d, J = 13.8 Hz), 3.07 (1 H, d, J = 13.8 Hz), 2.76 (1 H, d, J = 13.8 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 196.34, 170.65, 170.28, 153.63, 151.86, 151.15, 147.97, 142.32, 132.75, 132.54, 130.64, 128.00, 112.57, 108.97, 108.24, 102.10, 61.19, 61.03, 59.18, 56.22, 52.99, 52.89, 45.37, 36.50.

Similar treatment of 164 mg (0.34 mmol) of biaryl alcohol **16b** [R_f 0.23, hexane:ethyl acetate (1:1)] as described for **16a** afforded 82 mg (51%) of **19** as a light yellow oil that had identical physical properties.

Dibenzocyclooctanone Carboxylates 20 and 21. To a stirred solution of 5 mL of 2.7 M KOH and 5 mL of ethanol was added a solution of 72 mg (0.15 mmol) of the biaryl diester **19** in 2 mL of ethanol and the resultant solution was refluxed for 2 h under argon. The solution was cooled to ambient temperature and the aqueous layer washed with ether (2 mL). The aqueous layer was acidified with concentrated HCl and this mixture extracted with ethyl acetate (2 × 20 mL), washed with brine (20 mL), dried ($MgSO_4$), and filtered and the solvent evaporated to afford the crude diacid. This was heated to 205 °C under argon in a Kugelrohr oven for 15 min and then cooled to ambient temperature. The residue was esterified with excess diazomethane in ether (20 mL) to afford a 1:1 mixture of diasteromers (**20**, **21**) which were separated by flash chromatography [hexane:ethyl acetate (1:1)] to yield 18 mg (29%) of **20** [R_f 0.35, hexane:ethyl acetate (1:1)] which was recrystallized from methanol to afford white prisms followed by 19 mg (30%) of **21** [R_f 0.27, hexane:ethyl acetate (1:1)] as a clear glass.

20: mp 133-134 °C; $[\alpha]_{589}$ +5.2° (c 1.7, THF); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.69 (1 H, s), 6.67 (1 H, s), 6.47 (1 H, s), 6.08 (1 H, s), 6.05 (1 H, s), 3.92 (3 H, s), 3.86 (3 H, s), 3.72 (3 H, s), 3.58 (3 H, s), 3.17-3.12 (1 H, m), 3.07-2.93 (1 H, m), 2.84-2.76 (2 H, m), 2.66-2.56 (1 H, m); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 198.03, 173.77, 153.69, 151.62, 151.26, 147.93, 142.11, 133.50, 132.27, 131.33, 127.99, 113.25, 108.76, 108.54, 102.15, 61.29, 61.05, 56.28, 51.10, 43.63, 41.47, 33.33.

21: $[\alpha]_{589}$ -3.1° (c 1.3, THF); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.53 (1 H, s), 6.63 (1 H, s), 6.55 (1 H, s), 6.07 (1 H, d, J = 1.0 Hz), 6.04 (1 H, d, J = 1.0 Hz), 3.91 (6 H, s), 3.69 (3 H, s), 3.57 (3 H, s), 2.91-2.80 (4 H, m), 2.49-2.43 (1 H, m); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 197.93, 173.77, 154.11, 152.00, 150.85, 147.87, 141.95, 133.23, 132.12, 127.84, 112.25, 109.08, 108.76, 107.38, 102.05, 61.24, 61.08, 56.43, 52.10, 45.07, 42.37, 33.85.

Interconversion of 21 to 20. According to the previous observations,[5d,f,15] pure **21** was heated for 12 h in xylene to give a 1:1 mixture of **20** and **21** which was separated by flash chromatography as above.

(-)-Steganone (1). To a stirred solution of 70 mg (0.17 mmol) of monoester **20** [R_f 0.35, hexane:ethyl acetate (1:1)] was added 1 mL of 5% KOH and 0.3 mL of 37% formaldehyde and the resultant clear solution stirred for 2 h at ambient temperature. The solution was then acidified with 3 N HCl and extracted with chloroform (3 × 20 mL), dried ($MgSO_4$), and filtered and the solvent evaporated to afford a light yellow oil. The oil was dissolved in acetone (3 mL) and cooled to 0 °C and Jones reagent added slowly to the stirred solution until the orange color persisted. MeOH was added followed by water (5 mL) and this mixture extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were washed with 1 N NaOH (5 mL), dried ($MgSO_4$), and filtered and the solvent removed to afford a clear yellow oil. Flash chromatography [hexane:ethyl acetate (1:1)] afforded 14 mg (20%) of a clear oil that was recrystallized from methanol to afford 8 mg (11%) of (-)-steganone (**1**): mp 161-163 °C [lit. mp 155-156 °C,[4] 155-158 °C,[6a] 155.5-157 °C,[6b] 154-156 °C[6c]]; $[\alpha]_D$ -161° (c 0.8, $CHCl_3$) [lit. $[\alpha]_D$ -202° (c 0.76, $CHCl_3$),[4] $[\alpha]_D$ -191° (c 0.76, $CHCl_3$),[6a] $[\alpha]_D$ -197° (c 0.77, $CHCl_6$),[6b] $[\alpha]_D$ -140° (c 1.16, $CHCl_3$)[6c]]: ^{1}H NMR (270 MHz, $CDCl_3$) 7.53 (1 H, s), 6.63 (1 H, s), 6.54 (1 H, s), 6.11 (1 H, d, J = 1.3 Hz), 6.09 (1 H, d, J = 1.3 Hz), 4.48 (1 H, apparent t, J = 9.7 Hz), 4.37 (1 H, dd, J = 9.3, 7.0 Hz), 3.89 (3 H, s), 3.88 (3 H, s), 3.61 (3 H, s), 3.26-3.09 (2 H, complex m), 2.84-2.76 (2 H, m); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 195.39, 175.89, 154.38, 152.16, 151.62, 148.14, 141.95, 133.76, 132.28, 131.99, 127.10, 112.83, 108.81, 108.11, 102.36, 67.05, 61.13, 56.38, 50.14, 44.96, 30.48.

Acknowledgment. We are grateful to Professor Frederick Ziegler (Yale University) for providing us with spectral data of (+)-steganone for comparison and the National Institutes of Health for supporting this study. We also thank Dr. James Fry of the CSU Regional NMR Center for assistance with high-field (360 and 500 MHz) NMR spectra and Dr. Richard Himmelsbach for some preliminary experiments.

Polynitro-Substituted Strained-Ring Compounds. Synthesis, Mechanism of Formation, and Structure of *trans*-Dinitrocyclopropanes

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Abstract: 1,2-Dinitrocyclopropane, 1,2-dimethyl-1,2-dinitrocyclopropane, and 1,2-diethyl-1,2-dinitrocyclopropane have been prepared in 23-36% yield by oxidative cyclization of the corresponding open-chain 1,3-dinitronate dianions with iodine in DMSO. In each case only the trans isomer of the dinitrocyclopropane was obtained. Treatment of 2,4-dibromo-2,4-dinitropentane with the lithium salt of 2-nitropropane gave *trans*-1,2-dimethyl-1,2-dinitrocyclopropane, suggesting the intermediacy of a halonitro nitronate intermediate in the oxidative cyclization process. Further mechanistic studies using *m*-dinitrobenzene suggest either an internal single-electron transfer, nonchain pathway or an internal S_N2 process leading to the dinitrocyclopropanes. An X-ray crystallographic study performed on *trans*-1,2-dinitrocyclopropane indicates substantially shortened distal C-C bonds (1.47 Å) and bisected conformations for each nitro group. Ab initio calculations using a 4-31G basis set are in agreement with the X-ray data, except longer distal C-C bonds (1.49 Å) are calculated. Ab initio calculations using a variety of basis sets were performed on nitrocyclopropane as a model.

Strained-ring compounds substituted with multiple nitro groups are of interest as potential new high-energy materials and as compounds that might possess unusual chemical reactivity. Several such compounds have recently been synthesized,[1] typically in milligram quantities. The simplest strained-ring nitro compound, nitrocyclopropane,[2] and a number of its simple analogues have long been known. However, dinitrocyclopropanes, except for one brief report[3] on 1,1-dimethyl-2,3-dinitrocyclopropane which we became aware of after this study was in progress, have not been discussed in the literature. Since dinitrocyclopropanes are the simplest example of strained-ring polynitro compounds, their

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(1) (a) Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. (b) Paquette, L. A.; Fischer, J. W.; Engel, P. *Ibid.* **1985**, *50*, 2524. (c) Marchand, A. P.; Suri, S. C. *Ibid.* **1984**, *49*, 2041. (d) Marchand, A. P.; Reddy, D. S. *Ibid.* **1984**, *49*, 4078.
(2) Hass, H. B.; Shechter, H. *J. Am. Chem. Soc.* **1953**, *75*, 1382.
(3) Brown, W. G.; Greenberg, F. H. *J. Org. Chem.* **1966**, *31*, 394.

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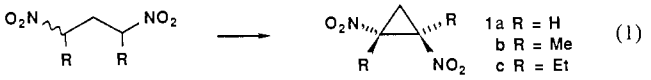
examination has been undertaken as a prelude to more complex systems.

A straightforward synthesis of 1,2-dinitrocyclopropanes employed the corresponding open-chain 1,3-dinitro compounds as precursors (eq 1). The dianion of the open-chain dinitro compound was generated by using 2 equiv of dimsylsodium in DMSO and was cyclized by dropwise addition of excess iodine in DMSO.[4] This procedure gave a 24% yield of *trans*-1,2-dinitrocyclopropane (**1a**) when applied to 1,3-dinitropropane. Similar elaboration of 2,4-dinitropentane and 3,5-dinitroheptane gave the corresponding cyclopropanes **1b** and **1c** in 36% and 23% yields, respectively. In the early work, a rather large variation in yield from run to run was noted. The rate of iodine addition appeared to be at least partly responsible for the variation; a slow, steady rate of addition over 6–8 min seemed to be most effective.



(1)

Oxidative cyclization of 1,3-dinitro compounds afforded only trans isomers of the dinitrocyclopropanes in every case. The stereochemical assignment is based on the lack of chemical shift difference for the ring methylene protons: for the trans isomer homotopic protons would be present whereas for the cis isomer two disimilar diastereotopic protons would be present.[5] Also, the stereochemical assignment for dinitrocyclopropane **1a** was confirmed by X-ray analysis.

The yields of dinitrocyclopropanes **1a–c** obtained from oxidative cyclization were somewhat low. Nevertheless, the route was efficient, since a one-pot procedure was carried out on the readily available corresponding open-chain 1,3-dinitro compounds. 1,3-Dinitropropane could be prepared by a well-established procedure[6] from 1,3-diiodopropane. In our hands, 3,5-dinitroheptane (the *R**,*R** diastereomer, based on ^{1}H NMR) could be prepared in 14% yield from 1-nitropropane and paraformaldehyde by the procedure of Bachman and Atwood.[7] Similar preparation of 2,4-dinitropentane from nitroethane was highly unsatisfactory: only a 1% yield was obtained and near-explosive decomposition of crude products was noted on two occasions. Only one diastereomer, the *R**,*R** isomer, was obtained owing to preferential crystallization from distilled material, although both diastereomers and several side products were present by NMR. A useful synthesis of 2,4-dinitropentane was developed based on condensation of excess lithium salt of nitroethane with 2-nitropropene (eq 2).

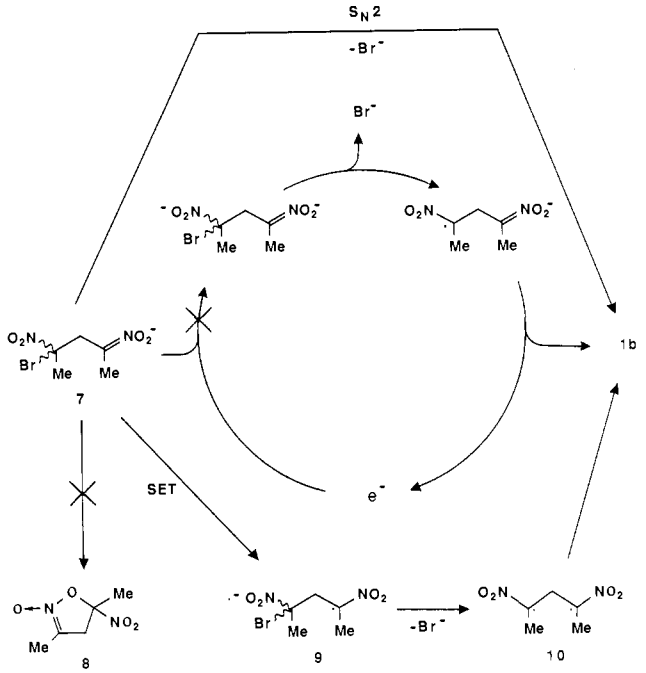

(2)

Four equivalents of the nitronate anion was employed to avoid further condensation of the product anion with 2-nitropropene, a process leading to oligomers. In this way a 71% yield of distilled product was obtained as a 55:45 mixture of *R*,*S* and *R**,*R** diastereomers, respectively. The diastereomers could be separated by preparative thin-layer chromatography, and the stereochemical assignment is based on ^{1}H NMR of the pure materials. The *R**,*R** diastereomer gave one methylene signal (homotopic protons), a doublet of doublets at δ 2.40, whereas the *R*,*S* diastereomer gave two methylene signals (diastereotopic protons), multiplets at δ 2.6–3.0 and 2.0–2.4. Only the *R**,*R** diastereomer was crystalline when pure.

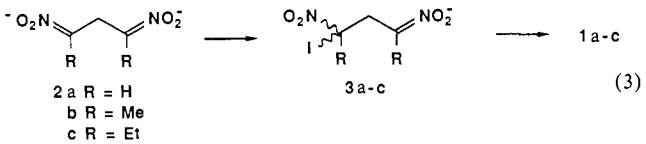
Mechanistic Studies

It seems likely that oxidative cyclization of the 1,3-dinitronates **2a–c** proceeded by monoiodination of the dianion and subsequent

Scheme I

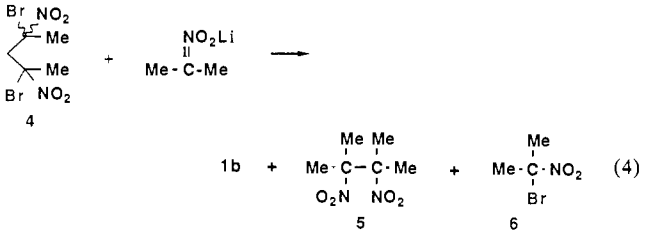


internal displacement of iodide from the resulting iodonitro nitronate intermediate **3** (eq 3). The intermolecular coupling



(3)

reaction of bromonitro compounds with nitronate anions is well-known;[8] coupling of iodonitro compounds with anions has also been observed.[9] In order to obtain further support for the intermediacy of halonitro nitronates in the oxidative cyclization process, an alternate scheme for their generation was devised. This depended on the known bromine atom transfer reaction[10] of bromonitro compounds and nitronates. The required substrate, 2,4-dibromo-2,4-dinitropentane (**4**), was synthesized by bromination of the open-chain dianion and was obtained as two diastereomers. A 50:50 mixture of the diastereomers was subjected to excess lithium 2-nitropropanate in DMSO for 3 min, affording a 15% yield of dinitrocyclopropane **1b** (eq 4). Simultaneously,



(4)

2,3-dimethyl-2,3-dinitrobutane (**5**) was obtained, arising from the known[8c] radical anion free radical chain substitution reaction of the anion of 2-nitropropane with 2-bromo-2-nitropropane (**6**) generated in situ. A small amount (<5% yield) of **6** also remained at the end of this reaction. It is therefore concluded that bromine transfer occurred to the anion of 2-nitropropane to generate **7**, which then cyclized. It is surmised from this result that iodonitro

(4) DMF and HMPA are compatible with cyclization. In the absence of a polar aprotic solvent, no dinitrocyclopropane was formed.

(5) The cis isomer of 1,2-dibromocyclopropane exhibits two different chemical shifts for the corresponding diastereotopic protons: Hammerschmidt, F.; Zbiral, E. *Monatsh. Chem.* **1977**, *108*, 79.

(6) (a) Feuer, H.; Leston, G. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. 4, p 368. (b) See also: Bordwell, F. G.; Bartmess, J. E. *J. Org. Chem.* **1978**, *43*, 3101.

(7) Bachman, G. B.; Atwood, M. T. *J. Am. Chem. Soc.* **1956**, *78*, 484.

(8) (a) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1968**, *90*, 347 and references cited therein. (b) Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *Ibid.* **1971**, *93*, 4318. (c) Russell, G. A.; Norris, R. K.; Panek, E. J. *Ibid.* **1971**, *93*, 5839.

(9) Kornblum, N.; Kestner, M. M.; Boyd, S. D.; Cattran, L. C. *J. Am. Chem. Soc.* **1973**, *95*, 3356.

(10) van Tamelen, E. E.; van Zijl, G. *J. Am. Chem. Soc.* **1949**, *71*, 835.

nitronates such as **3** are likely intermediates in the synthesis of the dinitrocyclopropanes **1a–c**. Of course, more than one pathway might be involved in cyclization.

Open-chain iodonitro and bromonitro compounds are known to undergo radical anion free radical chain substitution reactions.[8,9] On the basis of these observations, we first considered an intramolecular chain pathway for ring closure of bromonitro nitronate anion **7** (Scheme I) and by analogy, the one-pot oxidative cyclization of 1,3-dinitroalkanes. However, no support for this pathway could be obtained.

The bromine transfer cyclization of **4** was repeated in the presence of 78 mol % *m*-dinitrobenzene (*m*-DNB) and gave substantially different results under this condition. The yield of dinitrocyclopropane **1b** increased to 29% while only 5% of dinitro compound **5** and 50% of 2-bromo-2-nitropropane (**6**) were obtained. Apparently *m*-DNB inhibited the intermolecular radical anion free radical chain process while at the same time promoting the intramolecular cyclization. Except for the fact that one of the reactions is intramolecular while the other is intermolecular, they are closely related processes: the leaving group is located on a nitro-substituted secondary carbon and both anions are secondary. Surely for such similar processes to be so differently affected by *m*-DNB implies a different substitution mechanism. We conclude that cyclization of **7** is *not* a radical anion free radical chain process and that an alternate mechanism must operate. Alternative mechanisms must also be considered for the one-pot oxidative cyclization of 1,3-dinitro compounds.

It is possible that cyclization of **7** is simply a concerted internal S_N2 reaction, although an analogous intermolecular process is clearly precluded on steric grounds.[11] If the S_N2 mechanism does operate, the trans rather than cis isomer of **1b** presumably arises largely from unfavorable dipolar interactions between the oxygen atoms located on the nitronate and nitro groups. Since methyl and nitro groups are not vastly dissimilar in size (*A* values:[12] Me, 1.70; NO_2, 1.10), it is clear that a simple steric argument for exclusive (>97%) formation of trans product cannot be made.

Another possible cyclization mechanism would involve internal single-electron transfer (SET) in **7** from the nitronate group to the bromonitro moiety, generating a diradical anion. This internal SET process would be difficult at best to distinguish from an S_N2 pathway,[13] differing mainly in the assignment of diradical anion **9** as an intermediate rather than a transition state. If the SET mechanism operates, it can be assumed that the conformation of singlet diradical **10** does not alter prior to collapse, so that the preferred conformation of the diradical anion, controlled by unfavorable oxygen atom interactions on the two nitro groups, likely gives rise to the observed trans stereochemistry.

The increase in cyclization yield caused by *m*-DNB is attributed to protection of dibromodinitroalkane **4**, which would otherwise participate in intermolecular radical anion processes. The product, dinitrocyclopropane **1b**, was largely unaffected (70% recovery) when added to the reaction of 2-nitropropane anion and 2-bromo-2-nitropropane. Consequently, the increased yield is not simply due to protection of **1b** from radical anion processes.[8b,14]

Several mechanistic probes have been briefly examined for the oxidative cyclization of 1,3-dinitro compounds. Neither *m*-DNB nor di-*tert*-butyl nitroxide inhibited dinitrocyclopropane formation; cyclization to give **1a** proceeded readily in the dark. Thus, conditions that often hamper radical anion free radical chain substitution reactions did not prevent formation of **1a–c**.

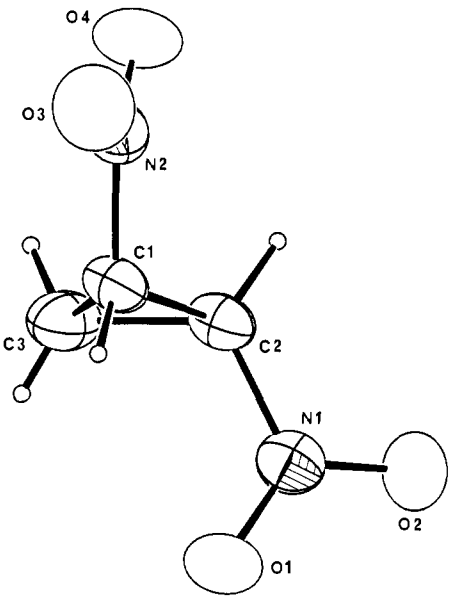


Figure 1. ORTEP drawing for *trans*-1,2-dinitrocyclopropane (**1a**). Only one enantiomer is shown. The numbering scheme is that used in Table I. For C, N, and O, 30% probability ellipsoids are shown; hydrogen atoms have been drawn artificially small.

Table I. Heavy-Atom Bond Lengths (Å) for Dinitrocyclopropane **1a**

bond	length, from X-ray data	calcd length 4-31G basis set
C1–C2 vicinal	1.506 (6)	1.502
C1–C3 distal	1.473 (7)	1.493
C2–C3 distal	1.477 (6)	1.493
C1–N2	1.474 (7)	1.450
C2–N1	1.452 (7)	1.450
N1–O1	1.223 (6)	1.227
N1–O2	1.226 (5)	1.214

Crystallographic Studies

Dinitrocyclopropane **1a** crystallizes in the monoclinic space group $P2_1/n$ with a = 5.212 (1) Å, b = 18.493 (4) Å, c = 6.220 (2) Å, β = 114.13 (2)°, and Z = 4. The density is calculated to be 1.603 g/cm^3 from the X-ray data, and the results were qualitatively confirmed [1.59 ± 0.01 g/cm^3] by the flotation density method using aqueous potassium iodide solutions. Interestingly, a calculation of density by Kitaigorodsky's method[15] using X-ray data[16] available for cyclopropane itself (calculated molar volume = 52.22 cm^3/mol), twice the atomic volume of hydrogen[1a] (3.60 cm^3/mol), and twice the nitro group volume[1a] (21.61 cm^3/mol) gave an estimated density of only 1.50 g/cm^3, in poor agreement with the actual value.

The most striking features of dinitrocyclopropane are the bisected conformation observed for each nitro group (Figure 1) and the shortened distal C–C bond lengths (Table I). The distal bonds are 0.04 Å shorter than in cyclopropane itself, a substantial substituent effect attributed largely to the π-acceptor ability of the nitro group. The vicinal C–C bond is also slightly shortened compared to cyclopropane.

Calculational Studies

The structure of dinitrocyclopropane **1a** was calculated by using ab initio molecular orbital theory at the 4-31G level.[17] Complete

(11) Nucleophilic displacement leading to a three-membered ring would be expected to have an effective molarity well in excess of 10^3 M. For a review concerning effective molarity, see: Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 123–278.

(12) Values were taken from: Hirsch, J. A. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley-Interscience: New York, 1967; Vol. 1, pp 199–222 [204, 216].

(13) S_N2 processes can be viewed as SET to the incipient leaving group with the remaining spin-paired electrons making up the new bond: the transition state is a radical–radical anion pair. (a) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702 (footnote 35). (b) Bilevitch, K. A.; Bubnov, N. N.; Okhlobystin, O. Yu. *Tetrahedron Lett.* **1968**, 3465. (c) Bilevitch, K. A.; Okhlobystin, O. Yu. *Russ. Chem. Rev. (Engl. Transl.)* **1968**, *37*, 954–968.

(14) (a) Ono, N.; Miyaka, H.; Tamura, R.; Hamamoto, I.; Kaji, A. *Chem. Lett.* **1981**, 1705. (b) Kornblum, N.; Cheng, L. *J. Org. Chem.* **1977**, *42*, 2944. (c) Fukunaga, K.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 107.

(15) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; pp 18–21.

(16) Bates, J. B.; Sands, D. E.; Smith, W. H. *J. Chem. Phys.* **1969**, *51*, 105.

(17) For an excellent review of ab initio molecular orbital theory, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

Table II. Calculated Bond Lengths (Å) for Nitrocyclopropane

bond	4-21G	4-31G	6-31+G	6-31G*
C1–C2 vicinal	1.514	1.504	1.508	1.497
C2–C3 distal	1.503	1.490	1.493	1.487

geometry optimization was carried out by using the GAUSSIAN 82 program[18] while imposing C_2 geometry. The nitro groups favored an orientation that bisected the three-membered ring as actually determined by X-ray analysis. Previous workers have found that the 4-21G and 4-31G basis sets give very good agreement between experimental and calculated values for the bond lengths in substituted cyclopropanes.[19]

Comparison of calculated and observed bond lengths for dinitrocyclopropane **1a** shows very good agreement, except for the distal cyclopropane bonds, which are calculated to be 0.02 Å longer than actually observed (Table I). This could be due to an underestimation of the π-accepting ability of the nitro group at the 4-31G level since the greater the π-accepting ability, the shorter the distal bond in cyclopropanes.[19] The cyano group has a π-electron accepting ability similar to (although somewhat less than) that of the nitro group. A microwave study of cyclopropanecarbonitrile revealed the distal bond to be 0.03 Å shorter than the vicinal bonds.[20] This difference is very similar to that which we observed for dinitrocyclopropane **1a**. A calculation of cyclopropanecarbonitrile at the 4-21G level only accounted for part of the difference.[19] A higher level of theory might correctly describe the π-accepting ability of the nitro groups in **1a**, although we were limited to the present method by the size of the calculation.

We investigated the effect of a larger basis set on the geometry of nitrocyclopropane as a model for compound **1a**. A calculation for nitrocyclopropane at the 4-21G level has already been reported.[21] A microwave study[22] has also been reported, although the large number of variables precluded assignment of a complete structure. We have calculated C–C bond lengths for nitrocyclopropane at the 4-31G, 6-31+G, and 6-31G* levels of theory using complete geometry optimiztion (Table II). The higher levels of theory examined here do not lead to any major changes in the carbon skeleton. The greatest difference in vicinal versus distal bond lengths (0.015 Å) is seen at the 4-31G and 6-31+G levels. Thus we are unable to account for the shortened distal bonds in dinitrocyclopropane **1a** at these levels of theory. It is possible that even higher levels that include electron correlation might have a major effect on the geometry of the three-membered ring. However, the bond length discrepancy may also be due simply to crystal packing forces.

Experimental Section

General Procedures. Crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer. NMR spectra were taken in $CDCl_3$ (TMS internal standard) on a JEOL FX-90Q instrument; sextet splitting patterns are apparent, and chemical shifts for the AB pattern are calculated. Gas chromatography (GC) was performed on a Varian 1420 instrument equipped with a 2 m × 0.64 cm 5% SE-30 column (preparative) and a 1 m × 0.32 cm 10% SE-30 column (analytical). Infrared spectra were recorded on a Perkin-Elmer 457 instrument. Elemental analyses were performed by Micro-Analysis, Inc. 1,3-Dinitropropane,[6] the lithium salt of 2-nitropropane,[23] and 2-bromo-2-nitropropane[9] were prepared according to published procedures. DMSO was distilled at reduced pressure from CaH_2. 2-Nitropropene was prepared by the method of Buckley and Scaife[24] and was twice distilled prior to use; a recommendation[25] concerning excess phthalic anhydride was followed, but the most critical factor involved using anhydride (mp 130–132 °C) free of phthalic acid.

Preparation of 2,4-Dinitropentane. Distilled nitroethane (17.58 g, 0.235 mol) was added to a cool (10 °C) methanolic solution of lithium methoxide, prepared from reaction of lithium (1.458 g, 0.208 mol) with absolute methanol (120 mL). The resulting stirred suspension was cooled (0–5 °C), and after 10 min a solution of 2-nitropropene (4.715 g, 0.054 mol) in methanol (20 mL) was added dropwise over 20 min. After 5 min of additional stirring, 50% aqueous acetic acid (80 mL) was added and the mixture was added to water (400 mL), which was then extracted with CH_2Cl_2 (three 100-mL portions). The combined extracts were washed (three 30-mL portions of H_2O), dried (anhydrous Na_2SO_4), and concentrated at reduced pressure. The resulting oil was distilled (**Caution**: *one batch of grossly impure material obtained by an alternate procedure vigorously decomposed at 130 °C*), care being taken to keep the pot temperature below 120 °C: bp 77–82 (0.05 mm). The 6.28 g (71% yield) of distillate was a mixture of two diastereomers [55:45 *R,S* to *R*,R** ratio], although early fractions had a higher precentage of the *R*,R** isomer while latter fractions contained more of the *R,S* isomer. More complete separation could be accomplished by preparative TLC (80:20 hexanes–ethyl acetate). The more mobile fraction was the *R*,R** isomer: mp 46–7.5 °C (lit.[7] mp 43–44 °C); ^{1}H NMR δ 4.61 (sextet, 2 H), 2.40 (dd, 2 H, J = 6.7, 5.9 Hz), and 1.60 (d, 6 H, J = 6.8 Hz). The less mobile fraction was the *R,S* isomer, isolated as an oil: ^{1}H NMR δ 4.62 (sextet, 2 H), 2.83 (m, 1 H), 2.0–2.5 (m, 1 H), and 1.63 (d, 6 H, J = 6.6 Hz).

A 1% yield of the *R*,R** isomer was also obtained from reaction of paraformaldehyde with nitroethane.[7] The crude product had to be steam-distilled (**Caution**: *vigorous decomposition occurred in one run when the distillation pot became too hot. Destruction of the pot residue from another run with nitric acid also led to vigorous decomposition*), vacuum-distilled, and recrystallized from aqueous ethanol.

Preparation of 3,5-Dinitroheptane.[7] A mixture of paraformaldehyde (30.3 g, 1 mol), 1-nitropropane (200 mL, 2.25 mol), and diethylamine (4.3 g) was heated at reflux for 2 h. The crude products were concentrated at reduced pressure and steam-distilled. The distillate (2.5 L) was extracted with CH_2Cl_2, and the extracts were dried (anhydrous Na_2SO_4) and concentrated at reduced pressure. Distillation of the resulting oil gave impure product: bp 150–160 °C (0.25 mm). Recrystallization of this material from aqueous ethanol gave a 14% yield of the pure *R*,R** diastereomer: mp 31.5–33.5 °C (lit.[7] mp 32 °C); ^{1}H NMR δ 4.39 (m, 2 H), 2.40 (dd, 2 H, J = 6.8, 5.7 Hz), 1.7–2.2 (m, 4 H), and 0.97 (t, 6 H, J = 7.5 Hz).

Preparation of *trans*-1,2-Dimethyl-1,2-dinitrocyclopropane (1b). A dimsylsodium[26] solution was prepared by reaction of hexane-washed 60% NaH–mineral oil dispersion (0.32 g, 8 mmol) with DMSO (15 mL) at 65–75 °C under Ar for 15 min. To the cooled (15 °C) solution was added a trace of triphenylmethane, and the resulting red solution was titrated over 2 min with 2,4-dinitropentane (mixture of diastereomers, 0.54 g, 3.35 mmol) until the red color just disappeared. The resulting cooled solution (water bath; internal temperature 15–18 °C) was stirred for 2 min and then iodine (3 g, 12 mmol) in DMSO (5 mL) was added dropwise over 6 min. After 2 min more, the reaction mixture was poured into ice water (200 mL) containing 5 g of sodium bisulfite, and the crude product was extracted with CH_2Cl_2 (three 30-mL portions). The combined extracts were washed (three 30-mL portions of H_2O), dried (anhydrous Na_2SO_4), and concentrated at reduced pressure. Preparative TLC (70:30 CCl_4–CH_2Cl_2 elution) gave pure **2** (195 mg, 36% yield) as an oil: IR (film) 1550 and 1340 cm^{-1} (NO_2); ^{1}H NMR δ 2.44 (s, 2 H) and 1.84 (s, 6 H).

A sample of **1b** was further purified by preparative GLC. Anal. Calcd for $C_5H_8N_2O_4$: C, 37.50; H, 5.04. Found: C, 37.53; H, 5.33.

An experiment performed on pure (*R*,R**)-dinitropentane gave **1b** in similar fashion.

Preparation of *trans*-1,2-Diethyl-1,2-dinitrocyclopropane (1c). 3,5-Dinitroheptane (0.62 g, 3.26 mmol) dissolved in DMSO (3 mL) was reacted as above to give crude **3**. Preparative TLC as above gave pure **3** (141 mg, 23% yield) as an oil: IR (film) 1550 and 1350 cm^{-1} (NO_2); ^{1}H NMR δ 2.61 (sextet, 2 H, J = 7 Hz), 2.26 (s, 2 H), 1.44 (distorted sextet, 2 H, J = 7 Hz), and 1.06 (t, 6 H, J = 7 Hz).

A sample of **1c** was further purified by preparative GLC. Anal. Calcd for $C_7H_{12}N_2O_4$: C, 44.68; H, 6.43. Found: C, 45.08; H, 6.57.

Preparation of *trans*-1,2-Dinitrocyclopropane (1a). 1,3-Dinitropropane (0.90 g, 6.72 mmol) was reacted at double the scale used to prepare **1b**. The crude product was purified by preparative TLC (CH_2Cl_2 elution) followed by recrystallization from CCl_4 to give pure **1a** (213 mg,

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24% yield): mp 60–61 °C; IR (melt) 1530 and 1350 cm^{-1} (NO_2); ^1H NMR δ 5.04 (t, 2 H, J = 7.2 Hz) and 2.42 (t, 2 H, J = 7.2 Hz); ^{13}C NMR δ 59.14 (2 CH) and 19.02 (CH_2); MS m/e 132 (M^+).

Anal. Calcd for $C_3H_4N_2O_4$: C, 27.28; H, 3.05. Found: C, 27.57; H, 3.13.

Starting 1,3-dinitropropane (41 mg, 5% recovery) was obtained as a less mobile fraction during preparative TLC.

This reaction was carried out in the presence of 5 mol % di-*tert*-butyl nitroxide with no change in results. It was carried out under sunlamp irradiation and in the dark also with no change in results. Attempts to carry out cyclization in water or methanol led to no formation of **1a**.

Preparation of 2,4-Dibromo-2,4-dinitropentane (4). Cleaned Na (149 mg, 6.49 mmol) was added to distilled 1-butanol (5 mL), and the mixture was refluxed for 20 min under Ar to attain complete reaction. The resulting stirred solution was cooled (0–5 °C) and 2,4-dinitropentane (55:45 mixture of diastereomers, 277 mg, 1.71 mmol) was added dropwise over 1 min. After 5 min, the resulting thick suspension was added portionwise over 5 min to a cold (0–5 °C) stirred solution of Br_2 (1.02 g, 6.4 mmol) in CH_2Cl_2 (5 mL), water (2 mL) being used to complete the transfer. After 5 min, water (10 mL) and excess sodium bisulfite were added. The mixture was extracted with CH_2Cl_2 (three 10-mL portions), and the combined extracts were washed (10 mL water), dried (anhydrous Na_2SO_4), and concentrated at reduced pressure. Kugelrohr distillation of the resulting oil gave **4** (434.1 mg, 79% yield) which was >95% pure (GC, NMR). A purer product (>99%; 249 mg, 50:50 mixture of diastereomers) was obtained by preparative TLC (70:30 CCl_4–CH_2Cl_2 elution) by taking the lower three-fourths of the main band: NMR δ 4.07 (s, 2 H, R^*,R^*) superimposed on 4.04 (d, 1 H, J = 16.7 Hz, R,S), 3.91 (d, 1 H, J = 16.7, R,S), 2.28 (s, 6 H, R,S), and 2.17 (s, 6 H, R^*,R^*). The remaining one-fourth of the main band partially overlapped a minor band; the material isolated (71 mg) consisted of the R^*,R^* diastereomer of **4** and a small amount of butoxylated material.

Dibromodinitro compound **4** could also be prepared by using sodium methoxide in methanol, but a small amount of methoxylated side product, which could not be separated by TLC or simple distillation, contaminated the product.

Reaction of Dibromodinitro Compound 4 with the Lithium Salt of 2-Nitropropane. Without Added *m*-DNB. A solution containing **4** (81 mg, 0.25 mmol) in DMSO (5 mL) was stirred under Ar at 18–20 °C while a second solution containing the lithium salt of 2-nitropropane (45 mg, 0.48 mmol) in DMSO (5 mL) was added dropwise over 3 min. The resulting pink solution was stirred for 0.5 min and was added to water (100 mL). This mixture was then acidified with dilute HCl and extracted with CH_2Cl_2 (three 10-mL portions). The combined extracts were washed, dried, and concentrated at reduced pressure to give a semisolid: NMR and GC analysis indicated 2,3-dimethyl-2,3-dinitrobutane (**5**) (70%), dinitrocyclopropane **1b** (25%), and a trace of 2-bromo-2-nitropropane (**6**) (5%). Small amounts of unidentified materials were apparent from the NMR. Preparative TLC gave **5** (35 mg, 88% yield) and **1b** (6 mg, 15% yield) as a more mobile fraction. A small amount of less mobile material (unidentified mixture, 2 mg) was also obtained.

In the Presence of 78 mol % *m*-DNB. A solution containing **4** (81 mg, 0.25 mmol) and *m*-DNB (33 mg, 0.2 mmol) in DMSO (5 mL) was treated with the lithium salt of 2-nitropropane as in the preceding experiment. Bright red coloration was noted as each drop of the nitronate solution was added. The crude product was a pale yellow semisolid: NMR and GC analysis indicated *m*-DNB (50%), dinitrocyclopropane **1b** (20%), 6 (25%), and **5** (5%). Several other materials in trace amounts were apparent from the NMR. Preparative TLC gave *m*-DNB containing **5** (95:5, respectively) (33 mg), **1b** (12 mg, 29% yield), and a little of the volatile **6** (11 mg, 25% yield).

X-ray Analysis of 1a. A crystal of **1a** was mounted in a capillary to minimize sublimation, and crystallographic data were collected at 299 K. A set of 1771 $\pm h,\pm k,l$ reflections were measured with a sphere limited by $2\theta = 120°$ using graphite-monochromated Cu Kα radiation (λ = 1.541 84 Å). Three standard reflections ($\bar{2}52$, $\bar{2}13$, $\bar{2}\bar{1}3$) measured every 2000 s of exposure showed an intensity decrease of 2.2%. A total of 718 unique reflections with $I > 3\sigma(I)$ were used during structure determination. These data were corrected for Lorentz and polarization effects but not for absorption.[27] The structure was solved by direct methods using the MULTAN 11/82 package, which revealed all nine heavy atoms. Hydrogen atoms were located from a subsequent difference Fourier synthesis. Full-matrix least-squares refinement on F for 98 variables converged to R = 0.069 and R_w = 0.082.

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Supplementary Material Available: Tables of crystallographic refined positional parameters, refined displacement (β) parameters, and bond distances and angles (3 pages). Ordering information is given on any current masthead page.

(27) The Enraf-Nonius Structure Determination Package, Delft, Holland (1986) was used for data collection, data reduction, structure solution, and structure refinement.

Automerization of Benzene[1]

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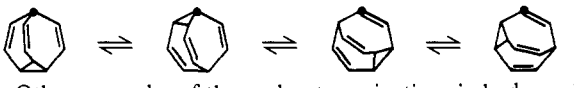
Abstract: It has been demonstrated that the atoms of benzene interchange positions *intra*molecularly (but not *inter*molecularly) at high temperatures in a quartz flow system. Thermolysis of benzene-*o*-$^{13}C_2$ at 1110 °C with a 2.0-s contact time gave ortho, meta, and para benzene-$^{13}C_2$ in a ratio of 72:24:4. The data point to a "1,2-switch" of atoms as the primary reaction pathway. Several mechanistic possibilities that could explain this automerization of benzene are considered. Of these, the reversible formation of benzvalene (eq 4) appears to be the most reasonable at this time.

Automerizations, the degenerate skeletal rearrangements of polyatomic molecules, have long held great fascination for organic chemists.[2] The degenerate Cope rearrangements of bullvalene that let every carbon atom in the molecule eventually occupy every possible site in the skeleton, for example, seem almost to mock the very concept that molecules have structure (eq 1).[3]



(1)

Other examples of thermal automerizations in hydrocarbons, heterocycles, and organometallic compounds abound.[4] For many

(1) Thermal Rearrangements of Aromatic Compounds: Part 10. For Part 9, see ref 12c. A preliminary account of this work was presented at the 190th National Meeting of the American Chemical Society, Chicago, Illinois, September 11, 1985, abstract ORGN 150.

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