Photoinduced Reactions. LXXIII. Solvent Dependence in the Photochemical Reaction of α-Nitroepoxides[1]

Isao SAITO, Masaaki TAKAMI, Toshiro KONOIKE, and Teruo MATSUURA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received June 21, 1973)

The photochemical reaction of α-nitroepoxides showed marked solvent dependence. The photolysis of (1,2-epoxy-2-nitropropyl)benzene (I) in 2-propanol led to the formation of three products 1-phenyl-1-isopropoxy-2-propanone (IIb), 1-phenyl-1,2-propanedione oxime (III) and 1-hydroxy-1-phenyl-2-propanone oxime (IV), whereas on irradiation in ether I gave exclusively IV. However, in *t*-butyl alcohol, benzene, acetone, acetonitrile or *n*-hexane, I was not susceptible to photolysis. The photolysis of α,α'-epoxy-α-nitrobibenzyl (V) in ether gave benzoin oxime (VII) in addition to benzaldehyde and benzoic acid, whereas in methanol it gave benzoin methyl ether (VI) in the dark. These reactions are interpreted in terms of effects of the acidity and hydrogen-donating property of solvents on the excited α-nitroepoxides. The pyrolysis of I and V were also examined.

The photochemical reaction of carbonyl compounds attached to a small ring has been extensively investigated.[2,3] Among these compounds, α,β-epoxyketones are known to give β-diketones and α-hydroxyketones[4-6] *via* mechanisms involving the initial n-π^* excitation followed by opening the epoxy ring.[5,6] In view of the similarity between photochemical behaviors of isoelectronic carbonyl and nitro groups,[7] such as photoreduction and α-cleavage, the photochemical behavior of α-nitroepoxides drew our attention. It also encouraged us that the solution photochemistry of aliphatic nitro compound has yet been little investigated.[8] The present paper deals with results obtained with certain α-nitro epoxides which undergo solvent-depending photochemical reactions.

Results and Discussion

Photolysis of (E)-(1,2-Epoxy-2-nitropropyl)benzene (I). In methanol, I[9] was found to be slowly converted into a methoxyketone IIa[10] with the participation of the solvent even in the dark, whereas I was stable to 2-propanol and ether in the absence of light. Irradiation of I in 2-propanol, ether and mixutres of them was carried out with light through Pyrex under bubbling nitrogen at room temperature. The ratio of photoproducts IIb,[10] III,[11] and IV[9] was solvent-dependent (Table 1). The photochemical conversions appear to occur in protic or hydrogen-donating solvents or ones having both properties since I was unsusceptible to photolysis in benzene, acetone, acetonitrile, and *n*-hexane, but was converted very slowly into III in *t*-butyl alcohol.

TABLE 1. PHOTOLYSIS OF I IN VARIOUS SOLVENTS

Solvent	Yields of products(%)[a]			
	II	III	IV	I
MeOH	85	—	—	12
i-PrOH	31	41	11	17
i-PrOH–Et_2O 9:1	20	25	15	39
i-PrOH–Et_2O 1:1	8	—	31	57
i-PrOH–Et_2O 1:9	—	—	30	67
Et_2O	—	—	20	80

a) The yields were determined by NMR analyses.

The conversion of I in methanol into IIa was accelerated by irradiation. The protic nature of solvents could be responsible for the formation of II. The decrease of the yield of II in the order, methanol > 2-propanol ≫ *t*-butyl alcohol, is probably due to steric hindrance of the solvents. The hydrogen-donating ability of solvents could be responsible for the formation of IV, since irradiation of I in ether gave exclusively IV. On the other hand, the formation of III should be ascribed to both protic and hydrogen-donating properties of solvents.

TABLE 2. QUENCHING EXPERIMENTS OF I WITH 1,3-PENTADIENE

Quencher concentration (mol/mol of I)	Yields of products (%)[a]					
	In 2-propanol				In ether	
	II	III	IV	I	IV	I
0	24	40	14	22	45	0
1.0	13	7	27	53	—	—
1.5	14	6	11	69	—	—
2.0	6	2	6	86	22	57
3.0	5	1	5	89	—	—
5.0	—	—	—	—	5	93

a) The yields were determined by NMR analyses.

1) Part LXXII: T. Matsuura, A. Horinaka, and R. Nakashima, *Chem. Lett.*, **1973**, 887. Part of this work was reported as a short communication; I. Saito, M. Takami, T. Konoike, and T. Matsuura, *Tetrahedron Lett.*, **1972**, 2689.

2) A. Padwa, "Organic Photochemistry," ed. by O.L. Chapman, Vol. 1, Marcel Dekker Inc., New York (1967), p. 91.

3) A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).

4) S. Bodforss, *Chem. Ber.*, **51**, 214 (1918).

5) C. Lehmann, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **45**, 1031 (1962).

6) H. Wehrli, C. Lehmann, K. Schaffner, and O. Jeger, *ibid.*, **47**, 1336 (1964).

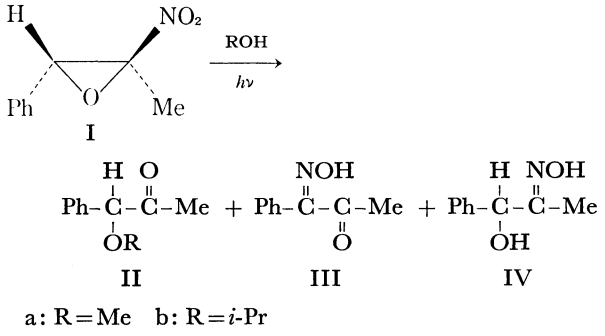
7) H.A. Morrison, "The Chemistry of the Nitro and Nitroso Groups", part 1, ed. by H. Feuer, Interscience, New York, N. Y., (1969), p. 165.

8) a) S. T. Reid and J. N. Tucker, *Chem. Commun.*, **1970**, 1286. b) S. T. Reid and E. J. Wilcox, *Tetrahedron Lett.*, **1972**, 1759. c) C. Chachaty and A. Forchioni, *ibid.*, **1968**, 1079.

9) H. Newmann and R. B. Angier, *Tetrahedron*, **26**, 825 (1970).

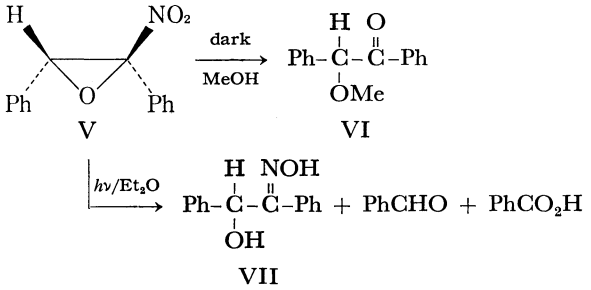
10) V. Auwers and L. Muller, *Ann. Chem.*, **524**, 155, 162, 170 (1936).

11) O. L. Chapman, *Pure Appl. Chem.*, **9**, 585 (1964).



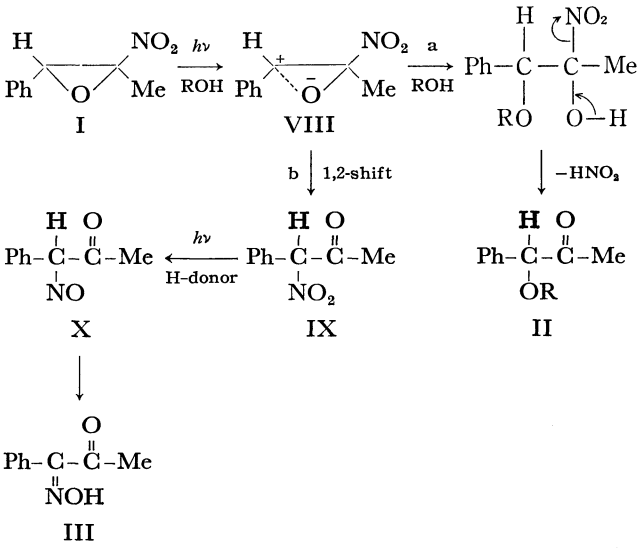
a: R=Me b: R=*i*-Pr

Photolysis of (E)-α,α'-Epoxy-α-nitrobibenzyl (V). Analogously to the dark reaction of I in methanol, V[9] reacted readily with methanol in the absence of light resulting in the formation of benzoin methyl ether (VI).[12] Irradiation of V in ether under similar conditions gave a complex mixture of products, from which benzoin oxime (35%) corresponding to IV, benzaldehyde (15%) and benzoic acid (11%) were isolated. The photolysis of V in 2-propanol was more complex and the isolation of pure products was unsuccessful, whereas V did not undergo photochemical change in *t*-butyl alcohol, benzene, and *n*-hexane under similar conditions.



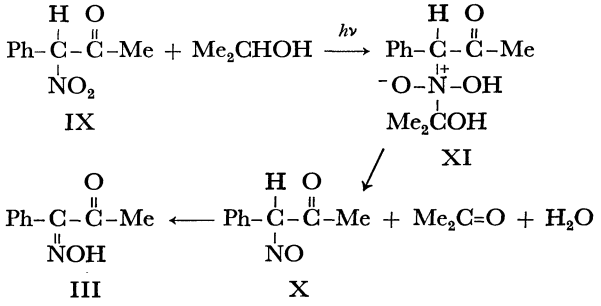
Mechanistic Consideration. As already pointed out, the presence of an aprotic solvent is requisite for the formation of II and III during the photolysis of I. This may be interpreted by considering on 1,3-dipolar intermediate VIII which is derived from the excited state of I, probably with the assistance of a solvent proton. The intermediate VIII may undergo two competitive processes, path a and path b shown in Scheme 1. In path a, VIII reacts with an alcohol to form II with the elimination of nitrous acid. Nitrogen oxides resulted from nitrous acid were experimentally detected. The photochemical addition of alcohols to simple epoxides has been reported,[13–15] although the reaction suffers auto-catalysis by a trace amount of acidic matter formed during the photolysis.[13,14] In methanol, which is more nucleophilic and has a more acidic proton than 2-propanol, the solvent can attack even in the ground state of I to the β-C–O bond having a considerably polar character attributable to the nitro group.

12) I. Wier, *J. Chem. Soc.*, **91**, 1391 (1905).
13) K. Tokumaru, This Bulletin, **40**, 242 (1967).
14) M. Hisaoka and K. Tokumaru, *Chem. Lett.*, **1973**, 351.
15) R. C. Petterson, C. S. Irving, A. M. Khan, G. W. Griffin, and I. M. Sarkar, 18th. National Meeting of the American Chemical Society, September, 1969, New York, ORGN-10.



Scheme 1.

In path b, the 1,3-dipolar intermediate VIII undergoes a 1,2-shift of the nitro group to form an α-nitro ketone IX in competition with the attack of an alcohol to the cationic β-carbon. An analogous rearrangement of I to IX is known to occur by acid catalysis with boron trifluoride.[9] The α-nitroketone IX may be photochemically reduced in a hydrogen-donating solvent to III possibly *via* an α-nitrosoketone X. Supporting this scheme, IX was found to be rapidly reduced upon irradiation in 2-propanol to give III in good yield. To the best of our knowledge, the photoreduction of an aliphatic nitro compound to an oxime is the first example. The photoreduction of IX to III may be rationalized by a mechanism involving the intermediary formation of a coupling product XI between IX and 2-propanol (Scheme 2). Similar intermediates have been proposed by Reid and co-workers.[8]

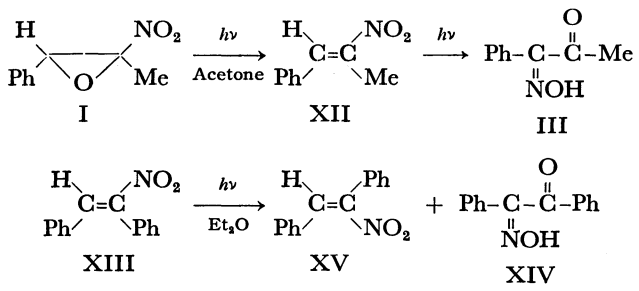


Scheme 2.

For the formation of III, an alternative pathway should be considered, which involves photochemical deoxygenation of the epoxy ring of I followed by rearrangement of a nitroolefin XII to form III (Scheme 3). In fact, the photochemical rearrangement of XII into III has been reported by Chapman and co-workers.[16] We found that *cis*-α-nitrostilbene (XIII) underwent the same rearrangement to benzil oxime (XIV) in addition to the known isomerization to

16) O. L. Chapman, P. G. Cleveland, and E. D. Hogauson, *Chem. Commun.*, **1966**, 101.

trans-α-nitrostilbene (XV).[17] Considering the fact that neither XIV nor XV was obtained by the photolysis of V, which is expected to form XIII according to Scheme 3, the pathway involving the initial deoxygenation is less probable than Scheme 1.



Scheme 3.

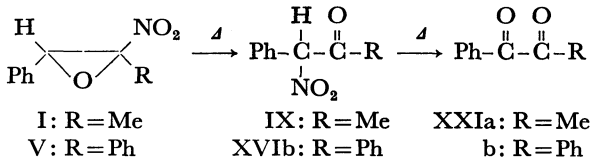
Four possible pathways were considered for the formation of α-hydroxyimino alcohols IV and VII by the photolysis in a hydrogen-donating solvent of I and V respectively (Scheme 4). Path a involves rearrangement to an α-nitroketone XVI analogous to the photorearrangement of α,β-epoxyketones to β-diketones,[4] followed by photoreduction leading to IV or VII. This pathway was eliminated by the finding that XVIb was unsusceptible to photolysis in ether. Path b involves reduction to an α-nitro alcohol XVII followed by further photoreduction leading to IV or VII. Path b was also excluded by the finding that neither XVIIa[9] or XVIIb[18] was susceptible to photolysis in ether.

Path c and path d involve photoreduction of the nitro group leading to a hydroxylamine XVIII and a nitrosoepoxide XIX respectively. The former will be tautomerized and the latter photoreduced to IV or VII. Attempts to synthesize these possible intermediates were unsuccessful. Available evidences at present cannot distinguish between path c and path d.

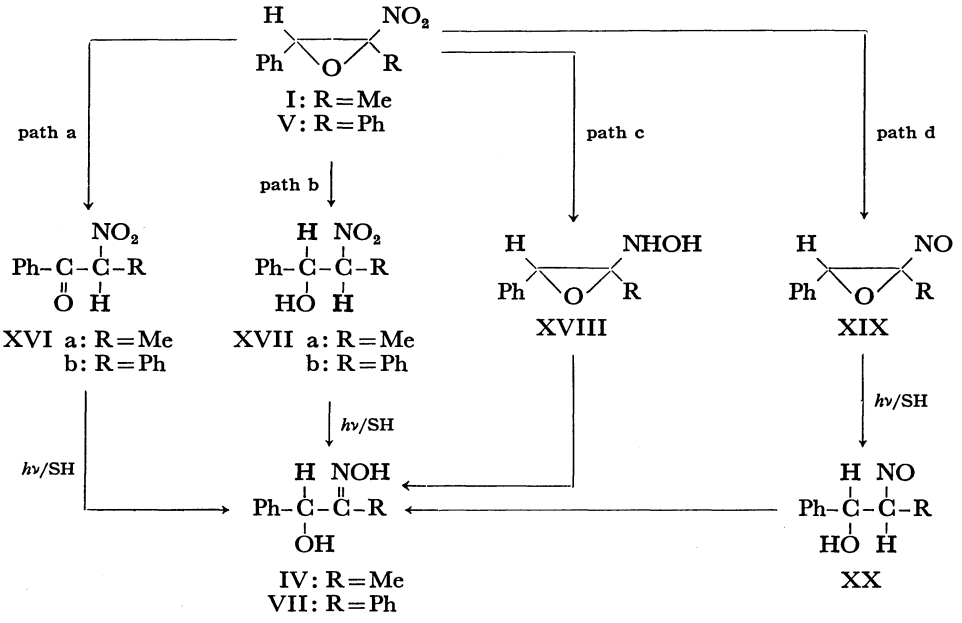
In order to obtain informations on the nature of the excited state of α-nitroepoxides, quenching experiments were carried out with I in 2-propanol and ether. Piperylene was found to quench both the disappearance of I and the formation of II, III, and IV in 2-propanol and of IV in ether. A triplet state of I may be responsible for the first step of the over-all reactions.

In conclusion, the photochemistry of α-nitroepoxides distinctly differs from that of α,β-epoxyketones, an isoelectronic analog. It may be reasonable to assume that the difference is due to a more polar character of nitro group which alters the electronic situation of the epoxy ring as already seen from the reactivity to methanol in the ground state.

Pyrolysis of α-Nitroepoxides I and V. When I was heated at 120—130 °C at atmospheric pressure, three products, IX (33%), XXIa[9] (21%) and benzaldehyde (6%) were obtained. Pyrolysis of I at 150 °C at 20 mmHg gave exclusively XXIa. A similar temperature dependence was observed in the pyrolysis of V. Thus XVIb was exclusively obtained on pyrolysis at 100 °C, while benzil (XXIb) (80%), benzaldehyde (15%) and benzoic acid (5%) were obtained at 150 °C.



It is evident that α-nitroketones IX and XVIb are an intermediate in the formation of XXI, since pyrolysis of IX at 150 °C and XVIb at 200 °C was found to give XXIa and XXIb respectively. The initial step



Scheme 4.

17) J. A. Sousa, J. Weinstein, and A. L. Bluhm, *J. Org. Chem.*, **34**, 3320 (1969).

18) F. G. Bordwell and E. W. Garbisch, Jr., *ibid.*, **27**, 2322 (1962).

of these pyrolysis reactions may be a homolytic cleavage of the C–NO_2 bond as seen in the pyrolysis of nitromethane.[19]

Experimental

All mps are uncorrected. IR spectra were obtained by a Japan Spectroscopic Co., Model IRS spectrometer. NMR spectra were obtained on a Varian T-60 NMR spectrometer with TMS as an internal standard. Elemental analyses were performed at Elemental Analysis Center of Kyoto University.

Dark Reaction of (E)-(1,2-Epoxy-2-nitropropyl)benzene (I) with Methanol. A solution of I[9] (20 mg) in 20 ml of anhydrous methanol in a Pyrex tube was let to stand for 21 hr at room temperature under nitrogen atmosphere. After evaporating under reduced pressure, the residue showed two spots on tlc. Analysis of the residue by NMR indicated that it consisted of unreacted I (59%) and IIa (41%). After purifying by glpc (DC-550 Silicone on Celite column at 160 °C), IIa was obtained as a colorless oil, which was identified by a comparison of its IR spectrum with that of an authentic sample.[10] ν_{max} (neat) 1720 cm^{-1}; NMR ($CDCl_3$): δ 2.13 (s, 1H), 3.60 (s, 3H), 6.67 (s, 1H), and 7.40 (s, 5H).

Irradiation of (E)-(1,2-Epoxy-2-nitropropyl)benzene (I). *A) In Methanol*: A solution of I [λ_{max}^{EtOH}: 290 nm (ε 450) and 230 nm (ε 4500)] (0.23 g) in 100 ml of purified methanol was irradiated with a 100 W high-pressure mercury lamp (Pyrex filter) under bubbling nitrogen for 5 hr. The gas outlet tube was connected to a trap containing a solution of sulfanilic acid (5 g) and *N,N*-dimethylnaphthylamine (5 g) in 200 ml of acetic acid. The trap solution was turned to red, indicating the liberation of nitrogen oxides.[20] The reaction mixture was evaporated to give a residue, the NMR spectrum of which showed the same spectral pattern as that of the dark reaction products. After purifying by glpc (DC-550 Silicone on Celite column at 160 °C), IIa was obtained as a colorless oil, which was identical with an authentic sample (IR).[10] The yields were determined by NMR analysis; IIa in 69% and I in 31%.

B) In 2-Propanol: A solution of I (0.50 g) in 5 ml of 2-propanol in a Pyrex tube was externally irradiated for 40 hr under nitrogen atmosphere with a 100 W high-pressure mercury lamp at room temperature. The reaction mixture was evaporated and the residue was chromatographed on neutralized alumina (15 g). Elution with benzene afforded 0.1 g of recovered I. Further elution with benzene yielded 0.15 g of IIb as a slightly yellow oil, which was identical with an authentic sample (IR).[10] Elution with chloroform gave a brown mass. After recrystallization from ethyl acetate colorless crystals were obtained (0.2 g), mp 160—161 °C, which were identified to be III by a comparison of its IR spectrum with that of an authentic sample.[11] ν_{max} (nujol) 3300 and 1670 cm^{-1}; NMR ($(CD_3)_2CO$): δ 2.47 (s, 3H), 7.36 (s, 5H), and 11.50 (s, 1H). Further elution with chloroform gave a brown mass. After recrystallization from ethyl acetate IV was obtained as colorless crystals (0.05 g), mp 111—112 °C, which were identical with an authentic sample (IR),[9] NMR ($(CD_3)_2CO$): δ 1.68 (s, 3H), 4.72 (s, 1H), 5.31 (s, 1H), 7.39 (s, 5H), and 11.40 (s, 1H).

C) In Ether: A solution of I (0.5 g) in 5 ml of anhydrous ether in a Pyrex tube was irradiated for 40 hr as above. The reaction mixture was evaporated and the resulting brown oil was chromatographed on neutralized alumina (15 g). Elution with chloroform gave colorless crystals. Recrystallization from ethyl acetate gave IV (0.15 g), mp 111—112 °C, which was identical with an authentic sample (IR).[9]

D) In Mixtures of 2-Propanol and Ether of Different Ratios: Solutions of I (50 mg) in each 20 ml of three solvent systems (2-propanol and ether; 9:1, 1:1, and 1:9) in Pyrex tubes under nitrogen atmosphere were irradiated for 40 hr with a 100 W high-pressure mercury lamp using a merry-go-round apparatus at room temperature. After evaporating, the yields of II, III, and IV were determined by NMR analysis. These results are shown in Table 1.

E) In Other Solvents (t-Butyl Alcohol, Benzene, Acetone, Acetonitrile, and n-Hexane): Solutions of I (50 mg) in each 20 ml of the solvents were externally irradiated under the same conditions as described in D). The reaction mixtures were monitored by tlc. After evaporating, the residues were analyzed by NMR indicating that I was recovered completely in benzene, acetone, acetonitrile, and *n*-hexane. Analyses of the product mixture obtained in *t*-butyl alcohol by tlc and NMR showed the existence of a small amount of III.

Dark Reaction of (E)-α,α'-Epoxy-α-nitrobibenzyl (V) in Methanol. A solution of V[9] (0.35 g) in 4 ml of anhydrous methanol in a Pyrex tube was let stand for 1 day at room temperature under nitrogen atmosphere. After evaporating, the residue showed a single spot on tlc and a single peak on glpc (DC-550 Silicone on Celite column at 160 °C). After purifying by glpc, the product VI was obtained as an oil, which was identical with an authentic sample (IR).[12] ν_{max} (neat) 1670 cm^{-1}; NMR ($CDCl_3$): δ 3.45 (s, 3H), 5.53 (s, 1H), and 8.20—7.20 (m, 10H).

Irradiation of (E)-α,α'-Epoxy-α-nitrobibenzyl (V). *A) In Methanol*: A solution of V [λ_{max}^{EtOH}: 290 (ε 800) and 232 nm (ε 6000)] (0.35 g) in 4 ml of anhydrous methanol was externally irradiated with a 100 W high-pressure mercury lamp for 40 hr under nitrogen atmosphere. After evaporating, glpc, tlc, and NMR analyses of the residue showed that it consisted of only IV.

B) In Ether: A solution of V (1.8 g) in 50 ml of dry ether was irradiated with a 100 W high-pressure mercury lamp under bubbling nitrogen at room temperature. After 11 hr V was completely consumed, which was monitored by tlc. The reaction mixture was evaporated and the residue was chromatographed on silica gel column (50 g). Elution with 90 ml of benzene afforded an oil (0.09 g), identified as benzaldehyde (IR). Elution with 800 ml of a mixture of benzene and chloroform (*ca.* 1:1) gave colorless crystals (0.28 g), identified as benzoic acid (IR). Elution with 100 ml of chloroform gave VII (0.63 g) as colorless crystals, mp 150—153 °C, which were identical with an authentic commercial sample (IR). NMR (DMSO-d_6): δ 5.60 (s, 1H), 7.27 (s, 10H), and 10.87 (s, 1H).

C) In 2-Propanol: A solution of V (0.1 g) in 20 ml of 2-propanol was externally irradiated with a 400 W high-pressure mercury lamp for 20 hr under nitrogen atmosphere at room temperature. After evaporating, the residue showed nine spots on tlc (silica gel with chloroform). The isolation of pure products was unsuccessful.

Irradiation of 2-Nitro-1-phenyl-1-propanol (XVIIa). A solution of XVIIa[9] (0.18 g) in 20 ml of ether in a Pyrex tube was externally irradiated with a 400 W high-pressure mercury lamp under nitrogen atmosphere for 50 hr at room temperature. After evaporating, the residue was analyzed by tlc and NMR showing that it consisted of only recovered XVIIa.

Irradiation of 1,2-Diphenyl-2-nitroethanol (XVIIb). A

19) a) C. G. Crawforth and D. J. Waddington, *Trans. Faraday Soc.*, **65**, 1334 (1969). b) K. Glänzer and J. Troe, *Helv. Chim. Acta*, **55**, 2884 (1972).

20) F. G. Germuth, *Ind. Eng. Chem., Anal. Ed.*, **1**, 28 (1929).

solution of XVIIb[18] (0.464 g) in 70 ml of ether was irradiated with a 100 W high-pressure mercury lamp (Pyrex filter) under bubbling nitrogen at room temperature for 20 hr. Analyses of the photolyzate by tlc, glpc, and NMR indicated no consumption of XVIIb.

Irradiation of 1-Nitro-1-phenyl-2-propanone (IX). A solution of IX[9] (50 mg) in 20 ml of 2-propanol in a Pyrex tube was externally irradiated for 22 hr with a 400 W high-pressure mercury lamp under nitrogen atmosphere at room temperature. After removal of 2-propanol under reduced pressure, a crystalline mass was obtained. Recrystallization from ethyl acetate gave III as colorless crystals (13 mg), mp 160—161 °C, which were identical with an authentic sample (IR and NMR).[11]

Preparation of 2-Nitro-2-phenylacetophenone (XVIb). To a solution of 1,2-diphenyl-2-nitroethanol (XVIIb;[18] 5 g) in 50 ml of acetone was added dropwise (30 min) under stirring a solution of chromium trioxide (13 g) in a mixture of 40 ml of water and 10 ml of conc. sulfuric acid at room temperature. After the addition of chromium trioxide, the reaction mixture was stirring for about 3 hr. The mixture was diluted with 150 ml of acetone and 150 ml of water, then extracted with ether. The ethereal layer was washed with water and dried over anhydrous sodium sulfate. After the removal of ether, a crystalline mass was obtained, which was recrystallized from a mixture of benzene and *n*-hexane gave 2 g of XVIb, mp 75 °C; ν_{max} (nujol) 1680, 1560, and 1350 cm^{-1}; NMR ($CDCl_3$): δ 7.3—8.0 (m).

Found: C, 69.51; H, 4.52; N, 5.83%. Calcd for $C_{14}H_{11}NO_2$: C, 69.70; H, 4.59; N, 5.80%.

Irradiation of 2-Nitro-2-phenylacetophenone (XVIb). A solution of XVIb (0.5 g) in 40 ml of ether in a Pyrex tube was externally irradiated with a 400 W high-pressure mercury lamp for 20 hr under nitrogen atmosphere at room temperature. After the removal of ether, analysis of the residue by tlc and NMR indicated no consumption of XVIb.

Quenching Experiments. *A) I with 1,3-Pentadiene in 2-Propanol*: 1,3-Pentadiene was distilled prior to use. Five solutions of I[9] (50 mg; 0.28×10^{-3} mol) in 20 ml of 2-propanol were prepared in Pyrex tubes. To each solution given amounts of 1,3-pentadiene, 0 μl, 30 μl (0.28×10^{-3} mol), 45 μl (0.42×10^{-3} mol), 60 μl (0.56×10^{-3} mol), and 90 μl (0.84×10^{-3} mol) were added. These five tubes were irradiated with a 400 W high-pressure mercury lamp using a merry-go-round apparatus for 13 hr under nitrogen atmosphere at room temperature. After evaporating, the residues were analyzed by NMR. The yields of recovered I and products were determined by NMR analysis. The results were summarized in Table 2.

B) I with 1,3-Pentadiene in Ether: Three solutions containing I (50 mg; 0.28×10^{-3} mol) and a given amount of 1,3-pentadiene (0 μl, 60 μl (0.56×10^{-3} mol) and 150 μl (1.40×10^{-3} mol), in 20 ml of ether were prepared in Pyrex tubes. These three tubes were irradiated for 18.5 hr as above. After evaporating each solution, the yields of recovered I and product IV were determined by NMR analysis. The results were summarized in Table 2.

Pyrolysis of (E)-(1,2-Epoxy-2-nitropropyl)benzene (I). *A) At 150 °C*: The pyrolysis of 20 mg of I[9] was done at 150 °C for 5 min under 20 mmHg. Analysis of the resulting yellow oil by NMR showed complete consumption of I and the yellow oil showed two peaks on glpc (DC-550 Silicone on Celite column at 150 °C). Glpc separation (DC-550 Silicone at 150 °C) gave XXIa as a yellow oil (13 mg), which was identical with an authentic sample.[9] ν_{max} (neat) 1710 and 1680 cm^{-1}; NMR (CCl_4): δ 2.13 (s, 3H) and 7.25—8.20 (m, 5H).

B) At 120—130 °C: A glass tube containing I[9] (25 mg) was heated at 120—130 °C for 10 min. Analysis of the resulting yellow oil by NMR showed that it consisted of recovered I (8%), XXIa (21%), benzaldehyde (6%), IX (33%), and an unknown product (30%). Among XXIa,[9] benzaldehyde, and the unknown product separated by glpc, the former two were identified by a comparison of the NMR and IR spectra with those of authentic samples. The methine proton peak of IX in the NMR spectrum of the product mixture was in accord with that of an authentic sample.[9] When an authentic sample of IX was heated at 150 °C for 5 min, XXIa was obtained quantitatively, which was monitored by NMR.

Pyrolysis of (E)-α,α'-Epoxy-α-nitrobibenzyl (V). *A) At 160 °C*: The pyrolysis of V[9] (24 mg) was done at 160 °C for 1 hr. Analysis of the resulting yellow oil by NMR showed complete consumption of V. Three products were isolated by glpc separation (DC-550 Silicone on Celite column at 160 °C), benzaldehyde (15%), benzoic acid (5%) and benzil (XXIb) (80%), which were identical with authentic samples (IR). The yields were determined by NMR analysis.

B) At 100 °C: The pyrolysis of V[9] (50 mg) was done at 100 °C for 2 hr under 20 mmHg. The reaction mixture solidified to give slightly yellow crystals, which were recrystallized from a mixture of benzene and *n*-hexane to give 25 mg of XVIb as colorless crystals, mp 75 °C, which were identical with an authentic sample (IR and NMR). Pyrolysis of XVIb at 200 °C in a glpc column gave a peak of XXIb.