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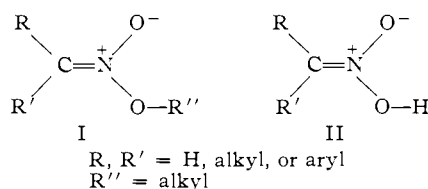
The Synthesis and Characterization of Nitronic Esters^{1,2}

BY NATHAN KORNBLOM AND R. ALAN BROWN

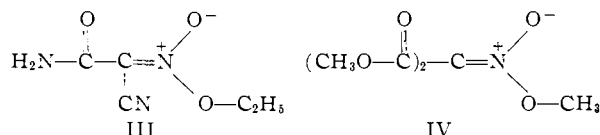
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Nitroparaffin salts react with trialkyloxonium fluoroborates to give nearly quantitative yields of nitronic esters. In this way nitronic esters derived from strictly aliphatic nitro compounds have been prepared for the first time. By the use of nuclear magnetic resonance spectroscopy it has been shown that nitronic esters exhibit *cis-trans* isomerism. Although stable indefinitely at -78° , nitronic esters decompose relatively rapidly at room temperature, particularly in the liquid state or in solution; nitronic esters derived from secondary nitro compounds appear to be less stable than those obtained from primary nitro compounds. Significant differences in decomposition rate are observed for stereoisomeric nitronic esters.

This paper is concerned with the preparation and characterization of nitronic esters (I), a little known group of compounds formally derived from *aci*-nitroparaffins (II).³ Hitherto the strictly aliphatic members

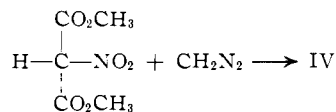


of this group have been unknown and, indeed, even those in which R (or R') is aryl have been prepared in but a few instances. Of the small number of nitronic esters known, most have electron-withdrawing groups present, *e.g.*, III and IV.⁴



In the past, nitronic esters have been obtained by three methods: (1) the reaction of nitro compounds with diazomethane, (2) alkylation of alkali metal salts of nitro compounds, and (3) treatment of the silver salts of nitro compounds with alkyl iodides.

The first of these methods succeeds with nitro compounds which are comparatively strong acids, *e.g.*⁵

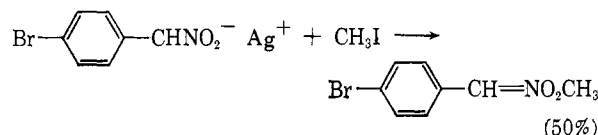


However, nitromethane and 2-nitrocamphane do not react with diazomethane⁶ and it has now been found that 3-phenyl-1-nitropropane, after being treated with diazomethane for 5 days, is recovered quantitatively.

The second method is less useful than the first. It has been reported, in two instances, that nitronic esters

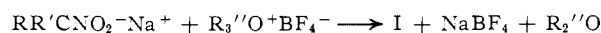
are obtained (yields unstated) on treatment of a nitroparaffin salt with dimethyl sulfate^{5a,7,8}; but the essential futility of this procedure is apparent when it is recalled that the reaction of alkyl halides with alkali metal salts of nitro compounds usually produces a carbonyl compound and an oxime. Indeed, this is a useful method for the synthesis of aldehydes and ketones.⁹

The third method, which employs silver salts, has been examined in but a few instances and, of these, only one involved a simple nitro compound.^{4,10} While



this method may have utility, reports of the instability of silver salts of nitro compounds¹¹ do nothing to foster optimism.

We here describe a new synthesis of nitronic esters which is achieved by treating the salts of nitroparaffins with trialkyloxonium fluoroborates at 0° . The reaction is rapid, and virtually quantitative yields are obtained (*cf.* Table I). The necessary oxonium fluoroborates



are readily prepared by the excellent procedure of Meerwein.^{12,13} In this synthesis of nitronic esters, methylene chloride is the solvent of choice. The sodium fluoroborate produced and the sodium salt of the nitroparaffin (which is employed in excess relative to the oxonium salt) are both insoluble in methylene chloride and are readily separated by filtration. Furthermore, methylene chloride is rapidly and easily removed from the nitronic ester by vacuum evaporation. Since nitronic esters are relatively unstable (*vide infra*), the simplicity of the work-up procedure which results from

(7) C. D. Nenitzescu and D. A. Isacescu, *Bul. Soc. Chem. Romania*, **14**, 53 (1932); *Chem. Abstr.*, **27**, 964 (1933).

(8) In the special case of γ -halonitro compounds instances of cyclization to give five-membered nitronic esters have been reported by E. P. Kohler and G. R. Barrett, *J. Am. Chem. Soc.*, **48**, 1770 (1926). (Also see M. S. Gibson, *Tetrahedron*, **18**, 1377 (1962), and ref. 4.)

(9) (a) C. D. Nenitzescu and D. A. Isacescu, *Ber.*, **63**, 2484 (1930); (b) L. Weisler and R. W. Helmkamp, *J. Am. Chem. Soc.*, **67**, 1167 (1945); (c) H. B. Hass and M. L. Bender, *Org. Syntheses*, **30**, 99 (1950); (d) S. V. Lieberman, *J. Am. Chem. Soc.*, **77**, 1114 (1955); (e) M. Montavon, *et al.*, *Helv. Chim. Acta*, **40**, 1250 (1957).

(10) C. H. Dale, Ph.D. Thesis, University of Rochester, 1936.

(11) H. Shechter and R. B. Kaplan, *J. Am. Chem. Soc.*, **75**, 3980 (1953).

(12) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and J. Willfang, *J. prakt. Chem.*, **154**, 83 (1939); also see ref. 13.

(13) L. G. Donaruma [*J. Org. Chem.*, **22**, 1024 (1957)], who treated the sodium salts of nitrocyclohexane, nitrocyclopentane, and 2-nitropropane with trimethyl- (and triethyl-) oxonium salts, generally at temperatures in the range 50 to 70° , did not obtain nitronic esters. Instead, he isolated the oximes of cyclohexanone, cyclopentanone, and acetone.

(1) This work was supported in part by the U. S. Army Research Office (Durham) and in part by the Air Force Office of Scientific Research.

(2) Paper XXI in the series, "The Chemistry of Aliphatic and Alicyclic Nitro Compounds." A preliminary account of this work appeared in *J. Am. Chem. Soc.*, **85**, 1359 (1963). For the preceding paper in this series see N. Kornblum and H. J. Taylor, *J. Org. Chem.*, **28**, 1424 (1963).

(3) The relationship is indeed formal since nitronic esters are not prepared by treating an *aci*-nitro compound with an alcohol. Nor, for that matter, can nitronic esters be hydrolyzed to nitro compounds.

(4) For a complete list of known nitronic esters the doctoral dissertation of R. A. Brown (Purdue University, June, 1963) should be consulted.

(5) (a) F. Arndt and J. D. Rose, *J. Chem. Soc.*, **1** (1935); (b) M. K. Shahova, M. I. Boudagyantz, G. I. Samahvalov, and N. A. Preobrashchenskii, *J. Gen. Chem. USSR*, **32**, 2832 (1962).

(6) J. L. Heinke, *Ber.*, **31**, 1395 (1898); W. J. Jones, Ph.D. Thesis, Purdue University, 1960.

the use of methylene chloride is crucial to the success of this synthesis.¹⁴

TABLE I

NITRONIC ESTERS PREPARED FROM OXONIUM FLUOROBORATES AND NITRO SALTS^a

Nitronic ester ^b	Yield, %	Nitronic ester ^b	Yield, %
CH ₃ CH=NO ₂ CH ₃	90-95	<i>p</i> -O ₂ NC ₆ H ₄ CH=NO ₂ C ₂ H ₅	92
CH ₃ CH=NO ₂ C ₂ H ₅	94	(CH ₃) ₂ C=NO ₂ C ₂ H ₅	75-80
CH ₃ CH ₂ CH=NO ₂ C ₂ H ₅	79	CH ₃ CH ₂ C=NO ₂ C ₂ H ₅	90-95
CH ₃ C(CH ₃) ₂ CH=NO ₂ C ₂ H ₅	90-95		
<i>p</i> -BrC ₆ H ₄ CH=NO ₂ C ₂ H ₅	95	CH ₃	

^a The yields of sodium fluoroborate were usually above 95%.

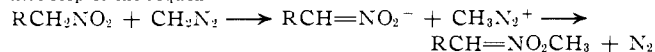
^b All the nitronic esters mentioned in this paper exhibit intense infrared absorption in the 6.05 to 6.2 μ region.

cis-trans Isomerism and Nuclear Magnetic Resonance Spectra of Nitronic Esters.—The reaction of the sodium salt of *p*-nitrophenylnitromethane with triethyloxonium fluoroborate produces a 92% yield of crude product which, although it melts over a wide range (82–88°), gives excellent carbon, hydrogen, and nitrogen analyses for the ethyl nitronic ester. Recrystallization of this "crude" gives a 65% yield of the nitronic ester which melts at 100–101°, and, not surprisingly, is analytically pure. Similarly, from the sodium salt of *p*-bromophenylnitromethane and triethyloxonium fluoroborate, a product is obtained (95% yield) which melts over the range 35–40°; yet it possesses the composition (C, H, N, Br analyses) of the pure ethyl nitronic ester.

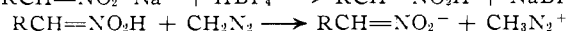
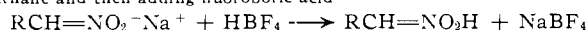
Nor is this characteristic only of nitronic esters prepared from trialkyloxonium fluoroborates. Nitronic esters synthesized by the action of diazomethane on relatively acidic nitro compounds also exhibit these characteristics. Thus, treatment of *p*-nitrophenylnitromethane with diazomethane produces a quantitative yield of the methyl nitronic ester which, even though it melts at 100–108°, has excellent carbon, hydrogen, and nitrogen analyses; recrystallization gives a 52% yield of analytically pure ester melting at 118–120°. In the same way, when the methyl nitronic ester of *p*-bromophenylnitromethane is prepared from the nitro compound and diazomethane, a crude product is isolated in quantitative yield and, although it melts at 20–43°, it is analytically pure; on recrystallization the melting point is raised to 66.5–67.5°, but the analysis remains unaltered.

These facts become intelligible on the basis that the crude nitronic esters are mixtures of geometric isomers,¹⁵

(14) Another synthesis of nitronic esters, although promising, has only been explored in a preliminary way. As noted above, diazomethane fails to react with simple, relatively weakly acidic nitro compounds, presumably as a consequence of the slowness with which proton transfer occurs in the first step of the sequence

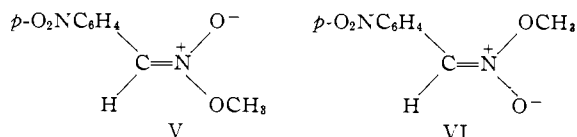


This difficulty is circumvented by treating a nitroparaffin salt with diazomethane and then adding fluoroboric acid



In the single experiment performed, the sodium salt of *p*-nitrophenylnitromethane gave the methyl nitronic ester when treated with diazomethane and fluoroboric acid; the yield (ca. 70%) is surely minimal. [This method is reminiscent of the procedure devised for the methylation of alcohols with diazomethane by M. Neeman, M. C. Caserio, J. D. Roberts, and W. S. Johnson, *Tetrahedron*, **6**, 36 (1959); see also M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5161 (1950), and E. Müller and W. Rundel, *Angew. Chem.*, **70**, 105 (1958).]

(15) Z. Buczkowski and T. Urbanski, *Spectrochim. Acta*, **18**, 1187 (1962), have suggested that sodium salts of primary nitroparaffins may exist in *cis* and *trans* forms. A. H. Lambertson and G. Newton, *J. Chem. Soc.*,

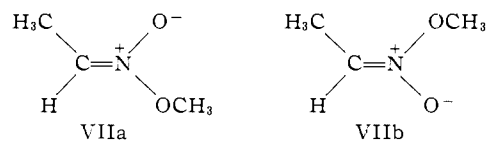


e.g., V and VI. Such stereoisomerism has not been reported previously, but this is not surprising considering the paucity of information regarding nitronic esters and their somewhat unstable character. The proposal that the "crude," albeit analytically pure, nitronic esters are mixtures of stereoisomers receives strong support from nuclear magnetic resonance (n.m.r.) studies.

We shall discuss first the n.m.r. spectra of nitronic esters derived from primary nitro compounds, *i.e.*, of the type RCH=NO₂R'. These are characterized by having a hydrogen atom on a carbon which is doubly bonded to nitrogen, *i.e.*, a "vinyl" hydrogen. This structural feature proves to be of particular value in establishing the presence of geometrical isomers, just as Phillips¹⁶ demonstrated for aldoximes, as Lustig¹⁷ showed for aldoximes and ketoximes, and as Slomp and Wechter¹⁸ and Mazur¹⁹ discovered for α,β-unsaturated oximes. Phillips¹⁶ found that a series of aliphatic aldoximes, RCH=NOH, exhibit two multiplets separated by about 0.6 p.p.m. in the vinyl hydrogen region and proposed that the *syn* isomer gives rise to one of these multiplets and the *anti* to the other. Lustig arrived at the same conclusion using the *syn*- and *anti*-*p*-chlorobenzaldoximes. In our hands the n.m.r. spectrum of acetaldoxime (neat) showed two vinyl hydrogen peaks, as quartets, centered at 6.84 and 7.42 δ.²⁰

Oxygen-alkylated oximes (RCH=NOR') are even better models for nitronic esters and, consequently, the n.m.r. spectrum of O-ethylacetaldoxime (CH₃CH=NOC₂H₅) was determined (neat). In the vinyl region two quartets are found, one at 6.62 and the other at 7.28 δ.

The methyl nitronic ester of nitroethane (VII) is a liquid whose n.m.r. spectrum shows two quartets



in the vinyl hydrogen region, one at 5.91 and the other at 6.25 δ, the latter being about five times the area of the former. Based on the vinyl hydrogen ratio, it follows that both stereoisomers of VII were produced and in about a 5:1 ratio, but whether the preponderant isomer is VIIa or VIIb cannot be stated. In addition, the peak due to the methyl group on the "vinyl" carbon atom appears as a doublet centered at 1.82 δ for the preponderant isomer and at 1.89 δ for the minor isomer. That these methyl groups in VIIa and VIIb are not equivalent is not surprising and is, in fact, consonant

1797 (1961), have proposed geometrical isomerism in the O,N-dialkylnitramine system RN=NO₂R' to explain the observed rates of alkali-induced decomposition.

(16) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958). For a very recent paper on this subject see G. J. Karabatsos, R. A. Taller, and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 2327 (1963).

(17) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).

(18) G. Slomp and W. J. Wechter, *Chem. Ind. (London)*, 41 (1962).

(19) R. H. Mazur, *J. Org. Chem.*, **28**, 248 (1963).

(20) Chemical shifts from the internal standard, tetramethylsilane (TMS), are reported in δ-units with TMS having a value of 0 δ.

with Lustig's¹⁷ finding that the two methyl groups of the anion derived from acetoxime, $(\text{CH}_3)_2\text{C}=\text{N}-\text{O}^-$, are not equivalent.²¹ Finally, for both stereoisomers, the methyl group on oxygen produces a singlet at 3.68 δ . In agreement with these assignments, the ratio of the areas of "vinyl" hydrogen to "vinyl" methyl hydrogen to methoxy hydrogen is 1:3:3.

As mentioned earlier, the "crude" ethyl nitronic ester obtained from *p*-nitrophenylnitromethane melts at 82–88° (even though it is analytically pure) and, on recrystallization, the melting point rises to 100–101° even though the elementary analysis is unchanged. The n.m.r. spectra of the "crude" and the recrystallized nitronic ester are very instructive. For, whereas the "crude" ester has "vinyl" singlets at 7.22 and 6.95 δ , the areas standing in the ratio 4:1, the recrystallized ester exhibits only one "vinyl" resonance, a singlet at 7.22 δ . Furthermore, for both the "crude" and the recrystallized ethyl nitronic ester, the ratio of aromatic hydrogen to "vinyl" hydrogen to methylene hydrogen to methyl hydrogen is 4:1:2:3, as expected.

In the same way, it becomes clear, on inspection of the n.m.r. spectra, that stereoisomeric mixtures are also produced when nitronic esters are synthesized by the direct reaction of diazomethane with a relatively acidic nitro compound. For instance, the "crude" methyl nitronic ester (analytically pure but of m.p. 100–108°) obtained from *p*-nitrophenylnitromethane and diazomethane exhibits "vinyl" singlets at 7.20 and 6.92 δ , in a 2:1 ratio, respectively, whereas the recrystallized nitronic ester (m.p. 118–120°) has only one "vinyl" hydrogen peak at 7.20 δ . The characteristics of the analytically pure "crude" methyl nitronic ester obtained by the action of diazomethane on *p*-bromophenylnitromethane (*vide supra*) also derive from the formation of both possible stereoisomers (*cf.* Table II and Experimental).

Table II summarizes the n.m.r. data for the vinyl hydrogen resonances of nitronic esters and related compounds. It must be emphasized that the remaining hydrogen resonances always exhibit a pattern consistent with what would be anticipated from the data of Table II (*cf.* Experimental).

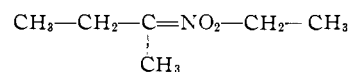
TABLE II
VINYL HYDROGEN RESONANCES

Compound	δ -Values	Multi- plicity of <i>H</i> lines	Approximate relative areas of the two <i>H</i> peaks
$\text{CH}_3\text{CH}=\text{NOH}$	6.84, 7.42	4	1.5:1
$\text{CH}_3\text{CH}=\text{NOC}_2\text{H}_5$	6.62, 7.28	4	1:1
$\text{CH}_3\text{CH}=\text{NO}_2\text{CH}_3$	5.91, 6.25	4	1:5
$\text{CH}_3\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	5.57, 6.27	4	1:2
$\text{C}_2\text{H}_5\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	6.05, 6.11	3	1.2:1
<i>n</i> - $\text{C}_6\text{H}_7\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	5.75, 6.04	3 ^a	1:7
<i>p</i> - $\text{BrC}_6\text{H}_4\text{CH}=\text{NO}_2\text{CH}_3$	6.72, 6.90	1	1:4
<i>p</i> - $\text{BrC}_6\text{H}_4\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	6.80, 7.03	1	1:3
<i>p</i> - $\text{O}_2\text{NC}_6\text{H}_4\text{CH}=\text{NO}_2\text{CH}_3$	6.92, 7.20	1	1:2
<i>p</i> - $\text{O}_2\text{NC}_6\text{H}_4\text{CH}=\text{NO}_2\text{C}_2\text{H}_5$	6.95, 7.22	1	1:4

^a In our preliminary communication² these triplets were inadvertently referred to as quartets.

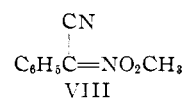
Only one ester derived from a secondary nitro compound was obtained analytically pure; this was the ethyl nitronic ester of 2-nitrobutane. A carbon tetra-

chloride solution of this liquid has an n.m.r. spectrum which can only be explained on the basis that we deal with a mixture of stereoisomers. Two singlets in the



"vinyl" methyl region (at 1.94 and 2.00 δ) due to the "vinyl" methyl hydrogens are observed.²² The "vinyl" methylene hydrogens are centered at 2.4 δ as a somewhat unsymmetrical quartet with rather broad peaks; the presumption that this multiplet consists of two overlapping quartets is supported by Lustig's¹⁷ findings for the analogous methylene of butanone oxime. The remaining hydrogens of this nitronic ester produce the expected resonances.

Stability of Nitronic Esters.—From the literature it is apparent that nitronic esters are not the most stable of organic compounds. But, aside from this rudimentary fact, the situation is far from clear. There appears to be no relationship between structure and stability; typical of the literature on this subject are the numerous and by no means concordant observations concerning the stability of VIII, the most extensively examined of the nitronic esters.^{23,10} About the only safe generalization appears to be that nitronic



esters decompose upon storage at room temperature and that decomposition rates vary widely from ester to ester. Rapid decomposition can, in general, be expected when a nitronic ester is heated to *ca.* 100°.

The nitronic esters prepared in the present study include the simplest ones yet described; consequently, their properties are of special interest. It turns out that none of the nitronic esters derived from primary nitro compounds (Table II) are stable for prolonged periods at room temperature, although at –80° they are stable indefinitely. For example, in carbon tetrachloride the ethyl nitronic ester of 1-nitrobutane decomposes completely in about 3 days at room temperature.

It appears that nitronic esters derived from secondary nitro compounds are less stable than those obtained from primary nitroparaffins. Indeed, only one nitronic ester derived from a secondary nitro compound could be obtained analytically pure—the ethyl nitronic ester of 2-nitrobutane. All efforts to isolate a pure sample of the ethyl nitronic ester of 2-nitropropane failed; the ester did, however, persist long enough at room temperature for its n.m.r. spectrum to be determined. The ethyl nitronic ester of nitrocyclohexane proved to be the least stable of all; although the reaction of the sodium salt of nitrocyclohexane with triethylxonium fluoroborate proceeds in the regular way, as evidenced by the quantitative yield of sodium fluoroborate and the fact that the yield of crude nitronic ester is virtually quantitative, within 1 to 5 min. after coming to room

(22) Lustig (ref. 17) has found that butanone oxime (*syn-anti* mixture) also exhibits two singlets in the "vinyl" methyl region.

(23) (a) A. Hantzsch, *Ber.*, **40**, 1541 (1907); (b) F. Arndt, L. Loewe, and H. Isik, *Rev. Fac. Sci. Univ. Istanbul* (New Series), **2**, No. 2, 139 (1937); (c) J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937); (d) S. K. Brownstein, Ph.D. Thesis, University of Chicago, 1955.

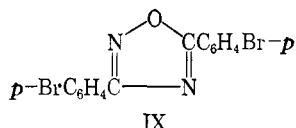
(21) Indeed, it has now been found that the methyl groups of acetoxime itself are not equivalent (E. Lustig, private communication).

temperature this yellow-green liquid evolves a colorless gas, turns yellow, and heats up.

Our n.m.r. studies of nitronic esters reveal that the stereoisomers of a given nitronic ester possess quite different stabilities. For example, in deuteriochloroform, one-half of the predominant isomer of the ethyl nitronic ester of *p*-nitrophenylnitromethane (m.p. 100–101°) decomposes in about 2 days at room temperature, whereas the minor stereoisomer (m.p. not known) is one-half decomposed in about 40 min. Consequently, any discussion of the stability of nitronic esters must take into account the matter of stereochemistry.

The most stable nitronic ester obtained in the present study is the 118–120° melting stereoisomer of the methyl nitronic ester derived from *p*-nitrophenylnitromethane. This, after 10 days at room temperature, undergoes no change in melting point; and after a month its melting point is only slightly depressed (*ca.* 115–118°). The 100–101° melting isomer of the ethyl nitronic ester of *p*-nitrophenylnitromethane is also relatively stable; only after 5 to 6 days at room temperature is there a perceptible (*ca.* 1°) drop in melting point. Not surprisingly, a nitronic ester is more stable in the crystalline state than in solution.

The decomposition of nitronic esters results in a variety of products. Thus, from the ethyl nitronic ester of *p*-bromophenylnitromethane, after 2 weeks at room temperature, a 60% yield of the pure oxadiazole IX is isolated. With the strictly aliphatic nitronic

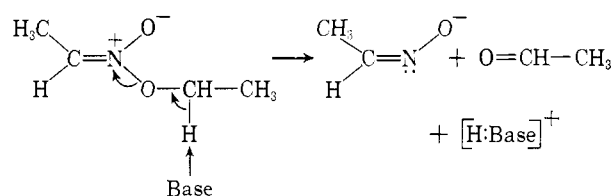


esters of Table I, the decomposition at room temperature was followed by n.m.r. spectroscopy; while an ester such as the ethyl nitronic ester of 1-nitrobutane produces the expected *n*-butyraldehyde oxime and acetaldehyde, the yields are low and other, unidentified, products are simultaneously generated in significant yields. Acetaldehyde is usually formed during the decomposition of ethyl nitronic esters; it is isolated (as the 2,4-dinitrophenylhydrazone) in about 20% yield from the decomposition of the ethyl nitronic ester of nitrocyclohexane.

These results are to be contrasted with the widely held view that nitronic esters disproportionate into oximes and carbonyl compounds.^{9b-d,24} This view



is based on the fact that the reaction of alkyl halides with alkali metal salts of nitroparaffins usually produces a carbonyl compound and an oxime (*vide supra*), it being assumed that nitronic esters are intermediates and that these disproportionate according to eq. 1. Even if the first of these two assumptions is correct, it must be recognized that nitronic esters produced by the reaction of alkyl halides with nitroparaffin salts are being subjected to alkaline conditions. Conceivably, the disproportionation of eq. 1 results from a base-catalyzed decomposition,²⁵ *e.g.*



The whole matter of the thermal and base-catalyzed decompositions of nitronic esters is now being investigated.

Experimental²⁶

All m.p.'s and b.p.'s are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 or 221 spectrophotometer. Unless otherwise specified, liquids were run neat and solids as Nujol mulls. The n.m.r. spectra were obtained using a Varian A-60 n.m.r. spectrometer. All gas chromatographic analyses were performed with a 5 ft. \times 0.25 in. column packed with Chromosorb W coated with GE-SF-96 silicone compound. Unless otherwise specified, all solvents were dried and distilled through a short column.

The 1-nitropropane and 2-nitrobutane employed were labeled 99.9% pure and were shown to be homogeneous by gas chromatography.²⁷ Eastman nitroethane was rectified; the fraction employed had b.p. 113.5–113.9° (749 mm.), n_D^{20} 1.3925, and was shown by gas chromatography to be 95% pure, the remainder being 2-nitropropane and a trace of nitromethane.²⁸ 2-Nitropropane (Commercial Solvents) was washed with 10% aq. sodium bicarbonate, with water, dried, and rectified. A cut, b.p. 119–120°, n_D^{20} 1.3948,²⁸ was used; by gas chromatographic analysis it was *ca.* 97% pure; the impurities were nitroethane and a high boiling material. In the same way 1-nitrobutane was purified; the center cut employed, b.p. 60–62° (30 mm.), n_D^{20} 1.4105,²⁸ was shown by gas chromatography to be at least 99% pure. Nitrocyclohexane (du Pont) was rectified at 3 mm.; a middle cut, b.p. 60–60.5°, n_D^{20} 1.4616, was used. It was about 99% pure by gas chromatography. *p*-Nitrophenylnitromethane was prepared according to Kornblum, *et al.*,²⁹ except that the reaction time was extended to 48 hr.; m.p. 89–90°. When a benzene solution of *p*-nitrophenylnitromethane is chromatographed on acid-washed alumina (Merck) the m.p. is raised to 90–91°. *p*-Bromophenylnitromethane was obtained by treating *p*-bromobenzyl bromide with silver nitrite in dry ethyl ether at *ca.* 5° for 40 hr. After filtration from silver bromide the ether solution was evaporated to dryness under reduced pressure and the residue recrystallized twice from absolute ethanol; m.p. 55.0–55.9°.

Preparation of Nitro Salts.—The preparation of the sodium salt of nitroethane is typical. Eight grams of nitroethane (0.106 mole) is treated with 103 ml. of 0.975 *M* methanolic sodium methoxide (0.10 mole) and then diluted to a total volume of 500–800 ml. with anhydrous ethyl ether. The slurry is filtered and washed well with anhydrous ether; during the washing a nitrogen atmosphere is maintained over the filter funnel. After washing, the white salt is pressed in the funnel, is partially dried by sucking nitrogen through, and it is then dried for at least 12 hr. *in vacuo*. Following this the salt is carefully (CAUTION)³⁰ ground to a fine powder in a mortar. The salt should be used at once or else stored only a short time *in vacuo* before being used.³⁰ The yield is nearly quantitative.

In several instances a variant of the "precipitation" method was employed; this "evaporative" procedure is exemplified by the preparation of the sodium salt of nitrocyclohexane. The nitrocyclohexane is treated with 1 equiv. of methanolic

(26) Analyses by Dr. C. S. Yeh, Purdue University, and Galbraith Micro-analytical Laboratories, Knoxville, Tenn.

(27) We are indebted to the Commercial Solvents Corp. for a generous gift of these very pure nitroparaffins.

(28) For the physical properties of the eight mononitroparaffins, nitromethane through the isomeric nitrobutanes, determined with highly purified samples, see E. E. Toops, Jr., *J. Phys. Chem.*, **60**, 304 (1956).

(29) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6277 (1955).

(30) A safety shield and goggles are recommended during this operation. Although none of our salts exploded, dry salts of nitroparaffins have been known to explode violently when allowed to stand for several weeks (see, for example, ref. 9d). On the other hand, attempts to explode salts of nitroethane and 2-nitropropane by impact are reported to fail. The situation is sufficiently confused that considerable care should be exercised.

(24) M. Bersohn, *J. Am. Chem. Soc.*, **83**, 2137 (1961).

(25) N. Kornblum and H. E. De La Mare, *ibid.*, **73**, 880 (1951).

sodium methoxide under nitrogen. After standing about 20 min. at room temperature the solution is evaporated to dryness at *ca.* 40° and 15 mm. The residual solid is carefully ground in a mortar (CAUTION)³⁰ and is then dried at 1 mm. for 3 hr. at 40°. Titration with acid reveals that the salt is pure.

Triethylxonium fluoroborate was prepared according to Meerwein¹² except that different proportions of reagents were employed. From 81.6 g. (0.882 mole) of epichlorohydrin and 152 g. (1.07 moles) of boron trifluoride ethyl etherate 145 g. (*ca.* 70%) of triethylxonium fluoroborate is obtained, m.p. 93–94° (sealed tube, bath preheated to 80°). Quite possibly this material is suitable for the preparation of nitronic esters, but this point was not investigated; instead the salt was recrystallized by dissolving it in 320 ml. of dry nitrobenzene at room temperature and then precipitating with anhydrous ethyl ether. The salt (70% recovery) now melts at 94.5–95° (sealed tube, bath preheated to 80°), lit.¹² m.p. 92°. All operations with this salt were conducted taking care to exclude moisture. The salt may be kept for many months if stored under anhydrous ethyl ether, the ether being replaced every few months; if stored *in vacuo* it liquified in several weeks.

Trimethylxonium Fluoroborate.—A 100-ml. flask was fitted with a stirrer, a dropping funnel, and a Dry Ice condenser protected by a drying tube. The system was flushed with nitrogen and then 11.46 g. (101 mmoles) of freshly distilled boron trifluoride methyl etherate was introduced. The flask was cooled with Dry Ice and gaseous methyl ether was passed in until the volume of liquid had increased by *ca.* 50 ml. The Dry Ice bath was removed and 7.00 g. (76 mmoles) of epichlorohydrin was added to the gently refluxing and vigorously stirred solution. A white solid formed and after stirring about 0.5 hr. the mother liquor was removed by inverted filtration using a sintered tube; the salt was then washed three times (inverted filtration) with anhydrous ethyl ether and dried in the reaction flask at 1 mm. and 25°. The yield was nearly quantitative: 11.0 g. This salt is extremely hygroscopic and usually decomposes after storing *in vacuo* for 1 day. It cannot be preserved by storing under ethyl ether since methyl ether will slowly evolve leaving the triethylxonium fluoroborate. Consequently, trimethylxonium fluoroborate was always used within a few hours after its preparation.

Nitronic Ester Syntheses Employing Trialkylxonium Fluoroborates.—The ethyl nitronic esters derived from primary nitro compounds were prepared at a reaction temperature of about 0°. Reaction times varied from 15 to 120 min., the average being *ca.* 50 min. While an extensive study of reaction time was not made, it appears that these reactions were often complete in 15 to 30 min. The one alkylation employing trimethylxonium fluoroborate was initiated at –75° and then allowed to proceed at 0° for 20 hr. In retrospect, it appears that a matter of minutes at 0° would likely be equally successful. The reaction of triethylxonium fluoroborate with the sodium salt of 2-nitrobutane was allowed to proceed at –60° for 80 min. and then at 0° for 30 min.

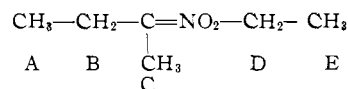
Two general procedures are illustrated by specific examples. The first employed the dry, finely powdered, nitroparaffin salt and it was used in almost every instance; it is recommended whenever an unstable nitronic ester is to be prepared. Even for preparing stable nitronic esters it is the method of choice if relatively small quantities, *e.g.*, 5 g., of the nitronic ester are required. For large scale preparations of stable nitronic esters the second procedure, in which the nitro salt is prepared *in situ*, is recommended.

Procedure 1. Preparation of the Ethyl Nitronic Ester of 2-Nitrobutane.—A stirred slurry of 7.5 g. (60 mmoles) of the dry, finely powdered, sodium salt of 2-nitrobutane in 60 ml. of methylene chloride is cooled to –60° under nitrogen and then an ice-cold solution of 9.1 g. (48 mmoles) of triethylxonium fluoroborate in 25 ml. of methylene chloride is run in rapidly. After being stirred under nitrogen at –60° for 80 min. the system is brought to 0° and stirred at that temperature for 30 min. The mixture is then filtered rapidly and the solid is washed with 10–15 ml. of cold methylene chloride. The combined filtrate and wash are rapidly evaporated *in vacuo* to constant volume at *ca.* 5 to 15°. The resulting very pale yellow liquid is subjected to a vacuum of *ca.* 1 mm. for another 5 min. at 15° and then stored at –78°; n_D^{20} 1.4513, yield 6.0 g. (94%).

Anal. Calcd. for $C_6H_{11}NO_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 55.09; H, 10.2; N, 10.52.

This nitronic ester is quite unstable. Thus, when a sample was placed in a refractometer at 20° the n_D^{20} fell from the initial value 1.4513 to 1.4373 in 20 min. And when 3 ml. of the neat liquid

was held at 25° in a closed vial it turned green in *ca.* 5 min. and a few minutes thereafter exothermically decomposed with vigorous gas evolution. However, it was possible to determine the u.m.r. spectrum of a dilute solution of this nitronic ester in carbon tetrachloride at room temperature. The D hydrogens appeared



as a quartet at 4.15 δ , the E hydrogens as a triplet at 1.18 δ , and the A hydrogens as a triplet at 1.09 δ . The C hydrogens appeared as two singlets (of about equal area) at 1.94 and 2.00 δ . Thus the *cis-trans* isomers had formed in about equal amounts. Since the C hydrogens of each isomer have slightly different δ -values, then it is to be expected that the B hydrogens of each isomer should also have slightly different δ -values. In fact, the B hydrogens appeared as a somewhat unsymmetrical quartet with rather broad peaks at 2.4 δ . In addition to these peaks, very weak peaks appeared at about 1.47, 1.77, 2.06, 2.08, and 2.11 δ , which could not be identified and were probably due to decomposition products. After only 80 min. at 25°, the peaks due to the nitronic ester had decreased to about one-half their original area; the two isomers decomposed at the same rate. In addition, many new, unidentifiable, peaks were also present. After 24 hr. at 25°, none of the ester's peaks remained; nearly all the peaks in the complex spectrum were in the 0.8 to 1.4 and 1.9 to 2.5 δ ranges.

Procedure 2. Preparation of the Ethyl Nitronic Ester of *p*-Nitrophenylnitromethane.—An ice-cold solution of 2.74 g. (15.0 mmoles) of *p*-nitrophenylnitromethane in 10 ml. of anhydrous methanol and 90 ml. of methylene chloride is slowly treated with 15.7 ml. (15.1 mmoles) of 0.959 *M* methanolic sodium methoxide. The orange slurry is stirred at 1° for 15 min., and then a cold (*ca.* 10°) solution of 3.00 g. (15.8 mmoles) of triethylxonium fluoroborate in 20 ml. of methylene chloride is added all at once. The temperature rises to 4° but drops back to 1° within 2 min. (When conducting a large scale preparation, *e.g.*, 10 to 20 times that here described, the exothermicity becomes significant and, therefore, the oxonium fluoroborate solution should be added cautiously.) After stirring for 30 min. more the solid is removed by filtration and washed with cold methylene chloride. The combined filtrate and wash are rapidly extracted with small portions of ice-cold water until the water washes are colorless. The aqueous washes are back extracted once with cold methylene chloride and then the combined methylene chloride solutions are dried rapidly first over sodium sulfate and then with Drierite. Vacuum evaporation of the solvent at *ca.* 15 to 20° yields 2.92 g. (92%) of a pale yellow powder. This "crude" nitronic ester is essentially pure.

Anal. Calcd. for $C_9H_{10}N_2O_4$: C, 51.40; H, 4.80; N, 13.34. Found: C, 50.89; H, 4.61; N, 13.23.

The "crude" ester melts from 82–88° (bath pre-heated to 65°), gas being evolved. The n.m.r. spectrum of a deuteriochloroform solution of the "crude" nitronic ester showed, in addition to the aromatic hydrogen peaks, two vinyl hydrogen singlets (at 7.22 and 6.95 δ with areas in about a 4:1 ratio, respectively) and two methyl hydrogen triplets (at 1.30 and 1.38 δ with areas in about a 4:1 ratio, respectively). The methylene hydrogen quartet appeared as a slightly broadened quartet at 4.35 δ . The solution was kept at room temperature and the n.m.r. spectrum recorded at frequent intervals. One-half of the minor isomer decomposed in about 40 min.; after 90 min. none could be detected, while the concentration of the major isomer did not appear to have changed. Acetaldehyde's doublet at 2.20 δ was easily seen after only 20 min.; after 20 hr. this doublet was quite strong. In addition a quartet at 9.8 δ appeared.

One gram of the "crude" nitronic ester was recrystallized by dissolving it in 25 ml. of toluene at *ca.* 25°, adding 20 ml. of absolute ethanol and cooling the solution to *ca.* –50°. After filtration, the very pale yellow powder was dried *in vacuo* at room temperature for *ca.* 1 hr.; yield 0.65 g. The recrystallized ester sintered at 98.5–99.5°, melted at 100–101°, vigorously evolved gas at 101–102°, and resolidified at 102–104°. Further recrystallization did not alter the m.p.

Anal. Calcd. for $C_9H_{10}N_2O_4$: C, 51.40; H, 4.80; N, 13.34. Found: C, 51.35; H, 4.83; N, 13.54.

The n.m.r. spectrum of a deuteriochloroform solution of the recrystallized nitronic ester was determined. In contrast to the spectrum of the "crude" ester, a lone vinyl hydrogen singlet ap-

pears at 7.22 δ and a lone methyl hydrogen triplet appears at 1.30 δ . The methylene hydrogen quartet appears at 4.35 δ . The peak areas of the aromatic, methyl, methylene, and vinyl hydrogens are in the expected 4:3:2:1 ratio. The solution was kept at room temperature and the n.m.r. spectrum recorded frequently. After about 2 days, one-half of this isomer had decomposed, and after about 15 days none of the ester remained. Thus the major isomer is much more stable than the minor isomer. During the decomposition acetaldehyde formed; the doublet at δ 2.20 could be seen after 4 hr. and after 15 days this doublet and a quartet at δ 9.8 were quite strong.

The recrystallized nitronic ester is stable at least 1 year at -78° . After 2 months at 0° , in the dark, the m.p. falls *ca.* 1° . At 25° the m.p. drops *ca.* 1° after 5 days and after 10 days the drop is *ca.* 3° . After 4 months at 25° the ester melts at 91 – 155° with no gas evolution or resolidification. Neither the nature of the storage vial nor the presence of light alters these results.

The recrystallized nitronic ester is easily soluble in CHCl_3 , CH_2Cl_2 , DMF, DMSO, acetone, THF, ethyl acetate, 1,2-dimethoxyethane, benzene, and nitromethane. It is sparingly soluble in ethyl ether, xylene, and CS_2 and insoluble in water, liquid NH_3 , CCl_4 , and pentane.

The ultraviolet spectrum of the recrystallized ester was determined in a solvent consisting of 99% by volume 95% ethanol and 1% by volume chloroform: λ_{max} 240 $\text{m}\mu$ (ϵ_{max} 0.93×10^4) and λ_{max} 337 $\text{m}\mu$ (ϵ_{max} 1.76×10^4), λ_{min} 280 $\text{m}\mu$.

The methyl nitronic ester of nitroethane was obtained by procedure 1.

Anal. Calcd. for $\text{C}_3\text{H}_7\text{NO}_2$: C, 40.44; H, 7.92; N, 15.72. Found: C, 40.76; H, 8.26; N, 15.84.

A sample placed in the refractometer at 20° gave an initial reading, n_D^{20} 1.4469, which was unchanged during the first 6 min.; after 14 min. the n_D^{20} was 1.4464 and after 131 min. the reading was n_D^{20} 1.4445.

The n.m.r. spectrum of a neat sample at 24° showed that only a trace of formaldehyde (9.7 δ) was present and that the amount present did not increase after 3 hr. at 24° . Both geometrical isomers of the ester had formed in about a 5:1 ratio. The methoxy hydrogens appeared as a singlet at 3.7 δ . The predominant isomer's "vinyl" hydrogen quartet was at 6.25 δ and its "vinyl" methyl hydrogen doublet at 1.8 δ . The minor isomer's "vinyl" hydrogen quartet was at 5.91 δ and its "vinyl" methyl hydrogen doublet at 1.9 δ . After 3 hr. at 24° only a trace of the minor isomer remained; but after 24 hr. at 24° the major isomer was still very easily detected. All the ester had vanished by 23 days at 24° and only a very complex spectrum could be seen.

The ethyl nitronic ester of 1-nitropropane was prepared by procedure 1.

Anal. Calcd. for $\text{C}_5\text{H}_{11}\text{NO}_2$: C, 51.20; H, 9.45; N, 11.97. Found: C, 51.40; H, 9.39; N, 12.16.

In the refractometer an initial value n_D^{20} 1.4455 fell to n_D^{20} 1.4444 in 20 min.

The ethyl nitronic ester of 1-nitrobutane was prepared by procedure 1.

Anal. Calcd. for $\text{C}_6\text{H}_{13}\text{NO}_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 55.16; H, 9.96; N, 11.02.

An initial n_D^{20} 1.4468 fell to n_D^{20} 1.4431 after 80 min. at 20° .

The n.m.r. spectrum of an approximately 15% solution of the ester in carbon tetrachloride at 25° completely supports the assigned structure. The two possible geometrical isomers formed in a 7:1 ratio; characteristic acetaldehyde peaks are absent. The δ -values are given in Table III. The isomer ratio is based on the relative areas of the "vinyl" hydrogen peaks at 6.04 and 5.75 δ . After 6 hr. at 24° the 5.75 δ peak has vanished and after 3 days at 24° the 6.04 δ peak vanishes. The 6-hr. old sample has a band at 9.8 δ , probably due to acetaldehyde. In the 3-day old sample the bands which appear at 6.8 and 7.4 δ (both slightly broad) and at 9.63 δ (weak) are evidently due to *n*-butyraldoxime since the n.m.r. spectrum of a neat sample of the oxime has the vinyl hydrogen peaks at 6.72 and 7.40 δ and the hydroxy hydrogen peak at 9.6 δ . A complex series of peaks in the 3-day old sample in the 3.5–4.2 δ region and a broad weak peak at 6.4–6.6 δ were not identified.

The ethyl nitronic ester of *p*-bromophenylnitromethane was obtained as a clear colorless liquid by procedure 1. Cooling below 0° produces a white crystalline mass (m.p. 35 – 40°).

Anal. Calcd. for $\text{C}_9\text{H}_9\text{BrNO}_2$: C, 44.28; H, 4.12; N, 5.74; Br, 32.74. Found: C, 44.47; H, 4.32; N, 5.88; Br, 32.70.

The infrared spectrum (Nujol mull) of the freshly prepared solid ester revealed the absence of any carbonyl component (no

TABLE III

N.M.R. SPECTRUM OF ETHYL NITRONIC ESTER OF 1-NITROBUTANE

Formula	Hydrogen label	δ -Values for predominant isomer	δ -Values for minor isomer	Multiplicity of peaks
CH_3	A	0.97	0.97	Triplet
CH_2	B	1.53	1.53	Quartet
CH_2	C	2.26	2.26	Quartet
C-H	D	6.04	5.75	Triplet
N				
O_2				
CH_2	E	4.10	4.14	Quartet
CH_3	F	1.17	1.17	Triplet

band in the 5.8 μ region), but after 20 min. at 20° a carbonyl band (5.80 μ) was easily discernible. The fresh ester showed a very strong band at 6.15–6.20 μ (presumably due to the nitronic ester function); the only other very strong band appeared at 12.0–12.15 μ . Storage of the ester at 0° for 1 day causes no change in its spectrum.

The n.m.r. spectrum of a deuteriochloroform solution of the liquid nitronic ester was determined. In addition to the aromatic hydrogen peaks, there were two vinyl hydrogen singlets (at 7.03 and 6.80 δ in about a 3:1 ratio, respectively) and two methyl hydrogen triplets (at 1.27 and 1.32 δ in about a 3:1 ratio, respectively). The methylene hydrogen quartet appeared at 4.31 δ . The peak areas of the methyl, methylene, and vinyl hydrogens were in the expected 3:2:1 ratio, respectively. When the solution was kept at *ca.* 24° for 1 day, n.m.r. revealed that the minor isomer had completely decomposed, but most of the major isomer remained.

The colorless liquid ester when stored for 1 hr. at *ca.* 30° in plastic, or Pyrex or soft glass, undergoes a change in n_D^{20} from 1.6150 to 1.608 with simultaneous yellowing and evolution of a small amount of acetaldehyde. (The nature of the storage vial does not affect the rate of decomposition.) After 3 hr. the initially colorless liquid becomes a pasty yellow mass and, when after 2 weeks the pasty-yellow-orange mixture is air-dried for 2 days, the resulting solid melts at 135 – 156° with slight gas evolution. When 3.42 g. of this solid is chromatographed on neutral alumina (Woelm), 1.65 g. (60% yield) of fluffy white needles, m.p. 184 – 185° , are obtained; lit. m.p. for 3,5-bis(*p*-bromophenyl)-1,2,4-oxadiazole: 181° ,^{6a} 183.5 – 184° .¹⁰ The n.m.r. spectrum of a deuteriochloroform solution of the 1,2,4-oxadiazole revealed the presence of only aromatic hydrogens, four doublets (each with $J = 8$ c.p.s.) at 7.62, 7.68, 8.03, and 8.06 δ .

Anal. Calcd. for $\text{C}_{14}\text{H}_8\text{N}_2\text{OBr}_2$: C, 44.24; H, 2.12; N, 7.37; Br, 42.06. Found: C, 44.34; H, 2.17; N, 7.31; Br, 42.34.

Nitronic Ester Syntheses Employing Diazomethane. The Methyl Nitronic Ester of *p*-Nitrophenylnitromethane. Method A.—An ice-cold solution of 2.18 g. (11.97 mmoles) of *p*-nitrophenylnitromethane in 230 ml. of ethyl ether is treated with 163 ml. of a freshly prepared, ice-cold, dry ethereal solution of diazomethane (2.44 g., 58 mmoles). After 17 hr. at 0° in the dark, the excess diazomethane and the ether are removed by vacuum evaporation. The residue is dissolved in *ca.* 30 ml. of methylene chloride, filtered to remove a trace of orange-brown solid, and vacuum evaporated to leave 2.40 g. (102%) of the "crude," yellow-orange nitronic ester.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$: C, 48.98; H, 4.11; N, 14.28. Found: C, 48.91; H, 4.35; N, 14.23.

Thus the "crude" ester is analytically pure. Its m.p. depends on the rate of heating. Immersed in a bath preheated to 78° and with a heating rate of $7^\circ/\text{min.}$, the ester sinters at 90° and melts at 100 – 108° with gas evolution. The n.m.r. spectrum of a deuteriochloroform solution of the "crude" ester exhibits, in addition to the aromatic hydrogen peaks, two vinyl hydrogen singlets (at 7.20 and 6.92 δ in about a 2:1 ratio, respectively) and two methoxy hydrogen singlets (at 3.88 and 3.98 δ in about a 2:1 ratio, respectively). Therefore both stereoisomers are present. All the minor isomer decomposes in the solution at room temperature within 1 day; the predominant isomer is much more stable (*vide infra*).

Recrystallization of 2.28 g. of the "crude" ester from 80 ml. of hot methanol as rapidly as possible gives 1.16 g. (52% yield) of yellow ester. With 105° preheat and a heating rate of 6°/min. the ester sinters at 116° and melts at 118–120° with gas evolution. When heated from room temperature at a rate of 14°/min., the m.p. is 112–113°.

*Anal.*³¹ Calcd. for C₈H₈N₂O₄: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.14; H, 4.06; N, 14.62.

The recrystallized ester, when kept at -78° for 4 months, shows no change in m.p. When held at 25° for a month in the light (or dark) in Pyrex, soft glass or plastic vials, the m.p. falls about three degrees. The n.m.r. spectrum of a deuteriochloroform solution of the recrystallized ester exhibits, in addition to the aromatic hydrogen peaks (a doublet at 8.25 and a doublet at 8.00 δ), a lone vinyl singlet at 7.20 and a lone methoxy hydrogen singlet at 3.88 δ. Thus only the predominant isomer is present. The peak areas of the aromatic, vinyl, and methoxy hydrogens are in the expected 4:1:3 ratio, respectively. The solution was kept at ca. 24° and the n.m.r. spectrum recorded at frequent intervals; one-half of the predominant isomer remains after 5 days, and only after 15 days has it completely decomposed.

Method B.—In the procedure referred to in footnote 14, a solution of the sodium salt of *p*-nitrophenylnitromethane in DMF is treated with ethereal diazomethane and then 1 equiv. of fluoroboric acid is added dropwise at 0°. Nitrogen evolves as fast as the acid is added. The DMF is largely removed by vacuum evaporation at 20° and the resulting sirup is taken up in benzene, washed with water, and dried. Removal of the benzene below 35° gives a tan solid which, on recrystallization from methanol, yields the nitronic ester, m.p. 118–120° dec.

In retrospect it is clear that DMF is a poor choice for the reaction medium. A simple procedure for the preparation of anhydrous solutions of fluoroboric acid in ethers has recently been published³² and it would appear that the use of anhydrous diethyl ether as the reaction medium will enhance the convenience and utility of this method.

The methyl nitronic ester of *p*-bromophenylnitromethane was prepared by method A using a reaction time of 4 days. The "crude" methyl ester is a yellow oil (100% yield) which, upon cooling to -80° and then warming to 0°, crystallizes; m.p. 20 to 43° with gas evolution at about 95°.

Anal. Calcd. for C₈H₈NO₂Br: C, 41.76; H, 3.50; N, 6.09; Br, 34.74. Found: C, 41.65; H, 3.46; N, 5.95; Br, 34.80.

The n.m.r. spectrum of a carbon tetrachloride solution of the "crude" nitronic ester reveals, in addition to aromatic hydrogen peaks, two vinyl hydrogen singlets (at 6.90 and 6.72 δ in about a

4:1 ratio, respectively) and two methoxy hydrogen singlets (at 3.75 and 3.85 δ in about a 4:1 ratio, respectively). Therefore both stereoisomers are present. The n.m.r. spectrum was recorded at frequent intervals. One-half of the minor isomer decomposed in about 1.5 hr., while the half-life of the major isomer was about 2 days.

A 1.12-g. sample of the "crude" ester was dissolved in about 8 ml. of methanol at 25°, filtered to remove dust, cooled to -60°, and the resulting slurry filtered. After washing with about 5 ml. of cold (ca. -60°) methanol, the white, crystalline solid was sucked partially dry in the funnel and then dried *in vacuo* at 25° for about 15 min.; yield 0.40 g.

Anal. Calcd. for C₈H₈NO₂Br: C, 41.76; H, 3.50; N, 6.09; Br, 34.74. Found: C, 41.89; H, 3.53; N, 6.36; Br, 35.00.

With 50° preheat and a heating rate of 3°/min. the recrystallized ester sintered at 65°, melted at 66.5–67.5°, and evolved gas above about 100°; lit. m.p. 65°,^{5a} 65.5°.¹⁰ When the recrystallized nitronic ester was kept at -78°, no change in the m.p. occurred after 1 month. When kept at 24° in a plastic vial, exposed to light, the m.p. drops about a degree in 24 hr. and after 11 days it has fallen to 60–63°. The n.m.r. spectrum in CCl₄ shows only one vinyl singlet (at 6.90 δ) and only one methoxy singlet (at 3.75 δ), in addition to the aromatic hydrogen peaks (two doublets at 7.46 and 7.71 δ). The peak areas of the aromatic, vinyl, and methoxy hydrogens are in the expected 4:1:3 ratio, respectively. The n.m.r. spectrum was recorded at frequent intervals; one-half of this (predominant) isomer remains after about 2 days. The ultraviolet spectrum of the recrystallized nitronic ester in 95% ethanol at 19° shows λ_{max} 288 mμ (ε_{max} 3.27 × 10⁴); λ_{sh} 299 mμ ε_{sh} (2.73 × 10⁴). From the rate of decrease of intensity of the peak at 288 mμ, the half-life of the major isomer of the nitronic ester is ca. 7 days at 19° in 95% ethanol.

3-Phenyl-1-nitropropane and Diazomethane.—An ice-cold solution of 8.26 g. (50 mmoles) of 3-phenyl-1-nitropropane³³ in 50 ml. of ether was allowed to stand with 65 mmoles of diazomethane in 190 ml. of dry ether at 0° (in the dark) for 5 days. The nitro compound was recovered quantitatively (8.40 g.) and shown by v.p.c. to be contaminated by a small amount of ethyl ether; other than this it was identical (v.p.c., *n*_D²⁰ 1.5205) with the original nitro compound.

Acknowledgment.—We are indebted to Mr. William E. Baitinger for determining many of the n.m.r. spectra and to Mr. Baitinger and Professor Norbert Muller for much assistance in interpreting these spectra.

(31) We are indebted to Dr. D. E. Hardies for this experiment.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, IOWA STATE UNIVERSITY, AMES, IOWA]

Small-Ring Organosilicon Compounds. I. A Comparison of the Reactivities of 1,1,2-Triphenyl-1-silacyclobutane and 1,1,2-Triphenyl-1-silacyclopentane

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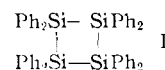
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The preparation of 1,1,2-triphenyl-1-silacyclobutane (II) and 1,1,2-triphenyl-1-silacyclopentane (III) and a comparison of the reactivities of these two compounds toward a variety of reagents is described. Compound II was found to undergo facile ring opening with most of the reagents used. In direct contrast, however, no cleavage could be observed with III under similar reaction conditions. A theoretical consideration of the factors contributing to the enhanced reactivity of silacyclobutanes is presented.

Introduction

Recently in this laboratory, attention has been given to the preparation, structural determination, and reactions of a compound originally prepared by Kipping¹ and designated by him as compound "A." This compound has been shown to be octaphenylycyclohexasilane (I).^{2,3}

(1) (a) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830, 848 (1921); (b) F. S. Kipping, *ibid.*, **123**, 2590, 2598 (1923); (c) F. S. Kipping, *ibid.*, **125**, 2291 (1924); (d) F. S. Kipping, *ibid.*, **2719** (1927); (e) F. S. Kipping, "Bakerian Lecture," *Proc. Roy. Soc. (London)*, **A159**, 139 (1937).



The highly reactive nature of this compound toward a variety of reagents⁴ prompted an investigation into

(2) H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960).

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(4) For a review of the chemistry of octaphenylycyclohexasilane see H. Gilman and G. L. Schwebke, in F. G. A. Stone and R. West, Eds., "At