Vacuum Pyrolysis of Nitrostyrenes

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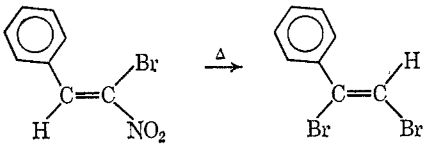
The gas-phase vacuum pyrolysis of a series of nitrostyrenes produced major products which are the result of intramolecular nonradical reactions, in contrast to the known behavior of alkylnitro compounds and nitroaromatic compounds. β-Methyl-β-nitrostyrene, for instance, yields benzaldehyde, acetonitrile, and methyl isocyanate as major products. Mechanisms for the major products are proposed and comparisons with mass spectral and photochemical processes are made and discussed.

The pyrolytic behavior of nitroalkanes[1b] has recently been reviewed, and that of nitroaromatics[2] has been the subject of much current interest. In both instances the main pyrolysis reaction involves cleavage of the nitro group to generate two radicals which lead to the observed products. Similarities in the mass spectral behavior of nitroaromatics[3] and nitrostyrenes[4] coupled with the known photochemical lability of nitro olefins[5,6] suggested that nitrostyrenes might exhibit thermal reactions analogous to those observed for nitroaromatics.

Two reports on the pyrolysis of nitrostyrenes have been published.[7,8] The pyrolysis of β-bromo-β-nitrostyrenes[7] reportedly yields α,β- or β,β-dibromostyrenes (eq 1 and 2) *via* the divalent carbon intermediate **1**, which adds bromine. The α,β-dibromo product (eq 1) was postulated to arise by a 1,2-hydrogen migration. A subsequent study on the pyrolysis of simple nitrostyrenes in the heated inlet (230°) of a mass spectrometer,[8] with product identification from the mass spectrum, revealed nitrostyrenes to be quite thermally stable. The only pyrolysis reaction observed was the elimination of HNO_2 from β-nitrostyrene itself.



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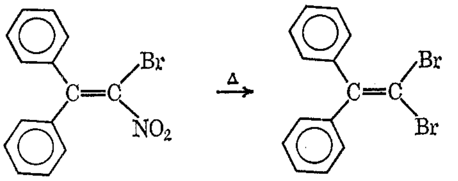

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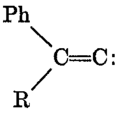


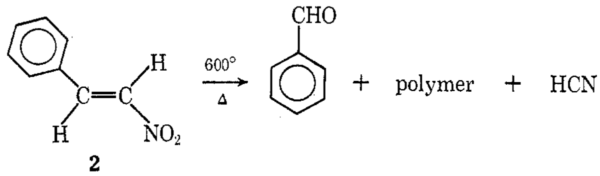
1, R = H, C_6H_5

Our observations of pronounced thermal effects on the mass spectra of nitrostyrenes prompted us to examine in more detail their thermal chemistry under conditions of high temperature and low pressure. The results are described below. Vapor phase chromatography, nuclear magnetic resonance, infrared and mass spectral techniques, along with authentic compound comparisons, were used to prove structures of products. Details, including a description of the apparatus used, are given in the Experimental Section.

Results and Discussion

The pyrolysis experiments were generally conducted at pressures in the range of 0.001–0.005 mm, but occasionally higher pressures were employed. The nitrostyrenes were found to be thermally quite stable and did not decompose at temperatures less than 400°, while even at 500° the pyrolysis reactions were often incomplete. At temperatures equal to or in excess of 600°, pyrolysis was complete. Generally 0.1–0.4 g of material was pyrolyzed during an 8–12-hr period. The yield of products was 60–70%, with the remainder being gaseous or carbonaceous materials.

Pyrolysis of β-nitrostyrene (**2**) at 600° resulted in the formation of benzaldehyde, a white, polymeric material, and a gas, probably hydrogen cyanide, as indicated in eq 3. The polymeric material changed to a red-brown color upon prolonged exposure to air, and could not be recrystallized from any of a variety of solvents. The pyrolysis of 1,1-diphenyl-2-nitroethylene (**3**) under similar conditions gave benzophenone, the same polymeric material, and probably hydrogen cyanide. The formation of the same polymeric material from **2** and **3** implicated the β-carbon atom for its formation. It was postulated that placing an alkyl group on the β-carbon atom might lead to more stable pyrolysis products.



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Indeed, this was borne out by the absence of any polymeric products in the pyrolysis of β-methyl-β-nitrostyrene (**4**), which yielded acetonitrile, benzaldehyde, benzene, methyl isocyanate, methyl phenyl-

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[1] (a) HEW Predoctoral Fellow, 1966–1969; (b) G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Usp. Khim.*, **37**, 1443 (1968).

[2] (a) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 724 (1967); (b) E. K. Fields and S. Meyerson, *ibid.*, **89**, 3224 (1968); (c) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **34**, 3114 (1967); (d) E. K. Fields and S. Meyerson, *Tetrahedron Lett.*, 1201 (1968).

[3] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 512.

[4] T. H. Kinstle and J. G. Stam, *Org. Mass Spectrom.*, in press.

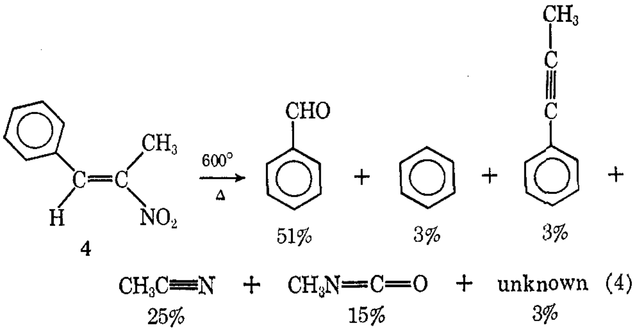
[5] O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Commun.*, 101 (1966).

[6] O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, **88**, 5550 (1966).

[7] C. F. H. Allen and C. V. Wilson, *J. Org. Chem.*, **5**, 146 (1940).

[8] C. F. H. Allen and G. P. Happ, *Can. J. Chem.*, **42**, 650 (1964).

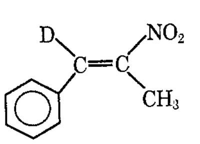
acetylene, and an unidentified material (less than 3.5% of total products) as indicated in eq 4. If the head temperature was increased above that indicated in the Experimental Section, additional unidentified products were formed, probably by intermolecular reactions. The pyrolysis of 1-(α-naphthyl)-2-nitropropene (**5**) and 1,1-diphenyl-2-nitropropene (**6**) under similar conditions gave products analogous to those described above for pyrolysis of **4**.



The formation of methylphenylacetylene (3%) among the pyrolysis products from β-methyl-β-nitrostyrene (**4**) can be explained as the elimination of nitrous acid. The formation of methyl-α-naphthylacetylene in the pyrolysis of **5** must occur in a similar manner. Apparently, β-nitrostyrene (**2**) does not decompose in this manner, since no phenylacetylene was detected among the pyrolysis products. Cleavage of the nitro group to give a vinyl radical with the subsequent loss of hydrogen is reminiscent of the pyrolytic behavior of nitroaliphatics[1b] and nitroaromatics,[2] but it constitutes only a minor decomposition pathway for nitrostyrenes.

The formation of benzene (3%) in the pyrolysis of β-methyl-β-nitrostyrene (**4**) can be explained in terms of a very similar mechanism. Instead of eliminating a nitro group and a hydrogen atom to give methylphenylacetylene, elimination of the nitro group can be followed by loss of a phenyl radical with the concurrent or subsequent abstraction of a hydrogen atom from another organic molecule. As is usual in such reactions, some tarry material is formed. No propyne is observed among the pyrolysis products of **4**. A similar reaction sequence can be envisioned for the formation of benzene and naphthalene in other pyrolysis reactions. The absence of benzene formation in the pyrolysis of β-nitrostyrene (**2**) and the formation of benzene in the pyrolysis of 1,1-diphenyl-2-nitropropene (**6**) demonstrate that benzene is not being formed by decarboxylation of benzaldehyde. Furthermore, benzaldehyde is not converted into benzene under the pyrolysis conditions.

The specifically deuterated compound **9** was pyrolyzed and the benzene which was formed contained no deuterium atom. This is further evidence against the benzaldehyde decarboxylation route to benzene and is strong evidence for hydrogen abstraction occurring from the β-methyl group of either **9** or the propyne obtained by elimination from **9**.



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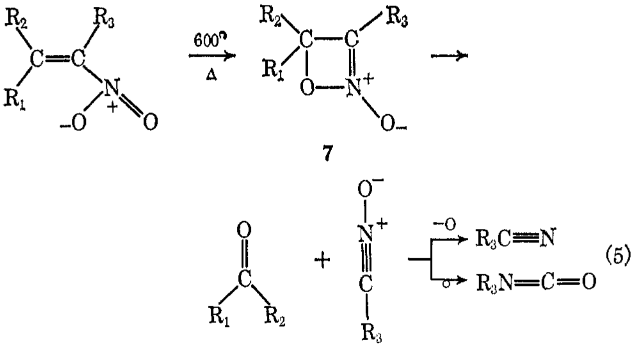
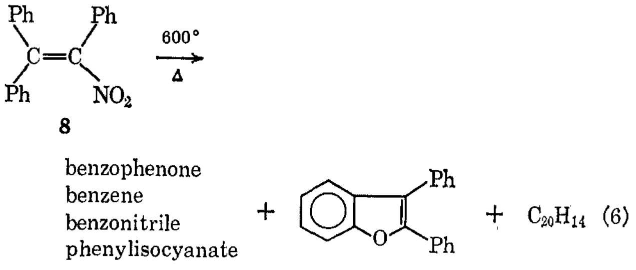
The isolation of carbonyl compounds as major products in the pyrolysis of **2**–**6** suggests that one of the oxygen atoms of the nitro group is acting as a nucleophile in an addition to the α-carbon atom of the nitrostyrenes, as depicted in generalized eq 5. In agreement with this proposal is the well-known propensity of nitroolefins to undergo addition reactions with a variety of nucleophiles.[9] The subsequent decomposition of the cyclic structure **7** formed in this way would give carbonyl compounds and nitrile oxides. Since nitrile oxides are known to rearrange thermally to isocyanates,[10] the origin of these products is easily explained. The nitriles observed as products in the pyrolysis reactions are probably formed by the thermal loss of oxygen from the nitrile oxides. Although this is not a known thermal reaction of nitrile oxides, chemical removal of oxygen is known to occur easily.[11] The polymer formed in the pyrolysis of β-nitrostyrene (**2**) and 1,1-diphenyl-2-nitroethylene (**3**) can be plausibly accounted for, since HNCO is known to polymerize spontaneously.[12] Also in accord with this mechanism is the fact that compound **9** gives only benzaldehyde-d_1 with all the label at the carbonyl carbon.



The effect of substituting a phenyl ring on the β-carbon atom was investigated by pyrolyzing nitrotriphenylethylene (**8**). Identified were the expected products benzene, benzophenone, benzonitrile, and phenyl isocyanate, undoubtedly formed by reactions whose mechanisms have been discussed above, as well the additional compounds 2,3-dibenzofuran and a $C_{20}H_{14}$ hydrocarbon of unproved structure (eq 6). The initial step in the formation of the $C_{20}H_{14}$ hydrocarbon is probably loss of the nitro group to form a vinyl radical. The vinyl radical can then rearrange with expulsion of a hydrogen atom to give the product, which is possibly 9-phenylphenanthrene.



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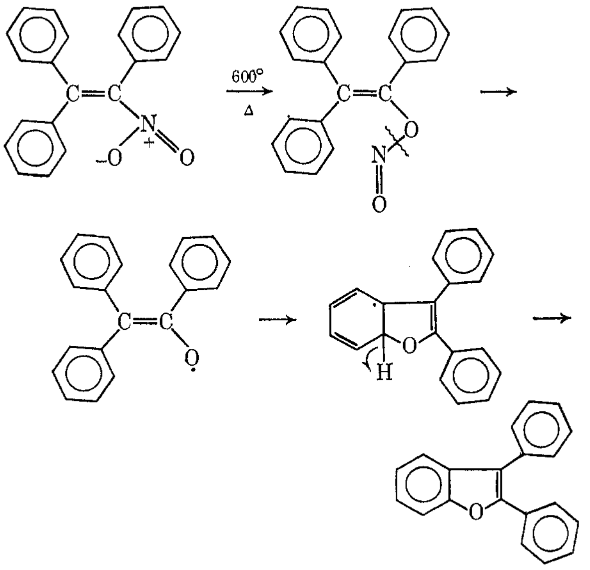
[9] V. V. Perekalin, "Unsaturated Nitro Compounds," Daniel Davey and Co., Inc., New York, N. Y., 1964.

[10] C. Grundman and S. K. Datta, *J. Org. Chem.*, **34**, 2016 (1969).

[11] C. Grundman, *Fortsch. Chem. Forsch.*, **7**, 62 (1966).

[12] E. E. Turner and M. M. Harris, "Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1952, p 117.

The formation of 2,3-diphenylbenzofuran from **8** results from a new type of decomposition. The first step must be a thermally induced nitro–nitrite rearrangement. A similar rearrangement has been proposed to explain some of the products from the thermal decomposition of nitrobenzene.[2b] The formation of a radical by breaking the nitrogen–oxygen bond of the nitrite is followed by attack on a phenyl ring with expulsion of a hydrogen atom to give 2,3-diphenylbenzofuran, as indicated in eq 7.



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These pyrolysis results from nitrostyrenes are quite different from those observed for nitroalkanes[1] and nitroaromatics, where only radical reactions are of importance. With nitrostyrenes, intramolecular reactions involving the double bond are of primary importance while radical reactions are of only secondary importance. Likewise, upon electron impact, nitrostyrenes[4] also exhibit important fragmentations involving the double bond.

There appear to be a number of correlations between the mass spectral fragmentations of nitrostyrenes and their thermal decomposition, for example, the observation of carbonyl and acetylenic ions. However, these ions are generally of low abundance in the absence of thermal effects. The nitro–nitrite rearrangement observed in the pyrolysis of nitrotriphenylethylene (**8**) is also observed in the mass spectrum of **8**.

The synthetic utility of the pyrolysis reaction is of limited value because of the variety of products obtained. However, it could be useful to obtain small quantities of unusual nitriles and isocyanates. We are presently exploring the scope and limitations of these interesting pyrolysis reactions.

Experimental Section

Description of Pyrolysis Apparatus.—All pyrolysis experiments were performed using a pyrolysis tube (12 × 1 in.) made from Vycor glass and filled with Vycor chips. The pyrolysis tube was heated with a Sola Basic Industries Lindberg Hevi-Duty Model 55035-A tube furnace, and the pyrolysis temperatures reported are those recorded by a Platinel II thermocouple. The temperature read is that between the pyrolysis tube and the heating element; thus the actual temperature inside the pyrolysis tube is probably slightly lower. The vacuum for the pyrolysis apparatus was created by a Consolidated Vacuum Corp. Type VMF oil diffusion pump backed by a Welch Duo-Seal vacuum pump. The samples were sublimed into the pyrolysis tube from an aluminum oven fitted with a buried thermometer and heated with a Glas-Col heating tape. Pyrolysis products were trapped in a U-tube cooled in liquid nitrogen.

β-Nitrostyrene (**2**).—The procedure of Worral[13] was used to prepare β-nitrostyrene (**3**), mp 55–56° (lit.[13] mp 57–58°).

β-Methyl-β-nitrostyrene (**4**).—An adaptation of Heinzelman's[14] procedure was used to prepare **4** by *n*-butylamine-catalyzed condensation of benzaldehyde and nitroethane in toluene using a Dean–Stark apparatus to remove water, mp 64° (lit.[15] mp 65°).

1-(α-Naphthyl)-2-nitropropene (**5**).—The desired compound was prepared by a modification of the method of McCarthy and Kahl.[16] A solution of 31.2 g of 1-naphthaldehyde (Aldrich), 15.0 g of nitroethane, 1 ml of butylamine, and 20 ml of absolute ethyl alcohol was kept in the dark at room temperature for 2 weeks. The red bottom layer was separated and concentrated to a red oil at reduced pressure. Dissolution of the oil in ethyl alcohol and cooling gave dark brown crystals. Charcoal decolorization and several recrystallizations from ethanol gave 28.7 g of light yellow needles: mp 65–67°; ir (CCl_4) 6.02 (C=C), 6.6 (NO_2), and 7.55 μ (NO_2); nmr (CCl_4) δ 2.3 (d, 3, CH_3), 7.3–7.9 (m, 7), and 8.5 (s, 1, *peri* H).

Anal. Calcd for $C_{13}H_{11}NO_2$: C, 72.90; H, 5.21; N, 6.58. Found: C, 72.88; H, 5.30; N, 6.64.

1,1-Diphenyl-2-nitroethylene (**3**).—This compound was prepared from 1,1-diphenylethylene according to the procedure of Govindachari, Pai, and Rao.[17] Light yellow needles were obtained after recrystallization, mp 86.5° (lit.[17] mp 87°).

1,1-Diphenyl-2-nitropropene (**6**).—The desired compound was prepared from 1,1-diphenylpropene using the procedure for **3**.[17] The oil resulting from decomposition of 5.1 g of nitrosite was vacuum distilled at 139–142° (1 mm) to give 1.85 g of thick yellow oil which was dissolved in ethanol and cooled in an acetone–Dry Ice bath to yield light yellow crystals: mp 49–50°; ir (CCl_4) 6.01 (C=C), 6.60 (NO_2), and 7.4 μ (NO_2); nmr (CCl_4) δ 2.3 (s, CH_3) and 7.0–7.4 (m, C_6H_5).

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.32; H, 5.44; N, 5.86. Found: C, 75.39; H, 5.47; N, 5.79.

Nitrotriphenylethylene (**8**).—This compound was prepared from triphenylethylene according to the procedure of Govindachari, Pai, and Rao.[17] The product obtained by decomposition of the nitrosite was recrystallized from ethanol to give light yellow needles, mp 176–177° (lit.[17] mp 178°).

α-Deuterio-β-methyl-β-nitrostyrene (**9**).—The method of Wiberg[18] was used to prepare 1.25 g of α-deuteriobenzaldehyde, which was condensed with 1.5 g of nitroethane using the procedure of Heinzelman[14] to yield 0.97 g of **9**: mp 63.5–64°; ir (CCl_4) 6.02 (C=C), 6.57 (NO_2), and 7.55 μ (NO_2). Low-voltage mass spectrometry indicated the following deuterium incorporation: 1.2% d_0, 98.8% d_1.

2,3-Diphenylbenzofuran.—This compound was prepared according to the procedure of Wacek and Daubner.[19] The product was purified by elution from a silica gel (Baker) chromatography column using petroleum ether. Evaporation of petroleum ether at reduced pressure gave light white crystals, mp 123–124° (lit.[19] mp 122–124°).

Pyrolysis of β-Nitrostyrene (**2**).—Pyrolysis of β-nitrostyrene (**7**) at 400° (0.001 mm)[20] with a head temperature of 50–52° resulted in the recovery of only starting material, as shown by nmr. The pyrolysate of **2** at 600° (0.005 mm) with a head temperature of 50–55° was washed from the cold trap with several milliliters of carbon tetrachloride. This solution became warm and then hot as white, amorphous precipitate formed. The precipitate isolated by filtration exhibited spectral characteristics of a polymer and turned dark red upon prolonged exposure to air. Nmr analysis of the filtrate revealed the presence of benzaldehyde: nmr (CCl_4) δ 7.2–7.8 (m, 5, C_6H_5) and 9.92 (s, 1, HCO).

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[13] D. E. Worral, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N.Y. 1932, p 413.

[14] R. V. Heinzelman, ref 13, Coll. Vol. IV, 1963, p 573.

[15] H. Hass, A. G. Susie, and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

[16] W. C. McCarthy and R. J. Kahl, *ibid.*, **21**, 1118 (1956).

[17] T. R. Govindachari, B. R. Pai, and U. R. Rao, *Proc. Indian Acad. Sci., Sect. A*, **48**, 111 (1958).

[18] K. B. Wiberg, *J. Amer. Chem. Soc.*, **76**, 5371 (1954).

[19] A. Wacek and H. Daubner, *Monatsh. Chem.*, **81**, 246 (1951).

[20] These pressure measurements were taken on the pump side of the pyrolysis column. Although the pressures at the point of pyrolysis were undoubtedly somewhat higher, the sublimination rate was held very low in order to minimize the pressure increase.

Pyrolysis of 1,1-Diphenyl-2-nitroethylene (3).—The pyrolysis of 1,1-diphenyl-2-nitroethylene (**3**) was effected at 600° (0.001 mm) with a head temperature of 75–78°. The pyrolysate was washed from the cold trap with carbon tetrachloride and gave the same white precipitate observed for **2**. Nmr analysis of the filtrate revealed the presence of benzophenone: nmr (CCl_4) δ 7.2–7.8 (m, C_6H_5). The pyrolysate obtained from the pyrolysis of **3** at 700° (0.002 mm) with a head temperature of 78–80° was identical with that obtained at 600°.

Pyrolysis of β-Methyl-β-nitrostyrene (4).—The pyrolysis of β-methyl-β-nitrostyrene was effected at 600° (0.001 mm) with a head temperature of 50–55°. Analysis of the pyrolysate by vpc indicated the presence of at least six components and the following peaks were observed in the mass spectrum (70 eV): *m/e* 106, 105, 78, 77, 76, 57, 52, 51, 50, 41, 40, and 39. The pyrolysate was shown to consist of acetonitrile, benzaldehyde, benzene, methyl isocyanate, and methylphenylacetylene by comparison of vpc retention times and spectral data with those of authentic samples. The following were recorded for the pyrolysate: ir (CCl_4) 4.25–4.55 (broad band) and 5.85 μ (CO); nmr(CCl_4) δ 1.9 (s, CH_3CN), 2.02 (s, $C_6H_5CCCH_3$), 2.1 (s, unknown), 3.0 (s, CH_3NCO), 7.15–7.3 (m, $C_6H_5CCCH_3$), 7.27 (s, C_6H_6), 7.4–7.8 (m, C_6H_5CHO), and 9.92 (s, C_6H_5CHO). A sixth minor product was not identified. The product ratios were determined by nmr. The pyrolysis of **4** at 500° (0.250 mm) with a head temperature of 60–70° was shown to give starting material and the aforementioned products by nmr analysis. Pyrolysis of **4** at 400° (0.100 mm) with a head temperature of 65–70° returned starting material only.

Pyrolysis of 1-(α-Naphthyl)-2-nitropropene (5).—The pyrolysis of 1-(α-naphthyl)-2-nitropropene (**5**) was accomplished at 600° (0.001 mm) with a head temperature of 52–53°. Nmr analysis of the pyrolysate indicated the presence of acetonitrile, methyl isocyanate, and naphthaldehyde. Vpc analysis of the pyrolysate (BDS, 175°) established the presence of naphthalene. Vpc data also suggested the presence of methyl-α-naphthylacetylene, which was confirmed by an ir absorption at 4.5 μ ($C\equiv C$) in the absence of acetonitrile and methyl isocyanate. A minor component of the pyrolysate was not identified. The following nmr data were obtained for the pyrolysate: nmr (CCl_4) δ 1.9 (s, CH_3CN), 2.15 (s, $C_{10}H_7CCCH_3$), 2.2 (s, unknown), 7.2–8.2 (m, $C_{10}H_7CHO$ and $C_{10}H_8$), and 10.33 (s, $C_{10}H_7CHO$).

Pyrolysis of 1,1-Diphenyl-2-nitropropene (6).—Pyrolysis of 1,1-diphenyl-2-nitropropene (**6**) was carried out at 700° (0.001 mm) with a head temperature of 50–51°. Nmr and vpc analyses of the pyrolysate indicated the presence of acetonitrile, benzene, benzophenone, methyl isocyanate, and an unidentified product: nmr (CCl_4) δ 1.9 (s, CH_3CN), 2.1 (s, unknown), 3.0 (s, CH_3NCO), 7.28 (s, C_6H_6), and 7.2–7.9 [m, $(C_6H_5)_2CO$].

Pyrolysis of Nitrotriphenylethylene (8).—Pyrolysis of nitrotriphenylethylene was accomplished at 600° (0.001 mm) with a head temperature of 101–105°. Vpc analysis of the pyrolysate demonstrated the presence of benzene, benzonitrile, benzophenone, and phenyl isocyanate. The presence of benzonitrile, phenyl isocyanate, and benzophenone was further confirmed by ir data: ir (CCl_4) 4.35–4.60 (nitrile–isocyanate) and 6.02 μ (CO). A considerable portion of the pyrolysate solidified before reaching the cold trap. Analysis of this material by mass spectrometry revealed the presence of 2,3-diphenylbenzofuran (*m/e* 270) and a $C_{20}H_{24}$ hydrocarbon (*m/e* 254).

Registry No.—**2**, 102-96-5; **3**, 5670-69-9; **4**, 705-60-2; **5**, 23854-03-7; **6**, 15795-69-4; **8**, 5670-70-2.

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Photochemical Oxidations. III. Photochemical and Thermal Behavior of α-Hydroperoxytetrahydrofuran and Its Implications Concerning the Mechanism of Photooxidation of Ethers[1a]

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The suspected intermediate peroxide in the photooxidation reaction of tetrahydrofuran (THF) was synthesized, and its thermal and photochemical behavior was studied. Liquid-phase thermal decomposition of a dilute peroxide solution gives rise to α-hydroxytetrahydrofuran, whereas vpc decomposition produces α-hydroxytetrahydrofuran and butyrolactone. Photochemically, the peroxide yields only α-hydroxytetrahydrofuran and the rate of production follows first-order kinetics. Using ir analysis and iodimetry, the rates of formation of the products in the photooxidation of THF were determined, and a modified mechanism was proposed for this reaction.

In previous papers of this series it was postulated that the photooxidation of ethers proceeds through the α-hydroperoxides of ethers.[2,3] In order to obtain further experimental data on the role of peroxides in these reactions, the thermal and photochemical behavior of α-hydroperoxytetrahydrofuran (I) has been studied. It was hoped that the hydroperoxide of diethyl ether could also be studied, but this was not possible, since the compound is too unstable to be prepared. In our previous work,[3] the rate of accumulation for the two products formed in the photooxidation of tetrahydrofuran (THF), *i.e.*, butyrolactone (II) and α-hydroxytetrahydrofuran (III), had been followed by vpc. However, since peroxides were also found in the reaction mixture, there was the possibility that thermal decomposition of these peroxides may have occurred during the vpc analysis and given rise to a portion of the products found. Therefore, it was necessary that the thermal decomposition of α-hydroperoxytetrahydrofuran, the postulated peroxide, be studied.

Compound I was prepared and a solution of it in THF was injected into a gas chromatograph with the injection chamber at 100°. It was found that both II and III were produced under these conditions. Also no trace of I could be detected in the vpc spectrum. The molar ratio of products obtained (II to III) was *ca.* 3:1, with the exact ratio depending on the experimental conditions and techniques. Therefore, it is obvious that the vpc results for rates of product accumulation during the photooxidation contain an

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[1] (a) Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; (b) Taken in part from the Ph.D. thesis of C. T. Wang, University of North Dakota, June 1969.

[2] V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1967).

[3] N. Kulevsky, C. T. Wang, and V. I. Stenberg, *ibid.*, **34**, 1345 (1969).