added to cold bromine water. Recrystallization of the solid product gave 0.46 g of **7a**. From the filtrate more **7a** (total 0.69 g, 1.8 mmol, 61%), mp 130–131°, **7b** (0.20 g, 0.54 mmol, 18%), mp 124–125°, and *cis,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene (0.09 g, 0.24 mmol, 8%), mp 124–125°, all identified by ir spectra, were isolated chromatographically.

A solution of **11**, prepared at 10° by the reaction of mixed **10a** and **10b** (0.81 g, 2.7 mmol) in 75 ml of tetrahydrofuran with sodium hydroxide (100 ml, 0.031 *N*), was added to cold chlorine water. From the solid product (0.86 g) was isolated by recrystallization and chromatography **8a** (total 0.44 g, 1.3 mmol, 48%), identified by its ir spectrum.

Interconversion of 7a and 7b. Solutions of **7a** in acetone and in dimethyl sulfoxide were kept 6 days at 25° and then mixed with dilute hydrochloric acid to precipitate the solutes. The solid products were dissolved in benzene, filtered, concentrated, and then analyzed. The mixture recovered from acetone contained 42% **7a**, 8% **7b**, and 51% *cis,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene.[7] The mixture recovered from dimethyl sulfoxide contained 12% **7a**, 29% **7b**, 41% *cis,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene, and 19% *trans,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene. Similarly, **7b** in dimethyl sulfoxide after 1 day at 25° gave a mixture containing 12% **7a**, 82% **7b**, and 5% *cis,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene. Interconversion of **7a** and **7b** also occurred in benzene in the presence of triethylamine. In a preparative isomerization 12.5 g of **7a** in a mixture containing 200 ml of dimethyl sulfoxide and 100 ml of dimethylformamide was stored at 5° for 5 days and then poured into dilute hydrochloric acid. The solid was collected, dissolved in benzene, filtered, and poured into 1200 ml of cold hexane. The resulting yellow precipitate (unchanged **7a**, 9.5 g) was filtered, dissolved in mixed dimethyl sulfoxide–dimethylformamide, and stored for 5–10 days at 5°. After the fourth such cycle there was recovered unchanged **7a** (2.5 g, 20%), mp 128–131°, as the hexane-insoluble product. The combined hexane-soluble material was purified by chromatography and fractional crystallization, giving **7b** (3.50 g, 28%), mp 123–125°, *cis,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene[7] (2.75 g, 22%), mp 122–124°, *trans,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene (0.15 g, 1.2%), mp 148–150°, and a further isomer (unknown structure, *cf.* ref 7) (0.08 g, 0.6%), mp 130–132°.

Cyclopropanols. IX. Cyclopropoxy Radicals from Cyclopropyl Nitrites

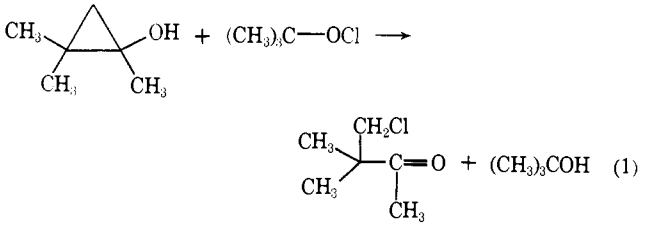
C. H. DePuy,* H. L. Jones,[1] and D. H. Gibson

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received September 13, 1971*

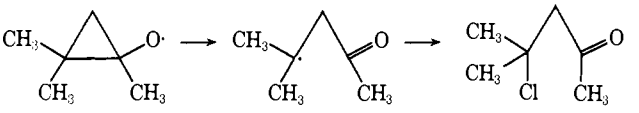
Abstract: Cyclopropyl nitrite esters decompose homolytically at very low temperatures (−80 to +20°) compared to ordinary aliphatic nitrite esters. The relative stability of the esters and the direction of ring opening are dependent upon the substitution pattern of the cyclopropanol. Those nitrite esters which give, upon ring opening, the most stable radicals decompose at the lowest temperatures. It is concluded that homolysis of the O–N bond of the nitrite ester occurs synchronously with carbon–carbon bond cleavage of the ring, and that release of strain in the transition state accounts for the rapid homolysis rates.

Cyclopropanols have been shown to be highly reactive toward acids and bases[2] and toward a variety of electrophilic agents.[3] In all of these ionic reactions isomerization occurs with fission of one of the carbon–carbon bonds of the ring.

Part of the evidence for the electrophilic nature of the reaction of cyclopropanol with halogenating agents was the structure of the reaction product when 1,2,2-trimethylcyclopropanol was allowed to react with *tert*-butyl hypochlorite (eq 1). Had the reaction involved free-radical attack on the hydroxyl group, it was argued that ring opening to the more stable tertiary radical should have occurred (eq 2). In order to confirm whether in fact this direction of ring opening would occur, it was decided to attempt to generate cyclopropoxy radicals and to study their ease of formation and direction of ring opening.[4]



(1)



(2)

As early as 1932 Lipp and coworkers[5] reported that both the hydrate and hemiketal of cyclopropanone give positive "silver mirror" tests when treated with ammonical silver nitrate. In more recent work Schaafsma and DeBoer[6] examined metal ion oxidations of several cyclopropanone hydrates and hemiketals. They observed rapid ring openings with any of a variety of one-electron oxidizing agents including silver(I), copper(II), and iron(III). Working with a fast-flow esr system, they were able to detect some of the alkyl

(1) NSF Traineeship, 1965–1967; Conoco Fellowship, 1967–1968.

(2) (a) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Amer. Chem. Soc.*, **88**, 3347 (1966); (b) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

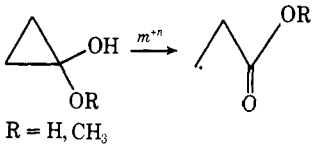
(3) (a) C. H. DePuy, W. C. Arney, Jr., and D. H. Gibson, *J. Amer. Chem. Soc.*, **90**, 1830 (1968); (b) A. DeBoer and C. H. DePuy, *ibid.*, **92**, 4008 (1970).

(4) C. H. DePuy, H. L. Jones, and D. H. Gibson, *ibid.*, **90**, 5306 (1968).

(5) D. Lipp, J. Buchkremer, and H. Seeles, *Justus Liebigs Ann. Chem.*, **499**, 1 (1932).

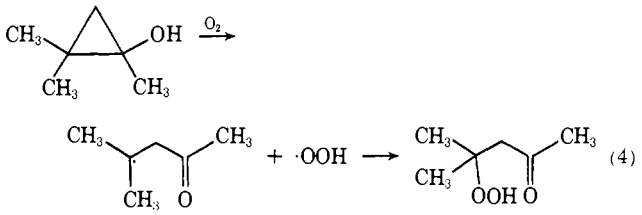
(6) (a) S. E. Schaafsma, H. Steinberg, and Th. J. DeBoer, *Recl. Trav. Chim. Pays-Bas*, **85**, 70 (1966); (b) S. E. Schaafsma, Ph.D. Thesis, University of Amsterdam, Amsterdam, The Netherlands, 1968.

radicals resulting from the isomerizations (eq 3). Gib-



(3)

son and DePuy[7] have demonstrated that cyclopropanols are also subject to oxidation by ground-state molecular oxygen. These reactions are also believed to occur *via* free-radical intermediates (eq 4). It seemed



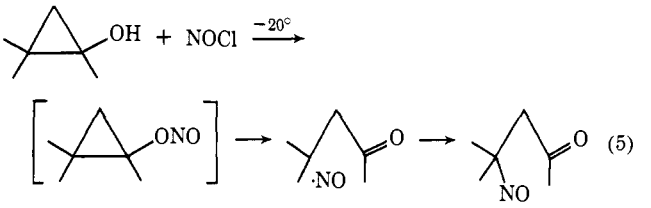
(4)

pertinent to generate cyclopropoxy radicals by means of a reaction whose approximate rate could be measured, in order to determine whether there is any special stability associated with these species.

Results and Discussion

Cyclopropyl Nitrites. Nitrite esters were chosen for study for several reasons. In the first place they are well established as precursors to alkoxy radicals, being cleaved thermally or photochemically to give the radical and nitric oxide.[8] Secondly, the esters can be formed directly from alcohols by reaction with nitrosyl chloride in the presence of a weak base such as pyridine. Under these conditions, devised by Barton[9] for steroid reactions, all of the numerous substituted cyclopropanols available are quite stable and thus a considerable variety of cyclopropyl nitrites can be prepared. Further, Kabasakalian and Townley[10] have reported the photolysis of nitrite derivatives of a series of cyclic alcohols including cyclobutyl nitrite, making possible comparison of our results to analogous systems of larger ring size.

In a typical preparation of an aliphatic nitrite ester, the alcohol, dissolved in pyridine, is treated at −20° with 1 equiv of gaseous nitrosyl chloride, the reaction mixture is poured into water, and the ester is isolated in the usual way, giving the pure ester after distillation. It can then be decomposed either thermally (by heating to approximately 200°) or photochemically by irradiation in solution. Thus, nitrite esters of most alcohols are stable and readily isolable. When nitrosyl chloride is added to a pyridine solution of 1,2,2-trimethylcyclopropanol, however, the solution immediately turns deep blue, indicating that a nitroso compound is being formed rapidly even at low temperatures (eq 5). If, however, the cyclopropanol is dissolved in an inert solvent ($CHCl_3$, $CDCl_3$, CS_2, CCl_4) containing 1 equiv of pyridine and NOCl added at −60°, a pale yellow solution of the nitrite ester forms, and pyridine hydrochloride precipitates. If a portion of the solution is transferred to the variable-temperature probe of an

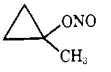
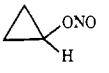
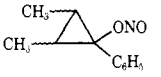
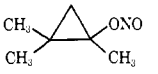
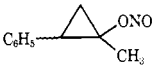
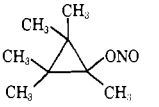
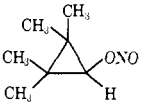
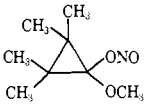


(5)

A-60A nmr spectrometer precooled to −60°, a spectrum of the ester can be obtained (*vide infra*). If now the temperature of the probe is gradually raised, the thermal rearrangement of the nitrite ester to the nitroso compound (and its dimer) can be followed.

Since the chemical shifts of substituents and the spin–spin coupling patterns of intact three-membered rings differ markedly from the spectra of isomerized products, there is little difficulty associated with the observations. The stability of the entire series of cyclopropyl nitrites is unusually low, and within those examined there are significant substituent effects. As one may deduce from a study of Table I, the relative reac-

Table I. Decomposition Temperatures of Cyclopropyl Nitrites ($t_{1/2} \cong 1$ hr)

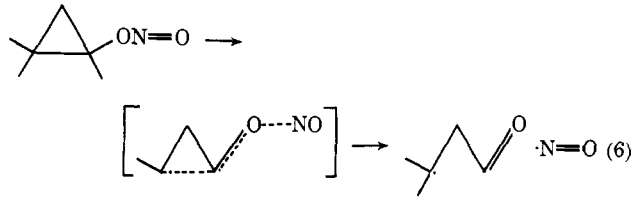
Nitrite	Temp, °C	Product
	+20	Nitroso dimer
	>0	5-Hydroxy-2-isoxazoline
	−5	Nitroso dimer
	−25	Nitroso dimer
	−40	Isoxazoline
	−45	Nitroso monomer
	−55	Nitroso monomer
	<−80	Nitroso monomer

tivity of cyclopropyl nitrites can be rationalized as corresponding to the normal order of reactivity for the alkyl radicals formed on ring opening. Thus, those nitrites which can form tertiary or benzylic radicals are more reactive than those which can form secondary or primary alkyl radicals. In addition, those cyclopropyl nitrites which may cleave either the 1–2 or the 1–3 bond to give *tert*-alkyl radicals are appreciably more reactive than those in which only one bond may

(7) D. H. Gibson and C. H. DePuy, *Tetrahedron Lett.*, 2203 (1969).
(8) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).
(9) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Amer. Chem. Soc.*, **83**, 4076 (1961).
(10) P. Kabasakalian and E. R. Townley, *J. Org. Chem.*, **27**, 2918 (1962).

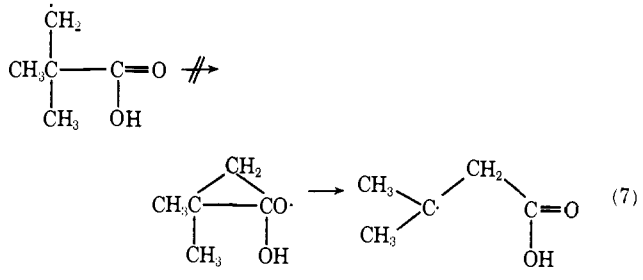
be broken, an effect which is probably steric in origin. This substituent effect, which is also present in the reaction of cyclopropanols with oxygen,[7] and the high reactivity of these nitrites at temperatures 100–250° lower than for nitrites not associated with three-membered rings are the principle findings of this study.

Two explanations for the very great rate enhancement for thermal homolysis of cyclopropyl nitrites as compared to nitrite esters of other aliphatic alcohols occurred to us. First, it might be postulated that there is some special stability of the cyclopropoxy radical, analogous to that of the cyclopropylcarbinyl cation, which lowers the activation energy for its formation. Alternately it is possible that carbon–carbon bond breaking is synchronous with O–N bond breaking, leading to a general enhancement of reactivity derived from energy released when the ring is opened and a carbonyl group is formed (eq 6). We strongly favor the second of these



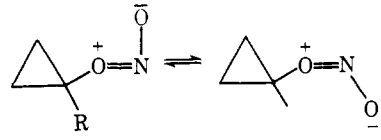
(6)

two explanations. In the first place the effect of substituents in the 2 position is readily accommodated if partial alkyl-radical character develops in the transition state. Secondly, the detection of only the alkyl radical by esr[11] spectroscopy argues against the closed form being the more stable one. The fact that no rearrangement is observed when a radical is generated on the methyl group of pivalic acid (eq 7) also argues against a highly stable cyclopropoxy radical.



(7)

Evidence for the Formation of Cyclopropyl Nitrites. A simple observation indicating nitrite formation is the color change which occurs during the formation and decomposition. Preparations are carried out in solution at temperatures well below the point of rapid isomerization of the nitrite ester. Slow addition of 1 equiv of nitrosyl chloride to a very cold solution of the cyclopropanol and 1 or 2 equiv of pyridine causes immediate discharge of the bright red color of NOCl and, depending on the solvent used, usually some solid pyridine hydrochloride is formed. Solutions of the nitrite esters are colorless or light yellow. In cases where the decomposition products are monomeric nitroso compounds, bright blue or blue-green solutions result upon warming. By appropriate choice of solvents and conditions, most of the ester preparations can be carried out at temperatures of from −35 to −80°. Only in the case of 1-methoxy-2,2,3,3-tetramethylcyclopropyl nitrite, prepared from tetramethylcyclopropanone methyl hemiketal, is real difficulty encountered in preparation and transfer of the sample to the probe of the nmr spectrometer. Further, the nmr spectra for all of the various cyclopropyl nitrites studied closely resemble the spectra of corresponding cyclopropanols and cyclopropyl acetates. Taking pentamethylcyclopropanol as an example, and using deuteriochloroform–pyridine-d_5 as solvent at a probe temperature of −60°, the alcohol spectrum consists of three singlets due to ring methyl groups at τ 8.66, 8.97, and 9.08 in the ratio of 3:6:6. Under identical solvent–temperature conditions, pentamethylcyclopropyl nitrite exhibits a spectrum of three singlets at τ 8.38, 8.88, and 9.06, likewise in the ratio of 3:6:6. Deshielding of the nmr signals due to groups at C-1 after nitrosation is consistently observed in the compounds studied and is rationalized as an effect of the N–O double bond. In other cyclopropyl nitrites where complex coupling patterns of ring protons are present in the nmr spectra of the alcohols, these patterns are preserved except for slight differences caused by chemical-shift changes. Several of the nitrites, especially those whose spectra could be observed over a wide temperature range, exhibited temperature-dependent effects in the nmr spectrometer. This is most notably a broadening of signals due to substituents at C-1. At −60 to −40°, C-1 signals due to methyl groups were about two–three times greater in width at half-height than were signals due to methyls on other ring atoms and in some cases signals of C-1 protons were lost in the base-line noise. Where the esters could be observed at higher probe temperatures, the signals narrowed and resolution improved to levels commensurate with the rest of the spectrum. Such temperature dependence is a characteristic of alkyl nitrites and is ascribed to "freezing out" of cis and trans isomers of the O–NO bond (eq 8).



(8)

This bond has considerable double bond character due to resonance. The observed temperature dependence of the spectra of cyclopropyl nitrites closely parallels that of benzyl nitrite as reported by Phillips;[12] however, we were not able to obtain spectra at low enough temperatures (*ca.* −90°) to resolve signals of the cis and trans isomers.

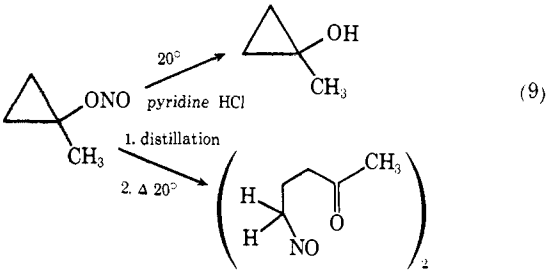
Nitrite esters may also be hydrolyzed to the alcohols if heated in the presence of weak acids. Barton accomplished this while attempting thermal homolysis of a steroid nitrite in a high boiling (150°) solvent.[13] With those cyclopropyl nitrites which are stable to about 0°, the pyridine hydrochloride formed during esterification can effect hydrolysis of the nitrite to the starting cyclopropanol. In a study of this, again using temperature-controlled nmr spectrometry, a solution of cyclopropyl nitrite containing 1 equiv of pyridine hydrochloride was first determined to be pure by recording its spectrum, and was then warmed to 0° for 30 min. Analysis, again by nmr, indicates the pres-

(11) R. Van Lanen, unpublished results.

(12) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, 70, 817 (1958).

(13) D. H. R. Barton, G. C. Ramsey, and D. Wege, *J. Chem. Soc.*, 265 (1964).

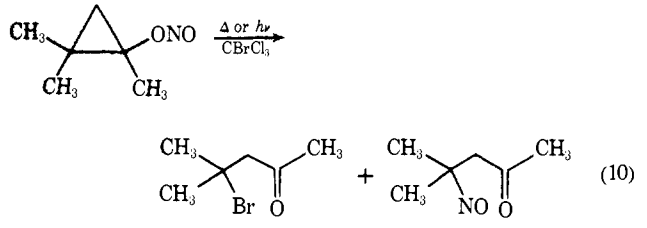
ence of 27% cyclopropyl nitrite, 38% cyclopropanol, and 35% ring-opened homolysis product. In another case, that of 1-methylcyclopropyl nitrite, only 1-methylcyclopropanol is obtained if solutions of the ester are allowed to warm to room temperature with pyridine hydrochloride present. If, however, a low-temperature bulb-to-bulb distillation is carried out first, only the ring-opened nitroso compound is formed (eq 9).



(9)

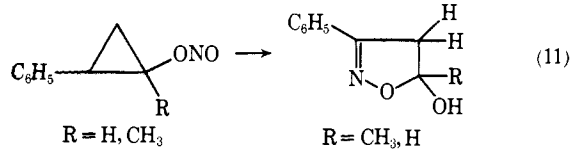
The spectroscopic and physical evidence seems clearly to indicate the formation of cyclopropyl nitrites at low temperatures.

Radical Trapping and Photochemical Homolysis. The intermediacy of ring-opened alkyl radicals is demonstrated when the nitrites are allowed to isomerize in solutions containing 5–10 mol equiv of a good radical trapping agent such as bromotrichloromethane. The products then contain 30–50% of β-bromocarbonyl compounds. Irradiation of nitrite solutions at temperatures well below those at which thermal decomposition occurs gives products which are identical with those from thermal processes. Again, in the presence of bromotrichloromethane, halogenated products are formed (eq 10).



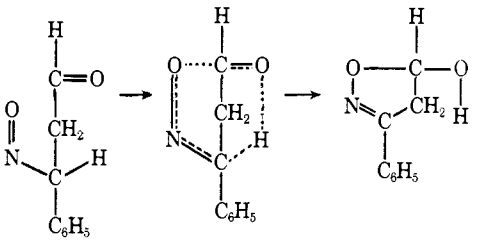
(10)

Isoxazoles and Isoxazolines as Products. When decomposition of the cyclopropyl nitrite gives a nitroso compound which is attached to a primary or secondary carbon atom, there is the potential for further isomerization to an oxime. Ordinarily, however, such isomerization does not occur under the conditions of the reaction and the nitroso dimer is the sole product. In three cases, during the decomposition of *cis*- and *trans*-2-phenylcyclopropyl nitrite and *trans*-1-methyl-2-phenylcyclopropyl nitrite the product was not a nitroso dimer but rather an isoxazoline (eq 11) formed even at −30 to −50°.



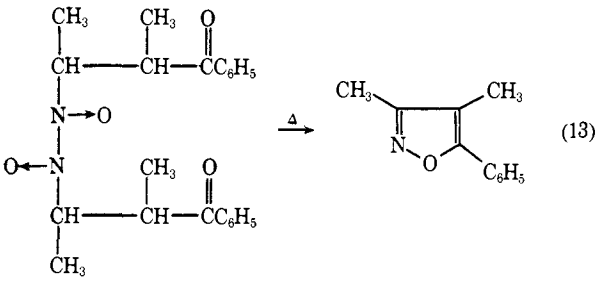
(11)

The structure of the product from the two 2-phenylcyclopropyl nitrites was verified by independent synthesis of the compound. In a formal sense this product can be imagined to be formed by isomerization to an oxime which cyclizes. We do not believe, however, that the oxime is an intermediate in this transformation. It seems very unlikely that a nitroso oxime tautomerism could occur under these conditions (inert solvent, −30 to −50°, no catalyst) and even when the reaction is carried out in an nmr tube no evidence for an intermediate can be found. We favor a concerted tautomeric shift by way of a bicyclo-[2.2.1] transition state analogous to the type postulated by Newman[14] (eq 12).



(12)

In other examples nitroso dimers are the initial products, but upon standing, or with some heating, isomerize to isoxazoles (eq 13). The structure of this product was also confirmed by an independent synthesis.



(13)

Experimental Section

Spectral Data. All infrared (ir) spectra were recorded on a Beckman IR-10 spectrophotometer using matched sodium chloride cells of 0.05, 0.10, or 0.25 mm path length. Mass spectra were obtained using a Varian CH-7 spectrometer. Nuclear magnetic resonance (nmr) studies were carried out using a Varian A-60-A spectrometer with a variable-temperature accessory.

Gas-Phase Chromatography (Gpc). All gpc analyses were performed on an F & M Scientific Model 700 gas chromatograph.

Nitrite Esters of Cyclopropanols. A. General Procedure for Nmr Studies. A weighed amount of a cyclopropanol was dissolved in enough carbon tetrachloride, chloroform, chloroform-d_1, carbon disulfide, or methylene chloride to make about a 10% solution. To this solution was added 1 or 2 equiv of pyridine-d_5. The reaction of the alcohol with nitrosyl chloride was carried out in a 25-ml two-necked flask equipped with an extension tube with a side arm sealed with a calcium sulfate filled drying tube. A mechanical stirrer was used, with the shaft passing through the extension tube.

Because excess NOCl was found to cause decomposition of the cyclopropyl nitrites, the amount which was added was carefully controlled. In some cases, a measured amount of the reaction solvent was pipeted into a small flask, which was sealed and weighed. Then, at −25°, NOCl was introduced into the flask. After a second weighing, the volume containing 1 equiv of NOCl was calculated, and this amount was removed by a graduated pipet and introduced into the reaction, under nitrogen, through an addition funnel. Direct addition of NOCl was carried out by employing a small, heavy-walled capsule equipped with two outlets fitted with Teflon stopcocks. Nitrosyl chloride was condensed into the tared capsule and then vented until exactly 1 equiv remained. One of the outlets was equipped with a 19/22 joint. This was fitted to the neck of the reaction flask and a slow stream of nitrogen was introduced through the other outlet and into the flask. The rate addition was controlled by alternate cooling or warming of the base of the capsule. The reactions were carried out with the flask immersed in a Dry Ice–

(14) M. S. Newman, S. Mladenovic, and L. K. Lala, *J. Amer. Chem. Soc.*, 90, 747 (1968).

isopropyl alcohol bath at the lowest temperature which was compatible with the solvent, down to −80°.

A special reaction flask was constructed and used in a few experiments. It was similar to an ordinary 25-ml two-necked flask, but was fitted with a sintered glass disk in the bottom leading to a second 25-ml bulb. The second bulb had one long neck. The reaction was carried out in the top section, in the cold bath, then a slight vacuum was applied to the neck of the lower portion, and the solution was filtered into the second bulb, removing most of the pyridine HCl formed.

Samples were removed by means of pipets which had been sealed in an argon-filled tube and cooled to −80°. Rapid transfer of an aliquot to an nmr sample tube in a bath at −80° resulted, except in the most extreme cases, in no thermal destruction of the cyclopropyl nitrites.

The nmr studies were carried out by first equilibrating the probe at a low temperature and then raising it in 5° increments until an appreciable rate of decomposition was observed in sequential spectra taken at about 10-min intervals usually at 500-Hz sweep width and 250-sec sweep times.

B. Tetramethylcyclopropanone Methyl Hemiketal–NOCl. A satisfactory nmr study was not obtained on the corresponding nitrite ester due to its extreme thermal sensitivity. In a typical reaction, 0.57 g (0.0039 mol) of the alcohol (prepared by the method of Turro, *et al.*[15]) and 0.35 g (0.0043 mol) of pyridine were combined in 5 ml of chloroform in the usual apparatus at −67 to −70°. Nitrosyl chloride, 0.27 g (0.004 mol), in 6.0 ml of chloroform was added dropwise over 15 min. The solution, which was allowed to warm slowly to room temperature over several hours, had become increasingly blue-green starting immediately upon introduction of the first portion of nitrosyl chloride. The material was taken up in 50 ml of pentane, washed free of pyridine with water, and dried over $MgSO_4$. After stripping the solvent, 0.63 g (94%) of a blue liquid monomer, methyl 3-nitroso-2,2,3-trimethylbutyrate, was obtained: ir (CCl_4) 1740 (C=O), 1585 cm^{-1} (N=O); nmr (CCl_4) τ 6.40 (s, 3, OCH_3), 8.40 (s, 6), 9.12 (s, 6).

C. Pentamethylcyclopropyl Nitrite. In the determination of the product yield, 0.35 g (0.003 mol) of the alcohol and 0.23 g (0.003 mol) of pyridine in 20 ml of chloroform were treated with 0.18 g (0.003 mol) of nitrosyl chloride at −70°. After work-up, 0.34 g (90%) of material was isolated which consisted of a 45:55 mixture of 2-nitroso-2,3,3-trimethyl-4-pentanone (nmr (CCl_4) τ 7.90 (s, 3), 8.45 (s, 6), 9.23 (s, 6)) and 2,3,3-trimethyl-1-penten-4-one (nmr (CCl_4) τ 5.03 (m, 2), 8.00 (s, 3), 8.35 (m, 3), 8.79 (s, 6)). The olefin was formed from the nitroso ketone through a short silica gel column resulted in its complete conversion to the olefin. Pure nitroso monomer was obtained by chromatography on florisil.

Pentamethylcyclopropyl nitrite was prepared, in the manner described (section A), from 0.50 g (0.0039 mol) of the alcohol, 0.7 g (0.009 mol) of pyridine, and 0.27 g of nitrosyl chloride in 30 ml of chloroform at −70°, and an nmr sample was removed. A reference spectrum of the alcohol was recorded: pentamethylcyclopropanol; nmr ($CHCl_3$–pyridine, −63°) τ 8.66 (s, 3), 8.97 (s, 6), 9.08 (s, 6). After NOCl addition, only the nitrite ester was present: pentamethylcyclopropyl nitrite; nmr ($CHCl_3$–pyridine, −63°) τ 8.38 (s, 3, broad), 8.88 (s, 6), 9.06 (s, 6). After 1 hr during which the probe temperature was raised from −63 to −45°, new peaks, due to the nitroso monomer in 1:1 ratio with the nitrite, were observed: nmr ($CHCl_3$–pyridine) τ 7.80, 8.42, and 9.22. Further spectra were recorded at 10–15-min intervals until after another hour the ratio of nitrite to nitroso compound by integration of the spectrum was 1:3. After briefly warming the sample to complete the conversion, the nitroso compound and its elimination product were the only detectable products. The olefin, 2,3,3-trimethyl-1-penten-4-one, was present in the ratio of 1:9 with the nitroso ketone.

D. 2,2,3,3-Tetramethylcyclopropyl Nitrite. Using the method described in part C, the corresponding blue nitroso monomer from this nitrite was prepared and isolated: 3-nitroso-2,2,3-trimethylpentanal; nmr (CCl_4) τ 0.03 (s, 1, CHO), 8.72 (s, 6), 9.10 (s, 6).

For the nmr study, the nitrite was prepared at −65° from 1.37 g (0.012 mol) of the alcohol, 1.5 g (0.019 mol) of pyridine, and 0.8 g (0.122 mol) of NOCl in 25 ml of $CHCl_3$, and an aliquot was then transferred to the nmr spectrometer at −60°. The spectrum of the cyclopropanol was obtained for reference: nmr ($CHCl_3$–pyridine, −60°) τ 7.10 (s, 1), 8.95 (s, 6), 9.00 (s, 6). The nmr spectrum of the NOCl reaction sample was recorded: nmr ($CHCl_3$–pyridine, −60°) τ 8.87 (s, 6), 9.13 (s, 6). After about 1 hr at −55° the nitrite was 50% converted to the nitroso compound: nmr ($CHCl_3$–pyridine, −55°) τ 8.72, 8.87, 9.10, 9.13 (singlets, 1:1:1:1). Finally, conversion was completed by briefly warming the sample to room temperature: nmr ($CHCl_3$–pyridine, −55°, 1000-Hz sweep width) τ −0.1 (s, 1), 8.72 (s, 6), 9.10 (s, 6).

E. 1,2,2-Trimethylcyclopropyl Nitrite. The nitrite was prepared from 1.05 g (0.011 mol) of the alcohol, 1 g (0.013 mol) of pyridine, and 0.75 g (0.011 mol) of NOCl in 20 ml of $CHCl_3$. The thermal decomposition of an aliquot of this solution was observed in the nmr spectrometer. The half-life was about 1 hr at −25° and the pertinent nmr data are given: 1,2,2-trimethylcyclopropanol, nmr ($CHCl_3$–pyridine, −63°) τ 8.56 (s, 3), 8.80 (s, 3), 8.97 (s, 3), 9.70 (AB, 2); 1,2,2-trimethylcyclopropyl nitrite, nmr ($CHCl_3$–pyridine, −50°) τ 8.32 (s, 3, broad), 8.79 (s, 3), 9.00 (s, 3), 9.18 (AB, 2, partially obscured by a methyl singlet); 2-methyl-2-nitroso-4-pentane, nmr ($CHCl_3$–pyridine, −20°) τ 6.74 (s, 2), 7.80 (s, 3), 8.73 (s, 6).

The nitroso ketone was isolated as the colorless dimeric solid, mp 74–76°. It was prepared independently by the oxidation of an aqueous solution of 2-hydroxylamino-2-methyl-4-pentanone oxalate with mercuric oxide in the manner of Aston[16] giving 2-nitroso-2-methyl-4-pentanone: mp 72–74° [lit.[16] mp 75–76°]; ir (CCl_4) 1720 (C=O), 1565 cm^{-1} (N=O); nmr (CCl_4) identical with the cyclopropyl nitrite product; mmp 73–76°.

F. *trans*-2-Phenylcyclopropyl Nitrite. The nitrite was prepared, as usual, from 0.41 g (0.003 mol) of alcohol, 0.79 g (0.009 mol) of pyridine-d_5, and 0.20 g (0.003 mol) of nitrosyl chloride in 5 ml of carbon disulfide. After transfer of a sample, the decomposition of the nitrite was observed in the nmr at −40°, where the half-life was about 1 hr. The nitrite exhibited the following nmr spectral features at −60°: τ 2.7 (m, phenyl protons), 5.70 (broad, unresolved peak, C-1 cyclopropane proton), 7.85 (septet, poorly resolved, C-2 benzylic cyclopropane proton), 8.6 (m, well-resolved, C-3 cyclopropane protons). At −40° the resolution of the spectrum of the nitrite was improved, but the C-1 ring proton was still somewhat broad. The signals due to the decomposition product were observed at τ 4.09 (q) and 6.78. The product was identified as 3-phenyl-5-hydroxy-2-isoxazoline: mp 122–123°; nmr ($CDCl_3$) τ 2.3–2.5 (m, 5), 3.5 (s, 1, broad, OH), 3.0 (q, 1, ABX), 6.75 (m, 2, ABX); mass spectrum *m/e* (relative intensity) 163 (30), 103 (25), 77 (100).

G. 3-Phenyl-5-hydroxy-2-isoxazoline. Benzaldoxime was prepared by heating 21.2 g (0.20 mol) of benzaldehyde, 20.0 g (0.30 mol) of hydroxylamine hydrochloride, and 28 g of potassium hydroxide in 200 ml of ethanol, under reflux for 1 hr. The solvent was evaporated and the organic materials were dissolved into ether. Evaporation of the solvent and distillation *in vacuo* gave 22 g (90%) of benzaldoxime: bp 60–61° (0.3 mm).

Benzhydroxamic acid chloride was prepared by passing chlorine gas through a solution of 11.0 g of benzaldoxime in 60 ml of 8 *N* hydrochloric acid for 30 min. The product was filtered from the solution giving 11.7 g (88%) of the acid chloride; mp 42–48°.

The acid chloride, 11.7 g (0.08 mol), and 6.5 g (0.08 mol) of vinyl acetate were combined in 75 ml of ether. To this solution was added, dropwise, 50 ml of 14% sodium hydroxide in water. After stirring for 45 min, the ether layer was separated, washed with water, and dried over $MgSO_4$. Two crystallizations from absolute ethanol gave 3-phenyl-5-acetoxy-2-isoxazoline: mp 89–92°; nmr ($CDCl_3$) τ 2.52 (m, 5), 3.17 (q, 1, ABX), 6.50 (m, 2, ABX), 7.82 (s, 3). The nmr spectral pattern was very similar to that of the 2-phenylcyclopropyl nitrite product.

Reduction of the acetate in ether with methyllithium gave, on work-up, a material which was identical by its nmr spectrum and melting point (121–123°) with the isoxazoline from 2-phenylcyclopropyl nitrite.

H. *cis*-2-Phenylcyclopropyl Nitrite. The nitrite was prepared as described in parts A and F. The thermal decomposition was followed in the nmr spectrometer, and the nitrite was found to have a half-life of 1 hr at −50°. The product of the decomposition was determined to be 3-phenyl-5-hydroxy-2-isoxazoline, identical with that from *trans*-2-phenylcyclopropyl nitrite.

I. *trans*-2-Phenyl-1-methylcyclopropyl Nitrite. The nitrite was prepared from 0.30 g (0.002 mol) of the alcohol, 0.25 g (0.003 mol) of pyridine-d_5, and 0.15 g (0.0023 mol) of nitrosyl chloride in the usual apparatus (part A) in 6 ml of $CDCl_3$. A sample had the fol-

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lowing nmr spectrum: ($CDCl_3$–pyridine-d_5, −56°) τ 2.61 (s, 5), 7.30 (t, 1, AB*X*), 8.14 (5), 8.50 (m, *ABX*). The observed half-life was 1 hr at −40°. The sole product of the reaction was 2-phenyl-5-hydroxy-5-methyl-2-isoxazoline: nmr (CCl_4) τ 2.4–2.9 (m, 5), 4.30 (s, 1, O*H*), 2.60 (s, 1), 2.67 (s, 1), 8.38 (s, 3).

J. *cis,trans*- and *trans,trans*-2,3-Dimethyl-1-phenylcyclopropanol. The nitrites were prepared in the usual way and found to have half-lives of 1 hr at −5°. About 25% of the decomposition products were the starting cyclopropanols resulting from hydrolysis of the nitrite ester. Distillation of the solvent and the nitrites from a bath at −80° to a liquid nitrogen cooled trap using a diffusion pump, gave, after thermolysis, products containing only 5% of the alcohols. The main products were dimeric nitroso compounds: ir (CCl_4) 1685 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.0–2.5 (m, 5), 4.35 (m, 1), 5.84 (m, 1), 8.70 (m, 6). The product mixtures from each isomeric nitrite were the same. On standing at room temperature, or at −20°, the nitroso dimers were converted to 3,4-dimethyl-5-phenylisoxazole: nmr ($CDCl_3$) τ 2.5 (m, 5), 7.88 (s, 3), 8.02 (s, 3); nmr (CCl_4) τ 2.55 (m, 5), 7.80 (s, 3), 7.89 (s, 3). Irradiation of *cis,trans*- and *trans,trans*-2,3-dimethyl-1-phenylcyclopropyl nitrites, in solution, below −20°, gave product mixtures which were identical by nmr spectroscopy with those from thermal decompositions, and were also easily converted to the isoxazole.

K. 3,4-Dimethyl-5-phenylisoxazole. To a solution of 4.9 g (0.03 mol) of benzoylacetone in 30 ml of ether was added 0.7 g (0.03 g-atom) of sodium wire. The product was isolated by filtration giving 5.4 g (100%) of the product.

Treatment of 5.4 g (0.03 mol) of the salt with 4.0 g (0.028 mol) of methyl iodide in acetone gave, after work-up and distillation, 2.63 g (50%) of methylbenzoylacetone: bp 124–130° (8 mm); nmr (CCl_4) τ 2.05 (m, 2), 2.50 (m, 3), 5.49 (q, 1, J = 7 Hz), 7.93 (s, 3), 8.67 (d, 3, J = 7 Hz).

Treatment of 2.63 g (0.015 mol) of the diketone with 1.04 g (0.015 mol) of hydroxylamine hydrochloride and 1.6 g (0.02 mol) of sodium bicarbonate gave, on work-up, 2.85 g of a material which was identical by nmr spectroscopy with the isoxazole obtained from the cyclopropyl nitrites.

L. Cyclopropyl Nitrite. The nitrite was prepared as usual (part A) from 1.95 g (0.034 mol) of the alcohol, 2.8 g of pyridine, and 2.2 g (0.034 mol) of nitrosyl chloride in 25 ml of chloroform. The thermal decomposition of a sample was observed in the nmr spectrometer. Some representative nmr data consisted of the following: cyclopropanol, nmr ($CHCl_3$–pyridine, −60°) τ 6.47 (septet, 1), 9.43 (m, 4); cyclopropyl nitrite, nmr ($CHCl_3$–pyridine, −60°) τ 5.59 (broad, unresolved), 9.08 (m, 14 lines); nmr ($CHCl_3$–pyridine, −45°) τ 5.6 (broad, J = 25 Hz, unresolved), 9.0 (m, 15 well-resolved lines); nmr ($CHCl_3$–pyridine, −35°) τ 5.6 (septet, barely resolved), 9.0 (m, 17 lines); nmr ($CHCl_3$–pyridine, −15°) τ 5.6 (septet, well resolved), 9.1 (m, 20 lines). The final product mixture consisted of a 1:1 ratio of cylopropanol (from acid hydrolysis) and a product which was identified as 5-hydroxy-2-isoxazoline: nmr ($CHCl_3$) τ 1.8 (m, 1), 3.9 (quartet of lines of equal intensity, 1), 6.8 (m, 6 lines, 2). This isoxazoline was not synthesized independently, but its structure was assigned on the basis of its resemblance to the isoxazoline from the 2-phenylcyclopropyl nitrites.

M. 1-Methylcyclopropyl Nitrite. The nitrite was prepared as usual from 0.72 g (0.01 mol) of alcohol, 0.86 g (0.011 mol) of pyridine, and 0.66 g (0.01 mol) of nitrosyl chloride in 10 ml of carbon disulfide. The flask containing the nitrite ester solution was attached to the side arm of a trap which was immersed in liquid nitrogen and attached to a vacuum pump. The nitrite ester solution was maintained at −75° and was distilled at 0.005 mm of pressure. A clear, pale-yellow solution was found in the trap after distillation and warming from −196 to −78°. This solution was used for the nmr study of the nitrite. A previous attempt had failed as no thermal decomposition was observed in the nmr spectrometer below +10° and above this temperature extensive hydrolysis to 1-methylcyclopropanol occurred. The distilled nitrite solution which was free from pyridine hydrochloride exhibited no hydrolysis and the nitrite was determined to have a half-life of about 1 hr at near room temperature (20–25°). The product was the nitroso dimer: mp 102–106°; ir (CCl_4) 1720 (C=O), 1590 cm^{-1} (N=O); nmr ($CDCl_3$) τ 5.54 (t, 2, J = 6.5 Hz), 7.00 (t, 2, J = 6.5 Hz), 7.75 (s, 3). A sealed nmr sample tube containing the dimer was heated to 52° in boiling acetone for 24 hr, but no change was observed. The sample was then heated at 80–110° for 8 hr and complete conversion to 5-methylisoxazole occurred: nmr ($CDCl_3$) τ 1.87 (m, 1), 4.05 (m, 1), 7.55 (s, 3). In benzene-d_6, coupling to the methyl group was observed: nmr (C_6D_6) τ 2.26 (m, 1), 4.70 (m, 1, J = 0.75 Hz), 8.20 (m, 3, J = 0.75 Hz).

N. *cis,trans*- and *trans,trans*-2,3-Dimethyl-1-phenylcyclopropyl Nitrite–$CBrCl_3$. In the usual manner, the cis,trans nitrite was prepared from 0.51 g (0.0032 mol) of alcohol, 0.38 g (0.0048 mol) of pyridine, and 0.22 g (0.0034 mol) of nitrosyl chloride in 100 ml of ether to which 12.5 g (0.06 mol) of bromotrichloromethane had been added. The solution was irradiated at −80° for 1 hr with a 450-W Hanovia lamp. The ether solution was washed with water and dried over $MgSO_4$. Removal of the solvent gave 0.67 g of a liquid residue; an nmr spectrum of the residue indicated it was largely *threo*-α-methyl-β-bromobutyrophenone. Chromatography on silica gel gave 0.5 g (78%) of an 80:20 mixture of *erythro*- and *threo*-α-methyl-β-bromobutyrophenones[3] and 0.14 g (20%) of the nitroso dimer.

The photolysis of the trans,trans nitrite under the same conditions resulted in a crude product mixture which was identical with that from the cis,trans isomer.

O. Pentamethylcyclopropyl Nitrite–$CBrCl_3$. The nitrite was prepared from 0.64 g (0.005 mol) of alcohol, 0.60 g (0.001 mol) of pyridine, 10.0 g (0.050 mol) of bromotrichloromethane, and 0.33 g (0.005 mol) of nitrosyl chloride in 30 ml of ether at −70°. The solution was allowed to warm slowly over several hours after which it was washed, dried over $MgSO_4$, and stripped of solvent. Analysis by nmr spectrometry of the crude material gave the following product distribution: 44% of 2-bromo-2,3,3-trimethyl-4-pentanone, nmr (CCl_4) τ 7.82 (s, 3), 8.23 (s, 6), 8.72 (s, 6); 25% of 2-nitroso-2,3,3-trimethyl-4-pentanone, nmr (CCl_4) τ 7.95 (s, 3), 8.45 (s, 6), 9.23 (s, 6); 15% of an unknown product, nmr (CCl_4) τ 7.90 (s, 3), 8.41 (s, 6), 8.77 (s, 6); and 16% of another unknown product, nmr (CCl_4) 7.82 (s, 3), 8.72 (s, 6), 8.82 (s, 6). The bromo compound was identified by comparison to the product from a reaction known to cleave cyclopropanols with formation of β-bromocarbonyl compounds.

P. 1-Methoxy-2,2,3,3-tetramethylcyclopropyl Nitrite–$CBrCl_3$. The nitrite was prepared from 0.73 g (0.005 mol) of the alcohol, 0.6 g (0.0075 mol) of pyridine, 12 g (0.06 mol) of bromotrichloromethane, and 0.37 g (0.0056 mol) of nitrosyl chloride in 30 ml of ether at −80°. The solution was allowed to warm slowly and was then worked up. The residue after removal of the solvent was analyzed by nmr spectrometry and gave the following product distribution: methyl 3-bromo-2,2,3-trimethylbutyrate, 30%, nmr (CCl_4) τ 6.37 (s, 3), 8.17 (s, 6), 8.65 (s, 6); methyl 3-nitroso-2,2,3-trimethylbutyrate, 40%, nmr (CCl_4) τ 6.38 (s, 3), 8.42 (s, 6), 9.15 (s, 6); and an unknown product, nmr (CCl_4) τ 6.35 (s, 3), 8.39 (s, 6), 8.73 (s, 6). The bromo ester was identified by comparison to the product from the *N*-bromosuccinimide reaction of the alcohol.

Acknowledgment. We wish to thank the National Science Foundation for a grant (No. GP-13783X) in support of this work.