The Cyclic Addition of Hetero Radicals. II. Cyclic Additions of Alkoxy Radicals in Alkenes[1]

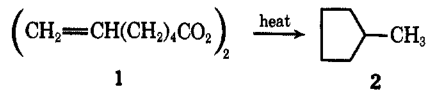
REUBEN D. RIEKE* AND NED A. MOORE[2]

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514

Received June 17, 1971

A series of alkenyl nitrite esters were photolyzed to study the cyclic additions of the resulting alkoxyl radicals. The photolysis of 4-pentenyl-1 nitrite ester resulted in a high yield of tetrahydrofurfural oxime. The apparent preference for formation of five-membered rings over six-membered rings is discussed. Cyclic addition of the 5-hexenyl alkoxy radical only occurs in the presence of iodine. The importance of the photolysis of the nitroso monomer intermediate is discussed. The use of various radical traps as well as quantum yields for cyclic addition *vs.* Barton reaction is also discussed.

Intermolecular addition of radicals to olefins results in the most stable radical intermediate,[3] *e.g.*, the classical example of anti-Markovnikov addition of hydrogen bromide to a double bond. Many free-radical cyclic addition reactions violate this principle. Pyrolysis of 6-heptenoyl peroxide (1) resulted in methylcyclopentane (2), not the expected cyclohexane (eq I).[4]



(I)

Other studies[5-10] have also noted a definite preference for the formation of five-membered ring in the cyclic addition of carbon radicals. Julia[11] has made one of the more thorough studies of the problem and has provided an excellent review.

Capon and Rees[12] have suggested that five-membered ring formation is favored because the addition of the radical to a double bond is so fast that the radical attacks the first termus of the double bond presented to it and that there are simply more conformations presenting the carbon five termus than the carbon six termus.

Surzur and coworkers[13] found the five-membered ring to be preferred to the six by a four to one ratio in the cyclic addition of nitrogen radicals, but in the cyclic addition of sulfur radicals the six-membered ring was generally preferred.[14,15] However, they were able to show conclusively that the addition of the sulfur radical was reversible.

In this paper, we present some of our observations on the cyclic addition of alkoxy radicals generated by the photolysis of nitrite esters.

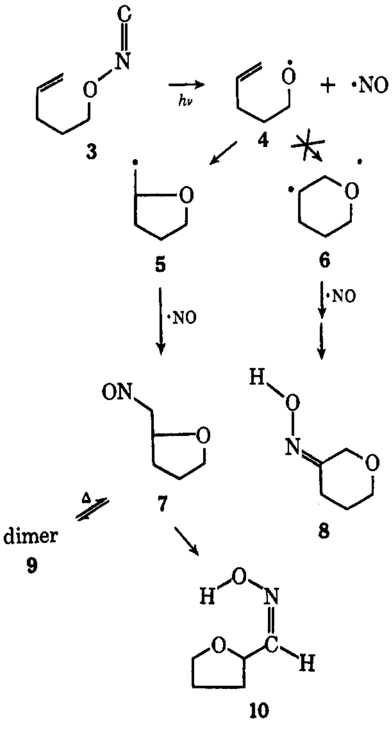
Results

Preparation of the Nitrite Esters.—The nitrite esters of *n*-pentanol, 5-hexan-1-ol, and 4-penten-1-ol were prepared[16] (crude yields from 72 to 93%). All of these nitrite esters proved to be stable when protected from light and stored in a deep freeze.

The nitrites were readily identified by their very characteristic series of low intensity peaks from 310 to 385 mμ in the uv and by their characteristic doublet at 1650 and 1610 cm^{-1} in the ir.[17] Nmr indicated that no migration of terminal double bonds occurred during synthesis. All nitrites were checked for purity by vpc prior to their photolysis, and thick film ir was used to check for the presence of any alcohol in the nitrite.

4-Pentenoxy Radical.—Irradiation of 4-pentenyl-1 nitrite (**3**, Scheme I) yielded as the major product tetrahydrofurfural oxime (**10**).

SCHEME I



Compound **10** was identified by its ir, mass spectrum, and nmr. Nmr was most definitive. Due to the syn and anti isomers, the trigonal carbon proton exhibited

---

[1] For part I of this series, see R. D. Rieke and Ned A. Moore, *Tetrahedron Lett.*, 2035 (1969).

[2] NASA Fellow, 1966–1969; Allied Chemical Fellow, 1969–1970.

[3] W. A. Pryor, "Introduction to Free Radical Chemistry," Prentice Hall, Englewood Cliffs, N. J., 1966, p 23.

[4] R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, **85**, 3483 (1963).

[5] C. Walling and M. S. Pearson, *ibid.*, **86**, 2263 (1964).

[6] N. O. Brace, *ibid.*, **86**, 524 (1964).

[7] N. O. Brace, *J. Org. Chem.*, **31**, 2879 (1966).

[8] N. O. Brace, *J. Org. Chem.*, **32**, 2711 (1967).

[9] R. F. Garwood, C. J. Scott, and B. C. L. Weedon, *Chem. Commun.*, **14** (1965).

[10] R. C. Lamb, J. C. Pacifici, and R. W. Ayers, *J. Org. Chem.*, **30**, 3099 (1965).

[11] M. Julia, *Pure Appl. Chem.*, **15**, 167 (1967).

[12] B. Capon and C. W. Rees, *Ann. Rep. Chem. Soc.* (*London*), **61**, 261 (1964).

[13] J. M. Surzur, P. Tordo, and L. Stellay, *Bull. Soc. Chim. Fr.*, 111 (1970).

[14] J. M. Surzur, M. P. Crozet, and C. DuPuy, *C. R. Acad. Sci.*, 264 (1967).

[15] Some of our preliminary results on the oxidation of unsaturated Bunte salts indicate that the initial ring closure may strongly favor the five-membered ring product.

[16] L. Hunter and J. H. Marriott, *J. Chem. Soc.*, 281 (1936).

[17] P. Kabasakalian and E. R. Townley, *J. Amer. Chem. Soc.*, **84**, 2711 (1962).

TABLE I

COMBINED RESULTS OF VARIOUS 4-PENTENYL-1 NITRITE IRRADIATIONS

Type	Concn	Wt loss,[a] %	% oxime in mixture	% oxime, theory	4-Penten-1-ol	Unknown III, %	Unknown IV, %	Unknown V, %
Normal	8.52×10^{-3}	13.2	62	54	Trace	Trace	8.6	7.3
Normal	7.52×10^{-2}	0	68	68	3.3	Trace	4.3	10
Normal	7.87×10^{-1}	20	61	48	*b*	*b*	*b*	*b*
O_2	8.80×10^{-2}	7.5	35	33	6.5	5.8	8.5	18.8
Filter A	7.54×10^{-2}	*c*	71	*c*	5.1	3.4	Trace	Trace

[a] Weight loss is actually greater than this since some benzene is always present in the mixture recovered after stripping. [b] Additional unknowns appeared. [c] Not irradiated to completion.

two chemical shifts, each a doublet. In DMSO, the oxime proton also exhibited two chemical shifts due to the syn and anti isomers. A 3 to 7 anti to syn ratio was indicated. This procedure was developed by Kleinspehn and coworkers.[18] Compound **10** was also converted into its *p*-nitrophenylhydrazone derivative, which had the same melting point as reported in the literature.[19]

The highest yield, 68% of **10** was obtained when a 7.5×10^{-2} *M* solution of the nitrite ester **3** was irradiated. Four other products were indicated by vpc. One of these, 3.3%, was identified as 4-penten-1-ol. Mass spectral analysis indicated that two of these, totaling 14.3%, were not monomeric. The fourth was only present in a trace amount at this concentration.

A definite concentration effect was observed. Both increasing and decreasing the concentration of nitrite ester by a factor of ten resulted in a decreased yield of the oxime **10**. Results are tabulated in Table I.

The intermediate carbon radical in the Barton reaction has been trapped with various free-radical trapping agents.[20] Similar experiments were tried in the photolysis of the nitrite esters.

A 1.5:1 atomic ratio of iodine to nitrite **3** resulted in a 61% yield of the one major product, 2-iodomethyltetrahydrofuran (**1**), and a 2.5% yield of oxime. Uv indicated no nitroso dimer formation. The pentenyl nitrite **3** proved to be quite stable when stirred in the dark with iodine. Compound **11** was identified by infrared comparison to a known sample prepared by the method of Staninets and Shilov.[21]

Photolysis of the pentenyl nitrite **3** in carbon tetrachloride resulted in a 52% yield of oxime **10**, a 3% yield of 4-penten-1-ol, and only a 7% yield of 2-chloromethyltetrahydrofuran (**12**) which was identified by infrared comparison to a known sample.[22]

The photolysis of a 40:1 molar ratio of bromotrichloromethane to pentenyl nitrite **3** through a sodium nitrate filter solution resulted in a blue solution and no nitroso dimer formation. The sodium nitrate filter solution was used to prevent the photochemical addition of bromotrichloromethane to the carbon–carbon double bond.[23] The blue color, indicating the presence of nitrosotrichloromethane,[20] stripped over with the benzene. A 51% yield of the one major product, 2-bromomethyltetrahydrofuran (**13**), was found. Compound **13** was identified by infrared comparison to a known sample of **13** prepared by the method of Paul.[24] Only a 1% yield of oxime **10** was found.

Effect of Oxygen.—Kabasakalian and Townley[17] noted during their study of the photolysis of *n*-octyl nitrite that in the presence of oxygen *n*-octyl nitrate was the major product and there was no nitroso dimer formation. The photolysis of pentenyl nitrite **3** in a solution that had been purged with oxygen and under an atmosphere of pure oxygen resulted in definite nitroso dimer formation and a 33% yield of tetrahydrofurfural oxime (**10**). Results are tabulated in Table I.

Possible Photolysis of the Nitroso Monomer Intermediate.—In 1935 Anderson and coworkers[25] found that, in the case of tertiary nitroso compounds, light caused the elimination of HNO to form a double bond. Their tertiary nitroso compounds exhibited a broad absorption band from 580 to 740 mμ with maximum absorption at 695 mμ. A filter solution blocking transmission in this region but allowing photolysis of the nitrite ester was prepared. The transmission spectrum of this solution is given in Table II (Experimental Section).

A photolysis, using the filter solution of pentenyl nitrite **3** at the concentration normally resulting in the best yield of tetrahydrofurfural oxime (**10**) was found to result in 10% decrease in the yield of **10**. A similar photolysis at lower concentration resulted in a 4% increase in the yield of **10**. Results, including minor products, are tabulated in Table I.

5-Hexenoxy Radical.—We were unable to isolate any cyclic addition product from the photolysis of the hexenyl nitrite **14** and were only able to separate and identify the corresponding alcohol, 5-hexen-1-ol, in low yield. Similar results have been reported by Surzur and coworkers,[26] who suggested that this was the result of the Barton reaction producing an allyl radical. Our efforts indicate that neither oximes or isoxazolines, both of which could be expected to result from the Bargon reaction, were formed in any significant amount.[27]

Quantum Yield Studies.—It was decided to compare the quantum yield of 4-pentenyl-1 nitrite (**3**) to that

---

[18] G. C. Kleinsphen, J. A. Jung, and S. A. Studniarz, *J. Org. Chem.*, **32**, 460 (1967).

[19] A. Gerrecs and L. Somolyi, *Acta Chim. Acad. Sci. Hung.*, **24**, 73 (1960).

[20] M. Akhtar, D. H. R. Barton, and P. G. Sammes, *J. Amer. Chem. Soc.*, **87**, 4601 (1965).

[21] V. I. Staninets and E. A. Shilov, *Ukr. Khim. Zh.*, **31**, 1286 (1965).

[22] A sample of 2-chloromethyltetrahydrofuran was generously provided by Dr. Burgess Cooke of this laboratory.

[23] C. Walling and E. S. Huyser, *Org. React.*, **13**, 91 (1963).

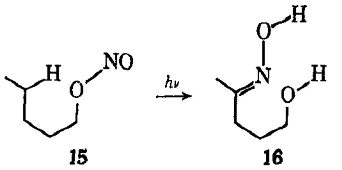
[24] M. R. Paul, *Ann. Chim. (Paris)*, **18**, 303 (1932).

[25] K. D. Anderson, C. J. Crumpler, and D. L. Hammich, *J. Chem. Soc.*, 1679 (1935).

[26] J. M. Surzur, M. P. Bertrand, and R. Nouguier, *Tetrahedron Lett.*, 4197 (1969).

[27] The photolysis of 5-hexenyl nitrite (**14**) in the presence of iodine yielded 42% of 2-iodomethyltetrahydropyran and 14% of 5-hexen-1-ol. Bromination of the stripped off benzene yielded 10% 2-(1,2-dibromo)-ethyltetrahydrofuran. Details of this reaction and other attempts to trap the 5-hexenoxy radical will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

of a suitable saturated nitrite, which should undergo the Barton reaction. *n*-Pentyl nitrite (**15**, eq II)



15 **16**

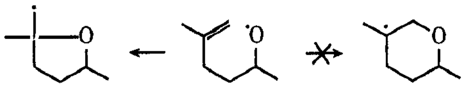
(II)

was chosen because it has a secondary hydrogen available for abstraction and because Kabasakalian and coworkers[28] had reported it to undergo the Barton reaction nicely as indicated by a strong nitroso dimer formation. They did not, however, isolate and identify any of the products. For this reason, and in order to determine a flame ionization detector correction factor for use in its quantum yield determination,[29] compound **15** was irradiated in a benzene solution. Ir indicated the major product to be the expected γ-hydroxypropyl methyl ketoxime (**16**), and vpc analysis indicated a 47% yield.

The quantum yields of both the pentenyl nitrite **3** and *n*-pentyl nitrite were run at the same time under the same conditions. A quantum yield of 0.71 was indicated for the unsaturated nitrite based on the appearance of tetrahydrofurfural oxime (**10**), while a quantum yield of 0.25 was indicated for the saturated nitrite based on the appearance of γ-hydroxypropyl methyl ketoxime (**16**).

Discussion

The pentenoxy radical apparently undergoes cyclic addition to form a five-membered ring with little or no six-membered ring compounds. This result parallels the carbon radical work but is somewhat surprising for the following two reasons. First of all, the five-membered ring product yields the thermodynamically less stable primary radical. Second, the Barton reaction, though admittedly a different type of reaction, requires exclusively a six-membered transition state.[17] Similar results have been reported on the cyclic addition of pentenoxy radical by Surzur and coworkers.[26] Furthermore, Surzur[26] found only five-membered ring cyclization *via* the primary radical **17**, even when cyclic addition *via* a six-membered ring would have resulted in the tertiary radical **18** (eq III).



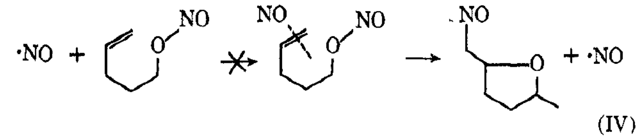
17 (62%) **18**

(III)

Thus, it appears that the observed product is the kinetically controlled product. A possible explanation for the lower energy of activation for the five-membered transition state is a more favorable activation entropy. The kinetic preference of five-membered transition states over six-membered transition states is a frequently observed occurrence in organic reactions.[30,31]

We can conclude that the cyclization observed is the result of photolysis and not thermolysis of the nitrite ester. Both 4-pentenyl-1 nitrite and 5-hexenyl-1 nitrite proved to be stable to refluxing benzene for up to 24 hr. Furthermore, the quantum yield is too low to allow the existence of a free-radical chain.

Also, there does not appear to be any interaction of nitric oxide with the double bond of another 4-pentenyl 1-nitrite involved in the cyclization. Such involvement would appear to require a chain mechanism (eq IV),



(IV)

and, as Surzur and coworkers[26] have suggested, such participation by nitric oxide should result in cyclization in the 5-hexenyl-1 nitrite system. Cyclization does not appear to occur in this system.

However, the best evidence that there is no interaction between nitric oxide and the double bond of another nitrite molecule is the fact that cyclic addition occurs even with other radical traps present. It would appear that there is no way such participation could have resulted in **11** with iodine as a trap and **12** when bromotrichloromethane was used as a trap.

At the same time, the addition of a bromine radical to the double bond of a nitrite molecule can be eliminated because this would require that the trichloromethyl radical, rather than a bromine, be abstracted when using bromotrichloromethane as a trap. It also seems unlikely that the addition of an iodine radical to the double bond of a nitrite molecule is involved in the formation of **11** because the addition of an iodide radical to a double bond is endothermic by 7 kcal[32] and because the nitrite was completely stable when stirred in the dark with iodine.

It is not unexpected that the use of carbon tetrachloride as a trap was largely unsuccessful. It is not a very efficient transfer agent. The bond energy of the C–Cl bond is 68 kcal compared to only 49 kcal for the C–Br bond of bromotrichloromethane.[33]

Possible Photolysis of the Nitroso Monomer Intermediate.—Unfortunately, filter solution A also reduced transmission in the region of the nitrite ester at the same time it blocked transmission in the nitroso monomer region. This makes it difficult to compare the results using the filter solution to those obtained with no filter solution. Use of the filter resulted in longer photolysis times. This means that at any given time there is going to be a lower concentration of reaction intermediates, and a concentration effect was observed in the photolysis of the pentenyl nitrite **3**.

At the concentration normally producing the best yield of oxime **10**, an 8% reduction in yield was observed when the filter solution was used. This was presumably due to the increased photolysis time. On the other hand, the use of the filter solution resulted in a 4% increase in yield at lower concentration.

It would be expected that at lower concentration the photolysis of the nitroso monomer intermediate **7**

---

(28) P. Kabasakalian, E. R. Townley, and M. D. Yudis, *J. Amer. Chem. Soc.*, **84**, 2716 (1962).

(29) H. M. McNair and J. Bonelli, "Basic Gas Chromatography," Varian Aerograph, Walnut Creek, Calif., 1967, p 124.

(30) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964), and references cited therein.

(31) H. Freundlich and H. Kroeplin, *Z. Phys. Chem.*, **122**, 39 (1926).

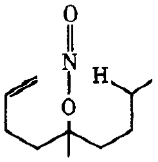
(32) D. H. R. Barton, J. M. Beaton, L. E. Seller, and M. M. Pechet, *J. Amer. Chem. Soc.*, **81**, 80 (1959).

(33) C. J. M. Stirling, "Radicals in Organic Chemistry," American Elsevier, New York, N. Y., 1965, p 167.

should be a greater problem because at lower concentration it should have a longer lifetime. Thus it would appear that, under certain conditions, slight increases in yield may be achieved by protecting the nitroso monomer from photolysis but, in general, it does not appear to be a major problem.

Cyclic Addition *vs.* the Barton Reaction.—The addition of an alkoxyl radical to a double bond is far more exothermic than is the abstraction of a hydrogen atom, 20 kcal as opposed to 8.5 kcal.[34] Also, the formation of the five-membered transition state required for cyclic addition should be faster than the formation of the six-membered transition state required for the Barton reaction. For these reasons, it would be expected that cyclic addition should be faster than the Barton reaction. The evidence indicates that this is indeed the case.

Surzur and coworkers[26] irradiate a molecule (**19**) that was capable of undergoing both cyclic addition and the Barton reaction. They found only the cyclic addition present even though they apparently looked very carefully for the Barton reaction product.



19

Kabasakalian and Townley[17] found the Barton reaction to be completely blocked by the presence of oxygen during their study of the photolysis of *n*-octyl nitrite. They found that the major product was *n*-octyl nitrate, presumably formed *via* reactions V, VI, and VII originally suggested by Hanst and Calvert.[35]

$$CH_3(CH_2)_6CH_2ON{=}O \xrightarrow{h\nu} CH_3(CH_2)_6CH_2O\cdot + \cdot NO \quad (V)$$

$$2\cdot NO + O_2 \longrightarrow 2\cdot NO_2 \quad (VI)$$

$$CH_3(CH_2)_6CH_2O\cdot \longrightarrow CH_3(CH_2)_6CH_2ONO_2 \quad (VII)$$

However, the presence of oxygen does not block cyclic addition during the irradiation of pentenyl nitrite **3**. This suggests that cyclic addition is faster than the oxidation of the nitrite to the nitrate and, hence, faster than the Barton reaction.[36]

Perhaps most conclusive is the large difference in quantum yields for these two processes. The quantum yield for formation of oxime **10** *via* cyclic addition of the pentenoxyl radical is 0.71. This number represents a minimum quantum yield for the cyclic addition process as the primary carbon radical is also most likely involved in the unidentified products. Since the per cent yield of the oxime **10** is about 70%, it is quite likely that the quantum yield for cyclic addition may be close to unity. The quantum yield for the Barton reaction product (**16**, eq II) from the photolysis of *n*-pentyl nitrite was only 0.25 with an observed yield of **16** of 48%. This would place a maximum value of the quantum yield for proton abstraction in the Barton reaction of 0.50 which is still substantially lower than the minimum quantum yield for cyclic addition. The measurement of quantum yields for the disappearance of the two nitrite esters proved to be experimentally too difficult to determine in our hands. Thus, if we make the assumption that the quantum yield for the initial cleavage of the two nitrite esters to the alkoxyl radicals is the same,[37] it would appear that the overall higher quantum yield for cyclic addition can only be explained in terms of a faster forward rate. In the case of the Barton reaction, the slower forward rate would allow more recombination of the alkoxyl radical with nitric oxide to give starting nitrite ester and a lower quantum yield.

Photolysis of 5-Hexenyl-1 Nitrite.[38]—Unfortunately, the results of the photolysis of hexenyl nitrite **14** are somewhat confusing and it is difficult to draw many definite conclusions from them. It is clear that the direct photolysis of the 5-hexenyl-1 nitrite does not yield any monocyclic nonpolymeric products. The results of the photolysis in the presence of radical trapping agents is less clear. The photolysis of the 5-hexenyl-1 nitrite in the presence of iodine is discussed in terms of a separate mechanism.[27]

Conclusions.—The cyclic addition of the 4-pentenoxyl radical has been shown to yield exclusively the five-membered ring product. The controlling factor in yielding a kinetically controlled product rather than a thermodynamically controlled product appears to be a more favorable activation entropy. It was demonstrated that the primary carbon radical resulting from the cyclic addition of the alkoxyl radical can be trapped with several radical traps. The effects of oxygen on the reaction and the quantum yield indicated that the cyclic addition was faster than the Barton reaction. It was demonstrated that the photolysis of the intermediate nitroso monomer was relatively unimportant. Finally, it was shown that the 5-hexenyl alkoxyl radical does not cyclize.

Experimental Section

Ir spectra were recorded on a Perkin-Elmer 237B, uv on a Unicam SP800B, and nmr on a Varian A-60. Quantitative analysis was accomplished using a Perkin-Elmer 881 vpc equipped with flame ionization and using a $^1/_8$ in. × 8 ft column of 5% SE-30 on Chromosorb G. Flame ionization correction factors[29] were determined in all cases unless specified otherwise. Vpc separations were accomplished on a Hewlett-Packard 5750 using thermal detectors and a 0.25 in. × 6 ft column of 10% SE-30 on Chromosorb P. Boiling and melting points are uncorrected.

4-Pentenyl-1 Nitrite.—4-Penten-1-ol (8.5 ml, Aldrich) was added to 8.65 g of sodium nitrite dissolved in 81 ml of water and stirred for 15 min in an ice bath. Concentrated hydrochloric acid (3.8 ml) was then injected with a hypodermic needle into the aqueous layer with stirring. The solution immediately turned a cloudy blue-gray, which rapidly faded to yellow. After 1 hr of vigorous mechanical stirring in the ice bath, a second 3.8-ml portion of acid was injected. Stirring was maintained for an

---

[34] P. Williams and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

[35] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 2071 (1959).

[36] The possibility remains that the difference between the effect of oxygen on the photolysis of *n*-octyl nitrite and the photolysis of pentenyl nitrite **3** lies in the interaction of oxygen with the excited nitrite ester, not with the effect of oxygen on the radical species after cleavage.

[37] Within the limits of the methods used, the uv spectrum and the extinction coefficient of the saturated and the unsaturated nitrite esters were the same.

[38] The photolysis of 3-butenyl-1 nitrite should provide an interesting comparison between cyclic addition to form a five-membered ring and β scission to form an allyl radical. However, Surzur and coworkers[26] reported finding only polymer. We undertook the photolysis of this nitrite with iodine present as a trap and found at least nine different products, no one of which could be called major. This would seem to indicate that there is no one major pathway available to the 3-butenoxy radical. We will endeavor to report on these products in the future.

additional 3 hr. The mixture was protected at all times from direct light. The crude yellow nitrite (8.7 g, 91%) was separated and vacuum distilled while protected from light: bp 53–55° (130 mm); ir (film) 1650, 1610 cm^{-1} (nitrite); uv (95% ETOH) low intensity peaks from 310 to 385 nm, λ_{max} 357 nm (ϵ 100); nmr (neat) τ 5.0 (m, 1 H), 5.7 (m,2 H), 6.0 (t, 2 H), 8.75 (m, 4 H).

Photolysis Precedure.—Irradiations were performed in a 350-ml capacity photolysis flask into which was slipped a quartz, water-jacketed immersion well containing a 450-W medium-pressure Hanovia mercury lamp. The lamp was surrounded by a Pyrex sleeve. Solvents were dried by refluxing over magnesium sulfate prior to their use and all apparatus, with the exception of the immersion well, was oven dried prior to use.

The solution was purged for 1 hr prior to photolysis with a stream of vanadate scrubbed nitrogen to remove all oxygen. If a radical was to be used, nitrogen flow was maintained during photolysis to sweep out as much nitric oxide as possible. If no trap was to be used, nitrogen flow was stopped and the system was sealed during photolysis. Magnetic stirring was used throughout both purging and photolysis.

All nitrites were checked for purity prior to photolysis by vpc and for the presence of alcohols by thick film ir. The disappearance of the nitrite could be followed by uv, and the formation of any nitroso dimer could be monitored by its characteristic peak at 294 nm.[17]

Photolysis of 4-Pentenyl-1 Nitrite.—Nitrite (3.08 g) was added to 350 ml of benzene, purged, and irradiated for 45 min. The solution turned to a deep yellow during photolysis and was stripped to 3.053 g of a viscous oil, which was injected directly into the vpc to reveal a 68% yield of **10**. The heat of the injector, 150°, was sufficient to break down all nitroso dimer into oxime.

Tetrahydrofurfural Oxime (10).—The above oil recovered from the photolysis of 4-pentenyl-1-nitrite was heated for 14 hr at 45° to cleave all nitroso dimer and isomerize it to the oxime. The disappearance of the dimer was followed by uv. Compound **10** was isolated by placing the mixture on a slurry packed column of Florisil activated at 500°F using chloroform as an eluent: ir ($CHCl_3$) 3300 (OH), 1640 (C=N), and 1050 cm^{-1} (CO); uv (95% ETOH) λ end absorption 210 nm (ϵ 1500); nmr (CS_2) 0.5 (s, 1 H, C=NOH), 2.75 (d, 0.7, J = 7 cps, syn CH), 3.3 (d, 0.3 H, J = 5 cps, anti CH), 5.9 (m, 3 H), 8.3 (m, 4 H); mass spectrum m/e 115 (M^+, 3%), 71 (C_4H_7O, 85%).

***p*-Nitrophenylhydrazone Derivative of 10.**—The method of Gerecs and Somobyi[19] was used, mp 146–147° (lit. 145–146°).

Anal. Calcd for $C_{11}H_{13}N_3O_3$: C, 56.16; H, 5.56; N, 17.86. Found: C, 56.41; H, 5.39; N, 18.09.

Photolysis of 4-Pentenyl-1 Nitrite in the Presence of Oxygen.—Nitrite (0.92 g) was added to 90 ml of benzene and the solution purged with oxygen for 30 min. The solution was then irradiated for 45 min with the oxygen turned off and the system sealed. Uv indicated that all nitrite was gone and indicated strong nitroso dimer absorption. Vpc analysis indicated a 34% yield of **10**.

Photolysis of 4-Pentenyl-1 Nitrite Using a Filter Solution.—Filter solution A consisted of 93 g of $Co(NO_3)_2 \cdot 6H_2O$, 131 g of $CoSO_4 \cdot 7H_2O$, 76 g of $Cr_2(SO_4)_3 \cdot 18H_2O$, and 97 g of $CuSO_4 \cdot 5H_2O$ per liter of water. The transmission spectrum of filter solution A is given in Table II. A pump circulated the filter solution through the immersion well and a cooling coil which was immersed on an ice bath.

TABLE II

TRANSMISSION SPECTRUM OF FILTER SOLUTION A[a]

Before photolysis		After 1.5 hr of photolysis	
mμ	% T	mμ	% T
190–320	0.0	190–320	0.0
330	10.6	330	10.3
348	30.7	348	25.0
360	10.6	360	10.4
384–434	0.0	385–432	0.0
466	10.6	466	10.7
485	23.0	485	23.0
506	10.6	506	10.7
548–640	0.0	554–620	0.0
656	1.2	655	2.3
665–850	0.0	696–850	0.0

[a] The per cent transmission has been corrected to the 0.5-cm path length of the immersion well.

Nitrite (3.08 g) was added to 350 ml of benzene. After 3 hr and 45 min of photolysis, uv indicated all nitrite had disappeared and that nitroso dimer had been formed. Vpc indicated a 60% yield.

Photolysis of 4-Pentenyl-1 Nitrite with Iodine.—Nitrite (2.44 g) was added to 350 ml of benzene in which 3.9 g of iodine had been dissolved. After 4.5 hr of irradiation, uv indicated no remaining nitrite ester and no nitroso dimer formation. Excess iodine was removed with a 10% aqueous solution of sodium thiosulfate. 2-Iodomethyltetrahydrofuran (**11**) was separated by preparative vpc and identified by ir comparison to a known sample prepared by the method of Staninets and Shilov:[21] ir ($CHCl_3$) 1060 cm^{-1} (CO); nmr ($CDCl_3$) τ 6.1 (m, 3 H), 6.75 (d, 2 H) 8.1 (m, 4 H). Vpc indicated a 61% yield of **11**, and nmr intergration of the mixture indicated a 2.5% yield of oxime.

Photolysis of 4-Pentenyl-1 Nitrite with Bromotrichloromethane.—A filter solution consisting of 120 g of sodium nitrite per liter of water was prepared and circulated through the immersion well and a cooling coil.

Nitrite (1.289 g) was added to a solution of 308 ml of benzene and 42 ml of bromotrichloromethane. After 25 min of irradiation, uv indicated no remaining nitrite and no nitroso dimer formation. The solution was a deep blue. This blue stripped over with the benzene and excess bromotrichloromethane.

2-Bromomethyltetrahydrofuran (**13**) was separated by preparative vpc and identified by ir comparison to a known sample prepared by the method of Paul.[24] Vpc analysis indicated a 51% yield of **13** and 1% yield of **10**.

Photolysis of 5-Hexenyl-1 nitrite.—Nitrite (3.286 g) was added to 350 ml of benzene and irradiated for 45 min. Uv indicated no remaining nitrite and nitroso dimer formation. The solution turned yellow during photolysis and became cloudy. The cloudiness cleared after sitting a few minutes. A very viscous red-brown oil settled out of solution, was taken up in methanol, and stripped to 0.77 g.

An oily material (2.81 g) was recovered after stripping off the benzene, but only trace amounts of material would come through the vpc. Only 5-hexen-1-ol was identified by comparison to a known sample.

The recovered oil was heated until uv indicated no remaining nitroso dimer, but all separation attempts, including preparative vpc, Florisil chromatography, paper chromatography, and extraction techniques, failed. Ir (film) of the mixture indicated no peaks in the vicinity of 1725 cm^{-1} (isoxazoline) and nmr in deuterated DMSO indicated no peak in the vicinity of τ 0 (oxime).

Photolysis of *n*-Pentyl Nitrite.—Nitrite (3.388 g) was added to 350 ml of benzene and irradiated for 1 hr. Uv indicated no remaining nitrite and nitroso dimer formation. A small amount of a brown oil settled out of solution and was taken up in methanol and combined with the benzene solution prior to stripping.

The major product was separated by preparative vpc. Ir indicated it to be the expected γ-hydroxypropyl methyl ketoxime (**16**), and vpc indicated a 47% yield: ir (film) 3400 (very strong, OH), 1665 cm^{-1} (C=N).

Quantum Yields.—4-Pentenyl-1 nitrite (**3**) and *n*-pentyl nitrite were irradiated in a merry-go-round apparatus at the same time and the same concentration, using a medium pressure mercury lamp and filters to isolate the 3660-Å line. The samples were sealed in Pyrex ampoules after three freeze-pump-thaw cycles using liquid nitrogen and a maximum pressure of 10^{-4} nm, and ferric oxalate actinometry was used. Half the tubes were irradiated for 5 min and half for 10 min. Blank tubes were made up and carried through the entire process for both nitrites.

Vpc analysis indicated a quantum yield of 0.71 for the unsaturated nitrite **3** based on the appearance of the aldoxime **10** and a quantum yield of 0.25 for the saturated nitrite **15** based on the appearance of the ketoxime **16**. No significant difference was noted between the tubes irradiated for 5 min and those irradiated for 10 min.

Registry No.—**3**, 29668-65-3; **4**, 23127-65-3; *anti*-**10**, 20728-36-3; *syn*-**10**, 23247-31-6; 5-hexenoxy radical, 32730-57-7; 5-hexenyl-1 nitrite, 32730-59-9.

Acknowledgment.—Financial support of this investigation by a National Science Foundation Grant and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Helpful discussions with Professor D. G. Whitten are gratefully acknowledged.

The Mechanism of the Rearrangement of Bis(diphenylphosphinyl) Peroxide[1]

RALPH L. DANNLEY,* ROBERT L. WALLER,[2] ROBERT V. HOFFMAN, AND ROBERT F. HUDSON[3]

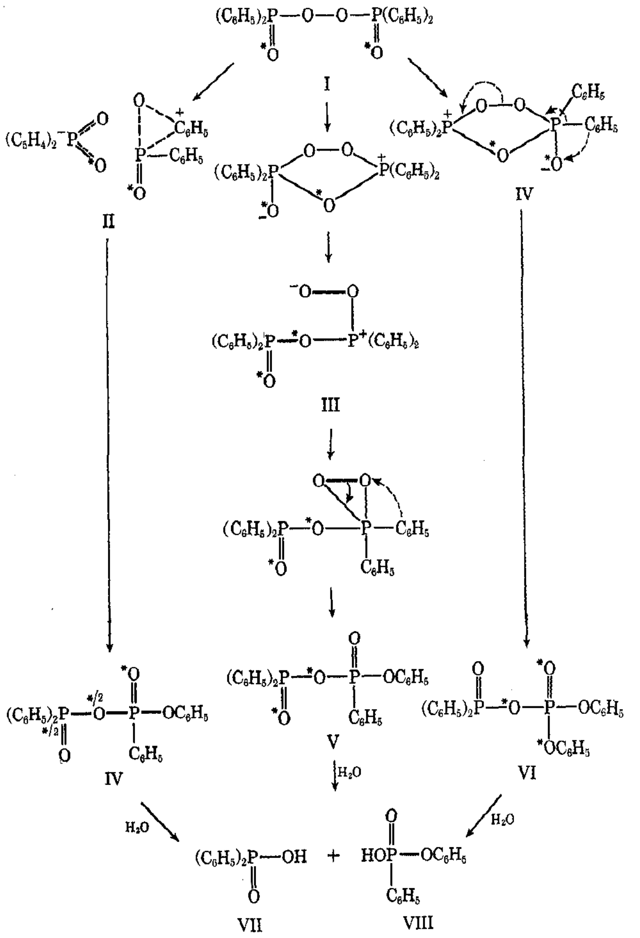
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received July 1, 1971

The thermal decomposition of bis(diphenylphosphinyl-^{18}O) peroxide in chloroform solution has been found to produce an unsymmetrical anhydride [$Ph_2P(=O)OP(=O)OPh_2$] in which all of the oxygen-18 label remains in the oxo oxygens. Only a concerted process or an ion pair so intimate as to prevent scrambling of the label is consistent with this labeling of the rearrangement product. In contrast, photolysis of the labeled peroxide in chloroform results in a much more rapid first-order decomposition which yields the same anhydride but with scrambling of the oxygen-18 label. This scrambling of the label corresponds to a free-radical intermediate for the photolytic process.

The thermal decomposition of bis(diphenylphosphinyl) peroxide (I) has been found[4] to yield, after hydrolysis of the reaction mixture, diphenylphosphinic acid (VII) and phenyl hydrogen phenylphosphonate (VIII). Evidence was presented that the reaction was ionic in nature and the following three alternative mechanisms (Chart I) were proposed. The present work was planned to establish whether one of these three mechanisms can be operative by labeling the oxo oxygens of the peroxide with oxygen-18 and determining the labeling in the product. The decomposition of the peroxide was also reported[4] to be accelerated by light and in the present work it was proposed, in addition, to elucidate this photolytic mechanism by oxygen-18 labeling experiments.

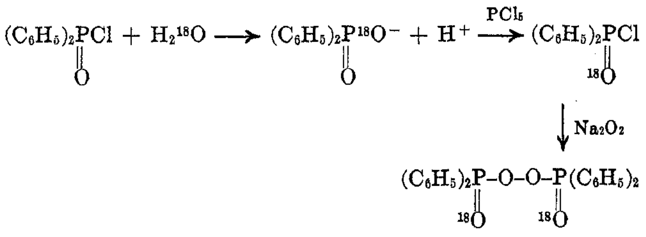
CHART I



appropriate labeling

Results and Discussion

Labeling of the Peroxide.—Labeling of the peroxide was accomplished by the following sequence of reactions. Since the phosphinyl peroxide is thermally too unstable to pass through a mass spectrometer, the incorporation of oxygen-18 in the oxo oxygen of the peroxide was assumed to be identical with that in the precursor phosphinyl chloride. Measurement of the oxygen-18 content of the diphenylphosphinyl chloride itself was found to be impractical, for the only peaks observed in the mass spectrometer corresponded to the chlorine cation (m/e 35, 37). However, treatment of the acid chloride with methanol gave the methyl ester which in the mass spectrometer produced a series of useful ions (Table I). The parent peaks (m/e 232, 234) were initially chosen for the analysis and, from the peak heights of multiple runs applying the statistical isotope occurrence formulas of Beynon,[5] the oxo oxygen enrichment with oxygen-18 above natural abundance was 5.3%. The base line at this portion of the spectrum was so poor and the correction for the m + 1 contribution of the 231 peak so large that the average



$$(C_6H_5)_2\underset{\underset{\displaystyle O}{\|}}{P}Cl + H_2{}^{18}O \longrightarrow (C_6H_5)_2\underset{\underset{\displaystyle O}{\|}}{P}{}^{18}O^- + H^+ \xrightarrow{PCl_5} (C_6H_5)_2\underset{\underset{\displaystyle {}^{18}O}{\|}}{P}Cl \xrightarrow{Na_2O_2} (C_6H_5)_2\underset{\underset{\displaystyle {}^{18}O}{\|}}{P}\text{-O-O-}\underset{\underset{\displaystyle {}^{18}O}{\|}}{P}(C_6H_5)_2$$

---

(1) Supported in part by National Science Foundation Grant No. GP-19018.

(2) Taken in part from the thesis of R. L. Waller, submitted in May 1971, to the Graduate School, Case Western Reserve University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(3) Preliminary work on this problem was performed at the American Cyanamid European Research Institute at Geneva, Switzerland.

(4) R. L. Dannley and K. R. Kabre, *J. Amer. Chem. Soc.*, **87**, 4805 (1965).

(5) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, p 296.