 AcOH–EtOH on silica gel column chromatography, and the structure of **8** was characterized as 3α-acetoxy-5α-androstan-17-one, and **9** as 3α-acetoxy-5α-androstane 17-oxime by comparison of the melting points with those of authentic samples.[13] The results indicate the stoichiometry and stereoselectivity of this photoreaction. Photochemistry of other steroidal nitro compound was also carried out. Irradiation of the B-ring nitro compound gave 6β-nitro-5α-cholestanyl 3β-acetate (**14**),[14] 6-aza-*B*-homocholestan-3β,6-dihydroxy-6a-one 3-acetate (**15**), cholesteryl acetate (**16**), and 3β-hydroxy-5α-cholestan-6-one (**17**).[14]

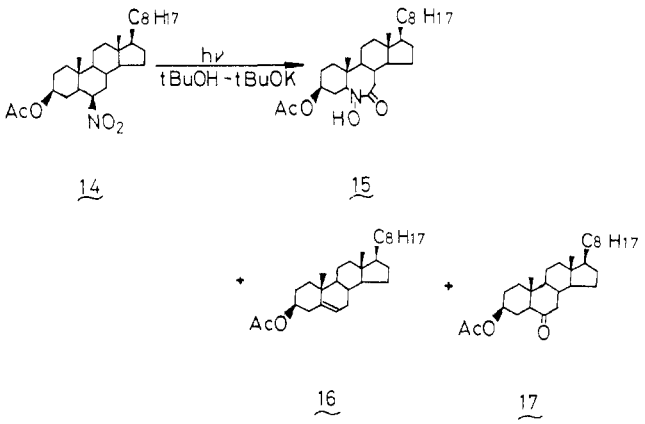
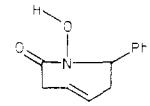
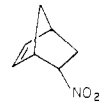
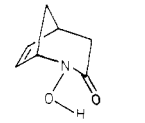
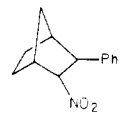
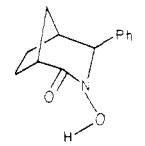
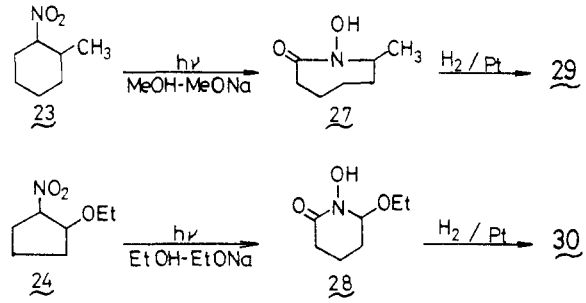


Table II. Product Yields from Irradiation of Various Nitroalkanes

nitroalkane			*N*-hydroxy lactam			
R	*n*		R	*n*		yield, %[a]
H	2	**31**	H	2	**32**	37
H	3	**33**	H	3	**34**	26
H	4	**25**	H	4	**26**	6.4
H	5	**22**				0
OEt	3	**24**	OEt	3	**28**	75
OEt	4	**35**	OEt	4	**36**	68
CH_3	4	**23**	CH_3	4	**27**	28
Ph	4	**37**	Ph	4	**38**	68
		18			**19**	76
		**39**			**40**	46
		**41**			**42**	95
		**43**			**44**	65

[a] Isolated yields.

Scheme III



High stereoselectivity was also observed from the photoreaction of 2-nitrobornane (**18**, Scheme II). Irradiation of **18** ($[\alpha]^{20}_D$ +9.4°) gave the *N*-hydroxy lactam 1,8,8-trimethyl-2-hydroxy-2-azabicyclo[3.2.1]octan-3-one (**19**, $[\alpha]^{18}_D$ −67.2°), which was identified by its melting point and comparison of its spectral data with those of the authentic sample.[15] Small amounts of byproducts, camphor (**20**) and camphor oxime (**21**), in this photoreaction were also obtained and were identified by comparing their melting points with those of authentic samples.[16] In this case, the C-1 carbon stereospecifically migrated to the nitrogen atom to give hydroxamic acid.

Anion Structure (Kinetic Acidity) and Selectivity of Migration. The structure of the nitronate anions seems to govern the yield of the hydroxamic acids. The order of the deprotonation rates of nitroalkanes is known to depend upon the ring size, 4 > 5 > 7 > 8 > 6 ≫ 3.[17] The

(11) Hassner, A.; Heathcock, C. *J. Org. Chem.* **1964**, *29*, 1350.
(12) Caglioti, L.; Grasselli, P.; Selva, A. *Gazz. Chim. Ital.* **1964**, *94*, 537.
(13) Ruzieka, L.; Goldberg, M. W.; Meyer, J.; Brüngger, H.; Eichenberger, E. *Helv. Chim. Acta* **1934**, *17*, 1395.
(14) Bull, J. R.; Jones, E. R. H.; Meakins, G. D. *J. Chem. Soc.* **1965**, 2601.
(15) Nakazaki, M.; Naemura, K. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 532.
(16) Auwer, K. *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 605.
(17) Flanagan, P. W. K.; Amburn, H. W.; Stone, H. W.; Traynham, J. G.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 2797.

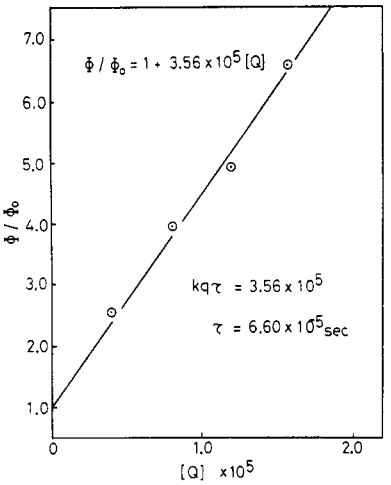


Figure 1. Stern–Volmer plots for the photoreaction of **5** with azulene as quencher.

relation between kinetic acidity and yield of photoreaction is shown in Table II. The results suggest that the faster the formation of nitronate anion, the higher yields of the hydroxamic acids. Although nitrocycloheptane (**22**), 2-methylnitrocyclohexane (**23**, Scheme III), and 2-ethoxynitrocyclopentane (**24**) are not totally consistent with this tendency, the effect of the substituent groups generally results in an increase in the yields of the hydroxamic acids. Typically, photolysis of the nitronate anion of nitrocyclohexane **25** gave *N*-hydroxy lactam **26** in low yield (6.4%), but incorporation of a methyl group (i.e., **23**) increases the yield of the hydroxamic acid (**27**, 18%). Irradiation of 2-ethoxynitrocyclopentane (**24**) in alkaline solution leads to *N*-hydroxy-6-ethoxy-2-piperidone (**28**, 75%). The reduction of **27** gave the known hexahydro-7-methyl-2*H*-azepin-2-one (**29**),[18] consequently the structure of *N*-hydroxy lactam **27** was assigned as hexahydro-1-hydroxy-7-methyl-2*H*-azepin-2-one. Also, compound **28** was derived from 6-ethoxy-2-piperidone (**30**).[19] The structure of the 2-substituted nitrocyclohexane in MeOH–MeONa has been discussed by Bordwell et al.[20] It was reported that 2-substituent groups are located in the axial position in order to avoid A strain between the substituent and the exocyclic double bond. This structural requirement indicates that the nitronates of 2-substituted nitrocycloalkanes are more strained and are therefore more slowly deprotonated than the nonsubstituted ones.

Nitrocyclopentane (**33**) was reported to be deprotonated 3 times faster than *trans*-2-phenyl-1-nitrocyclopentane.[21] Accordingly, *N*-hydroxy lactam formation was expected to be related to both the kinetic acidity and the strain of the ring systems.

The stereoselectivity of this photoreaction is given in Table II. From the table it can be seen that the predominant order of the migrating β-carbon is $CH(OC_2H_5) > CH_2$, $CH(CH_3) > CH_2$, $C(CH_3)CH_2 > CH_2$. This migration selectivity is very high. This is consistent with the results of the theoretical calculations,[22] in which the transient oxaziridine intermediate has little effect on the ease of Cα–Cβ bond cleavage.[22] Introduction of a 2-substituent group will increase the strain interaction between the nitronate carbon and the substituted β-carbon.

Table III. Quantum Yields and Lifetimes of Excited Nitronate Anions

compd	$10^2 I_0$ [a]	$10^{-5}K_q\tau$, [b,c] M^{-1}	τ, [d] s
1	14.00	0.29	0.54×10^{-5}
5	1.24	3.56	0.66×10^{-4}
18	2.54	6.80	1.26×10^{-4}
23	0.37	0.90	1.67×10^{-5}
45	8.60	3.24	0.60×10^{-4}

[a] In MeOH–MeONa (1:2–5 [$-NO_2$][Na]) at room temperature. [b] Azulene as quencher. [c] These standard deviations were $(3.40\text{–}6.57) \times 10^7$. [d] $k_q = 5.4 \times 10^9$ $M^{-1}\cdot s$ (MeOH).

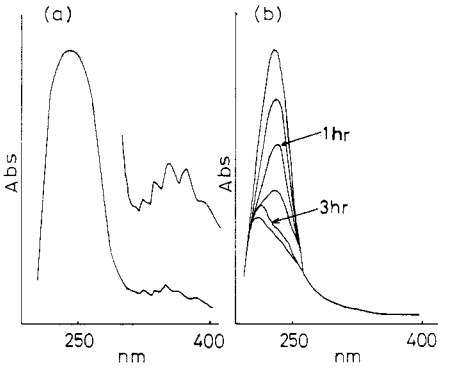


Figure 2. Absorption spectra of *dl*-bornyl nitrite (a) and 2-nitrobornane (**18**) (b) in EtOH–EtONa (irradiation at 2537 Å for 0, 0.5, 1, 2, 3, and 4 h).

Nature of the Excited State and Quantum Yield. The conversion of nitrones to oxaziridines was reported to be induced by singlet–singlet excitation.[23] Hydroxamic acid formation also implies a process in which the oxaziridine anion exists as an intermediate. Oxaziridine intermediate, however, was not observed spectroscopically. Quenching experiments were carried out with azulene and oxygen in order to elucidate the excited state of the nitronate anions. In a quenching experiment with azulene, Stern–Volmer plots (Figure 1) gave straight lines. From the slopes of these plots, the lifetimes of the excited nitronate anions of **1**, **5**, **18**, **23**, and 1-phenyl-2-nitropropane (**45**) were determined and found to have values between 0.54×10^{-5} and 1.26×10^{-4} s (Table III). These lifetimes are longer than those of most singlet excited species,[24] and thus the excited state of this reaction probably involves the triplet. The effect of oxygen on the quantum yield was also recognized, since there was a 65% difference in quantum yield between an experiment conducted in an aerated solution and one carried out with argon. For example, a solution under oxygen atmosphere in the case of the nitronate anion of 2-nitronorbornane (**46**) has $\Phi = 2.07 \times 10^{-3}$, and a solution under argon atmosphere is $\Phi = 5.69 \times 10^{-3}$. This result indicates that the triplet excited nitronate anion of **46** could be quenched by a small amount of oxygen in solution. The *N*-hydroxy lactam **19** was also obtained from *dl*-bornyl nitrite by a Barton reaction.[15,25,26] The photoreaction of the nitronate anion of **18** (Figure 2)

(18) Overberger, C. C.; Parker, G. M. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 513.
(19) Hubert, J. C. *Tetrahedron* **1975**, *31*, 1437.
(20) Bordwell, F. G.; Yee, K. C. *J. Am. Chem. Soc.* **1970**, *92*, 5939.
(21) Bordwell, F. C.; Yee, K. C. *J. Am. Chem. Soc.* **1970**, *92*, 5933.
(22) Kikuchi, O.; Yamada, K. *J. Fac. Eng., Chiba Univ.* **1981**, *32*, 53. Kikuchi, O.; Kanekiyo, T.; Tanaka, S.; Naruchi, K.; Yamada, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1509.
(23) Koyama, K.; Tanaka, I. *J. Phys. Chem.* **1965**, *69*, 2545.
(24) Fukuyama, M.; Flanagan, P. W. K.; Williams, F. T., Jr.; Frainier, L.; Miller, S. A.; Shechter, H. *J. Am. Chem. Soc.* **1970**, *92*, 4689.
(25) Robinson, C. H.; Gnoj, O.; Mitchell, A.; Oliveto, E. P.; Barton, D. H. R. *Tetrahedron* **1965**, *21*, 743.
(26) Kabasakalian, P.; Townley, E. R. *J. Org. Chem.* **1962**, *27*, 3562.

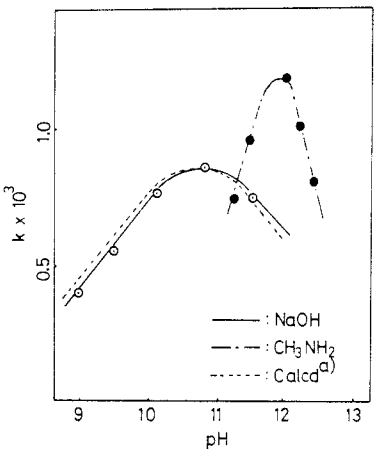


Figure 3. Plots of k vs. pH for the photoreaction of **47** with NaOH and $MeNH_2$. The broken line in this figure shows the calculated values when $k_{h\nu} = 8.5 \times 10^{-4}$ s^{-1} in eq 1.

had no absorption in the vicinity of 360 nm, in which the characteristic UV absorption of a nitrite occurs. Consequently, this photoreactioin does not proceed via *dl*-bornyl nitrite.

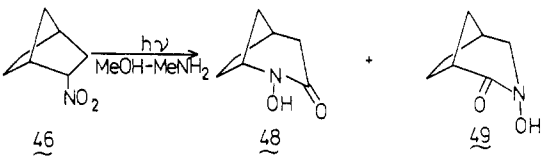
Rehybridization on Excitation. Nitronate anions show strong absorption at about 240 nm, as shown in Table IV. The intensity ($\sim 10^4$) indicates that the absorptions are due to π–π^* excitation.[24] The absorption maxima show an interesting relation with the ring size of the alkanenitronate (i.e., $5 > 4 \approx 7 > 6$).[27] This relationship and the calculated conformation of the excited methanenitronate imply that the exocyclic nitronates **22**, **25**, and **31** are more stable than structure **33**. In other words, rehybridization occurred on π–π^* excitation.

From the view point of I strain, rehybridization is less favorable for nitrocyclopentane (**33**) than for nitrocyclohexane (**25**). However, the order of strain release ΔE[28] is consistent with the yields of the *N*-hydroxy lactams. In the case of nitro compounds **5**, **23**, and **24**, 2-substituent groups are expected to enhance I strain in the nitrocycloalkane and maximize release of strain.

Base Dependency. Nitronate anion formation (kinetic acidity) is a key step in the photoreaction. One of the points worth clarifying was whether the nitronate anions are able to form any type of ion pair or not. There are no significant differences in absorption maxima when **23** is coupled with the alkali metals Li, Na, or K. This result implies that nitronate anions exist not as a contact ions but as solvent-separated ion pairs.

Irradiation of **1** and **3** in a solution of MeOH–$MeNH_2$ yielded the hydroxamic acids **2** and **4** almost quantitatively (Table I). The difference in the photobehavior of the nitronate anion of nitroethane (**47**) was examined in an aqueous sodium hydroxide solution and in an aqueous methylamine solution.[29] The pH vs. k (rate of the photoreaction) is plotted in Figure 3. This interesting curve indicates that the rate of the photoreaction depends on the pH value. A maximum rate occurs in both alkaline solutions. In the case of the NaOH solution, the rate of deprotonation (k_1) of **47** is too slow at lower pH values for enough nitronate anions to exist to undergo this photoreaction. Otherwise, at the high pH value the photoreaction proceeded completely. This tendency may be formulated as in eq 1–5.

Scheme IV



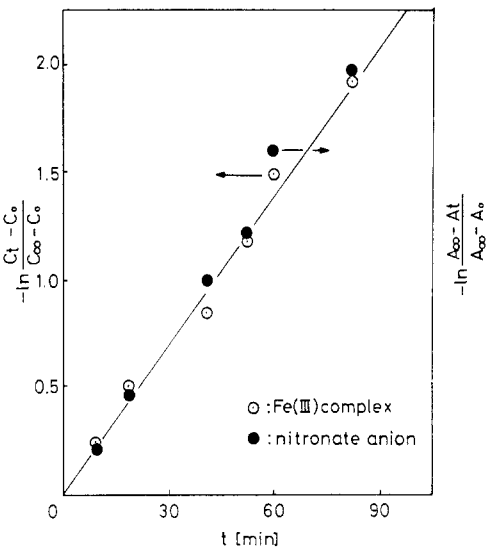


Figure 4. First-order plots of $-\ln(C_t - C_0)$ and $-\ln(A_\infty - A_t)/(A_\infty - A_0)$: C is the absorbance of the Fe(III) complex of **47** at 475 nm; A is the absorbance of anion of **23** at 237 nm.

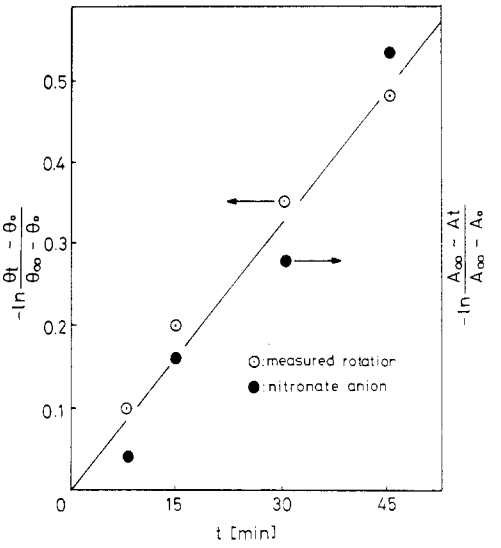


Figure 5. First-order plots of $-\ln(\theta_t - \theta_0)/(\theta_\infty - \theta_0)$ and $-\ln(A_\infty - A_t)/(A\infty - A_0)$: θ is the specific rotation of **19** in EtOH–EtONa; A is the absorbance of the anion of **18** at 238 nm.

$$CH_3CH_2NO_2 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CH{=}NO_2^- + H_2O \xrightarrow{k_{h\nu}} CH_3C(O)NH(OH) \quad (1)$$

$$K_a = [CH_3CH{=}NO_2^-][H^+]/[CH_3CH_2NO_2] \quad (2)$$

$$\frac{d}{dt}[CH_3CH{=}NO_2^-] = k_1[CH_3CH_2NO_2][OH^-] - k_{-1}[CH_3CH{=}NO_2^-][H^+] \quad (3)$$

$$-A/A_\infty k_{h\nu}[CH_3CH{=}NO_2^-] = -k_{obsd}[CH_3CH{=}NO_2^-] \quad (4)$$

$$k_{obsd} = k_1\, 10^{-14}[10^{pK_a - pH} - (A_\infty - A/A)10^{pH}] + A/A_\infty k_{h\nu} \quad (5)$$

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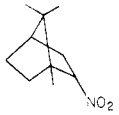
Table IV. UV Absorption of Some Nitroalkanes in Various Solvents

$(CH_2)_n$—NO_2		λ_{max}, nm (ϵ)[a]	λ_{max}, nm (ϵ)[b]	λ_{max}, nm (ϵ)[c]	hydroxamic acid	yield,[d] %	ΔE[e]
$n = 3$	**31**	237 (8.9×10^3)	229 (1.26×10^4)	231 (1.03×10^4)	**32**	35	20.1
$n = 4$	**33**	234 (9.6×10^3)	226 (1.32×10^4)	228 (1.35×10^4)	**34**	26	5.9
$n = 5$	**25**	238 (5.0×10^3)	231 (1.20×10^4)	233 (1.20×10^4)	**26**	6.4	−6.4
$n = 6$	**22**	237	235 (1.16×10^4)	230 (1.29×10^4)		0	−3.7
	**18**	238 (1.3×10^4)			**19**	76	23.8

[a] 2:1 EtONa:nitrocycloalkane. [b] H_2O.[27] [c] 1:1 H_2O:dioxane.[27] [d] Isolated yields. [e] ΔE, difference of total strain (kcal/mol).[28]

Yields of Products. The results of Table I imply that the photoreaction proceeds quantitatively. This is observed in the initial stages of the photoreaction of nitronate anions derived from **18**, **23**, and **46**. The rate of reaction of the nitronate anions of **18**, **23**, and **46** were followed by UV absorption. Similarly, the rates of reaction of **27**, *N*-hydroxy-2-azabicyclo[3.2.1]octan-3-one (**48**, Scheme IV), *N*-hydroxy-3-azabicyclo[3.2.1]octan-2-one (**49**), and **19** were followed by UV absorption (the characteristic absorption of the complex of *N*-hydroxy lactam **27** and Fe(III) ion), by using GC (*N*-hydroxy lactams **48** and **49**) and specific rotation. The results are plotted in Figures 4 and 5 and indicate that the photoreactions of the nitronate anions of **18** and **23** were proceeding quantitatively and stereospecifically. In other words, the quantum yield associated with the decrease of the anion was equal to the increase of the *N*-hydroxy lactam:

$$\Phi_{dec} = \Phi_{inc}$$

The byproducts of this reaction are mainly oximes and ketones. Cyclohexanone oxime and cyclohexanone were reported to be obtained from nitrocyclohexane **24** by irradiation.[30] The formation of cyclohexanone oxime and cyclohexanone will be explained, i.e., when the deprotonation of **25** is slow, free nitro-compound **25** will be subjected to a similar photoreaction as reported[30] and thus will form the oxime and ketone. Cycloandrostane **7** is also explained as the product from the nitroalkane **5**. In this case, hydrogen abstraction from the C-18 methyl group was found to occur.[31,32]

Experimental Section

All melting points are uncorrected. The optical rotations were measured with a Type DIP-140 (Japan Spectroscopic Co. Ltd.). UV spectra were recorded on Shimazu UV-200 and UV-180 spectrophotometers. IR spectra were taken on Model IR-S (Japan Spectroscopic Co. Ltd.) and Hitachi 215 type spectrometers. ^1H NMR spectra were recorded with a Hitachi R-24 instrument. Mass spectra were obtained with a Hitachi RMU-7M spectrometer (for high-resolution mass spectra) at 70 eV. The pH values, were given by a Model HM-5A pH meter (TOA Electronic Co. Ltd.) and a Hitachi-Horiba Model M-7 pH meter. Buffer solutions were chosen according to the required pH region; M/10 H_2NCH_2CO-OH–NaCl–NaOH (pH 8–12). Column chromatography was carried out with Merck's silica gel 7734, and flash-column chromatography[33] was carried out with Merck's silica gel 9385.

Photoreactions were carried out with an 80-W Ushio low-pressure mercury arc. Argon was bubbled into the reaction mixture before and during the irradiation. The photoreaction was followed by checking the decrease of the intensity on UV absorption due to π–π^* excitation of the nitronate anions. All yields were based on the conversion from the starting nitro compounds (mostly 70–80% conversion).

Materials. 1-Nitrooctane (**1**),[34] phenylnitromethane (**3**),[35] 6β-nitro-5α-cholestanyl 3β-acetate (**14**),[14] 2-nitrobornane (**18**),[36] nitrocycloheptane (**22**),[37] 2-methylnitrocyclohexane (**23**),[37] nitrocyclohexane (**25**),[37] nitrocyclobutane (**31**),[37] nitrocyclopentane (**33**),[37] 1-nitro-2-phenylcyclohexane (**37**),[38] 4-phenyl-5-nitrocyclohexene (**39**),[39] 5-nitrobicyclo[2.2.1]hept-2-ene (**41**),[40] 2-nitro-3-phenylnorbornane (**43**),[40] 1-phenyl-2-nitropropane (**45**),[41] and 2-nitronorbornane (**46**)[40] were prepared by literature methods.

3α-Acetoxy-17β-nitro-5α-androstane (5). Compound **5** was prepared by the method of Patchett.[42] To a slurry of 4.7 g of *N*-bromosuccinimide in 15 mL of dioxane and 15 mL of water was added simultaneously 3 g of 3α-acetoxy-5α-androstan-17-one oxime (**9**)[13] in 31 mL of dioxane and 2.7 g of potassium bicarbonate in 15 mL of water. The mixture was stirred for 48 h, diluted with water, and extracted with ether. After drying over anhydrous sodium sulfate the solvent was removed under vacuum to give a solid residue. This was dissolved in 77 mL of 80% tetrahydrofuran–water solution, and 1.35 g of sodium borohydride was added over 40 min with vigorous stirring. The mixture was stirred for 2.5 h, and 3.45 g of hydroxylamine hydrochloride in 51.6 mL of water was added slowly. The solution was extracted with ether and worked up as usual to give a solid residue (2.2 g), which was purified by silica gel column chromatography with 50:1 benzene–ethyl acetate to give pure **5** (1.6 g, 51%): mp 174–176 °C (white needles, from MeOH); $[\alpha]^{25}_D$ +48.18° (*c* 0.124, dioxane), $[\alpha]^{25}_D$ = +51.51° (*c* 0.053, MeOH); IR (CCl_4) 1745 ($\nu_{C=O}$), 1550 (NO_2 asym), 1380 (NO_2 sym), 1204 (AcO) cm^{-1}; NMR (CCl_4) δ 0.75 (s, 3 H, C-18Me), 0.80 (s, 3 H, C-19Me), 1.96 (s, 3 H, acetate), 4.9 (br s, $W_{1/2}$ = 6 Hz, 1 H, C-3H, equatorial), 4.24 (br s, $W_{1/2}$ = 17 Hz, 1 H, C-17 H, ax); UV λ_{max} (MeOH) 278 nm (ϵ 127); mass spectrum, calcd for $C_{19}H_{30}NO_2$ *m/e* 304.2286, found *m/e* 304.2285 ($M^+ - CH_3COO$). Anal. Calcd for $C_{21}H_{33}NO_4$: C, 69.24; H, 9.15; N, 3.85. Found: C, 69.24; H, 8.92; N, 3.69.

2-Ethoxynitrocyclopentane (24). 1-Nitrocyclopentene[43] (200 mg) was added to a solution of EtOH–EtONa (nitrocyclopentene:sodium = 1:1 molar ratio) and stirred at room temperature. After 10 min of stirring the reaction mixture was neutralized with 0.5 M HCl ethanolic solution followed by evaporation of ethanol and extraction with ether. The ether solution was concentrated to give a brown oil, which was chromatographed on silica gel to yield 65 mg of **24**: IR (CCl_4) 1550 (NO_2 asym), 1370 (NO_2

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sym) cm^{-1}; NMR (CCl_4) δ 4.7 (sext, J = 5 Hz, 1 H), 4.3 (sext, J = 5 Hz, 1 H), 3.5 (q, J = 8 Hz, 2 H), 2.3 (d, J = 8 Hz, 2 H), 1.5–2.1 (4 H), 1.2 (t, J = 8 Hz, 3 H); UV λ_{max} (EtOH) 272 nm (ϵ 18); mass spectrum, calcd for $C_7H_{13}O$ m/e 113.0965 (M – NO_2), found m/e 113.0928 (M^+ – NO_2). Anal. Calcd for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.80. Found: C, 52.55; H, 8.25; N, 8.48.

2-Ethoxynitrocyclohexane (35). A solution of 1.27 g of 1-nitrocyclohexene[43] in 300 mL of EtOH–EtONa was stirred for 3 h. The reaction mixture was concentrated and treated as usual to give pure **35**: IR (CCl_4) 1555 (NO_2 asym), 1385 (NO_2 sym) cm^{-1}; NMR (CCl_4) δ 4.2 (m, 1 H), 3.6 (m, 3 H), 1.3–2.5 (br s, 8 H), 1.2 (t, 3 H); mass spectrum, calcd for $C_8H_{15}O$ m/e 127.1124 (M – NO_2), found m/e 127.1122 (M^+ – NO_2). Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 54.70; H, 8.74; N, 8.11.

Irradiation of the Nitronate Anion of 1-Nitrooctane (1). General Irradiation Procedure A. A solution of 2.00 g of **1** in 500 mL of aqueous NaOH–EtOH solution was irradiated for 6 h. The solution was neutralized with acetic acid, and then ethanol was removed. The aqueous mixture was extracted with etyl acetate, and the resulting organic solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give an oily residue. This residue was purified by column chromatography on silica gel to afford caprylohydroxamic acid (**2**) (240 mg, 30%), mp 78–79 °C (lit.[4] mp 78.5–79 °C).

General Irradiation Procedure B. A solution of **1** (490 mg) in MeOH–$MeNH_2$ (500 mL, pH 12) was irradiated for 2 h. The reaction product was worked up as described above to afford pure **2** (285 mg, 85%).

Irradiation of the Nitronate Anion of Phenylnitromethane (3). By the general procedure A, 900 mg of **3** was irradiated for 7.5 h. Benzhydroxamic acid (**4**) (114 mg, 27%) was obtained as crystals, mp 125–126.5 °C (lit.[44] mp 125 °C). By general procedure B, compound **4** (300 mg, 91%) was also obtained from 480 mg of **3**.

Irradiation of the Nitronate Anion of 3α-Acetoxy-17β-nitro-5α-androstane (5). Nitrosteroid **5** (1.42 g) was dissolved in 550 mL of MeOH–MeONa solution (MeONa, 6.88 × 10^{-2} mol). This solution was irradiated for 3 h and worked up as in general procedure A. The resulting residue was separated by flash-column chromatography with 20:1 chloroform–ethanol as eluant to yield a brown semisolid (1.00 g), which was recrystallized from methanol to give 985 mg (78%) of 17α-aza-3α,17α-dihydroxy-D-homo-5α-androstan-17-one 3-acetate (**6**) as needles: mp 226–231 °C (lit.[6] mp 228–233 °C), $[\alpha]^{20}D$ –2.49° (dioxane; (lit.[8] $[\alpha]^{20}_D$ –2° (dioxane)). Other components, 3α-acetoxy-17,18-cyclo-5α-androstane (**7**; 215 mg, 17%), 3α-acetoxy-5α-androstan-17-one (**8**; 10 mg, 0.8%), and 3α-acetoxy-5α-androstan-17-one oxime (**9**; 29 mg, 2%), eluted ahead of hydroxamic acid **6**, were also separated by flash-column chromatography (**8**, mp 164–165 °C (lit.[13] mp 164.5–165.5 °C); **9**, mp 215 °C (lit.[13] mp 215 °C)). **7** was recrystallized from EtOH–Et_2O to yield needles: mp 98–103 °C; IR (CCl_4) 1745 ($\nu_{C=O}$), 1240 (δ_{C-O-C}) cm^{-1}; NMR ($CDCl_3$) δ 4.99 (br s, $W_{1/2}$ = 7 Hz, 1 H, C-3H, eq), 2.06 (s, 3 H, AcO), 0.80 (s, 3 H, C-19Me), 0.56 (m, 1 H), 0.29 (m, 1 H), –0.04 (m, 1 H); mass spectrum, calcd for $C_{21}H_{32}O_2$ m/e 316.2400 (M), found m/e 316.2389 (M^+). Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.50; H, 9.97%.

Hydrolysis of 7. Treating of **7** in 10% NaOH–MeOH gave 3α-hydroxy-17,18-cyclo-5α-androstane (**12**; 70%): mp 130–132 °C; IR (CCl_4) 3420 (ν_{OH}), 1456 (δ_{CH}) cm^{-1}; NMR (CCl_4)[45] δ 5.5–6.0 (m, 1 H), 4.10 (br s, $W_{1/2}$ = 10 Hz, 1 H, C-3H, eq), 0.83 (s, 3 H, C-19 Me), 0.32 (m, 1 H), 0.04 (m, 1 H), –0.04 (m, 1 H); mass spectrum, calcd for $C_{19}H_{30}O$ m/e 274.2295 (M), found m/e 274.2295 (M^+).

Irradiation of the Nitronate Anion of 6β-Nitro-5α-cholestanyl 3β-Acetate (14). A solution of **14** (616 mg) in 550 mL of t-BuOK–t-BuOH (K metal, 510 mg) was irradiated for 30 min and was treated by general procedure A to give 67 mg (12.2%) of 6-aza-3β,6-dihydroxy-B-homocholestan-6a-one 3-acetate (**15**): mp 175–178 °C; IR (CCl_4) 3250 (ν_{OH}), 1740 ($\nu_{C=O}$), 1640 ($\nu_{C=O}$), 1240 (δ_{C-O-C}) cm^{-1}; NMR ($CDCl_3$) δ 7.14 (br s, 1 H, OH), 4.60 (br s, $W_{1/2}$ = 20 Hz, 1 H, C-3H, ax), 2.33 (br s, 2 H), 2.03 (s 3 H, AcO), 0.84 (s, 3 H, C-19Me), 0.68 (s, 3 H, C-18Me); mass spectrum, calcd for $C_{29}H_{49}NO_2$ m/e 475.3658 (M), found m/e 475.3616 (M^+). Also byproducts cholesteryl acetate (**16**; 230 mg, 42%) and 3β-hydroxy-5α-cholestan-6-one (**17**; 201 mg, 36.7%) were obtained (**16**, mp 111–113 °C (lit.[46] mp 114–115 °C); **17**, mp 139–141 °C (lit.[14] mp 142–143 °C)).

Irradiation of the Nitronate Anion of 2-Nitrobornane (18). A solution of **18** (1.14 g) in 550 mL of EtONa–EtOH (1:2 18:EtONa) was irradiated for 4.5 h, and the reaction mixture was treated by general procedure A to afford pure 1,8,8-trimethyl-2-hydroxy-2-azabicyclo[3.2.1]octan-3-one (**19**; 710 mg, 76%), mp 212–214 °C (lit.[15] mp 214–215 °C). The optical rotations of **18** and **19** (both 9.5 × 10^{-4} mol) were obtained in the presence of 9.5 × 10^{-4} mol of EtONa in EtOH at 18 °C as –128.8 and –74.1°. Also from this reaction products camphor (**20**; 5 mg, 0.6%) and camphoroxime (**21**;[16] 20 mg, 2.3%) were obtained.

Irradiation of the Nitronate Anion of Nitrocycloheptane (22). By general irradiation procedure A, 1.43 g of **22** was irradiated for 3 h, and 210 mg (18%) of cycloheptanone oxime was obtained, mp 24 °C (lit.[47] 25 °C).

Irradiation of the Nitronate Anion of 2-Methylnitrocyclohexane (23). A solution of **23** (900 mg) in MeOH–MeONa (1:2 **23**:MeONa) was irradiated for 4 h. The reaction mixture was worked up according to general procedure A, and 160 mg (23%) of hexahydro-1-hydroxy-7-methyl-2H-azepin-2-one (**27**) was obtained as liquid: bp 140 °C (5 mmHg); IR (CCl_4) 3200 (ν_{OH}), 1640 ($\nu_{C=O}$) cm^{-1}; NMR (CCl_4) δ 8.7 (s, 1 H), 4.0 (m, 1 H), 2.4 (m, 2 H), 1.7 (m, 6 H), 1.3 (d, J = 7 Hz, 3 H); mass spectrum, calcd for $C_7H_{13}NO_2$ m/e 143.0852 (M), found m/e 143.0947 (M^+). N-Hydroxy lactam **27** was reduced with platinum oxide in AcOH–AcOEt solution under the atmospheric pressure. The crude residue was crystallized from petroleum ether to give hexahydro-7-methyl-2H-azepin-2-one (**29**) in 90% yield, mp 88 °C (lit.[18] mp 90–92 °C).

Irradiation of the Nitronate Anion of 2-Ethoxynitrocyclopentane (24). According to general procedure A, 200 mg of **24** was irradiated for 3 h. N-Hydroxy-6-ethoxy-2-piperidone (**28**) was obtained in 75% (150 mg) yield: mp 63.5–64.5 °C; IR (neat) 3200 (ν_{OH}), 1650 ($\nu_{C=O}$) cm^{-1}; NMR (CCl_4) δ 7.6 (m, 1 H), 4.9 (d, J = 4 Hz, 1 H), 3.8 (q, 2 H), 2.7–1.5 (6 H), 1.2 (t, 3 H); mass spectrum, calcd for $C_7H_{13}NO_3$ m/e 159.0894 (M), found m/e 159.0845 (M^+). Anal. Calcd for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.80%. Found: C, 52.55; H, 8.28; N, 8.47.

Hydrolysis of 28. A solution of 45 mg of **28** in AcOEt that contained a trace of hydrochloric acid was treated with hydrogen on platinum oxide at atmospheric pressure for 30 h. The catalyst was removed by filtration, and the resulting filtrate was worked up as usual to give 6-ethoxy-2-piperidone (**30**; 36 mg, 80%), mp 44.5–45 °C (from ether; lit.[19] mp 45 °C).

Irradiation of the Nitronate Anion of Nitrocyclohexane (25). By general procedure A, from 530 mg of **25**, N-hydroxy-ε-caprolactam (**26**; 6.4%), cyclohexanone oxime (40%) and cyclohexanone (10%) were yielded. Yields of these products were calculated by gas chromatography.

Irradiation of the Nitronate Anion of Nitrocyclobutane (31). By general procedure A, 400 mg of **31** (1:10 **31**:EtONa) was irradiated for 2 h. N-Hydroxy-2-pyrrolidine (**32**;[48] 110 mg, 37%) was obtained as crystals, mp 83–85 °C (lit.[48] mp 80–81 °C).

Irradiation of the Nitronate Anion of Nitrocyclopentane (33). According to general procedure A, 1.00 g of **33** was irradiated for 5.5 h. The reaction product was worked up as usual, and 26% (90 mg) of N-hydroxy-2-piperidone (**34**) was obtained as crystals, mp 45–47 °C (lit.[7,49] mp 50–51 °C).

Irradiation of the Nitronate Anion of 2-Ethoxynitrocyclohexane (35). A solution of 412 mg of **35** in 500 mL of

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(45) According to Misiti and co-workers,[10] NMR signals of the cyclopropane ring of 3β-acetoxy-17,18-cycloandrost-5-ene appear at δ 0.73, 0.28, and –0.04 ppm. The melting point of 3β-hydroxy-17,18-cyclo-5α-androstane was reported to be 153–155 °C. Furthermore, Hassner[11] reported that the half-height width of 3β-H proton signal is narrow (5–12 Hz).

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EtOH–EtONa (pH 12.6) was irradiated for 1 h and worked up as usual to give *N*-hydroxy-7-ethoxydihydroazepin-2-one (**36**; 193 mg, 68% at 70% conversion): bp 70 °C (1 mmHg); IR (CCl_4) 3200 (ν_{OH}), 1645 ($\nu_{C=O}$) cm^{-1}; NMR ($CDCl_3$) δ 9.2 (br s, 1 H), 5.0 (d, 2 H), 3.7 (m, 2 H), 2.5 (m, 2 H), 1.8 (m, 3 H), 1.2 (t, 3 H); mass spectrum, calcd for $C_8H_{15}NO_3$ m/e 173.1050 (M), found m/e 173.1047 (M^+). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 55.47; H, 8.73. Found: C, 55.85; H, 8.80.

Irradiation of the Nitronate Anion of 1-Nitro-2-phenylcyclohexane (37). According to general procedure A, 994 mg of **37** was irradiated for 15 h, and *N*-Hydroxy-7-phenyl-ϵ-caprolactam (**38**) was isolated: IR (CCl_4) 3200 (ν_{OH}), 1640 ($\nu_{C=O}$) cm^{-1}; NMR (CCl_4) δ 9.3 (br s, 1 H), 7.3 (s, 5 H), 5.1 (t, 1 H), 2.2 (m, 4 H), 1.5 (m, 4 H); mass spectrum, calcd for $C_{12}H_{15}NO_2$ m/e 205.1101 (M), found m/e 205.1086 (M^+).

Irradiation of the Nitronate Anion of 4-Phenyl-5-nitrocyclohexene (39). By general procedure A, 939 mg of **39** was irradiated for 11.5 h, and *N*-hydroxy-7-phenyl-3*H*,6*H*,7*H*-azepin-2-one (**40**; 239 mg, 46% at 55% conversion) was obtained: IR (CCl_4) 3200 (ν_{OH}), 1640 ($\nu_{C=O}$) cm^{-1}; NMR (CCl_4) δ 7.9 (s, 5 H), 5.7 (m, 2 H), 5.0 (t, 1 H), 3.2 (d, 2 H), 2.8 (q, 2 H); mass spectrum, calcd for $C_{12}H_{13}NO_2$ m/e 203.0945 (M), found m/e 203.0928 (M^+).

Irradiation of the Nitronate Anion of 5-Nitrobicyclo-[2.2.1]hept-2-ene (41). By general procedure B (pH 12.5), 504 mg of **41** was irradiated for 1 h, and *N*-hydroxy-2-azabicyclo-[3.2.1]oct-6-en-3-one (**42**; 475 mg, 95%) was obtained as crystals: mp 68 °C; IR ($CHCl_3$) 3120 (ν_{OH}), 1650 ($\nu_{C=O}$) cm^{-1}; NMR ($CDCl_3$) δ 9.12 (m, 1 H), 6.39 (q, 1 H), 6.03 (q, 1 H), 4.10 (m, 1 H), 2.70 (m, 1 H), 2.39 (m, 1 H), 2.16 (m, 1 H), 1.85 (m, 2 H); mass spectrum, calcd for $C_7H_9NO_2$ m/e 139.0632 (M), found m/e 139.0614 (M^+). Anal. Calcd for $C_7H_9NO_2$: C, 60.47; H, 6.57; N, 9.75. Found: C, 60.42; H, 6.52; N, 10.07.

Irradiation of the Nitronate Anion of 2-Nitro-3-phenylbicyclo[2.2.1]heptane (43). By general procedure A, 738 mg of **43** was irradiated for 6 h, and *N*-hydroxy-4-phenyl-3-azabicyclo[3.2.1]octan-2-one (**44**; 220 mg, 65% at 45% conversion) was obtained by silica gel column chromatography with AcOEt as an eluant: mp 159 °C; IR (CCl_4) 3200 (ν_{OH}), 1650 ($\nu_{C=O}$), 1360 (δ_{N-O}) cm^{-1}; NMR ($CDCl_3$) δ 8.6 (br s, 1 H), 7.2 (s, 5 H), 4.5 (s, 1 H), 2.9 (m, 1 H)[, 2.0 (5 H), 1.3 (1 H); mass spectrum, calcd for $C_{13}H_{15}NO_2$ m/e 217.1102 (M), found m/e 217.1104 (M^+). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.56; H, 6.92; N, 6.42.

Irradiation of the Nitronate Anion of 1-Phenyl-2-nitropropane (45). According to general procedure A, *N*-benzylacetohydroxamic acid (137 mg, 17%) was obtained as crystals, mp 125–127 °C (lit.[50] mp 124 °C), from 1.11 g of **45**.

Irradiation of the Nitronate Anion of 2-Nitronorbornane (46). By general procedure B (pH 12.5), 509 mg of **46** was irradiated for 1.5 h. The resulting product was purified by flash-column chromatography with AcOEt as eluant to give a mixture of 290 mg (78%) of *N*-hydroxy-2-azabicyclo[3.2.1]octan-3-one (**48**) and *N*-hydroxy-3-azabicyclo[3.2.1]octan-2-one (**49**). Yields of **48** and **49** were determined by NMR spectra as 41% and 37%. NMR ($CDCl_3$) δ 9.12 (s, 1 H), 4.02 (br s, 0.53 H, C-1 of **48**), 3.70 (q, J = 11.0, 3.6 Hz, 0.47 H, exo-C-4H of **49**), 3.32 (d, J = 11.0 Hz, 0.47 H, endo-C-4H of **49**), 2.75 (br s, 0.47 H, C-1H of **49**), 2.54 (br s, 1.06 H, C-4H of **48**), 2.3–1.5 (7 H); mass spectrum, calcd for $C_7H_{11}NO_2$ m/e 141.0789 (M), found m/e 141.0779 (M^+); UV λ_{max} (MeOH) 214 nm (ϵ 2120). Accompanied with the mixture of **48** and **49**, norcamphor[51] (41 mg, 11%) and norcamphoroxime[51] were isolated and identified by comparison of the spectral data with those of authentic samples.

Oxygen Effect. A solution of 2-nitronorbornane (**46**) in 25 mL of MeOH–$MeNH_2$ (pH 12.36) was irradiated in an aerobic condition by using the merry-go-round (6.0-cm distance from the 80-W low-pressure mercury lamp). Quantitative determination of *N*-hydroxy lactams **48** and **49** was performed by using GC. A solution of a mixture of **48** and **49** in 15 mL of absolute ether was added dropwise to a stirred suspension of 32.6 mg of $LiAlH_4$ in 10 mL of absolute ether. The mixture was refluxed for 3 h and then allowed to stand at room temperature for 12 h. The reaction mixture was added to carefully diluted NaOH solution in order to quench the excess $LiAlH_4$ until the mixture resulted in a clear solution. The resulting semisolids were separated by preparative TLC with AcOEt as eluant. 3-Azabicyclo[3.2.1]octane (**50**) (R_f 0.41, 6.3 mg) and 2-azabicyclo[3.2.1]octane (**51**; R_f 0.17, 11.3 mg) were obtained. Hydrochlorides **50** and **51** were identified by their NMR spectra.[52]

Quenching Experiments. A solution of 2-methylnitrocyclohexane (**23**; 164 mg, 1.15×10^{-3} mol) in MeOH–MeONa (48.3 mg of sodium in 500 mL MeOH) was pipetted into four 25-mL volumetric flasks, and a solution of azulene (1.5×10^{-4} mol in MeOH) was added to these flasks at 6.0×10^{-6}, 4.8×10^{-6}, 3.6×10^{-6}, and 2.4×10^{-6} M in H_2O, respectively. The stock solution was irradiated by the general procedure, and the reaction was followed by UV spectrum. The first-order rate constants obtained by the quenching experiments were substituted in the following equation:

$$\Phi = C_0 \cdot k / I_{abs}$$

where C_0 is the concentration of nitronate **23** (mol/4 mL), I_{abs} is the number of absorbed photons (einsteins/4 mL), and Φ is the quantum yield. In this case, measurement of the absorbed photon number was carried out by use of a ferric oxalate actinometer.[53]

Registry No. 1 nitronate anion, 83705-37-7; **3** nitronate anion, 12413-18-2; **5**, 79929-65-0; **5** nitronate anion, 83705-38-8; **7**, 79935-75-4; **9**, 49566-82-7; **12**, 79929-73-0; 14 nitronate anion, 83705-39-9; **15**, 83705-40-2; **18** nitronate anion, 83705-41-3; **22** nitronate anion, 83705-42-4; **23** nitronate anion, 29916-51-6; **24**, 74221-91-3; **24** nitronate anion, 83705-43-5; **25** nitronate anion, 12349-47-2; **27**, 74221-92-4; **28**, 74221-97-9; **31** nitronate anion, 83705-44-6; **33** nitronate anion, 29916-56-1; **35**, 74221-89-9; **35** nitronate anion, 83705-45-7; **36**, 74221-95-7; **37** nitronate anion, 29916-52-7; **38**, 74221-93-5; **39** nitronate anion, 83705-46-8; **40**, 76784-68-4; **41** nitronate anion, 29916-53-8; **42**, 83705-47-9; **43** nitronate anion, 83705-48-0; **44**, 83705-49-1; **45** nitronate anion, 83705-50-4; **46** nitronate anion, 29916-54-9; **48**, 74222-01-8; **49**, 74221-99-1; 1-nitrocyclopentene, 22987-82-2; 1-nitrocyclohexene, 2562-37-0.

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