The Products and Stereochemistry of Reactions of Dinitrogen Tetroxide with $\Delta^{9,10}$-Octalin, Norbornene, Cyclooctatetraene, 6,6-Diphenylfulvene, and Indene

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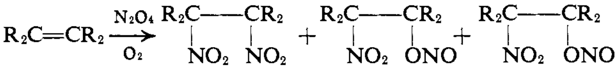
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio, and the Central Research Department, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota. Received December 19, 1966

Abstract: $\Delta^{9,10}$-Octalin and dinitrogen tetroxide in ethyl ether in the presence of oxygen yield *trans*-9,10-dinitrodecalin (II) and 10-nitro-9-decalyl nitrate (III). Norbornene and dinitrogen tetroxide give, after hydrolysis and chromatography, *exo,cis*- (IX, major) and *trans*- (X, minor) 2,3-dinitrobicyclo[2.2.1]heptanes and 2-hydroxy-3-nitrobicyclo[2.2.1]heptane (stereochemistry unestablished). Cyclooctatetraene and dinitrogen tetroxide result in the formation of 5,8-dinitro-1,3,6-cyclooctatriene (XXII) of probable *trans* stereochemistry. The mechanisms of these reactions are consistent with homolytic addition of dinitrogen tetroxide or nitrogen dioxide to the olefinic centers to give vicinal nitrocycloalkyl radicals which then react selectively with the nitrating agent(s) from the more sterically accessible direction. Reaction of 6,6-diphenylfulvene and dinitrogen tetroxide leads to 4-benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX), 2-nitro-6,6-diphenylfulvene (XXX), and 2,5-dinitro-6,6-diphenylfulvene (XXXI). Indene and dinitrogen tetroxide and subsequent aqueous hydrolysis yield *cis*-2-nitro-1-indanol (XXXVI). The *cis* stereochemistry of the products derived from addition of dinitrogen tetroxide to 6,6-diphenylfulvene and to indene may indicate that with rigid planar cycloolefins (charge transfer) coordination with dinitrogen tetroxide, and subsequent collapse to *cis* adducts, becomes an important reaction mechanism.

Dinitrogen tetroxide reacts with olefins (eq 1) in ether or ester-type solvents and in the presence of oxygen to give vicinal dinitro compounds, nitro nitrites, and nitro nitrates.[2] These reactions involve coordination of dinitrogen tetroxide with the electron-donor solvents and subsequent homolytic addition of the nitrating agent(s) to the olefins.[2] Dinitrogen tetroxide adds stereoselectively to a number of olefins and cycloolefins. Cyclohexene and cyclopentene give both *cis* and *trans* products.[3] 1-Methylcyclohexene yields 1-methyl-*trans*-2-nitrocyclohexyl nitrite exclusively.[3] *cis* and *trans*-stilbenes and dinitrogen tetroxide give mixtures of the *dl*- and *meso*-dinitro adducts in a 3:2 ratio and the *threo* and *erythro* nitro nitrites in a 2:1 ratio.[4] It has been suggested that the major stereochemical adducts are formed more rapidly because the structure of the transition state for homolytic reaction of an intermediate nitroalkyl radical ($R_2\dot{C}-CR_2NO_2$) and the nitrating agent (NO_2, N_2O_4) resembles the reactants and thus attack occurs at the greater rate from the more accessible direction.[2,4a,5]

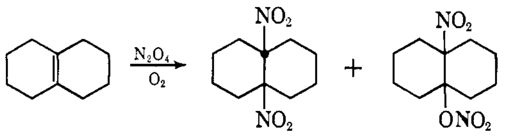


$$R_2C{=}CR_2 \xrightarrow[O_2]{N_2O_4} \underset{NO_2}{R_2C}-\underset{NO_2}{CR_2} + \underset{NO_2}{R_2C}-\underset{ONO}{CR_2} + \underset{NO_2}{R_2C}-\underset{ONO_2}{CR_2} \qquad (1)$$

In the present study the stereochemistry of addition of dinitrogen tetroxide to $\Delta^{9,10}$-octalin, bicyclo[2.2.1]-heptene-2, cyclooctatetraene, 6,6-diphenylfulvene, and indene has been investigated. The principal objectives of this research are to evaluate possible charge-transfer and steric effects in reactions of dinitrogen tetroxide with the particular olefins. The chemistry of the products of these reactions has also been determined.

Discussion

$\Delta^{9,10}$-Octalin. Addition of $\Delta^{9,10}$-octalin (I) in ethyl ether to dinitrogen tetroxide in ethyl ether at −20° in the presence of oxygen (eq 2) yields *trans*-9,10-dinitrodecalin (II, 76% conversion of I) as the principal product; small amounts of 10-nitro-9-decalyl nitrate (III, eq 2; stereochemistry unknown) were isolated (see Experimental Section) in certain experiments. Upon inverting the order of addition of reactants at 0° in the absence of oxygen, *trans*-9,10-dinitrodecalin (II, 74%) is also obtained. · The order of addition of reagents does not significantly affect the types and stereochemistry of the products formed. When oxygen is passed rapidly through the reaction mixture, there is a significant change in the course of addition and 10-nitro-9-decalyl nitrate (III) is a major product.



I II III (2)

The stereochemistry of *trans*-9,10-dinitrodecalin (II) was assigned upon its hydrogenation (eq 3) over Raney

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[1] (a) The studies of reactions of dinitrogen tetroxide with $\Delta^{9,10}$-octalin and norbornene have been abstracted in part from the Ph.D. dissertation of J. J. Gardikes, The Ohio State University, Columbus, Ohio, 1960. This research was supported by the Office of Naval Research. (b) The investigations of dinitrogen tetroxide with cyclooctatetraene, 6,6-diphenylfulvene, and indene were effected by T. S. Cantrell, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1964. (c) National Science Foundation Cooperative Fellow, 1961–1962 and 1963–1964, and National Science Foundation Graduate Fellow, 1962–1963. (d) The nuclear magnetic resonance spectra of *exo,cis*- and *exo,trans*-2,3-dinitrobicyclo[2.2.1]heptanes and *exo,cis*- and *exo, trans*-2,3-diacetamidobicyclo[2.2.1]heptanes were studied by G. V. D. Tiers of the Minnesota Mining and Manufacturing Co., St. Paul, Minn.

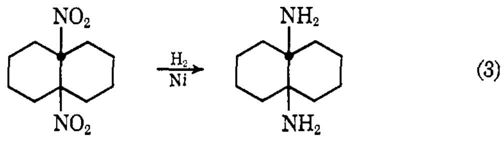
[2] H. Shechter, *Record Chem. Progr.*, 25, 55 (1964).

[3] J. C. D. Brand and I. D. R. Stevens, *J. Chem. Soc.*, 629 (1958).

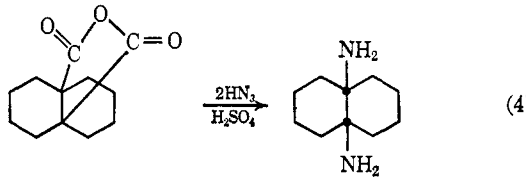
[4] (a) H. Shechter and J. J. Gardikes, *J. Am. Chem. Soc.*, 81, 5420 (1959); (b) T. Stevens, *ibid.*, 81, 3593 (1959).

[5] Reaction of *trans*-stilbene with dinitrogen tetroxide to give *dl*-1,2-dinitro-1,2-diphenylethane and *threo*-1-(2-nitro-1,2-diphenylethyl) nitrite as the principal products may be formally classified as that in which *cis* addition is preferred.[4a]

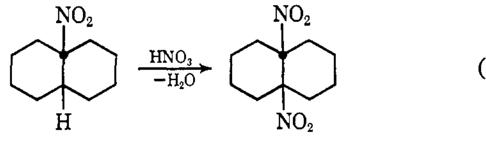
nickel to *trans*-9,10-diaminodecalin (IV, 97% yield) and subsequent conversion to *trans*-9,10-diacetamidodecalin and *trans*-9,10-diaminodecalin dipicrate. The assignment of structure of *trans*-9,10-diaminodecalin (IV) was made after synthesis of *cis*-9,10-diaminodecalin (VI) and *cis*-9,10-diacetamidodecalin by reaction of *cis*-decalin-9,10-dicarboxylic anhydride (V) with hydrazoic acid[6] and sulfuric acid (eq 4) and subsequent acetylation of the product. The stereochemical assignments of structure of II, IV, and VI are in agreement with previous intuitive assignments for these products as obtained from (1) nitration of *cis*- and *trans*-decalins[7] and *trans*-9-nitrodecalin[7c] (eq 5) and (2) reduction of 1,6-cyclodecanedione dioxime with sodium and ethyl alcohol[8] (eq 6).



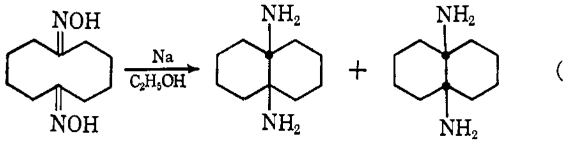
II IV (3)



V VI (4)

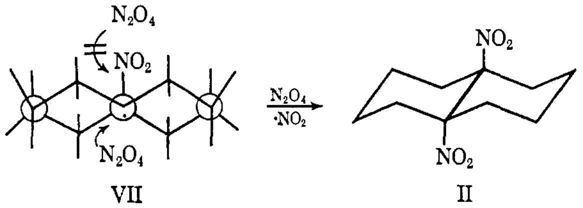


II (5)



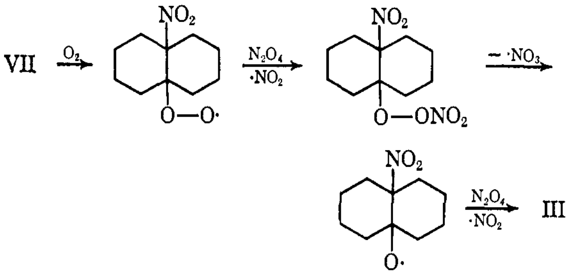
IV VI (6)

The formation of *trans*-9,10-dinitrodecalin (II) from $\Delta^{9,10}$-octalin indicates that dinitrogen tetroxide adds to the unsaturated center by a *trans* process. The stereochemical results thus exclude a concerted or bimolecular reaction involving coordinative *cis* attack of dinitrogen tetroxide on the carbon–carbon double bond. Synthesis of *trans*- (II) rather than *cis*-9,10-dinitrodecalin may be interpreted in terms of a homolytic addition process involving initial formation of the 10-nitro-9-decalyl radical (VII) and subsequent exchange with dinitrogen tetroxide or electron pairing with nitrogen dioxide. On the basis that radical pairing or exchange processes involve small activation energies and are usually exothermic, it is anticipated that the structure of the transition state for reaction of the 10-nitro-9-decalyl radical (VII) with the nitrating agent is close to reactants and will reflect the trigonal (sp^2) character of the tertiary radical which results in partial flattening of each of the fused cyclohexane rings from their chair forms. In the reaction of the 10-nitro-9-decalyl radical (VII) to give the *trans* adduct (II, eq 7), a maximum of four partial 1,3 interactions with the nitrating agent will be involved, whereas for formation of the *cis*-dinitro adduct, there will be three more prohibitive 1,2 interactions, one of which is with a bulky nitro group.[9] It is also of note that the generation and fate of VII in the present system are identical with that proposed for liquid-phase nitration of *trans*-9-nitrodecalin to II.[7c]



VII II (7)

10-Nitro-9-decalyl nitrate (III) can be made a minor or major reaction product by the amount of oxygen introduced during addition. Its structure was assigned from its quantitative and infrared analyses and upon consideration of its probable origin. 10-Nitro-9-decalyl nitrate (III) may possibly arise (eq 8) from addition of oxygen to the 10-nitro-9-decalyl radical (VII), reaction of the 10-nitro-9-decalylperoxyl radical with dinitrogen tetroxide or nitrogen dioxide, homolytic decomposition of 10-nitro-9-decalyl pernitrate, and exchange or electron pairing of the resulting 10-nitro-9-decalyloxy radicals with the nitrating agent(s).[2] An additional or alternate source of III may be reaction of VII with nitrogen trioxide ($\cdot NO_3$).[2]



(8)

Norbornene. Reaction of norbornene (VIII) with dinitrogen tetroxide in ethyl ether at 0°, rapid aqueous hydrolysis of the initial adducts, and chromatography of the products on silica gel (eq 9) results in formation of *exo,cis*-2,3-dinitrobicyclo[2.2.1]heptane (IX, 22% conversion of VIII; mp 108°), *trans*-2,3-dinitrobicyclo[2.2.1]heptane (X, 12%; mp 127°), and 2-hydroxy-3-nitrobicyclo[2.2.1]heptane (XI, 33%; stereochemistry unestablished). There is net isomerization of IX to X on chromatography; however, under conditions of near-kinetic control involving rapid chromatography and minimal handling of the products, the principal

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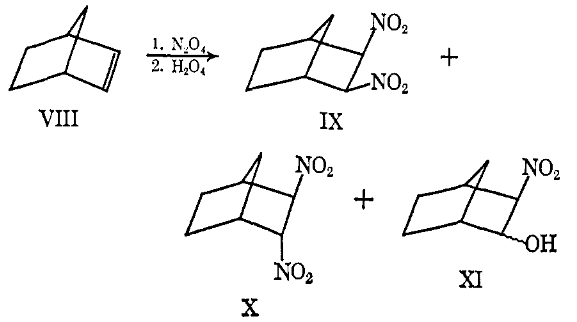
[6] Schmidt reactions of hydrazoic acid with carboxylic acids give amines with retention of configuration: H. Wolff, *Org. Reactions*, **3**, 307 (1946).

[7] (a) S. Nametkin and O. Madaeff-Ssitscheff, *Ber.*, **59**, 370 (1926); (b) W. Huckel and M. Blohm, *Ann.*, **502**, 114 (1933); (c) H. Shechter and D. Brain, *J. Am. Chem. Soc.*, **85**, 1806 (1963).

[8] P. A. Plattner and J. Halstkamp, *Helv. Chim. Acta*, 27, 200 (1944).

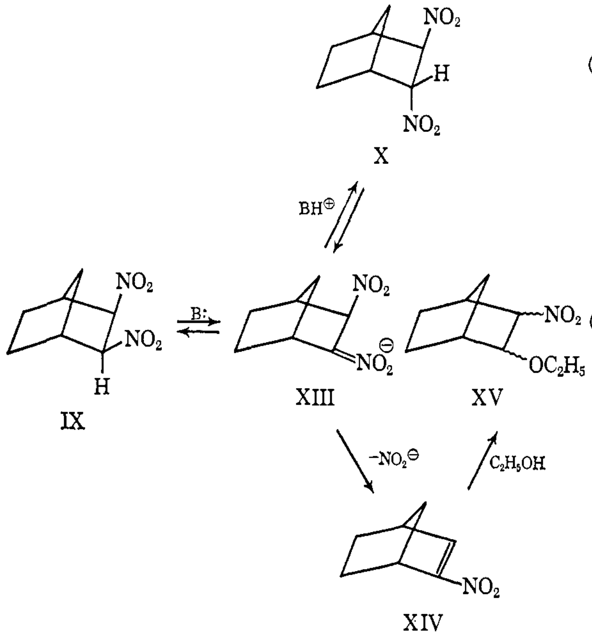
[9] (a) The relative thermodynamic stabilities of *cis*- and *trans*-9,10-dinitrodecalins are not known. *trans*-Decalin is 2.1 kcal more stable than is *cis*-decalin;[9b] however, *cis*-9-methyldecalin derivatives are slightly more stable than are *trans*-9-methyldecalin derivatives.[9c] *cis*-9-Decalylcarboxylic acid is also thermodynamically more stable than the *trans* isomer.[9d] (b) G. F. Davies and E. C. Gilbert, *J. Am. Chem. Soc.*, **63**, 1585 (1941); (c) A. Ross, P. A. S. Smith, and A. S. Dreiding, *J. Org. Chem.*, 20, 905 (1955); (d) R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 6332 (1959).



(9)

dinitro adduct was of *exo,cis* (IX) rather than of *trans* (X) stereochemistry. *endo,cis*-2,3-Dinitrobicyclo[2.2.1]-heptane(XII) was not found.

The gross structures of IX and X were indicated from their analyses and infrared properties; that the adducts are related stereochemically was established by isomerization of X to IX[10] (eq 10a) on chromatography or by the action of catalytic quantities of piperidine, cyclohexylamine, sodium methoxide, and potassium *t*-butoxide. The fact that addition of dinitrogen tetroxide to VIII occurs without carbon-skeleton rearrangement[11] is demonstrated by oxidation of IX and X with alkaline potassium permanganate to *cis*-1,3-cyclopentanedicarboxylic acid in excellent yields. Behavior of IX as a vicinal dinitro compound which will undergo base-catalyzed elimination of nitrous acid (eq 10b) is indicated by its reaction with equivalent amounts of sodium ethoxide to give 2-ethoxy-3-nitrobicyclo[2.2.1]heptane (XV, stereochemistry unknown).



(10a)

(10b)

The stereochemistries of IX and X are assigned on the basis of their chromatography properties and their dipole moments. The nuclear magnetic resonance of IX and X and of their derivatives in which there has been no stereochemical alteration about the functional centers corroborate the structural assignments.[12] The evidence for the structures of IX and X is as follows.

It has been previously observed that rigid cyclic compounds having dinitro groups in *cis* positions are much more strongly adsorbed[13] than are their corresponding *trans* isomers. The enhanced adsorptive properties of such *cis* derivatives have been attributed to their greater dipole moments and to the relatively favorable steric circumstances for interaction of the polar nitro groups with the adsorbent.[13] Chromatography of the vicinal dinitro products of the present research revealed quickly that the adduct melting at 108° is more strongly adsorbed on silica gel than is the isomer of 127° melting point. The assignments initially made are that the isomers melting at 108 and 127° are the *exo,cis* (IX) and the *trans* (X) adducts, respectively. The stereochemical designations are compatible with the dipole moments subsequently determined for IX (6.1 D.) and X (3.4 D.).[14]

The structures of IX and X also agree with their nuclear magnetic resonance properties. The spectrum of the isomer melting at 108° (IX) shows, *inter alia*, a doublet of area 2 at τ 5.09 ($J \sim 2$ cps) attributable only to the hydrogens on the carbon atoms C-2 and C-3 containing the nitro groups. The observed equivalence of these hydrogens indicates that IX is either the *exo,cis* or *endo,cis* isomer. The corresponding hydrogens in the isomer melting at 127° (X) exhibit significantly different chemical shifts, appearing at τ 4.52 (pair of doublets, $J \sim 4$ cps) and τ 4.93 (pair of doublets, $J \sim 3.9$ cps, $J \sim 1.4$ cps);[15] X, therefore, possesses the *trans* stereochemistry.

The hydrogen signals at C-7 provide evidence for the assignment of the *cis* nitro groups of IX as *exo* rather than *endo*. The apical hydrogens (C-7) of X occur as a complex multiplet overlapping the signals of the C-5 and C-6 methylenes at τ 8–8.5. In the spectrum of IX, on the other hand, one apical hydrogen is half of a broadened AB quartet at τ 7.45; the other half is partially masked by the C-5 and C-6 methylenes at τ 8.4 but appears to occur at *ca.* τ 8.56. The low-field position of one hydrogen at C-7 in IX is consistent with its location as *syn* to the two *exo* nitro groups. Models reveal that the nitro groups of IX are probably parallel to each other and perpendicular to the C-2–C-3 bond; the *syn* C-7 hydrogen is thus in the deshielding region. An effect of the magnitude found in IX would not be expected from proximity to only one nitro group (as in the *trans* isomer) or for the *endo,cis*-dinitro adduct.

trans-2,3-Diacetamido[2.2.1]heptane, mp 272–274°, has been previously prepared.[16] A chemical proof of

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[10] This appears to be the first recorded example of base-catalyzed isomerization of a vicinal dinitro compound. Such dinitro compounds are usually converted to conjugated nitroolefins by bases. In the present system isomerization of the vicinal dinitro compound may be allowed because collapse of XIII to XIV is a relatively slow process because of the strain involved.

[11] Possibly anticipated if addition of dinitrogen tetroxide occurred by an electrophilic process.

[12] Efforts to resolve either of the 2,3-dinitrobicyclo[2.2.1]heptanes by reaction of insufficient brucine, α-phenethylamine, and potassium menthylate were unsuccessful.

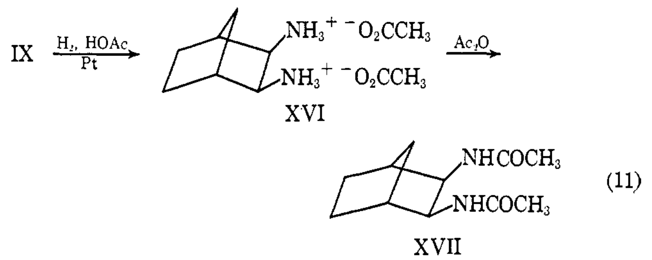
[13] D. B. Miller, Ph.D. Dissertation, The Ohio State University, 1957.

[14] The theoretical moments of IX and X as calculated using simple trigonometric methods involving vector addition of group moments are 6.3 and 2.2 D., respectively. It is not yet clear why the observed value for X is somewhat greater than that calculated. The enhanced dipole moment obtained for X does not affect the stereochemical assignments given to IX and X.

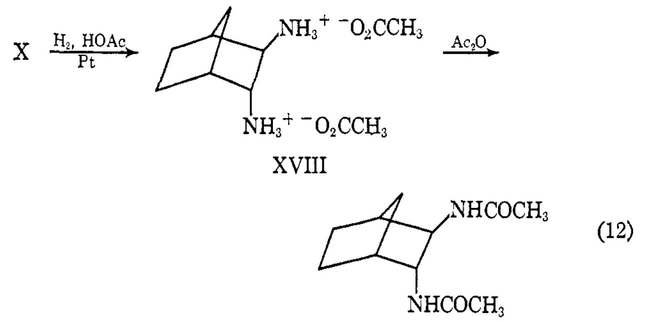
[15] The coupling constants are consistent with those previously observed in norbornane systems; see P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

[16] (a) From *trans*-2,3-bicyclo[2.2.1]heptanedicarboxylic acid and from dimethyl *endo,cis*-2,3-bicyclo[2.2.1]heptanedicarboxylate. (b) K. Alder and G. Stein, *Ann.*, 514, 211 (1934). (c) C. S. Inglessis, Ph.D. Dissertation, Clark University, 1959.

the stereochemistry of compounds IX and X was initiated. Hydrogenation of IX and X over platinum in glacial acetic acid[17] gives the corresponding diamines as isolated in near-quantitative yields as dibasic acetates (XVI and XVIII, eq 11 and 12). Reactions of XVI and XVIII with acetic anhydride (eq 11 and 12) yield



XVII (11)

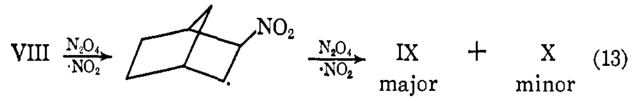


XIX (12)

the corresponding diacetylated derivatives, *exo,cis*-2,3-diacetamidobicyclo[2.2.1]heptane (XVII, mp 272° uncor; 83% yield) and *trans*-2,3-diacetamidobicyclo-[2.2.1]heptane (XIX, mp 280° uncor; 84% yield). A mixture of XVII and XIX results in melting point depression.

Since there are only small differences in melting points for the diacetamido derivatives prepared previously[16] and presently, it is not possible to make structural assignments on such evidence.[18] The nuclear magnetic resonance for XVII and XIX are decisive, however, and corroborate the stereochemical assignments given IX and X. In the spectrum of XVII (in trifluoroacetic acid) the equivalent hydrogens at C-2 and C-3 appear as a broadened doublet at τ 5.64; in the spectrum of XIX the hydrogens at C-2 and C-3 are nonequivalent and occur as separate unresolved multiplets at τ 5.81 and 6.23. Thus XIX is assigned the *trans* structure and XVIII the *cis* for reasons analogous to that discussed for the nuclear magnetic resonance of IX and X.

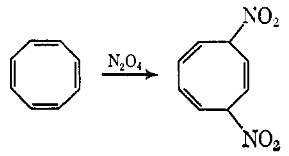
Isolation of IX as the major dinitro adduct from dinitrogen tetroxide and VIII indicates that the principal stereochemical path involves *exo–cis* addition. *exo–cis* processes involving free-radical mechanisms have been observed in reactions of *p*-thiocresol,[19a] ethyl bromoacetate,[19b] and bromotrichloromethane,[19c] respectively, with VIII, and in homolytic reaction of hydrogen bromide and 2-bromo-2-norbornene.[19d] The major stereochemical path in the present system thus may be interpreted in terms of a homolytic process involving sterically preferred *exo* attack on VIII by the nitrating agent to give the *exo*-3-nitro-2-norbornyl radical (XX, eq 13), and subsequent exchange with dinitrogen tetroxide or electron pairing with nitrogen dioxide from the more accessible directions (eq 13). An alternate possibility is that a portion of the *exo,cis* product (IX) is formed *via* coordination of the olefinic center of VIII with dinitrogen tetroxide from the lesser hindered direction (*exo*) and subsequent *cis* addition. Sysfems in which this latter mechanism appears to be important have been found and will be discussed in this paper.



XX

The 2-hydroxy-3-nitrobicyclo[2.2.1]heptane (XI) obtained from VIII and dinitrogen tetroxide is presumably derived from hydrolysis of 2-(3-nitrobicyclo[2.2.1]-heptyl) nitrites. The structure of XI is confirmed by its analysis and infrared absorption (see Experimental Section), its oxidation by basic potassium permanganate to *cis*-1,3-cyclopentanedicarboxylic acid, and its conversion by acetic anhydride to 2-acetoxy-3-nitrobicyclo-[2.2.1]heptane[20] in 70% yield. The stereochemistry and isomeric composition of XI were not determined. It is probable that XI is a mixture of *exo,cis*-2-hydroxy-3-nitro and *endo*-2-hydroxy-*exo*-3-nitro isomers.

Cyclooctatetraene. Dinitrogen tetroxide and cyclooctatetraene (XXI) in ethyl ether at −70° give 5,8-dinitro-1,3,6-cyclooctatriene (XXII, eq 14) in >34% yield; other products formed decompose rapidly at room temperature and cannot be handled readily.[21]



(14)

XXI XXII

Use of inverse addition techniques or excess XXI does not improve the yield of XXII or result in other tractable products. XXII decomposes rapidly and often violently in 1–2 hr; its ability to be handled is generally improved when it is purified.

From its analysis and spectral properties the product of reaction of XXI and dinitrogen tetroxide must be a 1:1 dinitro adduct. Its probable structure includes XXII, 1,2-dinitro-3,5,7-cyclooctatriene (XXIII), 1,8-dinitro-1,3,5,7-octatetraene (XXIV), derivatives of bi-

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(17) The acidic solvent is necessary to prevent isomerization during the reductions.

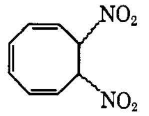
(18) Authentic XIX was no longer available from ref 16c and its synthesis is laborious.

(19) (a) S. J. Cristol and G. D. Brindel, *J. Am. Chem. Soc.*, 76, 5699 (1954); (b) J. Weinstock, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., 1955, p 190; (c) V. A. Rollen, *Dissertation Abstr.*, 19, 960 (1958); (d) N. A. LeBel, *J. Am. Chem. Soc.*, 82, 623(1960).

(20) (a) Ethanolic solutions of 2-acetoxy-3-nitrobicyclo[2.2.1]heptane and of IX in excess base give ultraviolet absorption with maxima at 245 mμ; the extinction coefficients (max) are 11,310 and 11,428, respectively. Since salts of primary and secondary nitro compounds usually absorb at 229–235 mμ with λ_{max} ~11,000, it is believed that the bathochromic shifts in absorption of the present bicyclic nitronates result from the diminished π-bond order of the C–N bonds in these strained ground states in excitation processes involving further dimunition of the π order. (b) F. T. Williams, P. W. K. Flanagan, W. J. Taylor, and H. Shechter, *J. Org. Chem.*, 30, 2674 (1965).

(21) Adducts such as 1,2-dinitro-3,5,7-cyclooctatriene (XXIII) and 1-nitrito-2-nitro-3,5,7-cyclooctatriene are expected to isomerize to unstable products such as 1,8-dinitro-1,3,5,7-octatetraene (XXIV) and 1-nitrito-8-nitro-1,3,5,7-octatetraene. Multiple addition of dinitrogen tetroxide to these rearrangement products and to XXI also probably occurs.

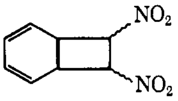
cyclo[4.2.0]octadiene (XXV and XXVI), and those containing phenyl or cycloheptatriene groups.[22] The



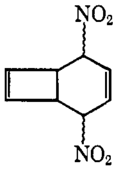
XXIII

$O_2N(CH{=}CH)_4NO_2$

XXIV



XXV

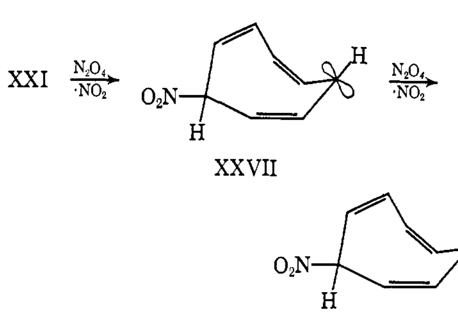


XXVI

ultraviolet spectrum of the present adduct exhibits no true maximum but only a shoulder at 240–245 mμ and strong end absorption; its infrared spectrum indicates strong bands for nitro groups (6.46 and 7.48 μ) at saturated carbon but none for aromatic nuclei or conjugated nitroolefins. The spectral properties of the dinitro compound strongly suggest that it is a 1,3,6-cyclooctatriene.[23] Its ultraviolet spectrum is very similar to that of 5,8-bis(2-cyano-2-propyl)-1,3,6-cyclooctatriene, the product of 1,4-homolytic addition of 2-cyano-2-propyl radicals and XXI.[24]

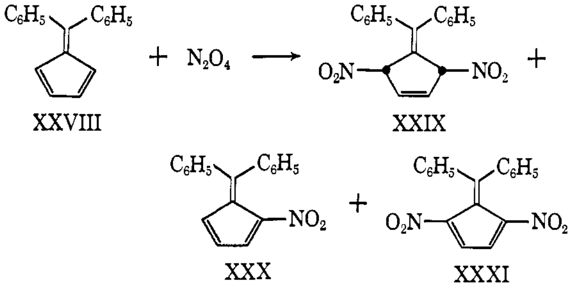
The nuclear magnetic resonance of the adduct clearly excludes benzenoid, cycloheptatriene, and bicyclo[4.2.0]octadiene structures. The absence of aryl hydrogen signals at τ 2.5–3.0 eliminates any benzene derivative; the lack of resonance in the τ 5.0–6.5 region indicates the absence of tertiary hydrogen on carbon atoms which do not bear nitro groups, thus ruling out any bicyclooctadiene or cycloheptatriene structural possibilities. The complex absorption in the τ 3.6–4.7 region is consistent with the structure assigned as XXII.

No direct experimental evidence is available on the stereochemistry of XXII; its instability precludes determination of its dipole moment. *cis*-Bimolecular attack of dinitrogen tetroxide on XXI appears unlikely because of steric features of the cyclooctatetraene ring. The stereochemistry of XXII is probably *trans* because the 4-nitro-2,5,7-cyclooctatrien-1-yl radical (XXVII, eq 15), a presumed intermediate, will strongly reflect a conformation in which the nitro group is quasi-equatorial rather than quasi-axial, and subsequent reaction with the nitrating agent can proceed most readily from the quasi-equatorial direction.[25]



(15)

6,6-Diphenylfulvene. Addition of dinitrogen tetroxide to 6,6-diphenylfulvene (XXVIII) in ethyl ether at 0° in the absence of oxygen and subsequent hydrolysis of the initial products (eq 16) give 4-benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX, 22–28%), 2-nitro-6,6-diphenylfulvene (XXX, 2–4%), and 2,5-dinitro-6,6-diphenylfulvene (XXXI, 9–12%). Inverse addition of the reagents in the absence of oxygen at 0° yields the same product but in different proportions: XXIX (14–16%), XXX (1–2%), and XXXI (15–16%). There is considerable oxidation and polymerization of XXVIII by dinitrogen tetroxide. Direct addition using 10–15% excess XXVIII leads to the highest yields of tractable products: XXIX (45–52%), XXX (3–4%), and no XXXI.



(16)

The elemental analysis, molecular weight, and absorption spectra of 4-benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX), a white solid, are consistent with its structure. The infrared absorption bands of XXIX at 6.42 and 7.31 μ are characteristic of saturated secondary nitro groups. Its ultraviolet spectrum exhibits a shallow maximum at 250 mμ (ϵ 10,200)[26a] and is similar to that of 1,1-diphenylethylene [λ_{max} 251 mμ (ϵ 12,000)]; its absorption is quite different from that of 3-benzhydrylidenecyclopentene [λ_{max} 290 mμ (ϵ 19,000)].[26b] It is thus apparent that XXIX possesses the 1,1-diphenylethylene chromophore and is the product of 1,4 addition of dinitrogen tetroxide across the five-membered ring of XXVIII. The stereochemistry of XXIX is assigned on the basis of its dipole moment. The calculated moments for the *cis* and *trans* isomers of 4-benzhydrylidene-3,5-dinitrocyclopentene are 5.60 and 0.98 D., respectively. The moment determined experimentally is 5.71 D., nearly identical with that anticipated for XXIX. Products obtained under relatively mild conditions were searched for 4-benzhydrylidene-*trans*-3,5-dinitrocyclopentene, but none was found. Some may have been formed initially and subsequently transformed to XXX and XXXI. Even if such an unlikely circumstance leads exclusively to the XXX and XXXI isolated, these products are formed in such minor amounts that it can be concluded that addition of dinitrogen tetroxide to XXVIII occurs primarily by a *cis* reaction path.

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(22) For a summary of the types of structures derivable by addition to cyclooctatetraene, see R. A. Raphael in "Nonbenzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 10.

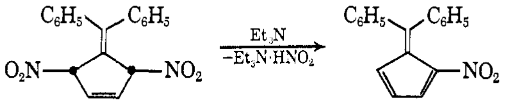
(23) 1,3,5-Cyclooctatriene, bicyclo[4.2.0]octadiene, and cycloheptatriene chromophores possess strong absorption maxima in the 265–275-mμ region; see M. Kamlet and H. Ungnade, Ed., "Organic Electronic Spectral Data," Vol. I and II, Interscience Publishers, New York, N. Y., 1960.

(24) J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, **85**, 2298 (1963).

(25) When the nitro group is quasi-equatorial in XXVII or if the product is of *cis* stereochemistry (one of the nitro groups must take a quasi-axial position), models reveal that severe steric interference will exist between the quasi-equatorial nitro group and the carbon atoms across the ring.

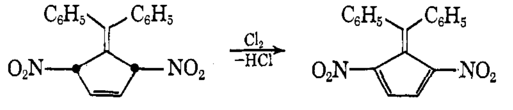
(26) (a) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 2014 (1950); (b) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **80**, 3792 (1958).

2-Nitro-6,6-diphenylfulvene (XXX) is a brick red solid. Its infrared spectum shows bands for a conjugated nitro group at 6.61 and 7.40 μ. Its ultraviolet spectrum exhibits maxima at 374, 290, and 254 mμ (ϵ 23,500, 11,100, and 12,000) and is similar in shape to that of XXVII with a bathochromic shift of *ca.* 50 mμ. Further evidence for the structure of XXX is that it is obtained in 63% yield by treating XXIX with triethylamine in benzene (eq 17). When triethylamine is added to a reaction mixture of XXVIII and dinitrogen tetroxide (without hydrolysis), XXX is isolated in 55% yield.



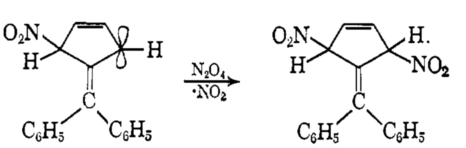
XXIX XXX (17)

2,5-Dinitro-6,6-diphenylfulvene (XXXI), an orange solid, has infrared absorption for conjugated nitro groups at 6.69 and 7.53 μ. Its ultraviolet absorption maxima at 399 and 308 mμ (ϵ 29,000 and 12,700) are shifted bathochromically as anticipated upon comparison with that of XXX. The structure of XXXI is established chemically upon effecting its synthesis from XXIX by chlorination in warm chloroform (eq 18).



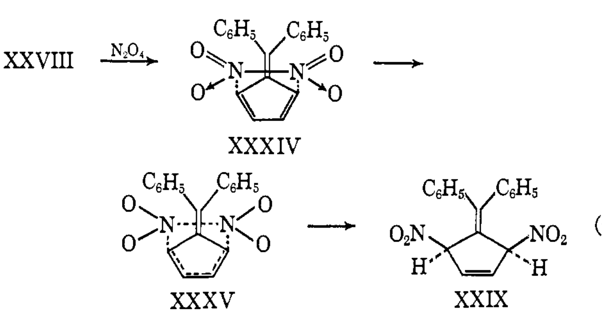
XXIX XXXI (18)

The result of particular interest in the present system is that the major (or sole) initial product of reaction of XXVIII and dinitrogen tetroxide is derived from *cis* rather than *trans* 1,4 addition. The stereochemistry is unexpected on the basis of stepwise homolytic addition of nitrogen dioxide and subsequent stereochemical control since attack of the nitrating agent from the lesser hindered side of the intermediate nitrocycloalkenyl radical XXXII will yield the *trans* adduct XXIII (eq 19).



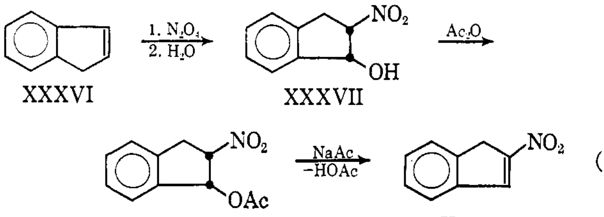
XXXII XXXIII (19)

It is possible that the *cis*-dinitro compound XXIX is formed *via* a process in which the dinitrogen tetroxide first forms a charge-transfer or addition complex with the diene system of XXVIII (eq 20). Dinitrogen tetroxide does give 1:1 adducts with benzene, mesitylene, and nitrobenzene which are believed to be derived from orbital overlap[27] of the π-electron systems of the compounds with dinitrogen tetroxide. Coordination of dinitrogen tetroxide and XXVIII as indicated (eq 20) may indeed occur since the cyclopentadienylidene moiety is a rigid and electron-rich planar π system. Formation and collapse *via* XXXIV and XXXV may thus possibly be favored because the process allows maximum overlap and minimal steric restriction of the reactants.



XXXIV XXXV XXIX (20)

Indene. Addition of dinitrogen tetroxide in ethyl ether to indene (XXXVI) in ethyl ether at 0° and subsequent hydrolysis of the initial products gives *cis*-2-nitro-1-indanol (XXXVII, eq 21) as the only well-defined product. Major reactions result in amorphous products and black resins[28a] containing nitro groups. Inverse addition enhances formation of intractables[28b] and decreases the nitroindanol XXXVII. Attempts to convert the primary products advantageously to 2-nitroindene (XXXIX) by treatment of the reaction mixture with triethylamine were unsuccessful.



XXXVI XXXVII XXXVIII XXXIX (21)

The gross structure of 2-nitro-1-indanol (XXXVII) is derived from its analytical and spectral properties (infrared bands at 6.50 and 2.98 μ for nitro and hydroxyl groups) and its conversion (eq 21) to *cis*-1-acetoxy-2-nitroindane (XXXVIII) and to 2-nitroindene (XXXIX), a previously established structure,[29] by reaction with acetic anhydride and subsequent elimination by sodium acetate.

The stereochemistry of XXXVIII, and consequently of XXXVII, is assigned on the basis of the nuclear magnetic resonance properties of the hydrogen atoms at C-3. The nuclear magnetic resonance of a number of 1,2-disubstituted indanes of known stereochemistry has been recently determined.[30] For the *trans* compounds containing either electronegative or electropositive substituents, the signals due to the hydrogens at C-3 occur as quartets with differences of chemical shifts of 23–44 cps; the methylene hydrogens, however, of the corresponding *cis* isomers absorb as doublets at very nearly the same field, the difference in chemical shifts being only 0–3 cps for the compounds studied. In the spectrum of XXXVIII, the methylene hydrogens absorb as doublets centered at τ 6.37 (J = 7.4 cps) and 6.40 (J = 7.0 cps) with a difference of 2 cps. On the basis of the generalization reported,[30] the stereochemistries of XXXVII and XXXVIII are assigned as *cis*.

That the sole tractable product of reaction of indene (XXVI) and dinitrogen tetroxide is derived from *cis* addition is not in agreement with a stepwise homolytic

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(27) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1941 (1956).

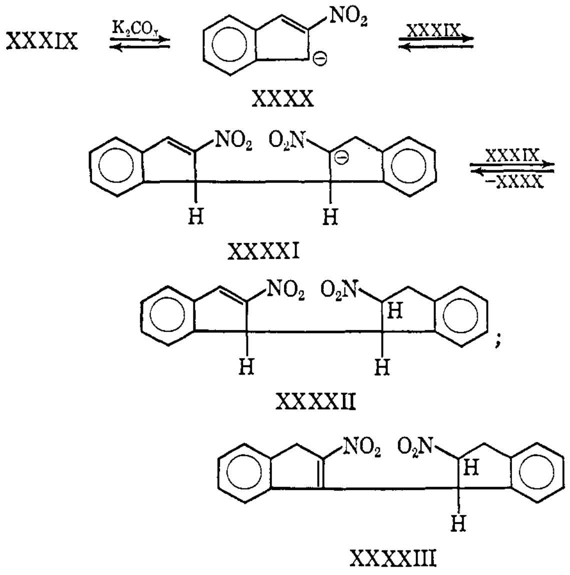
(28) (a) Indene is polymerized by free-radical or electrophilic reagents.[28b] (b) "Encyclopaedia of Organic Chemistry," Vol. 12A, Elsevier Publishing Co., Inc., New York, N. Y., 1948, p 101.

(29) O. Wallach and E. Beschke, *Ann.*, **336**, 2 (1904).

(30) W. E. Rosen, L. Dorfman, and M. Linfield, *J. Org. Chem.*, **29**, 1723 (1964).

process; attack of the nitrating agent from the preferred direction by such a mechanism would give the *trans* adduct. As has been suggested for reaction of XXVIII and dinitrogen tetroxide, the *cis* stereochemistry of XXXVII may result from initial coordination of dinitrogen tetroxide with XXXVI, a nearly flat rigid cycloolefin having considerable π electron activity, and subsequent intramolecular collapse with minimum reorganization. It is of note that the *cis* stereochemistry of reaction of dinitrogen tetroxide and indene (XXXVI) is analogous to that observed for addition of performic acid[30] and of deuterium bromide[31] to XXXVI. It has been suggested that the latter reaction occurs by a classical carbonium ion process involving ion pairs. It is conceivable that reaction of dinitrogen tetroxide with XXXVII (and with XXVIII) involves collapse of an initial π adduct *via* an intimate ion pair process or *via* transition states having considerable cationic rather than homolytic character.

cis-1-Acetoxy-2-nitroindane (XXXVIII) is also of interest in that it is converted by potassium carbonate to 1-(2-nitro-1-indenyl)-2-nitroindane (XXXII, eq 22), the product of self-Michael addition of 2-nitroindene (XXXIX). Analytical, molecular weight, and spectral data allow the structural assignment of XXXXII. The infrared spectrum of XXXXII has strong bands at 6.47 and 6.66 μ indicating the presence of both conjugated and unconjugated nitro groups. Maximum ultraviolet absorption of XXXXII occurs at the same wavelength as does 2-nitroindene (XXXIX; 338 mμ) but of only one-half the intensity. The adduct is assigned structure XXXXII rather than as the isomer XXXXIII on the basis that the nmr spectrum showed only one methylene signal of intensity 2.



(22)

Experimental Section

Reaction of $\Delta^{9,10}$-Octalin (I) with Dinitrogen Tetroxide. Inverse Addition. $\Delta^{9,10}$-Octalin mixture[32] (68 g, 0.277 mole of I, n^{20}D 1.4938) in ethyl ether (250 ml) was added dropwise to dinitrogen tetroxide (138 g, 1.5 moles) in ethyl ether (750 ml) at −20°. Oxygen was passed through the reaction mixture only while the octalin was added. The mixture was then kept between −10 and 20° for 45 hr. A bluish crystalline solid was filtered which, after having been washed with a small quantity of cold ethyl ether and air dried, was identified as *trans*-9,10-dinitrodecalin (II, 33.4 g), mp 150–159°. After the reaction solution had been poured on ice, washed with water, 10% aqueous sodium bicarbonate, and water, dried over magnesium sulfate, and concentrated, additional II (16.0 g) was obtained, mp 149–159°. The total II isolated was 49.4 g (0.217 mole). Recrystallization of II from hot ethanol gave 47.7 g of pure material (76% conversion of I to II, mp 168° cor, lit.[7] 164°).

Complete evaporation of the ethereal filtrate left a yellow oil (50.6 g) from which no solid could be crystallized. Distillation of an aliquot of the material allowed separation of decalin,[33] n^{20}D 1.4695, equivalent to 11.3 g (0.083 mole) in the evaporated filtrate. The remaining material exhibited absorption for olefin, nitro (6.47 μ), and nitrate (6.13 μ) groups; its various components could not be adequately resolved (see subsequent Experimental Section) because of their drastic decomposition upon chromatography on silica gel or on vacuum distillation.

In a similar experiment in which oxygen was bubbled through the mixture for the entire reaction period, a solid of different composition was obtained. From this solid, after several recrystallizations from alcohol, was isolated II, mp 161–164°, and an analytically pure product, 9-nitrato-10-nitrodecalin (III), mp 122–124°, of unknown stereochemistry (probably *trans*). The infrared spectrum of III exhibits absorptions for a nitro group at 6.45 μ and for nitrate at 6.13 and 7.8 μ.

Anal. Calcd for $C_{10}H_{16}N_2O_5$: C, 49.17; H, 6.60; N, 11.45. Found: C, 49.31; H, 6.41; N, 11.45.

Direct Addition. Dinitrogen tetroxide (13.8 g, 0.15 mole) in ethyl ether (75 ml) was added in 1 hr at 0° to $\Delta^{9,10}$-octalin reagent[32a] (13.6 g, 0.055 mole of I) in ethyl ether. After 8 hr, II precipitated (6.1 g), mp 155–160°, and was filtered. The filtrate was handled as described previously to give additional II (3.7 g), decalin, and nitro derivatives.[34]

Reduction of *trans*-9,10-Dinitrodecalin (II). *trans*-9,10-Diaminodecalin (IV), *trans*-9,10-Diacetamidodecalin, and *trans*-9,10-Diaminodecalin Dipicrate. *trans*-9,10-Dinitrodecalin (II, 2.0 g, 0.0088 mole) in 15% absolute ethanol in benzene (50 ml) was hydrogenated over Raney nickel (45 psi) at room temperature for 6 hr. Filtration of the catalyst and evaporation of the solvents gave crude *trans*-9,10-diaminodecalin (IV, 1.435 g, 0.0085 mole), mp 65–67°, 96.6% conversion of II. Pure IV was obtained as white needles upon one recrystallization from cold ethyl ether, mp 70°, lit.[7] 70°. *trans*-9,10-Diacetamidodecalin (white crystals) prepared from reaction of IV with acetic anhydride and 10% sodium hydroxide melted above 360°; the *trans*-9,10-diaminodecalin dipicrate prepared melted at 262–264°, lit.[8] 262–264°.

Synthesis of *cis*-9,10-Diaminodecalin (VI) and *cis*-9,10-Diacetamidodecalin. Sodium azide (1.95 g, 0.03 mole) in concentrated sulfuric acid (25 ml) was added dropwise to a stirred mixture of decalin-9,10-dicarboxylic anhydride (2.08 g, 0.01 mole, mp 89–91°, lit.[35] mp 95–96°) and fuming sulfuric acid at 56–60°. After 7 hr, evolution of gas had ceased, and the reaction mixture was cooled and poured on ice. The solution was made basic and then extracted several times with ethyl ether. The ether extract was dried over magnesium sulfate and evaporated to give crystalline *cis*-9,10-diaminodecalin (VI, 0.4 g, 0.0024 mole), mp 41°, lit.[8] 41°, 24.0%

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(31) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2248 (1963).

(32) (a) The I used was a mixture of $\Delta^{9,10}$-octalin (I, 55.4%), $\Delta^{1,9}$-octalin (28%), and decalin (16.6%) prepared by reduction of naphthalene with lithium in ethylamine.[32b] The presence of $\Delta^{1,9}$-octalin complicated separation and identification of the products of reaction with dinitrogen tetroxide but did not affect the principal stereochemical objectives of this study. (b) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, 77, 3230 (1955); W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958); A. S. Hussey, J. F. Sauvage, and R. H. Baker, *ibid.*, **26**, 256 (1961); see R. A. Benkeser and E. M. Kaiser, *ibid.*, **29**, 955 (1964).

(33) Its infrared spectrum and refractive index are essentially identical with that of authentic decalin.

(34) A considerable portion of the noncrystalline product, as separated by chromatography on silica gel, is soluble in excess sodium hydroxide. The ultraviolet absorption of an alkaline solution of this material in ethanol shows a minimum at 234 mμ and a maximum at 283 mμ (λ_{max} 9700) analogous to that of conjugated nitroanates.[20b] The ultraviolet absorption and the nuclear magnetic resonance of this material indicate the presence of a carbon–carbon double bond and a $CHNO_2$ function. It is probable that a constituent of the reaction product is 1-nitro-$\Delta^{9,10}$-octalin. For further experiments on the products, see ref 1a.

(35) K. Alder and K. H. Backendorf, *Ber.*, 71, 2199 (1938).

conversion of decalin-9,10-dicarboxylic anhydride. Reaction of VI with acetic anhydride and 10% sodium hydroxide yielded *cis*-9,10-diacetamidodecalin, mp 243°, lit.[8] 242°.

Reaction of Norbornene (VIII) with Dinitrogen Tetroxide. Dinitrogen tetroxide (4.6 g, 0.6 mole) in ethyl ether (200 ml) was added in 2 hr at 0–5° to norbornene (VIII, 37.6 g, 0.4 mole) in ethyl ether (500 ml). After 4 hr the mixture was poured into water (500 ml), stirred for 0.5 hr, and washed quickly with 5% aqueous sodium bicarbonate (400 ml),[36] dilute hydrochloric acid, and water. After the ether solution was evaporated, the oily residue was stirred several hours with water (three 400-ml portions). The water-insoluble oil was redissolved in ether, dried over magnesium sulfate, evaporated to about 200 ml, and cooled with ice. The white solid which separated was filtered, washed with a small quantity of cold ether, air dried, and then identified as *exo,cis*-2,3-dinitrobicyclo[2.2.1]heptane (IX, 7.7 g), mp 108°, infrared absorption for an aliphatic nitro group at 6.45 μ.

Anal. Calcd for $C_7H_{10}N_2O_4$: C, 45.16; H, 5.41; N, 15.04. Found: C, 45.47; H, 5.46; N, 15.09.

The remaining ethereal filtrate was evaporated and the yellow residue (28.8 g) chromatographed on silica gel (G. F. Smith Co., 3.5 × 21 cm) prewashed with 1:1 Skellysolve B–methylene chloride (200 ml). The following eluents were used: 1:1 Skellysolve B–methylene chloride (1200 ml), methylene chloride (1000 ml), and 4:1 methylene chloride–ethyl acetate (500 ml). Seven equal fractions (about 400 ml) were collected. Fractions 1 (16.7 g) and 2 (2.3 g) show identical spectra for a mixture of IX and X. Fractions 3 (0.5 g), 4 (1.0 g), 5 (2.4 g), 6 (1.7 g), and 7 (3.5 g), though different, show bands for hydroxyl, nitro, and carbonyl (5.8 μ) groups; their principal component is 2-hydroxy-3-nitrobicyclo[2.2.1]heptane (XI).

Fraction 1 (1.0-g aliquot) was rechromatographed on silica gel (V_{280} = 160 ml) prewashed with Skellysolve B (200 ml).[37] The following solvents were used: Skellysolve B (150 ml), 4:1 Skellysolve B–methylene chloride (150 ml), 3:2 Skellysolve B–methylene chloride (150 ml), 3:2 methylene chloride–Skellysolve B (150 ml), and methylene chloride (100 ml). Ten fractions (1′–10′) of approximately 70 ml each were collected. Fractions 1′ and 2′ contained only a small amount of product (0.03 g); this material exhibited bands for nitro (6.48 μ) and possibly nitrate (6.12 μ) groups. Fractions 3′–5′ yielded a white solid, *trans*-2,3-dinitrobicyclo[2.2.1]heptane (X, 0.46 g), mp 127–130°.

Anal. Calcd for $C_7H_{10}N_2O_4$: C, 45.16; H, 5.41; N, 15.04. Found: C, 45.03; H, 5.43; N, 15.21.

The total amount of X in fractions 1 and 2 is 8.73 g, 0.047 mole, 11.8% conversion of VIII. Fractions 6′–10′ yielded *exo,cis*-2,3-dinitrobicyclo[2.2.1]heptane (IX, 0.46 g), mp 108–110°; the amount of IX calculated in fractions 1 and 2 is 8.7 g. The total amount of IX isolated from the reaction is 16.4 g, 0.008 mole, 22% conversion of VIII.

From the aqueous washes of the initial reaction product after addition of sodium chloride, extraction with ether, drying of the ether extracts over magnesium sulfate, and vacuum evaporation of the ether, was isolated crude 2-hydroxy-3-nitrobicyclo[2.2.1]heptane (XI, 20.6 g, 0.131 mole, 33% conversion of VIII).[38] Distillation of VIII at greatly reduced pressures resulted in its extensive decomposition. The proof of structure of XI is described in subsequent experiments.

Oxidation of IX, X, and XI to Cyclopentane-*cis*-1,3-dicarboxylic Acid with Potassium Permanganate. To a solution of potassium permanganate (3.16 g, 0.02 mole) in water (50 ml) was added *exo,cis*-2,3-dinitrobicyclo[2.2.1]heptane (IX, 1.86 g, 0.01 mole). The mixture was warmed on a steam bath for 2 hr and then kept at 25–30° for 4 hr. The manganese dioxide was filtered, the solution was acidified, further traces of manganese dioxide were filtered, and finally the solution was extracted several times with ether. The ether solution was dried over magnesium sulfate and evaporated; the white solid (mp 118°) obtained was washed with a small quantity of cold Skellysolve F–ether, air dried, and then identified as cyclopentane-*cis*-1,3-dicarboxylic acid (1.01 g, 0.0064 mole), mp 120°, no depression by an authentic sample, 64% conversion of IX.

By procedures essentially identical with that described, X and XI were each oxidized by potassium permanganate to cyclopentane-*cis*-1,3-dicarboxylic acid, mp 118°, no depression by an authentic sample.

2-Acetoxy-3-nitrobicyclo[2.2.1]heptane. Concentrated sulfuric acid (five drops) was added to XI (8.4 g, 0.53 mole) in acetic anhydride (25 ml). The reaction mixture became hot and was heated (about 50°) further for 1.5 hr, and then stored at 25–30° for 24 hr. The resulting black solution was poured into water (100 ml), and the mixture stirred for 0.5 hr. After the mixture had been extracted with ether, the combined ether extracts were washed with 5% aqueous sodium bicarbonate, water, dilute aqueous hydrochloric acid, and water, dried over magnesium sulfate, and evaporated. The yellow oil obtained was distilled at reduced pressure to give 2-acetoxy-3-nitrobicyclo[2.2.1]heptane (7.4 g, 0.37 mole), bp 92–93° (0.3 mm), $n^{20.9}\mathrm{D}$ 1.4807, 70% conversion.

Anal. Calcd for $C_9H_{13}NO_4$: C, 54.24; H, 6.58; N, 7.04. Found: C, 54.01; H, 6.51; N, 7.19.

Isomerization of *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX) with Piperidine. *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX, 1.86 g, 0.01 mole) in ethyl ether (160 ml) was treated with piperidine (0.21 g, 0.0025 mole) in ether (20 ml). A solid formed immediately upon addition of piperidine. After 5 min the mixture was filtered; the ether solution was washed with water, excess aqueous hydrochloride acid, and water, and dried over magnesium sulfate and the solvent evaporated. The white solid isolated upon recrystallization from Skellysolve B was *trans*-2,3-dinitrobicyclo-[2.2.1]heptane (X, 1.20 g, 0.00645 mole), mp 127°, 64.5% conversion of IX.

Attempted Isomerization of *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX) with Pyridine. *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX, 0.93 g, 0.005 mole, in ethyl ether (80 ml) was treated with pyridine (0.2 g, 0.0025 mole). There was no precipitation. After 5 min the ether solution was washed with water, excess aqueous hydrochloric acid, and water, dried over magnesium sulfate, and evaporated. All of the starting material was recovered, mp 108°; its infrared absorption spectrum was identical with that of authentic IX.

Attempted Thermal Isomerization of *exo,cis*-2,3-Dinitrobicyclo-[2.2.1]heptane (IX). *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX, 0.5 g), mp 108°, was heated slowly to 160° (20 min) and then allowed to cool to room temperature. Upon heating IX slowly turned red and sublimed. Both the sublimed and recovered solids gave the same melting point, 106°; their infrared spectra were identical with the starting material.

Reaction of *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX) with Sodium Ethoxide. Sodium methoxide (1.62 g, 0.03 mole) was added portionwise to *exo,cis*-2,3-dinitrobicyclo[2.2.1]heptane (IX, 5.58 g, 0.03 mole) in absolute ethanol (50 ml) and stored for 0.5 hr. The resulting yellow mixture was poured in water (200 ml) and extracted with ether. After the extract had been washed with water, dilute acid, and water, dried over magnesium sulfate, and evaporated, the remaining oil was distilled. A colorless fraction (1.5 g, 27% yield) which analyzed for 2-ethoxy-3-nitronorbornane was obtained, bp 63–64° (0.3 mm), $n^{22}\mathrm{D}$ 1.4748, infrared absorption bands for nitro (6.49 μ) and possibly ether (9.16 μ) groups; there was no absorption for a carbon–carbon double bond.

Anal. Calcd for $C_9H_{15}NO_3$: C, 58.35; H, 8.16; N, 7.56. Found: C, 58.37; H, 8.35; N, 7.77.

Reduction of *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX). *exo,cis*-2,3-Dinitrobicyclo[2.2.1]heptane (IX, 1.86 g, 0.01 mole) in glacial acetic acid (50 ml) was hydrogenated over platinum (45 psi) at room temperature for 24 hr. After the catalyst had been filtered, the mixture was frozen, and the solvent sublimed under reduced pressure. A white ether-insoluble, water-soluble solid was obtained which begins melting at 110°. After having been washed with ether and air dried, the total solid weighed 2.36 g, 96% conversion of IX, based on the diacetate salt of *exo,cis*-2,3-diaminobicyclo[2.2.1]heptane (XVI). Treatment of the salt with picric acid in ethanol gave the dipicrate of *exo,cis*-2,3-diaminobicyclo[2.2.1]heptane, mp 245°.

Anal. Calcd for $C_{19}H_{20}O_{14}N_2$: C, 39.05; H, 3.45; N, 19.17. Found: C, 39.59; H, 3.43; N, 18.50.

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(36) Prolonged treatment (24 hr) of IX and X in ethyl ether with 5% aqueous sodium bicarbonate gave oils which exhibit absorption for hydroxyl and nitro groups.

(37) When large amounts of IX (4.7 g) are chromatographed on silica gel (3.5 × 20 cm) with Skellysolve B, there is some isomerization to X; this isomerization is not observed when a small amount (1.0 g) of IX is chromatographed on a similar column. Solutions of IX and X in ethyl ether and in methylene chloride upon standing for long periods turn yellow. The infrared spectra of the yellow solids isolated upon evaporation of the solvents, however, show no change of IX and X. There is depression in melting point upon mixing IX with X.

(38) The XI in fractions 3–7 is not included in the per cent conversion reported; the value thus quoted is believed to be minimal. In other experiments in which the initial reaction mixture was extracted thoroughly with water, the conversion of VIII to XI is considerably greater than 40%.

Synthesis of *exo,cis*-2,3-Diacetamidobicyclo[2.2.1]heptane (XVII). A mixture of the diacetate salt of *exo,cis*-2,3-diaminobicyclo[2.2.1]-heptane (XVI) (0.74 g, 0.003 mole) and acetic anhydride (5 ml) was stored overnight.[39] The solution was cooled, the white solid which precipitated was filtered, the solvents were evaporated, and the residual solid was washed with cold acetone. The combined solids upon recrystallization from hot acetone yielded pure *exo,cis*-2,3-diacetamidobicyclo[2.2.1]heptane[40] (XVII, 0.56, g, 2.48×10^{-3} mole), mp 272°, 82.6% conversion.

Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 62.81; H, 8.63; N, 13.32. Found: C, 62.66; H, 8.79; N, 13.17.

Reduction of *trans*-2,3-Dinitrobicyclo[2.2.1]heptane (X). *trans*-2,3-Dinitrobicyclo[2.2.1]heptane (X, 1.86 g, 0.01 mole) in glacial acetic acid (50 ml) was hydrogenated over platinum (45 psi) at room temperature for 24 hr. After filtering the catalyst and freezing and subliming the solvent under reduced pressure, a white ether-insoluble, water-soluble solid was obtained which began to melt at 118°. After the solid had been washed with ether and air dried, its weight was 2.30 g, 94% conversion of X assuming the product to be the diacetate salt of *trans*-2,3-diaminobicyclo[2.2.1]-heptane (XVIII).

Synthesis of *trans*-2,3-Diacetamidobicyclo[2.2.1]heptane (XIX). A mixture of diacetate salt of *trans*-2,3-diaminobicyclo[2.2.1]-heptane (XVIII, 0.74 g, 0.003 mole) and acetic anhydride (5 ml) was stored overnight.[48] The mixture was cooled, the white solid which precipitated was filtered, the solvents were evaporated, and the residual solid was washed with cold acetone. The combined solids upon recrystallization from hot acetone yielded pure *trans*-2,3-diacetamidobicyclo[2.2.1]heptane (XIX, 0.57 g, 2.52×10^{-3} mole), mp 280°, 84% conversion.

Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 62.81; H, 8.63; N, 13.32. Found: C, 62.72; H, 8.52; N, 13.27.

Reaction of Cyclooctatetraene (XXI) and Dinitrogen Tetroxide. Dinitrogen tetroxide (9.2 g, 0.100 mole) in ethyl ether (25 ml) was added in 1 hr to stirred cyclooctatetraene (XXI, 10.4 g, 0.100 mole) in ethyl ether (150 ml) at −70 to −78° under nitrogen. The solution was allowed to warm to −20° and then stirred at this temperature for 2 hr. The now orange solution was filtered to give crude 5,8-dinitro-1,3,6-cyclooctatriene (XXII, 6.4 g, 0.33 mole, 33%) as a yellow solid which was washed twice with cold ether. Darkening of the crude material occurred rapidly and the compound was recrystallized by the following procedure, working as rapidly as possible. The crude XXII was dissolved in *ca.* six parts of lukewarm oxygen-free ethyl acetate, and ethyl ether was added until the mixture was faintly turbid. The solution was then cooled, first at −15°, then at −78°. Two recrystallizations in this manner gave pure XXII (3.22 g, 0.0164 mole, 16.4%) as white prisms, mp 57–58° dec, which turned yellow on standing at room temperature for a short while, and which decomposed violently after standing for periods ranging from 1 hr to overnight. The compound could be stored overnight at −20° with little visible change, but some decomposition had nevertheless occurred and spectral and analytical work was performed immediately on freshly crystallized material.

Anal. Calcd for $C_8H_8N_2O_4$: C, 48.97; H, 4.08; N, 14.27. Found: C, 48.66; H, 4.22; N, 14.11.

The infrared spectrum of XXII shows strong bands at 6.45, 7.47, and 7.54 μ. Its ultraviolet spectrum displays no true maximum, but only strong end absorption, with a shoulder at 240–245 mμ (ϵ 1500). The nmr spectrum of XXII consists of a doublet centered at τ 3.65 (area 2, hydrogens on C-2 and C-3, $J = 7.4$ cps) overlapping a singlet at τ 3.74 (area 2, hydrogens on C-6 and C-7), a broadened doublet at τ 4.16 (area 2, hydrogens on C-5 and C-8), and an unresolved multiplet at τ 4.3–4.5 (area 2, H on C_1 and C_4).

The ethereal filtrate from the reaction was evaporated at 10° to give a dark red oil which fumed and turned to a black tar when allowed to stand at 0°. Use of the inverse addition technique or excess XXI gave no other tractable product, nor was the yield of XXII improved.

Reaction of 6,6-Diphenylfulvene (XXVIII) with Dinitrogen Tetroxide. Normal Addition, Equimolar Quantities of Reactants. Dinitrogen tetroxide (0.92 g, 0.010 mole) in ethyl ether (10 ml) was added in 1 hr to a stirred solution of 6,6-diphenylfulvene (XXVIII, 2.30 g, 0.010 mole, freshly crystallized) in ethyl ether (60 ml) at 0° under nitrogen; the solution of XXVIII in ethyl ether had previously been flushed thoroughly with nitrogen. The mixture was stirred at 0° for 1 hr. The pale yellow solid formed was filtered, washed with cold ether, and air dried. The crude 4-benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX, 0.33 g, 0.0010 mole, mp 158° dec) was recrystallized from benzene or chloroform. Pure XXIX was obtained as white prisms, mp 165° dec.

Anal. Calcd for $C_{18}H_{14}N_2O_4$: C, 67.07; H, 4.35; N, 8.70. Found: C, 66.82; H, 4.41; N, 8.63.

Compound XXIX possesses an ultraviolet absorption maximum at 250 mμ (ϵ 10,200). Its nuclear magnetic resonance spectrum shows a singlet at τ 2.79 (area 10, aromatic hydrogens) and a pair of narrow doublets at τ 3.21 and 3.44 ($J = 1.2$ cps) representing the olefinic and methine hydrogens, respectively. It displays strong infrared absorption at 6.42, 7.29, 11.86, 12.52, 13.09, 13.31, and 14.12 μ.

The ethereal filtrate was washed with water, 5% aqueous sodium bicarbonate, 5% hydrochloric acid, and water and then dried. Cooling the solution at 5° gave 2,5-dinitro-6,6-diphenylfulvene (XXXI) as a red solid (0.36 g, 0.0011 mole), mp 225° dec. Recrystallization from ethyl acetate yielded pure XXXI as brilliant orange needles, mp 228° dec, which shows strong infrared bands at 6.37, 6.69, 7.52, 10.49, 13.17, and 14.18 μ. Its ultraviolet spectrum exhibits maxima at 374 and 308 mμ (ϵ 29,000 and 12,700).

Anal. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.74; N, 8.75. Found: C, 67.24; H, 3.83; N, 8.48.

The ether was evaporated from the filtrate. The residue was chromatographed on silica gel (24×260 mm) and eluted with hexane (100 ml), 9:1 hexane–methylene chloride (200 ml), 4:1 hexane–methylene chloride (200 ml), 2:1 hexane–methylene chloride (200 ml), 1:1 hexane–methylene chloride (150 ml), methylene chloride (200 ml), 8:1 methylene chloride–ethyl acetate (200 ml), and 2:1 methylene chloride–ethyl acetate (300 ml). Twenty-four fractions were collected and evaporated. Fractions 1–5 contained a dark red oil which crystallized on standing in the cold or on seeding. Recrystallization from 10% benzene–hexane gave 2-nitro-6,6-diphenylfulvene (XXX) as tiny brick red prisms, mp 111–113° dec (0.08 g, 0.0003 mole).

Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.61; H, 4.73; N, 5.10. Found: C, 78.46; H, 4.98; N, 5.36.

XXX has strong infrared bands at 6.32, 6.40, 6.69, 7.40, 7.58, 12.80, 13.16, and 14.23 μ. Its ultraviolet absorption maxima are at 374, 290, and 254 mμ (ϵ 23,500, 11,100, and 12,000).

Fractions 6–17 contained XXIX contaminated with XXXI. Recrystallization from benzene gave purer XXIX as off-white prisms (0.40 g, total 0.73 g, 0.00230 mole). Fractions 18–24 contained a red-black tar (1.86 g) which resisted crystallization and which exhibited infrared bands at 2.9 (broad), 6.41, 6.59, and 7.40 μ. Reaction of 6,6-diphenylfulvene (XXVIII) with dinitrogen tetroxide in ethyl ether thus yielded XXIX (0.0023 mole, 23% yield), XXX (0.0003 mole, 3% yield), and XXXI (0.0011 mole, 11% yield). Two additional experiments performed in the manner described gave similar results; XXIX (26 and 28%), XXX (2 and 4%), and XXXI (8.5 and 10%) were formed in the indicated yields.

Inverse Addition. A solution of XXVIII (2.30 g, 0.010 mole) in ethyl ether (50 ml, flushed with nitrogen) was added at 0° to stirred dinitrogen tetroxide (0.92 g, 0.010 mole) in ethyl ether (40 ml). The addition required 30 min, after which the solution was stirred for 1 hr. Filtration gave XXIX (0.27 g, 0.0084 mole) which was washed with cold ether. The combined ethereal filtrate and washings were washed with 5% sodium bicarbonate, 5% hydrochloric acid, and water, dried, and cooled to 5°. There was thus obtained XXXI (0.22 g, 0.00069 mole) identified by its melting point and its infrared spectrum. The solution was concentrated to *ca.* 40 ml and then cooled; additional XXXI (0.29 g, total XXXI: 0.51 g, 0.0016 mole, 16% yield) was obtained.

The mother liquors were evaporated and the residue was chromatographed on silica gel (British Drug House, Ltd., 24×250 mm). The column was eluted with 200 ml each of hexane, 9:1 hexane–methylene chloride, 6:1 hexane–methylene chloride, 3:1 hexane–methylene chloride, 2:1 hexane–methylene chloride, and imethylene chloride. The 9:1 hexane–methylene chloride fractions gave XXX (~1%). The 3:1 and 2:1 hexane–methylene chloride fractions yielded, on evaporation, additional XXIX (0.24 g, total XXIX: 0.51 g, 0.0016 mole, 16% yield). The reaction of XXVIII with dinitrogen tetroxide in ethyl ether, adding the fulvene to the dinitrogen tetroxide, thus gave XXIX (16% yield). A second experiment conducted in the described manner gave XXIX (14%), XXX (1%), and XXXI (15%); the results are similar to that of the first experiment.

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(39) Formation of the product appeared to have taken place during the first few minutes after mixing.

(40) There was depression in melting point upon mixing with *trans*-2,3-diacetamidobicyclo[2.2.1]heptane (XIX). The infrared spectra of the two show some differences in absorption in the fingerprint region.

Normal Addition, Excess XXVIII. Dinitrogen tetroxide (12.4 g, 0.135 mole) in ethyl ether (35 ml) was added in 1 hr under nitrogen to a stirred solution of XXVIII (34.5 g, 0.150 mole) in ethyl ether (700 ml) at 0°. The mixture was stirred at 0° for 1.5 hr and then filtered. The crude XXIX (3.41 g) was washed twice with cold ether and air dried. The combined ethereal washings and filtrate were washed with water, dried, and concentrated to *ca.* 400 ml. Cooling to 5° gave additional crude XXIX (7.47 g). The mother liquor was concentrated to *ca.* 125 ml and cooled again. There was obtained a total of 11.87 g of an orange solid which was mainly XXIX contaminated with a little XXX. Further concentration and cooling of the mother liquors gave only red tar. The final crop of orange solid obtained above was ground and triturated with 4:1 hexane–benzene. The yellow residue, crude XXIX (11.03 g, total crude XXIX: 21.91 g, 0.0682 mole, 50% yield), was combined with the two crops obtained earlier and the whole recrystallized from chloroform–ethyl acetate (charcoal) to give pure XXIX, mp 165° dec. The total yield of pure XXIX was 20.0 g (0.062 mole, 46% based on dinitrogen tetroxide).

The benzene–hexane washings from the trituration of the third crop of XXIX were evaporated to give XXX (0.66 g, 0.0024 mole, 1.4% based on dinitrogen tetroxide). The reaction of dinitrogen tetroxide with excess XXVIII in ethyl ether at 0° thus gave XXIX (46% yield) and XXX (1.4% yield). Two additional experiments repeated as indicated gave analogous results: XXIX (45 and 52%) and XXX (1 and 3.5%).

Reaction of 4-Benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX) with Triethylamine. A solution of 4-benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX, 0.50 g, 0.00155 mole) and triethylamine (0.20 g, 0.0020 mole) in benzene (15 ml) was refluxed under nitrogen for 15 min. The dark red solution was evaporated to dryness under reduced pressure. The residue was taken up in a small amount of benzene and chromatographed on neutral alumina (20 × 200 mm, activity II). The column was eluted with hexane (100 ml) and 6:1 hexane–benzene (300 ml). A broad red band which moved down the column with the benzene–hexane was collected and evaporated to dryness. The residue was dissolved in warm 10% benzene–hexane (3 ml). On cooling the solution at −15°, 2-nitro-6,6-diphenylfulvene (XXX) crystallized as tiny dark red prisms, mp 111–113° dec; a total of 0.27 g (0.00098 mole, 63% yield) was obtained.

Conversion of 4-Benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX) to 2,5-Dinitro-6,6-diphenylfulvene (XXXI). 4-Benzhydrylidene-*cis*-3,5-dinitrocyclopentene (XXIX, 0.62 g, 0.00193 mole) was dissolved in boiling chloroform (25 ml) and a stream of chlorine was passed through the refluxing solution for 2 hr. The solvent was then evaporated and the red semicrystalline residue was chromatographed on silica gel (20 × 220 mm). Elution with 2:1 hexane–methylene chloride gave an orange solid identified as 2,5-dinitro-6,6-diphenylfulvene (XXXI, 0.19 g, 0.00058 mole, 31%) by its infrared spectrum.

Reaction of 6,6-Diphenylfulvene (XXVIII) and Dinitrogen Tetroxide and Subsequent Treatment with Triethylamine. A solution of 6,6-diphenylfulvene (XXVIII, 4.60 g, 0.020 mole) in ethyl ether (150 ml) was flushed with nitrogen, and dinitrogen tetroxide (1.70 g, 0.0185 mole) in ethyl ether (10 ml) was added at 0° under nitrogen. The addition required 40 min, after which the mixture was stirred for 20 min; triethylamine (2.2 g, 0.022 mole) was then added, and the mixture was stirred at 0° for 0.5 hr and at room temperature for 2 hr.

After the mixture had been evaporated to *ca.* 10 ml, it was chromatographed on neutral alumina (30 × 300 mm, activity II). Elution with 20% ether–hexane (400 ml) developed a deep red zone, leaving a dark brown zone at the top of the column. The red zone was eluted with 20% ether–hexane and the solvent evaporated. The residue was recrystallized from 20% benzene–hexane at −15° to give 2-nitro-6,6-diphenylfulvene (XXX, 2.91 g, 1.04 moles, 52%), mp 111° dec.

Reaction of Dinitrogen Tetroxide with Indene (XXXVI). Dinitrogen tetroxide (18.4 g, 0.02 mole) in ethyl ether (40 ml) was added in 1 hr to a stirred solution of indene (XXXVI, 24.0 g, 0.21 mole) in ethyl ether (200 ml) at 0° in the absence of oxygen. The solution was stirred for 1.5 hr and filtered. The polymeric white solid formed (0.81 g) was washed with cold ether and air dried. The substance melted with decomposition over a broad range, exhibited the behavior of polymers, and was not further studied.

The filtrate was washed with water, dried, and concentrated to *ca.* 50 ml. Cooling to 5° and trituration with hexane resulted in partial crystallization. The solid, after having been washed with cold 1:2 ether–hexane, weighed 6.5 g. The mother liquor was combined with the wash liquid, reconcentrated, and cooled to −15°. A second crop of 2-nitro-1-indanol (XXXVII, mp 115–117°) was obtained which weighed 1.7 g; total yield, 8.2 g (0.046 mole, 23%). Two recrystallizations from ethyl acetate gave pure XXXVII as white silky needles, mp 117–118°.

Anal. Calcd for $C_9H_9NO_3$: C, 60.51; H, 5.02; N, 7.84. Found: C, 60.88; H, 5.15; N, 7.82.

Chromatography of the mother liquor on silica gel and elution with various solvents gave only brown gums. Use of the inverse addition technique gave increased amounts of the polymer and greatly decreased yields of nitro alcohol.

Acetylation of 2-Nitro-1-indanol (XXXVII). Sulfuric acid (three drops) was added to 2-nitro-1-indanol (XXXVII, 4.00 g, 0.022 mole) in acetic anhydride (75 ml). The solution was stored at room temperature overnight and then poured into ice water (300 ml). The suspension was stirred for 1 hr and extracted with ether. The combined ethereal extracts were washed with 5% sodium bicarbonate and water, dried, and evaporated to dryness. The residue crystallized on scratching and was recrystallized twice from ethanol (charcoal) to give 1-acetoxy-2-nitroindane (XXXVIII, 4.34 g, 0.0194 mole, 87%) as large colorless prisms, mp 62–63°.

Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.75; H, 4.98. Found: C, 60.22; H, 4.91.

Conversion of 1-Acetoxy-2-nitroindane (XXXVIII) to 2-Nitroindene (XXXIX). A solution of 1-acetoxy-2-nitroindane (XXXVIII, 2.00 g, 0.009 mole) in ethyl ether (40 ml) was refluxed over sodium acetate (0.3 g) for 35 hr. The solution was filtered, washed twice with water, dried, and evaporated to give a yellow solid residue. Recrystallization from benzene gave 2-nitroindene (XXXIX, 1.04 g, 0.0066 mole, 73%) as stout yellow needles, mp 139–140°. The ultraviolet spectrum of XXXIX showed $\lambda_{max}^{CH_3OH}$ 336 and 241 mμ (ϵ 26,000 and 35,000). The nmr spectrum showed, in addition to the aromatic hydrogen signals at τ 2.4–2.8, a triplet of area 1 at τ 2.11 (vinyl hydrogen), and a doublet of area 2 at τ 6.08 (methylene hydrogens); $J = \sim 1.4$ cps.

Preparation of 1-(2-Nitro-1-indenyl)-2-nitroindane (XXXXIII) from 1-Acetoxy-2-nitroindane (XXXVIII). A solution of 1-acetoxy-2-nitroindane (XXXVIII, 0.90 g, 4.1 mmoles) in ethyl ether (20 ml) was refluxed over potassium carbonate (0.70 g, 7.8 mmoles) for 3 hr. The dark brown solution was filtered while still warm. The residue was extracted twice with ether, and the extracts were combined with the filtrate. The combined ether solution was treated with charcoal, filtered, and evaporated to give a brown oil which partially solidified on trituration with 1:1 benzene–hexane. Recrystallization of the solid from 1:1 benzene–hexane gave 1-(2-nitro-1-indenyl)-2-nitroindane (XXXIII, 0.16 g, 0.51 mmole, 22%)) as tiny, dull yellow prisms, mp 193–194° dec. The compound exhibited strong infrared bands at 6.47 and 6.66 μ; the ultraviolet spectrum shows λ_{max} 338 mμ (ϵ 11,000).

Anal. Calcd for $C_{18}H_{14}N_2O_4$: C, 67.92; H, 4.41. Found: C, 68.16; H, 4.31.