Reaction of 3,3-Diphenyl-1,2-*trans*-bis(*N*-nitrosourethano)cyclopropane with Methanolic Sodium Methoxide. Ring Opening between the Nitrogen Functions

DEWEY J. NORTHINGTON[1] AND W. M. JONES*

Department of Chemistry, University of Florida, Gainesville, Florida 32601

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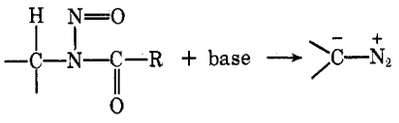
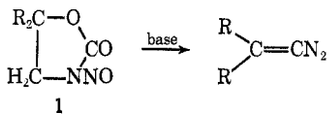
Reaction of 3,3-diphenyl-1,2-*trans*-bis(*N*-nitrosourethano)cyclopropane (**2**) with sodium methoxide in methanol has been found to give a mixture of 3,3-diphenyl-1-diazopropanone and 4,4-diphenyl-3-methoxy-1-pyrazoline 1-oxide. The structural assignment of the latter, which requires cleavage of the cyclopropane between the nitrogen functions, is based on spectral and chemical properties. The origin of the pyrazoline oxide is briefly discussed in terms of the diazabicyclo[2.1.0]pentene oxide **7**.

One of the more general methods of generating diazoalkanes is by the base-induced decomposition of *N*-nitrosoamine derivatives.[2] In our hands[3] this method has



not been found generally useful for the generation of diazoalkenes because most vinyl amines exist primarily in the imine form,[4,5] thus precluding amine nitrosation. In a series of recent papers, Newman[6] has reported a method to generate diazoalkenes by allowing *N*-nitrosooxazolidones **1** to react with base. This method cleanly circumvents the problem mentioned above by generating the double bond after the amine function is nitrosated.



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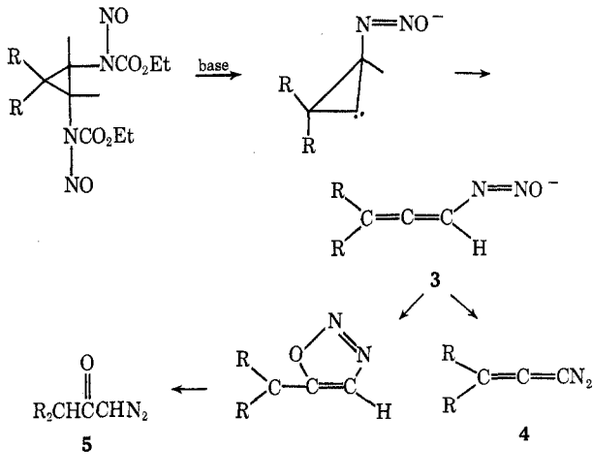
We have recently reported[7] our modestly successful attempts to generate a diazoallene by allowing 3,3-diphenyl-1,2-*trans*-bis(*N*-nitrosourethano)cyclopropane (**2**) to react with base, in this way attempting to generate the allene moiety *after* nitrosation of the amine function. Under many conditions, the reaction apparently proceeded well as far as the allenyl diazotate **3**, and, although a small portion gave the diazoallene **4**, most of the diazotate is believed to have undergone a unimolecular ring closure followed by opening to give diphenyldiazopropanone **5**. However, when the reaction was carried out in a dilute solution of sodium methoxide in methanol, in addition to the diazopropanone, a new material, 4,4-diphenyl-3-methoxy-1-pyrazoline 1-oxide (**8**), was formed as the major product. At this time we report a proof of structure of this material and some of its very interesting chemistry.



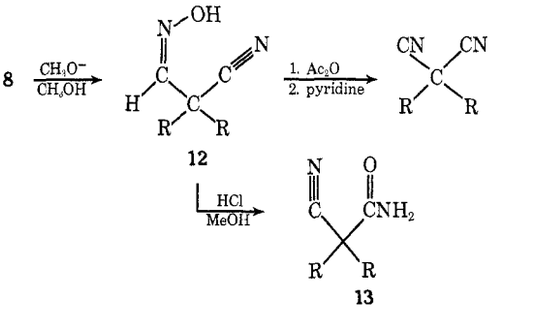
5 **3** **4**

Results

3,3-Diphenyl-1,2-*trans*-bis(urethano)cyclopropane (**2**) was synthesized by conventional methods[8] from 3,3-diphenylcyclopropyl-1,2-*trans*-dicarboxylic acid *via* the bis acid chloride, acid azide, and isocyanate. Nitrosation was effected with N_2O_4 in ether.[9]

Treatment of the nitrosourethane **2** with a dilute solution of sodium methoxide in methanol gave as principal products 4,4-diphenyl-3-methoxy-1-pyrazoline 1-oxide (**8**) and diazopropanone **5** (several very minor unidentified products were formed). As reported previously,[7] reaction in a concentrated solution of sodium methoxide in methanol gave as the only identifiable product the diazopropanone **5** (*ca.* 70% yield).

The structure proof of **8** was difficult at best. Thus, although the nmr (see below) was completely consistent



12 **13**

(1) Support for this work by the National Science Foundation is gratefully acknowledged. Presented in part to the 1970 Meeting in Miniature of the Florida Section of the American Chemical Society. Taken from the Ph.D. Dissertation of D. J. Northington, University of Florida, 1970.

(2) *Cf.* A. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961; P. A. S. Smith, "Open-Chain Nitrogen Compounds," W. A. Benjamin, New York, N. Y., 1966.

(3) Unpublished results of T. G. Squires.

(4) In cases where the vinyl amine is the more stable tautomer,[5] nitrosation of the amine function gives the vinylidene, presumably *via* the diazoalkene.

(5) *Cf.* D. Y. Curtin, J. A. Kampmeir, and B. R. O'Connor, *J. Amer. Chem. Soc.*, **87**, 863 (1965).

(6) M. S. Newman and T. B. Patrick, *ibid.*, **92**, 4312 (1970); M. S. Newman and C. D. Beard, *ibid.*, **92**, 4309 (1970); M. S. Newman and T. B. Patrick, *ibid.*, **91**, 6461 (1969); M. S. Newman and A. O. M. Okorodudu, *ibid.*, **90**, 4189 (1968); *J. Org. Chem.*, **34**, 1220 (1969).

(7) D. J. Northington and W. M. Jones, *Tetrahedron Lett.*, **No. 4**, 317 (1971).

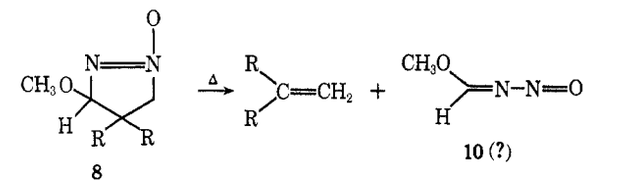
(8) For example, see J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Amer. Chem. Soc.*, **90**, 2895 (1968).

(9) E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, **83**, 1174, 1179, (1961).

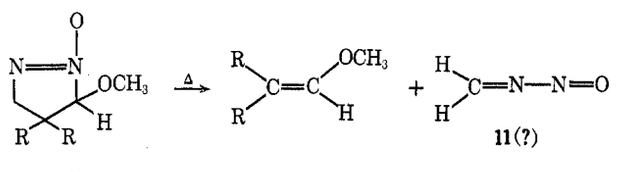
with **8**, it neither identified the basic ring structure nor the position of the oxygen of the *N*-oxide. The carbon skeleton was ultimately determined by its chemistry. Isolation of diphenylmalonodinitrile[10] and its oxime precursor **12**[11] leave little doubt but that the cyclopropane opened between the two nitrogen functions. Strong ir absorption at 1525 cm^{-1}, an M − 16 peak in the mass spectrum, and strong end absorption in the uv indicate an azoxy function.[2,12] Finally, nmr absorptions at τ 4.25 (s, 1 H) for the methyne proton, 4.97 and 5.35 (AB quartet with J_{AB} = 13.5 cps) for nonequivalent geminal methylene protons, and 6.40 (s, 3 H) for the methoxy protons support the structural assignment of **8**. However, it should be noted that spectral data are no help in differentiating between the two possible oxide isomers (**8** *vs.* **9**).

Two experiments, one of which may be generally applicable, led us to identify the pyrazoline oxide as **8**.

First, pyrolysis of **8** yielded 1,1-diphenylethylene and no detectable amount of 1,1-diphenyl-2-methoxyethylene, whereas its photoisomer[13] (the isomeric pyrazoline oxide **9**) gave 1,1-diphenyl-2-methoxyethylene and no trace of diphenylethylene. Thermal fragmentation of **8** to give diphenylethylene should give, in addition, a valence-satisfied nitrosoimine **10**. On the other hand, fragmentation of **8** to give diphenylmethoxyethylene requires initial formation of a diradical. The same arguments can, of course, also be made for the formation of 1,1-diphenyl-2-methoxy-



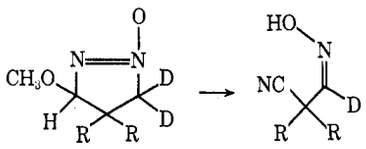
8 **10 (?)**



9 **11 (?)**

ethylene from **9**. These conclusions were further supported by the mass spectra of **8** and **9** in that the former showed a peak at *m/e* 180 with a relative intensity of 100 and none at 210, whereas the latter showed only a small peak at 180 (relative intensity 10) and a substantial peak (relative intensity 22) at *m/e* 210.

The assignment of structure **8** to the initial pyrazoline oxide was further supported by allowing it to react with sodium methoxide in MeOD. As noted above, reaction of **8** with base gives the aldoxime **12**. Assuming that the nitrogen bearing the oxide moiety in **8** becomes the aldoxime function in **12**, the following results are meaningful. When the reaction of sodium methoxide with **8** in MeOD was quenched with water at approximately the midpoint in the reaction, it was found that the starting material had incorporated deuterium into the methylene position to the extent that no absorptions in the nmr were noted for these protons, whereas no deuterium had been incorporated into the methyne position. Further, it was found that the product aldoxime had incorporated deuterium to the extent of 96% (nmr). Finally, undeuterated oxime did not exchange under the reaction conditions. Thus, unless some intermediate undergoes rapid and total deuterium exchange, these results point to structure **8** for the oxide.



8

Discussion

Of primary interest from these results is the origin of the pyrazoline oxide **8**. Although we do not have direct evidence, a number of arguments lend support to the series of reactions in Scheme I.

Certainly, the first step in the reaction must be conversion of one *N*-nitrosocarbamate group to a diazotate.[2] We further suggest that the second nitrosourethane is also converted to its diazotate prior to reactions leading to **8**.[14] The bisdiazotate would be expected to undergo two different types of reactions under our conditions. It could either react further with base and alcohol to ultimately give diazopropanone **5** (a reaction which should be favored by a high concentration of base[15]), or it could react with alcohol alone to give a cyclopropyldiazonium ion. This, in turn, would be expected to lose nitrogen to give a cyclopropyl cation,[15] which, in light of Moss and Landon's[16] recent work with diazotates, could give the azoxy compound **7**.

The steps in the conversion of **7** to **8** must, at this time, remain open. Recent work of Dolbier and Williams[17] on the photolysis of 4*H*-pyrazole oxides (analogous to **14** but highly substituted) led them to the conclusion that heterocycles analogous to **7** open thermally at temperatures as low as −30° to give two products, one of which is the starting 4*H*-pyrazole oxide. This suggests as one very real possibility ring opening to **14** followed by base-induced addition of MeOH.[18] On the other hand, direct attack of methoxide on the cyclopropane ring[19] of **7** cannot at this

(10) *Cf.* C. R. Hauser and E. Jordan, *J. Amer. Chem. Soc.*, **58**, 1772 (1936).

(11) Assignment of the anti configuration to the aldoxime is based on dehydration by acetic anhydride followed by pyridine as well as HCl in methanol. None of the Beckman rearrangement product predicted for the syn configuration was observed.

(12) V. T. Bandurco and J. P. Snyder, *Tetrahedron Lett.*, 4643 (1969); F. D. Greene and S. S. Hecht, *ibid.*, 575 (1969); W. R. Dolbier and W. M. Williams, *J. Amer. Chem. Soc.*, **91**, 2818 (1969).

(13) For a discussion on the photolysis of azoxy compounds, see F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970).

(14) For convenience, the precursor to **5** is also pictured as the bisdiazotate. In fact, it could be a monodiazotate without changing the arguments. The bisdiazotate is the preferred precursor to **8**.

(15) W. Kirmse and H. Schutte, *J. Amer. Chem. Soc.*, **89**, 1284 (1967).

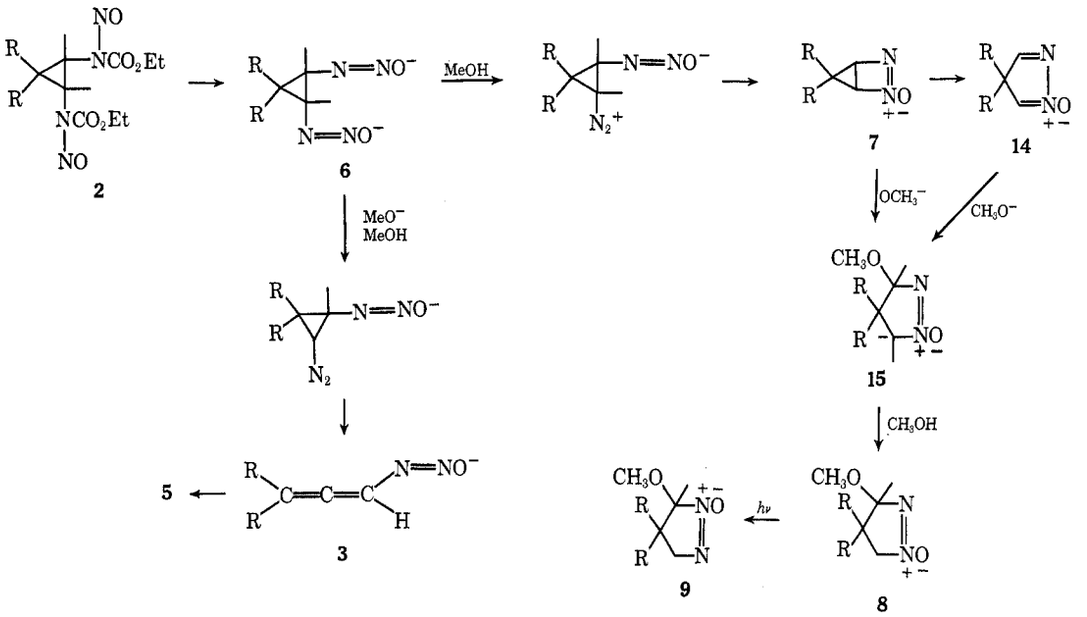
(16) R. A. Moss and M. J. Landon, *Tetrahedron Lett.*, 3897 (1969).

(17) W. R. Dolbier, Jr., University of Florida, private communication.

(18) To the best of our knowledge, the chemistry of 4*H*-pyrazole oxides with base has not been studied.

(19) Base-induced ring opening of cyclopropane, while rare, is not unknown in strained ring systems in which opening leads to a stable anion. For examples, see R. P. Blanchard, Jr., and A. Cairncross, *J. Amer. Chem. Soc.*, **88**, 587 (1966). The strain of the ring systems involved (bicyclobutane) and the probable sluggishness of the reaction (*e.g.*, 1-cyanobicyclobutane was opened by methoxide in methanol after 63 hr at room temperature) argues against direct attack on the cyclopropane ring.

SCHEME I



time be excluded. Preferential formation of **8** by either mechanism is certainly reasonable, since the observed facile and exclusive base-induced deuterium exchange at the methylene position in **8** leaves little question but that anion **15** is more stable than its counterpart which would lead to the isomeric oxide **9**.

Experimental Section

General.—Melting points were taken in a Thomas–Hoover capillary melting point apparatus and are uncorrected. A Beckman Model IR-10 was used to obtain infrared spectra. Nuclear magnetic resonance spectra were obtained on a Varian A-60 high resolution spectrometer. Chemical shifts are reported in units of τ using tetramethylsilane as an internal standard. Ultraviolet spectra were obtained from a Cary 15 spectrophotometer. The Hitachi Perkin-Elmer RMU-6E mass spectrometer was used to record mass spectra. The molecular ion peak, the base peak, and large significant fragments are reported. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

3,3-Diphenylcyclopropane-1,2-*trans*-dicarboxylic Acid—To a solution of 33 g of diethyl fumarate in 200 ml of ether was added 1 equiv of diphenyldiazomethane. The solution was stirred at room temperature for a few hours until the red color disappeared. The ether was removed under reduced pressure and the residue was pyrolyzed by slowly heating it to 180° until the gas evolution was complete (about 0.5 hr). The residue from the pyrolysis was saponified by refluxing it with 24 g of potassium hydroxide in 300 ml of water for 5 hr. The water solution was extracted twice with 100 ml of ether, warmed to 70°, and slowly acidified with dilute hydrochloric acid. The solution was allowed to cool for several hours and the precipitate was filtered and dried under vacuum. This yielded 46 g (80%) of the acid, mp 285–290° (lit.[20] mp 290°).

3,3-Diphenyl-1,2-*trans*-bis(urethano)cyclopropane (1).—3,3-Diphenylcyclopropane-1,2-*trans*-dicarboxylic acid was converted to the acid chloride by refluxing 21 g (0.74 mol) of the acid in excess thionyl chloride for 3 hr. The excess thionyl chloride was removed under reduced pressure; the last traces of thionyl chloride were removed by high vacuum overnight. The residue was dissolved in 120 ml of acetone and cooled in an ice bath. To this solution was added 38 g (4 equiv) of sodium azide in a minimum amount of water and the mixture was stirred at room temperature for 1.5 hr. This was poured into 300 ml of water and extracted with three 100-ml portions of ether. The combined ether solutions were washed with 50 ml of saturated brine and dried (Na_2SO_4). The ether was removed under reduced pressure and the residue was refluxed in 200 ml of benzene until nitrogen evolution ceased. The benzene solution of the isocyanate was cooled to room temperature and 35 ml of ethanol were added. This was refluxed for about 3 hr or until an ir spectrum showed complete loss of the isocyanate peak at 4.4 μ. The benzene solution was allowed to cool slowly to room temperature, and the solid product was filtered. The residue was washed with two small portions of benzene and recrystallized from benzene. This yielded 19 g (70%) of a white solid having needle-like crystals: mp 216–217°; ir (KBr) 3290, 1672, 1525, 1250–1290, 1075, 1045, 715 cm^{-1}; nmr ($CDCl_3$) τ 2.4–2.9 (10 H), 5.20 (broad s, 2 H), 5.90 (q, 4 H), 6.41 (d, 2 H), 8.82 (t, 6 H).

Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57; N, 7.60. Found: C, 68.60; H, 6.58; N, 7.80.

3,3-Diphenyl-1,2-*trans*-bis(*N*-nitrosourethano)cyclopropane (2).—The urethane was nitrosated in the following manner. 1 (1.0 g) was dissolved in 50 ml of ether, and 0.5 g of sodium sulfate and 1.3 g of sodium acetate were added. This mixture was cooled in a Dry Ice bath and stirred. To this was added 1.0 g of N_2O_4 in 10 ml of ether. The mixture was stirred for 10 min and then allowed to warm to room temperature by replacing the Dry Ice bath with a water bath. The excess N_2O_4 was removed under reduced pressure using an aspirator. This was then added to a stirred slurry of ice and saturated sodium bicarbonate solution. This mixture was transferred to a separatory funnel and the ether layer was collected. The ether solution was washed with cold saturated sodium bicarbonate solution and with saturated brine and dried (Na_2SO_4). In most cases **2** was used directly as the crude yellow oil obtained by removing the ether under reduced pressure. The ether solution could, however, be concentrated and pentane added to obtain crystalline **2** by placing the flask in the freezer compartment of the refrigerator overnight. This gave pale yellow crystals in 75–90% yield: mp 76–78° dec; ir (KBr) 2895, 1755, 1510, 1400, 1375, 1340, 1315, 1190, 1165, 1095, 1055, 970, 940, 900, 815, 760, 705, 610 cm^{-1}; nmr ($CDCl_3$) τ 2.4–3.0 (10 H), 5.40 (s, 2 H), 5.68 (q, 4 H), 8.78 (t, 6 H). This solid was unstable when left at room temperature, but a solution of **2** in ether could be kept in the freezer for a few weeks without noticeable decomposition.

Base-Induced Decomposition of 2 in Methanol.—Compound **2** was decomposed in methanol as follows. (1) Approximately 1.15 g (2.7 mmol) of **2** was dissolved in 60 ml of methanol. This was cooled in an ice bath, and 2.0 equiv of sodium methoxide was added. Gas evolution was complete after 20–30 min. The reaction was poured into approximately 200 ml of brine and extracted with two 50-ml portions of ether. This was dried (Na_2SO_4) and concentrated under reduced pressure. Nmr analysis of the residue showed about 20% of a compound identified as 3,3-diphenyl-1-diazopropanone (**5**) and 35% of a compound identified as 4,4-diphenyl-3-methoxy-1-pyrazoline 1-oxide

(20) J. van Alphen, *Recl. Trav. Chim. Pays-Bas*, **62**, 210 (1943).

(8).[21] In an experiment where 3 equiv of sodium methoxide was used, the results were the same.

The pyrazoline oxide was isolated by crystallization from the reaction mixture in ether or CCl_4. This gave 0.13 g (18%) of a white, crystalline solid: mp 126–127°; ir (KBr) 1525, 1335, 1205, 1130, 790, 730, 715, 700 cm^{-1}; nmr ($CDCl_3$) τ 2.5–3.2 (10 H), 4.25 (s, 1 H), 4.97 and 5.35 (J_{AB} = 13.5 cps, 2 H), 6.40 (s, 3 H); uv (EtOH) shoulder on end absorption 222 mμ (ϵ 19,000); mass spectrum (9 eV) *m/e* 268, 252, 238, 224, 180 (100), 121.

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.42. Found: C, 71.62; H, 6.02; N, 10.44.

The diazopropanone was isolated by chromatographing the filtrate on silica gel eluting with pentane–ether mixtures. Crystallization from ether–pentane gave 0.078 g (11%) of a yellow solid: mp 67–68°; ir (KBr) 3070, 2090, 1625, 1485, 1440, 1335 and 1345 (doublet), 1280, 1130, 1060, 1030, 800, 745, 730, 710, 690 cm^{-1}; nmr (CCl_4) τ 2.81 (s, 10 H), 4.90 (s, 1, H), 5.20 (s, 1 H).

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.39; H, 5.26; N, 11.78.

(2) Addition of 1.0 g of **2** in 60 ml of methanol to 27 ml of 25% sodium methoxide in methanol gave after work-up diazopropanone (*ca.* 70%) as the only identifiable product.

Reaction of 8 with Sodium Methoxide.—Compound **8** (0.136 g, 0.51 mmol) was dissolved in 10 ml of methanol, and 4 ml of 25% sodium methoxide in methanol was added. This was stirred for 40 min at room temperature, after which 50 ml of water was added. The excess base was neutralized with acetic acid, and crystallization commenced. This gave 0.103 g of a white crystalline solid (**12**) (86% yield), mp 145–147°. This was recrystallized from carbon tetrachloride: mp 151–152°; nmr ($CDCl_3$) τ 1.52 (s, 1 H), 2.20 (s, 1 H), 2.64 (s, 10 H); ir (KBr) 3330, 2250, 1590, 1480, 1440, 1420, 1280, 1180, 1140, 1070, 1030, 1010, 995, 965, 935, 910, 840, 782, 755, 740 cm^{-1}; uv λ_{max} (CH_3CN) 245, 251, 257 (ϵ 505), shoulder at 266, 375 mμ (ϵ 1.9); mass spectrum (70 eV) *m/e* (rel intensity) 236, 218 (100), 164.

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.04; H, 5.14; N, 11.68.

Reaction of 8 with Sodium Methoxide in MeOD.—The pyrazoline oxide (35 mg) was dissolved in 1.5 ml of MeOD and a trace of NaOMe was added. Reaction was monitored by tlc. After 12 hr at room temperature (*ca.* half-life) the reaction mixture was poured into 50 ml of a mixture of dilute HCl and ether. The ether layer was washed with brine, dried, and evaporated to dryness. Preparative tlc of the residue yielded two fractions—starting material and oxime **12**. Analysis of recovered **8** by nmr showed no detectable retention of methylene protons with no detectable loss of the methyne proton. The spectrum of product **12** showed less than 5% aldehyde hydrogen.

In a parallel reaction, proteated oxime was exposed to the above reaction conditions. Recovered material showed no loss of aldehyde hydrogen.

Reaction of 12 with Acetic Anhydride and Pyridine.—Compound **12** (54 mg, 0.23 mmol) was heated with 1 ml of acetic anhydride overnight at 60°. Pyridine (5 ml) was then added and the mixture was heated for 20 hr at 100°. The reaction mixture was then added to ice. The crystals that were produced were filtered, washed with water, and dried under vacuum. This gave 32 mg (65%) of diphenylmalonodinitrile, a white, crystalline solid: mp 86–87° (lit.[22] mp 87.5°); ir (KBr) 3030 (m), 2920 (w), 2260 (w), 1950 (w), 1880 (w), 1800 (w), 1750 (w), 1590 (s), 1490 (s), 1450 (s), 770 (s), 745 (s), 702–691 cm^{-1} (doublet, s); mass spectrum (70 eV) *m/e* (rel intensity) 218 (100), 190, 165, 115.

Reaction of 12 with Hydrochloric Acid in Methanol.—Compound **12** (0.103 g, 0.44 mmol) was dissolved in 10 ml of methanol, and 2.0 ml of concentrated hydrochloric acid was added. This was refluxed for 1 hr, then poured into 50 ml of water and extracted with two 20-ml portions of chloroform. The chloroform was dried (Na_2SO_4) and concentrated. Ether was added to begin crystallization. This gave 0.045 g (45%) of the amide **13**, a white, crystalline solid: mp 159–160°; ir (KBr) 3390, 3320, 3200, 2260, 1960, 1350, 760, 700 cm^{-1}; nmr ($CDCl_3$) τ temperature dependent, at 35° 2.58 (s, 10 H), 4.30 (broad s, 2 H) (on cooling to −50° the broad singlet split into two broad singlets at τ 1.79 and 4.09); mass spectrum (70 eV) *m/e* (rel intensity) 194 (100), 166.

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.35; H, 5.09; N, 11.69.

Pyrolysis of 8.—Compound **8** (0.109 g) was dissolved in 30 ml of chloroform and added to 1.5 g of Chromosorb P AW 60–80 mesh. The chloroform was removed under vacuum and the residue was pyrolyzed by dropping down a tube heated to 350° in a stream of nitrogen (0.1 l./min) under vacuum (2–3 mm) over a period of 30 min. The effluent gases were collected in a trap cooled in liquid nitrogen. The trapped material was dissolved in $CDCl_3$ and analyzed by nmr. The spectrum showed 55% starting material and 17% of a product identified as 1,1-diphenylethylene. Tlc on silica and glpc on 5 ft, 5% SE-30 and 150 ft, capillary Apiezon L columns showed retention times which were identical with that of a known sample of diphenylethylene. This indicates that **1** pyrolyzes in 38% yield to 1,1-diphenylethylene. No 2,2-diphenylvinyl methyl ether[23] could be detected by nmr or tlc.

Photolysis of 8.—Compound **8** (0.25 g) was irradiated with a 450-W Hanovia medium pressure mercury lamp in 130 ml of benzene in a water-cooled Pyrex apparatus for 12 hr (*ca.* 60% conversion). Concentration of the solution and chromatography of the residue on silica gel gave 50 mg of a new crystalline compound, mp 132–133°, identified as 4,4-diphenyl-3-methoxy-1-pyrazoline 1-oxide: ir (KBr) 1525 (s), 1370 (s), 1220 (s), 1150 (s), 705 cm^{-1} (s); nmr ($CDCl_3$) τ 2.5–3.2 (10 H), 4.53 (s, 1 H), 5.20 and 5.67 (J_{AB} = 16 cps, 2 H), 6.06 (s, 3 H); uv λ_{max} (EtOH) end absorption 225 mμ (ϵ 37,000); mass spectrum (70 eV) *m/e* (rel intensity) 268, 252, 238, 224, 210, 192, 121 (100).

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.42. Found: C, 71.83; H, 5.94; N, 10.56.

Pyrolysis of 9.—Compound **9** was pyrolyzed using the same procedure that was used for **8**. Nmr analysis of the crude pyrolysate showed approximately 12% starting material and 33% 2,2-diphenylvinyl methyl ether (isolated by preparative tlc) identical in every way with a sample (except reported melting point) of authentic material prepared by the method of Wittig.[23] Both materials showed the following physical properties: nmr (CCl_4) τ 2.7–2.9 (m, 10 H), 3.67 (s, 1 H), 6.26 (s, 3 H); uv λ_{max} (EtOH) 264 mμ; mass spectrum (70 eV) *m/e* (rel intensity) 210 (100), 195, 167, 165, 152, 105.

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 84.50; H, 6.93.

Registry No.—**1**, 32640-76-9; **2**, 32640-77-0; **5**, 32640-78-1; **8**, 32640-79-2; **9**, 32640-81-6; **12**, 32670-71-6; **13**, 32640-80-5.

(21) Approximate yields based on total phenyl absorption as an internal standard.

(22) R. N. Bennett, *J. Chem. Soc.*, 2628 (1956).

(23) Wittig, *Chem. Ber.*, **94**, 1373 (1961). A crystalline material was reported. We were unable to induce crystallization and therefore carried out a complete characterization.