Structure and Chemistry of the Photodimer of *trans*-β-Nitrostyrene[1a,b]

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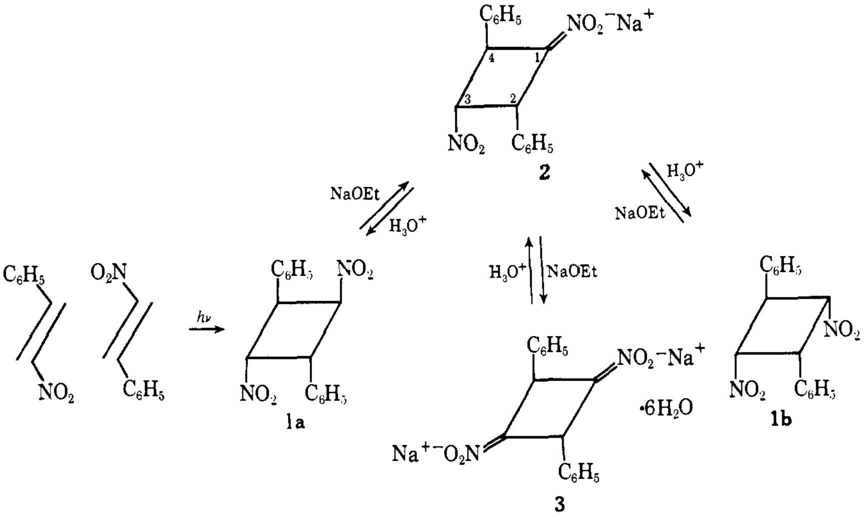
Abstract: The product of irradiation of solid *trans*-β-nitrostyrene is 1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (**1a**). Acidification of the mononitronate **2** of **1a** reveals steric kinetic control in that protonation occurs preferentially trans to the 3-nitro group to yield 1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (**1b**, major) along with **1a**. That **1a** and **1b** equilibrate to a mixture containing 48–51% of **1a** may indicate that their four-membered rings are not highly folded. Bromination of **2** occurs stereoselectively trans to the 3-nitro group to give 1-bromo-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (**4a**) and 1-bromo-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (**4b**, major). Chlorination of **2** occurs analogously to yield monochlorides **5a** and **5b** (major), respectively. The greater stability of **4b** than of **4a** upon equilibration is rationalized on the basis that the e,e conformation is more accessible to **4b** which has cis nitro groups and that the ring system of **4b** is highly folded. Bromination or chlorination of bromonitronate **6** (the conjugate base from **4a** and **4b**) and chloronitronate **7** (from **5a** or **5b**) to 1,3-dihalo-1,3-dinitro-2,4-diphenylcyclobutanes **8a**–**10b** leads preferentially to halogenation trans to the 3-nitro rather than the 3-halo groups. Halogenation of disodium 2,*trans*-4-diphenyl-1,3-cyclobutanedinitronate (**3**, the dinitronate of **1a** or **1b**) gives dihalides **8a**–**9b**. Monobromides **4a** and **4b** are resolved by brucine. The structures of **1a** and **1b** are corroborated by their stereospecific reduction to the diamines 1,*trans*-3-diamino-*cis*-2,*trans*-4-diphenylcyclobutane (**12a**) and 1,*cis*-3-diamino-*cis*-2,*trans*-4-diphenylcyclobutane (**12b**), respectively, characterized as diacetyl, dibenzoyl, and ditosyl derivatives **13a**–**15b**.

Solid *trans*-β-nitrostyrene dimerizes in sunlight.[2a,2b] The colorless product did not melt sharply (172–180° from ethanol,[2a] 179–187°)[2b] and was soluble in sodium methoxide; acidification with carbon dioxide resulted in "quantitative regeneration of the parent dimer."[2b] By analogy with head-to-tail photodimerization of solid cinnamic acid to α-truxillic acid,[3] it was postulated[2b] that the photodimer of the nitrostyrene is a 1,3-dinitro-2,4-diphenylcyclobutane. Since cinnamic acid also undergoes head-to-head photodimerization in the solid state, the analogy is ambiguous.[3]

The first objective of the present research was to establish the structure of the nitrostyrene photodimer. Expecting that the photoproduct would indeed be a dinitrodiphenylcyclobutane, we intended to explore its chemistry.[4] Since the proof of structure of the nitrostyrene photodimer is based on many aspects of its chemistry, the discussions of the structural proof and chemistry are combined. The structures of photodimer **1a** and its isomer **1b** are indicated at the outset (Scheme I). The chemistry of **1a**, **1b**, and their derivatives is then related to their structures; reactions that contribute to establishment of structure are noted in the course of the discussion. Since our initial report,[1b]

Scheme I



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(1) (a) Taken in part from the Ph.D. Dissertation of D. B. Miller, The Ohio State University, 1957 [*Diss. Abstr.*, 18, 1981 (1958)]; (b) presented in part at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, Abstracts, p 79N.

(2) (a) B. Priebs, *Justus Liebigs Ann. Chem.*, **225**, 339 (1894); (b) J. Meisenheimer and F. Heim, *ibid.*, **355**, 260 (1907).

(3) A. Mustafa, *Chem. Rev.*, **51**, 1 (1952), and references therein.

(4) Nitro olefin photodimers believed to have centrosymmetric head-to-tail structures have been reported by (a) W. E. Parham and P. L. Stright, *J. Org. Chem.*, **24**, 262 (1959); (b) M. Lahan and G. M. J. Schmidt, *J. Chem. Soc. B*, 239 (1967); (c) T. S. Cantrell and H. Shechter, *J. Org. Chem.*, **33**, 114 (1968).

work in this area has progressed continuously and there has been uncovered substantial new chemistry relating in particular to halo and to unsaturated derivatives of the nitrostyrene dimers.

Results and Discussion

Ultraviolet irradiation of solid *trans*-β-nitrostyrene gave a single photodimer, 1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (**1a**, Scheme I). With sunlight, conversion to product was $\sim$70% in 4–6 weeks; thus, **1a** was readily prepared in large quantities. Like cinnamic acid, β-nitrostyrene photodimerizes only in the solid state; in solution or as a melt, photoisomerization to *cis*-β-nitrostyrene occurs.[5,6]

Reaction of **1a** with 1 or 2 equiv of sodium hydroxide or ethoxide gave mononitronate **2**[7] or dinitronate **3**, respectively (Scheme I). Dinitronate **3** was isolated as a stable crystalline hexahydrate by precipitation from aqueous solution upon addition of tetrahydrofuran. Acidification of **2** or **3** with aqueous carbon dioxide yielded **1a** and its isomer, 1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (**1b**) in a 12:88 ratio (Scheme I). In warm ethanol or dimethyl sulfoxide containing 10–15% D_2O, **1a** and **1b** gave an equilibrated mixture containing 48–51% **1a**. These data reveal that (1) acidification of **2** is a kinetically controlled protonation process in which the nitro group in the 3 position retards proton transfer to nitronate **2** from the cis direction,[8] and (2) there is little free-energy difference between **1a** and **1b** in solution. These results thus indicate that the transition states for proton transfer make extensive use of trigonal stereochemistry[8] and are far more subject to steric influences than are the ground states of **1a** and **1b** in which the structural requirements of the ring atoms are all tetragonal. Cyclobutane rings are usually folded (20–35°) giving rise to conformational effects analogous to those of cyclohexanes.[9] As a result the cis-1,3-disubstituted cyclobutanes that have been studied have pseudo e,e conformations and are more stable than are their trans (pseudo a,e) isomers.[9] It is thus of note that **1a** and **1b** are practically of equal energies in various solvents. In **1b** it may be that the cyclobutane ring is not highly folded and the interaction of the *cis*-2-phenyl (pseudo a) group with the *cis*-1,3-dinitro (pseudo e,e) group is sufficient to make **1b** of energy comparable to that of **1a**.[10]

Isomers **1a** and **1b** are colorless, are separable chromatographically or by fractional crystallization, and melt at 185–187 and 192–198° dec, respectively.[11] The elemental analyses, molecular weights, and the chemical and spectral properties of **1a** and **1b** are in accord with their ascribed structures. Oxidation of **1a** to benzoic acid in 70% yield (2 equiv) showed that the phenyl groups were unaltered in the dimerization. The absence of benzil among the products of mild oxidation of **1a** indicated that the phenyl groups in the photodimer are not vicinal.[12] Similarly formation of stable anions **2** and **3** suggested that the nitro groups are not on adjacent carbon atoms;[13] a positive pseudo nitrole color test indicated the presence of a secondary nitro group.[14] The absence of an ultraviolet absorption maximum above 220 mμ showed that **1a** and **1b** do not have conjugation for a *trans*-β-nitrostyrene moiety; the absorption maxima near 250 mμ exhibited by **2** and **3** are attributed to the nitronate anion chromophores.[15] The facile interconversion of **1a** and **1b** is in accord with the reactions of Scheme I; since the isomerization involves only nitro groups, the stereochemistry of the phenyl groups in both isomers must be the same. The symmetry of **1a** is reflected in its nmr spectrum which exhibits an A_2B_2 pattern for its alicyclic protons and a relatively simple signal for phenyl hydrogen. In contrast the phenyl hydrogens of **1b** show a more complex signal indicative of unlike phenyl groups and the alicyclic proton signals of **1b** constitute three multiplets.

Reactions of mononitronate **2** with bromine and with chlorine gave colorless monobromides **4a** and **4b** and monochlorides **5a** and **5b**, respectively (Scheme II). Major products **4b** and **5b** were purified by recrystallization and constitute at least 80% of the monohalogen products formed in the individual reactions. Isolation of minor products **4a** and **5a** required chromatographic separations. As found for acidification, halogenation of **2** occurs preferentially from the direction trans to the nitro group in the 3 position.

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(5) D. B. Miller, P. W. Flanagan, and H. Shechter, to be submitted for publication.

(6) Solid-state photodimerizations are controlled by the crystal structure of the monomer. Photodimerization occurs only if the reacting ethylenic groups lie within $\sim$4 Å; G. M. J. Schmidt, *J. Chem. Soc.*, 2014 (1964). (b) β-Bromo-β-nitrostyrene and 2-nitro-1-phenylpropene fail to photodimerize, presumably because of their unfavorable crystal structures.

(7) In 50:50 dioxane–water at 0°, neutralization of **1a**, although too rapid for accurate measurement, is at least 30 times faster than neutralization of nitrocyclobutane: P. W. K. Flanagan, Ph.D. Dissertation, The Ohio State University, 1957; *cf.* P. W. K. Flanagan, H. W. Amburn, H. Stone, J. G. Traynham, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 2797 (1969).

(8) (a) On the basis of the large kinetic hydrogen–deuterium isotope effect for acidification of a nitronate,[7] the small activation energy required for conversion of a nitronate ion to a nitro compound, and the results of the present and prior investigations of steric control in protonation of a nitronate,[8b] it is clear that the transition state for protonation (and halogenation) reflects the structure of the reactant (nitronate) rather than the product. In the transition state for conversion of a cyclobutanenitronate to a nitrocyclobutane, it is thus likely that the four-membered ring will be nearly planar and the ring substituents will not assume highly equatorial conformations. The transition state for protonation will thus sense the steric interaction of the nitro group in the 3 position and the solvated hydronium ion. (b) For studies of steric effects in protonation of 2- and 4-substituted cyclohexanenitronates, see H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955); H. E. Zimmerman and T. E. Nevins, *J. Amer. Chem. Soc.*, **79**, 6559 (1957); and F. G. Bordwell and M. M. Vestling, *ibid.*, **89**, 3906 (1967).

(9) (a) K. B. Wiberg and G. M. Lampman, *ibid.*, **88**, 4429 (1966); (b) H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **44**, 865 (1966).

(10) On the basis of steric effects, if the cyclobutane rings in **1a** and **1b** are nearly planar, **1a** is expected to be the stable isomer; if the rings are highly folded and the nitro groups are equatorial, **1b** should be more stable than **1a**.

(11) The lower, less sharp melting points previously reported for the β-nitrostyrene photodimer[2a,b] signify that **1a** had become contaminated with **1b** during isolation. The assertion that the parent photodimer is regenerated quantitatively upon acidification of its basic solution[2a] is erroneous.

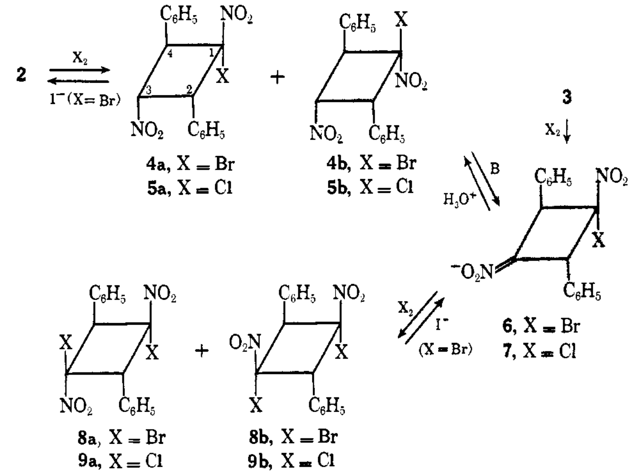
(12) Benzil is a major product of permanganate oxidation of β-truxinic acid, a head-to-head dimer of cinnamic acid; C. Liebermann, *Chem. Ber.*, **22**, 2240 (1889).

(13) In the presence of bases, vicinal secondary dinitro compounds usually eliminate nitrous acid; N. Levy, C. W. Scaife, and A. E. Wilderson, *J. Chem. Soc.*, 52 (1948). The finding that *exo,cis*-2,3-dinitrobicyclo[2.2.1]heptane is isomerized to *trans*-2,3-dinitrobicyclo[2.2.1]-heptane by various bases, presumably *via* a vicinal nitronitronate monoanion of some stability, introduces some ambiguity to the conclusion; H. Shechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, **89**, 3005 (1967).

(14) H. B. Hass and E. F. Riley, *Chem. Rev.*, **32**, 373 (1943).

(15) Cycloalkane nitronate anions generally show maxima at $\sim$230 mμ: F. T. Williams, Jr., P. W. K. Flanagan, W. J. Taylor, and H. Shechter, *J. Org. Chem.*, 30, 2674 (1965).

Scheme II

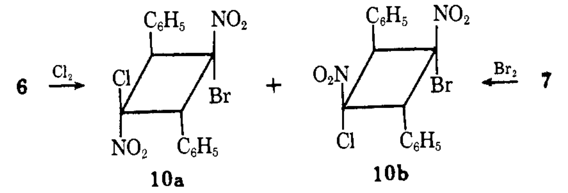


Isomers **4a** and **4b** equilibrate in ethanol; the major component of the resulting mixture was **4b**, the isomer having *cis*-nitro groups. The thermodynamic behavior of **4a** and **4b** is somewhat different than that of **1a** and **1b**. In the cyclobutane derivatives of the present study the conformation effect of a *cis*-phenyl group at C-2 is offset by the opposite effect of the *trans*-phenyl group at C-4. The most stable conformations of the bromine and nitro substituents at C-1 and C-3 should depend on the relative preferences of the different groups for axial or equatorial positions if the four-membered rings are significantly folded. In monosubstituted cyclohexanes the conformational energies for bromine and nitro groups are 0.38 and 1.10 kcal/mol, respectively.[16] Nitro groups will thus dominate bromine (and chlorine) in cyclic structures in which the substituents act in opposing directions. The greater stability of **4b** than of **4a** is thus rationalized on the basis that the e,e conformation is accessible to the isomer having *cis*-nitro groups and the ring system of **4b** is probably more folded than that of **1b**.

A study was then made of reactions of **4a**, **4b**, **5a**, and **5b** with bases and subsequent halogenation. It was expected that the initial actions of the bases on the monohalides would give nitronate salts and/or dehydrohalogenation products. Bromo compounds **4a** and **4b** react with bases to give bromonitronate salt **6** (Scheme II) or dehydrohalogenation (to be discussed later) depending on reaction conditions.[17] Bromination of bromonitronate **6** gave **8b**, the dibromide in which the nitro groups are cis, as the principal product. Similarly bromination of dinitronate **3** resulted in dibromides **8a** and **8b**.[18] The lower melting product **8a** was separated from **8b** by fractional crystallization; the major product **8b**, which has *cis*-nitro groups, constituted over 80% of the mixture. As previously,[8] the transition state for halogenation of a nitronate resembles the reactant and thus the 3-nitro group in competition with the 3-bromo substituent in the *trans*-2,4-diphenylcyclobutanenitronate (**6**) leads selectively to bromination trans to the 3-nitro group. The stereochemistry of **8a**, a centrosymmetrical product, was assigned on the basis that its two alicyclic hydrogens are identical and as expected a single alicyclic nmr signal is observed. The nmr spectrum of **8b** indicates the presence of two unlike alicyclic hydrogens.

Chloro compounds **5a** and **5b** and various bases gave chloronitronate salt **7** (Scheme II) as the principal product; chlorination of **7** yielded chiefly **9b** (Scheme II). The dinitronate salt **3** and chlorine (2 equiv) resulted in a mixture of dichlorides **9a** and **9b**; the proportion of isolated products suggests that the initially formed mixture contained at least 70% **9b**, the higher melting isomer. Chlorination of **7**, as for bromination of **6**, exhibits steric control in that chlorine is preferentially introduced trans to the 3-nitro rather than the 3-chloro groups. The stereochemistry of **9a** was established from its single alicyclic nmr absorption whereas **9b** exhibits nmr signals for two unlike alicyclic hydrogens.

Chlorination of **6** or bromination of **7** yielded mixtures of the bromochloro compounds **10a** and **10b** (eq 1). The lower melting isomer **10a** was the minor product in both experiments. The structures of **10a** and **10b** were deduced from their nmr spectra. The alicyclic hydrogens in **10a** differ in that one is cis to chlorine and the other cis to bromine. In **10b**, however, one of the cyclobutane hydrogens is cis to both halogens whereas the other is cis to both nitro groups. The structural assignments were thus based on the observation that the alicyclic hydrogen signals (4.95 and 6.18 ppm) of the isomer designated as **10b** were separated much more than the corresponding signals (5.69 and 5.80 ppm) of **10a**.



(1)

The nmr signals of the phenyl hydrogens of each of the five isomeric pairs of 1-halo (**4a**–**5b**) and 1,3-dihalo (**8a**–**10b**) derivatives are similar to those for **1a** and **1b** and corroborate the stereochemical assignments made. In each system the isomer having *cis*-nitro groups (**b** series) and thus by necessity having unlike phenyl groups, displays a single aromatic hydrogen signal having little or no structure superimposed on a complex multiplet. Isomers having *trans*-nitro groups (**a** series) on the other hand, exhibit single phenyl hydrogen signals that have relatively little structure. The effect is observable (Figure 1) even if both isomers of a pair have unlike phenyl groups as do monobromo compounds **4a** and **4b**.

Bromine atoms geminal to nitro groups are selectively reduced by iodide ion.[19] Upon use of sodium iodide in acetic acid, reduction occurs in an acidic medium which at the same time obviates dehydrohalogenation and ensures that the intermediate nitronate ion is protonated in a kinetically controlled step. A study was thus made of debromination of **8b**. As in Scheme II, dibromide **8b** gave principally **4b** which was subsequently converted primarily to **1b**. Accompanying the

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[16] J. A. Hirsch, *Top. Stereochem.*, **1**, 200, 216 (1967).

[17] Titration of 4b and 5b in ethanol–water consumed 10–20% more sodium hydroxide than required if the halonitro compounds were functioning only as monobasic acids. The intense red color accompanying titration and subsequent experiments indicate that some dehydrohalogenation accompanied formation of halonitronates **6** and **7**.

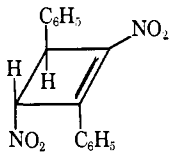
[18] Minor quantities of **4a** and **4b** accompany **8a** and **8b**.

[19] E. P. Kohler, *J. Amer. Chem. Soc.*, **38**, 889 (1916); R. A. Gotts and L. Hunter, *J. Chem. Soc.*, **125**, 442 (1925).

major products were minor amounts of **4a** and **1a**, respectively. The stereochemistry of protonation of nitronate **6** to yield **4b** as the major product thus parallels that for bromination of **2** (Scheme II). The kinetic steric control in reductive conversion of **4b** to **1b** corresponds to that described previously for generation of **1b** from **2** (Scheme I).

The structures assigned to **1a**–**10b** agree with observations that **4a** and **4b** are resolvable. Compounds **1a**, **1b**, or any of their derivatives with identical substituents at C-1 and C-3 have either a center of symmetry (**a** series) or a plane of symmetry through C-2 and C-4 (**b** series) and thus are incapable of optical isomerism. If the phenyl groups in these products were trans, the monobromides **4a** and **4b** each will lack an element of symmetry and should be resolvable. If, however, the phenyls were cis, a plane of symmetry would pass through C-1 and C-3 regardless of the substituents at C-1 and C-3 on the cyclobutane ring, and the bromides will be incapable of resolution.

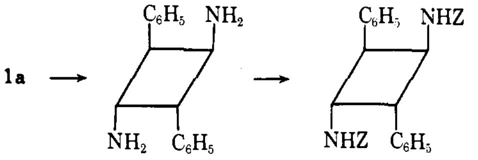
Amines in benzene effect dehydrohalogenation of **4a** and **4b**.[20a] Reaction of **4b** with less than an equivalent amount of brucine yielded 1,3-dinitro-2,*trans*-4-diphenylcyclobutene (**11**) as an optically inactive product



11

along with isomeric 1,3-dinitro-2,4-diphenylbutadienes.[20b] Unreacted **4b** and its isomer **4a** were also isolated from the brucine reaction and carefully purified; both **4a** and **4b** were now optically active ([α]D −32.5 and −20.8°, respectively). The phenyl groups at C-2 and C-4 of the monobromides must have trans geometry.

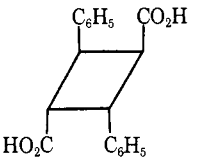
The structures of dimers **1a** and **1b** were confirmed by their reduction (eq 2 and 3) in acetic acid with zinc or



(2)

12a

13a, Z = CH_3CO
14a, Z = C_6H_5CO
15a, Z = $C_7H_7SO_2$



16a

hydrogen–Raney nickel to give isomeric diamines **12a** and **12b**,[21] respectively, isolated and characterized as their acetyl, benzoyl, and tosyl derivatives **13a**–**15b**.

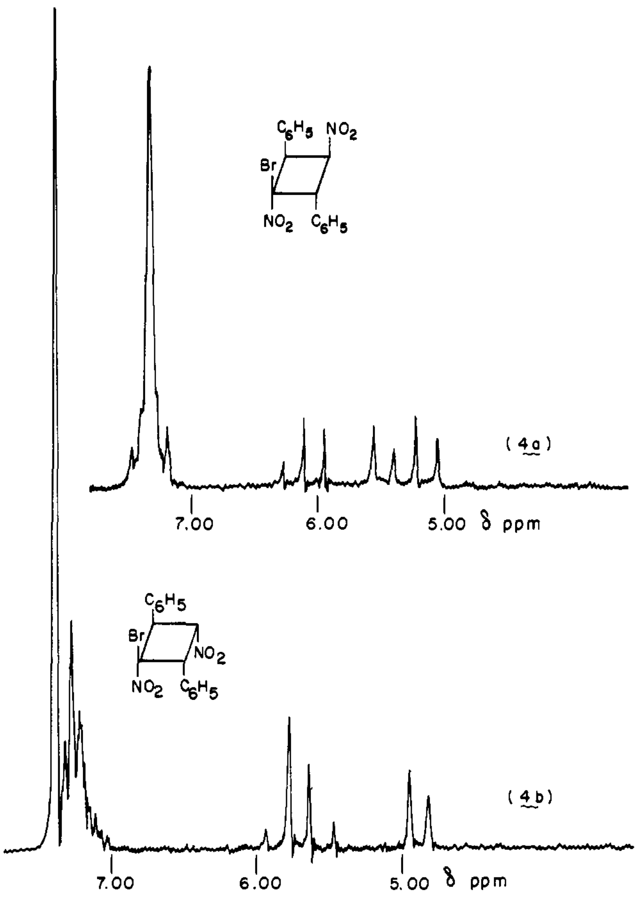
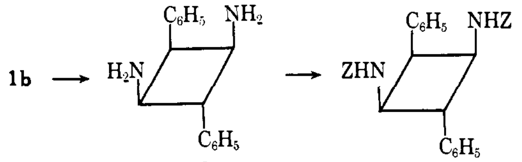


Figure 1. Nmr spectra of **4a** and **4b** at 60 MHz.

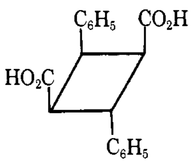
Diamine **12a** had been obtained with retention of configuration from α-truxillic acid (**16***a*) *via* Curtius reaction;[22] the *N*,*N*′-diacetyl derivative of this product was identical (melting point, mixture melting point, and ir spectra) with **13a**.[23]



(3)

12b

13b, Z = CH_3CO
14b, Z = C_6H_5CO
15b, Z = $C_7H_7SO_2$



16b

Experimental Section

General Techniques. Melting points are uncorrected. Chromatographic analyses and preparative separations with columns

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[20] (a) These dehydrohalogenation reactions are discussed in the accompanying paper; D. B. Miller, P. W. Flanagan, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 3919 (1972); (b) the structures and chemistry of the substituted butadienes will be described later.[5]

[21] Reduction of optically active secondary nitro compounds in acidic media proceeds with upward of 70% retention of configuration: N. Kornblum and L. Fishbein, *ibid.*, **77**, 6266 (1955).

[22] E. H. White and H. C. Dunathan, *ibid.*, **78**, 6055 (1956).

[23] After we had established that **13a** derived from **1a** was identical with that derived from α-truxillic acid, these results were confirmed by R. D. Campbell and R. F. Ofstead, *Proc. Iowa Acad. Sci.*, **71**, 197 (1964). These investigators also showed that **13b** obtained from **1b** was identical with that derived from γ-truxillic acid (**16b**).

were made on a mixture of 75% silicic acid (Mallinckrodt chromatographic grade) and 25% diatomaceous earth (Johns-Mansville Super-Cel or Hyflo Super-Cel). In later work thin-layer chromatography on silica gel (Brinkmann Instruments MN Polygram Sil S) was used extensively. For many separations, 5–15% ethyl ether in hexane or 20–50% benzene in hexane were suitable eluents, but one or the other eluent was more effective in certain separations. Streaking the chromatographic columns with 15–30% aqueous sodium hydroxide caused colors to form which located and frequently identified the compounds. Many of the compounds were also colored by 1 *N* sodium hydroxide, triethylamine, or sulfuric acid. Reaction mixtures in benzene were routinely filtered through 75% silicic acid–25% diatomaceous earth to remove water, tars, and extraneous materials. Unless otherwise indicated products were recrystallized from benzene–hexane.

Infrared spectra for characterization of products were obtained from Nujol mulls; for quantitative analyses, samples were dissolved in nitromethane and compared with known mixtures. The infrared spectra were recorded with Baird Associates Model B, Perkin-Elmer Model 21, and Perkin-Elmer Infracord spectrometers. Ultraviolet spectra were determined using Beckman DU and Cary Model 14M spectrometers. Nuclear magnetic resonance spectra of samples in chloroform-*d* containing tetramethylsilane were recorded with Varian Associates HR-60 or HA-100 spectrometers; chemical shifts are in parts per million with respect to tetramethylsilane. The compositions of reaction mixtures were determined by comparison of the intensities of the nmr signals of the nonaromatic hydrogens. Accuracy is low for values below 10%; "trace" signifies values on the order of 2% or less.

Optical rotations of substrates in chloroform were measured with a Schmidt and Haensch polarimeter. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Photodimerization of β-Nitrostyrene. Isolation of 1,*trans*-3-Dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (1a) and 1,*cis*-3-Dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (1b). A 5–10 mm layer of granular β-nitrostyrene[24] in trays with window glass covers was placed on an open roof and stirred several times a week. After 6 weeks of winter exposure,[25] the crude product (784 g) was worked up by fractional crystallization from tetrahydrofuran (1 crop, 415 g) and then from chloroform–benzene (2 crops, 92 g). The filtrate was washed with sulfuric acid to remove tar, then concentrated and crystallized from ethanol to give an additional 31 g of colorless product (total, 531 g, 69%). Freshly sublimed β-nitrostyrene sealed in Pyrex under nitrogen also photodimerized readily.[26] Recrystallization of the colorless dimeric product from ethanol gave pure **1a**: mp 185–187° (lit. mp 170–178°,[2a] 178–187°[2b]); mol wt calcd 298, found 321 (isopiestic method in benzene); nmr δ 4.98, 5.84 (two quartets, area 2 each, $J_{2,3} = 10.0$, $J_{3,4} = 6.2$, $J_{2,4} = \sim 1$ Hz, hydrogens geminate to phenyls at C-2,4 and to nitro at C-1,3, respectively), and 7.15–7.45 ppm (area 10, C_6H_5).[27] Further work-up of the ethanol solutions yielded a material melting from 160 to 180°. Chromatographic separation gave **1a** and a more slowly eluted second dimer **1b**: dec 192–198°; mol wt calcd 298, found 294; nmr δ 4.74, 5.53 (symmetrical multiplets, area 1 each, hydrogens geminate to phenyl at C-2,4), 5.12 (multiplet, area, 2, hydrogens geminate to nitro, C-1,3), and 7.15–7.45 ppm (multiplet, area 10, C_6H_5). Slow crystallization of the 160–180° materials from ethanol–acetone resulted in large prismatic crystals of pure **1a** and pure **1b** which could be manually separated from each other and from accompanying columnar mixed crystals. No **1b** could be detected in the initial photodimerization product by chromatographic or infrared methods.

Anal. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.40. Found, **1a**: C, 64.59; H, 4.80; N, 9.40. Found, **1b**: C, 64.33; H, 4.69; N, 9.50.

Oxidation of **1a** (0.78 g, 2.6 mmol) by hot potassium permanganate[28] gave benzoic acid (0.45 g, 3.7 mmol, 70%), mp 119–121°.

Equilibration of 1a and 1b. After 3 days at 65–75° an ethanolic solution of **1a** was swamped with dilute hydrochloric acid; infrared analysis of the resulting precipitate showed that it contained **1a** and **1b** in a 50:53 ratio. Equilibration starting with pure **1b** gave an identical mixture. Neither dimer was detectably isomerized after 3 days in acetic acid at 80°. Equilibration of **1a** in dimethyl-d_6 sulfoxide containing ~15% deuterium oxide gave, in 15 days, a mixture of 1,3-dideuterio **1a** and **1b** containing 49.5% **1a** (average of three nmr integrations). After 30 days at 25°, the mixture contained 49.7% **1a** (average of two integrations; all values for **1a** were between 48 and 51%).[29]

Reaction of 1a and 1b with Base. Sodium 3-Nitro-2,*trans*-4-diphenyl-1-cyclobutanenitronate (2) and Disodium 2,*trans*-4-Diphenyl-1,3-cyclobutanedinitronate (3). Titration of ethanolic **1a** with dilute aqueous sodium hydroxide did not give a distinct end point. The great rapidity of the neutralization reaction was demonstrated by the absence of drift in the pH meter as increments of base were added. The ultraviolet spectrum of **1a** in ethanol did not exhibit a maximum in the 220–400 mμ region. Solutions of **1a** in ethanol were treated with dilute sodium hydroxide (1–10 equiv) and diluted with water to give 5×10^{-5} *M* solutions containing 99% water: $\mathrm{uv_{max}}$ 1 equiv of NaOH, 246 mμ (ε 9,000); 2 equiv of NaOH, 245 mμ (ε 14,000); and 10 equiv of NaOH, 252 mμ (ε 18,000). Isolation of monoanion **2** from the reaction of **1a** with 1 equiv of base was not attempted.

Mixed **1a** and **1b** (32 g, 0.11 mol) in a mixture of tetrahydrofuran (400 ml) and water (30 ml) was treated at 0–10° with ethanolic sodium ethoxide (prepared from 5.2 g, 0.23 g-atom of sodium). After filtration, the granular pink precipitate was dissolved in a minimum quantity of ice water; reprecipitation by addition of excess tetrahydrofuran gave 50 g of colorless hexahydrated dinitronate salt **3**: nmr (D_2O) δ 5.21 (singlet, area 1, hydrogen geminate to phenyl) and 7.40 ppm (single signal, area 5, C_6H_5).

Anal.[30] Calcd for $C_{16}H_{24}Na_2N_2O_{10}$: C, 42.67; H, 5.31; N, 6.22. Found: C, 42.45; H, 5.28; N, 6.16.

On storage, **3** became cream or pinkish colored; warming an aqueous solution of **3** rapidly decomposed it. Acidification of an aqueous mixture of **3** and sodium nitrite and extraction with ether gave a blue-green ether layer, indicative of a secondary nitro group.[14] Cold aqueous **3** was treated first with permanganate (1 equiv) and then with bisulfite. The neutral, nearly colorless solution was acidified with concentrated hydrochloric acid and extracted with ether. Concentration of the ether extract gave benzoic acid, mp 121°, and several unidentified products, but at no point was there any indication of the presence of benzil.

Preparation of 1b from 2 and 3. Addition of aqueous **3** (0.28 g) to a cold aqueous mixture of acetic acid and urea gave a nearly colorless precipitate (0.17 g) which consisted of 20% **1a** and 80% **1b** (ir analysis). Addition of a solution of **3** in deuterium oxide to a solution of carbon dioxide in deuterium oxide gave a mixture of deuterated **1a** and **1b** which contained 88% **1b** (nmr analysis). In a preparative experiment, a cold solution of **1a** (11.9 g, 40 mmol) in tetrahydrofuran (250 ml)–ethanol (120 ml) was treated with aqueous sodium hydroxide (0.25 *N*, 45 mmol), filtered, and slowly added to an aqueous solution of acetic acid and urea. Recrystallization of the precipitate from benzene gave colorless **1b** (7.9 g, 65%), mp 185–190°, which contained only a trace of **1a** (chromatographic analysis).

1-Bromo-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (4a) and 1-Bromo-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (4b). Addition of **2** (from 5.96 g, 20 mmol of **1a** and 20 mmol of sodium hydroxide) in ethanol–tetrahydrofuran–water to cold bromine water gave a suspension that was freed of excess bromine and precipitated by agitation with a stream of air. Along with traces of **1a** and **1b**, the product contained two new compounds, the more rapidly eluted **4a** and the more slowly eluted principle product **4b** (chromatographic analysis). Recrystallization yielded **4b** (4.1 g, 11 mmol) slightly contaminated with **1a** and **1b**; several recrystallizations gave colorless, pure **4b**: mp 169–170°; nmr δ 5.81, 4.86, 5.63 (multiplet, hydrogens geminate to phenyl, C-2,4 and nitro, C-3, $J_{2,3} = 10.3$, $J_{3,4} = 9.9$ Hz), and 7.1–7.4 ppm (multiplet, C_6H_5). The combined filtrates were chromatographed, giving mixed **4a** and **4b** (1.5 g, 4 mmol) and **4a** (0.3 g, 0.8 mmol). Repeated recrystallization of the latter material led to pure **4a**: mp 166–168° (mmp with **4b** 138–143°); nmr δ 5.14, 5.48, 6.12 (multiplet, hydrogens geminate to phenyl, C-2,4 and nitro, C-3, $J_{2,3} = 10.1$, $J_{3,4} = 9.7$ Hz), and 7.34 ppm (singlet

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[24] D. E. Worall, *Org. Syn.*, **9**, 66 (1929).

[25] The poor yields of **1a** from dimerizations in the summertime arise from liquification of the monomer that occurs after a few days irradiation.

[26] The photodimerization did not require or benefit from the presence of water or ethanol; *cf.* ref 2b.

[27] Assignments were established from the spectrum of **1a**, deuterated at C-1,3.

[28] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, Wiley, New York, N. Y., 1948, p 198.

[29] We thank Mrs. L. D. Stietzel and Dr. H. C. Barrett, Stanford Research Institute, for recording some of the nmr spectra.

[30] Analysis by Miss E. M. McCarthy, Stanford Research Institute.

signal, C_6H_5). The approximate composition of the initial bromination product was 12% (or less) **4a** and 65% **4b** (ir analysis).

Anal. Calcd for $C_{16}H_{13}BrN_2O_4$: C, 50.95; H, 3.45; Br, 21.20; N, 7.43. Found, **4a**: C, 50.98; H, 3.55; Br, 20.78; N, 7.51. Found, **4b**: C, 50.70; H, 3.27; Br, 21.29; N, 7.54.

1-Chloro-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (5a) and 1-Chloro-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (5b). Chlorination of **2** (from 45 mmol of sodium hydroxide and 11.9 g, 40 mmol of mixed **1a** and **1b**) gave a product (13.4 g) containing a minor component **5a** and a more slowly eluted major component **5b** in 5 and 69% yields, respectively (chromatographic analysis). Fractional crystallization initially yielded pure **5b**: mp 155–156°; nmr δ 5.51, 4.72, 5.93 (multiplet, hydrogens geminate to phenyl, C-2,4 and nitro, C-3, $J_{2,3}$ = 10.7, $J_{3,4}$ = 9.05 Hz), and 7.1–7.4 ppm (multiplet, C_6H_5), but subsequent fractions contained both isomers. Pure **5a** was isolated chromatographically: mp 151–153° (mmp with **5b** 128–135°); nmr δ 5.14, 5.42, 6.08 (multiplet, hydrogens geminate to phenyl, C-2,4, and nitro, C-3), and 7.33 ppm (single signal, C_6H_5).

Anal. Calcd for $C_{16}H_{13}ClN_2O_4$: C, 57.75; H, 3.95; Cl, 10.67; N, 8.42. Found, **5a**: N, 8.37. Found, **5b**: C, 57.87; H, 4.12; Cl, 9.96; N, 7.65.

Attempts to isolate **4a** and **5a** by fractional crystallization from their mixtures with **4b** and **5b**, respectively, were unsuccessful.

Interconversion of 4a and 4b. Ethanolic solutions of pure **4a** and pure **4b** were heated 3 days at 50° and 2 days at 60° and then precipitated with dilute hydrochloric acid. The product from **4a** contained 60% **4b** and 25% **4a**; the product from **4b** contained 71% **4b** and 19% **4a** (ir analysis).

1,*trans*-3-Dibromo-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (8a) and 1,*cis*-3-Dibromo-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (8b). Addition of cold aqueous **3** from mixed **1a** and **1b** (44.4 g, 0.149 mol) to cold bromine water yielded a light colored solid. Fractional crystallization initially gave pure colorless **8b** as needles or oblong prisms: dec 175–200°; nmr δ 5.03, 5.87 (two singlets, hydrogens geminate to phenyl, C-2,4), and 7.0–7.5 ppm (multiplet, C_6H_5). Continued slow crystallization led to more **8b** along with colorless diamond-shaped prisms of **8a**: mp 150–152°; nmr δ 5.71 (singlet, hydrogens geminate to phenyl, C-2,4) and 7.41 ppm (single signal, C_6H_5). The chromatographic behavior of compounds **8a** and **8b** was very similar. Although **8b** was eluted slightly faster than **8a**, the overlapping zones made separation of the isomers by this procedure impractical. Fortunately, the distinctive habits of **8a** and **8b** permitted manual separation of individual crystals. After chromatography to remove tars and by-products, further crystallizations gave more **8a** (total 4.1 g, 9.0 mmol, 6.1%) and **8b** (total 55.5 g, 0.12 mol, 82%).[31]

Anal. Calcd for $C_{16}H_{12}Br_2N_2O_4$: C, 42.13; H, 2.66; Br, 35.04; N, 6.14. Found, **8a**: C, 42.20; H, 2.62; Br, 35.12; N, 6.05. Found, **8b**: C, 42.13; H, 2.70; Br, 34.67; N, 5.99.

1,*trans*-3-Dichloro-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (9a) and 1,*cis*-3-Dichloro-*trans*-1,*trans*-3-dinitro-*cis*-2,-*trans*-4-diphenylcyclobutane (9b). Chlorination of **3** (from 25.6 g, 88 mmol of mixed **1a** and **1b**) gave colorless **9a** (3.1 g, 8.5 mmol, 9.6%) (mp 153–155°; nmr δ 5.79 (singlet, hydrogens geminate to phenyl, C-2,4) and 7.40 ppm (single signal, C_6H_5)) and colorless **9b** (19.9 g, 54 mmol, 61%); mp 181–185°; nmr δ 4.83, 5.43 (two singlets, hydrogens geminate to phenyl, C-2,4) and 7.0–7.5 ppm (multiplet, C_6H_5)). The reaction conditions and the work-up procedures were essentially the same as those for the preceding bromination reaction. Again the distinctive crystal habits permitted manual separation of the isomers. Comparison of their chromatographic behavior showed that compound **9b** eluted slightly faster than **9a**.[32]

Anal. Calcd for $C_{16}H_{12}Cl_2N_2O_4$: C, 52.33; N, 3.30; Cl, 19.31; N, 7.63. Found, **9a**: N, 7.73. Found, **9b**: C, 52.20; H, 3.30; Cl, 19.19; N, 7.52.

Sodium 3-Bromo-3-nitro-*cis*-2,*trans*-4-diphenyl-1-cyclobutanenitronate (6) and Sodium 3-Chloro-3-nitro-*cis*-2,*trans*-4-diphenyl-1-cyclobutanenitronate (7). 1-Bromo-*trans*-3-chloro-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (10a) and 1-Bromo-*cis*-3-chloro-*trans* 1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (10b). The potentiometric titration of **4b** (0.20 g, 0.53 mmol in 60 ml of ethanol) with 0.01 *N* aqueous sodium hydroxide gave an apparent end point at 0.62 mmol of added base. The apparent end point in the titration of **5b** (0.20 g, 0.60 mmol in 60 ml of ethanol) was at 0.66 mmol of added base. In duplicate titrations, the pH of **4b** at the half-neutralization point was 9.8 and 9.9, while the pH of **5b** at half-neutralization was 9.5 and 9.6. Both solutions became bright red during the titrations.

A clear, red, aqueous methanolic solution containing bromonitronate anion **6** (from 1.0 g, 2.65 mmol of **4b** and 3.75 mmol of sodium hydroxide) was divided into 25 and 75% portions which were added, respectively, to bromine water and chlorine water. Recrystallization of the brominated product gave **8b** (0.18 g, 0.40 mmol, 60%) identical with that prepared previously. Recrystallization of the chlorinated product gave **10b** (0.47 g, 1.15 mmol, 58%): dec 180–195°; nmr δ 4.95, 6.18 (two singlets, hydrogens geminate to phenyl, C-2,4), and 7.0–7.6 ppm (multiplet, C_6H_5). Similarly, the cloudy red mixture containing chloronitronate anion **7** (from 1.0 g, 3.0 mmol of **5b** and 3.75 mmol of sodium hydroxide) was divided into 25 and 75% portions which were added, respectively, to chlorine water and bromine water. Recrystallization of the chlorinated product gave **9b** (0.10 g, 0.27 mmol, 36%) identical with that obtained previously. Recrystallization of the bromination product gave **10b** (0.35 g, 0.85 mmol, 38%) identical with the **10b** prepared from **6**. Chlorination of **6** and bromination of **7** (from a total of 29 mmol of **4a**, **4b**, **5a**, and **5b**) gave, in total, 7.6 g of **10b** (18.5 mmol, 64%), which was isolated by fractional crystallization. Later crops contained **10b** and an isomer **10a** (0.8 g, 1.9 mmol, 6.7%): mp 151–153°; nmr δ 5.69, 5.80 (two singlets, hydrogens geminate to phenyl, C-2,4), and 7.40 ppm (single signal, C_6H_5). As with **8a** and **8b**, the distinctive crystal habits of **10a** and **10b** facilitated manual separation of the isomers.

Anal. Calcd for $C_{16}H_{12}BrClN_2O_4$: N, 6.80. Found, **10a**: N, 6.26. Found, **10b**: N, 6.46.

Dehalogenation of 8b and 4b with Sodium Iodide. Dibromo compound **8b** (0.23 g, 0.5 mmol) in 30 ml of acetic acid was treated with sodium iodide (0.25 g, 1.8 mmol) for 25 min on a steam bath. The dark reddish-brown mixture was quenched with ice water. Recrystallization of the precipitate gave colorless crystals (0.05 g, mp 145–165°) which consisted almost entirely of **4b** (ir analysis). The filtrate (0.03 g) was predominantly **4b**, but contained small proportions of **4a** and **1b**.

Treating **4b** (0.30 g, 0.8 mmol) in acetic acid with sodium iodide (0.60 g, 4 mmol) for 40 min on a steam bath and then quenching with ice water gave a crude product (0.22 g, 92%) which consisted of **1b** and a small proportion of **1a** (ir analysis). No **4b** was detectable in the product (chromatographic analysis).

Optical Resolution of 4a and 4b. Brucine tetrahydrate (1.24 g, 2.66 mmol) in 40 ml of benzene was mixed at 25° with **4b** (1.52 g, 4.0 mmol), also in 40 ml of benzene. After 3 hr the colorless precipitate was removed by filtration and the filtrate was washed four times with dilute hydrochloric acid. Unreacted **4b** and lesser amounts of **4a**, 1,3-dinitro-2,*trans*-4-diphenylcyclobutene (**11**), and *trans*,*trans*-1,3-dinitro-2,4-diphenylbutadiene[20b] were isolated chromatographically. Successive recrystallization from benzene–hexane, ethanol, and benzene–hexane gave 0.2 g of pure **4b**: mp 164–168°; $[\alpha]_D$ −20.8° (*c* 3.8, chloroform), $[\alpha]_D$ −24.9° (*c* 1.4, chloroform). In another experiment **4b** (1.65 g, 4.4 mmol) and brucine tetrahydrate (1.35 g, 2.9 mmol) were allowed to react as above. Separation and purification as before gave recovered **4b** (0.14 g), mp 163–166°, $[\alpha]_D$ −15.2° (*c* 3.9, chloroform), and lesser amounts of **4a** and **11**. The **4a** from both experiments was combined, rechromatographed, and recrystallized to give 0.04 g of product: mp 158–161°; $[\alpha]_D$ −32.5° (*c* 2.5, chloroform). This **4a** contained not over a few per cent **4b** (chromatographic analysis). Recrystallization of crude **11** combined from both experiments gave pure **11** (0.44 g), mp 110–112°, and *cis*,*cis*-1,3-dinitro-2,4-diphenylbutadiene (0.05 g), mp 105–106°.[20b] Recrystallization of *trans*,*trans*-1,3-dinitro-2,4-diphenylbutadiene from the first brucine reaction gave 0.04 g of product, mp 143–144°. No rotation was observed for solutions of **11** and the two butadienes in chloroform.

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(31) Accompanying **8a** and **8b** were monobromo compounds **4a** and **4b** (2.1 g, 3.7%). Mixed **4a** and **4b** were separated chromatographically from the more rapidly eluted **8a** and **8b**.

(32) Iodine reacts with **3** to give a mixture from which were isolated 1-iodo-1,3-dinitro-2,4-diphenylbutadiene (yellow, dec 130–133°, uv$_{max}$ 223 (EtOH) (ϵ 18,000) and 320 mμ (ϵ 16,000). *Anal.* Calcd for $C_{16}H_{11}IN_2O_4$: C, 45.49; H, 2.63; I, 30.06; N, 6.64. Found: C, 45.24; H, 2.62; I, 29.83; N, 6.46), 3-iodo-1,3-dinitro-2,4-diphenylcyclobutene (yellow, mp 129–131°. *Anal.* Calcd for $C_{16}H_{11}IN_2O_4$: C, 45.49; H, 2.63; I, 30.06; N, 6.64. Found: C, 47.07; H, 2.57; I, 29.06; N, 6.47), and 1-iodo-1,3-dinitro-2,4-diphenylcyclobutane (light tan, dec 180–187°. *Anal.* Calcd for $C_{16}H_{13}IN_2O_4$: C, 45.30; H, 3.10; I, 29.92; N, 6.61. Found: C, 45.57; H, 3.18; I, 29.64; N, 6.46). Reaction of the latter product with triethylamine gave **1a**, **1b**, and 1,3-dinitro-2,*trans*-4-diphenylcyclobutene (**11a**). The iodo compounds were difficult to purify and were not studied further.

1,*trans*-3-Diamino-*cis*-2,*trans*-4-diphenylcyclobutane (12a), 1,*cis*-3-Diamino-*cis*-2,*trans*-4-diphenylcyclobutane (12b), and Their Acetyl (13a and 13b), Benzoyl (14a and 14b), and Tosyl (15a and 15b) Derivatives. A. Catalytic Reduction. **1a** (3.0 g, 10 mmol) in 80 ml of tetrahydrofuran and 40 ml of acetic acid was hydrogenated (100 atm, 25°, 15 hr) over Raney nickel in a rocking bomb. After the hydrogen was vented, the reaction mixture was filtered and made strongly alkaline with aqueous sodium hydroxide. Extraction with ether gave a solution of diamine **12a** that was used for preparing derivatives.

B. Reduction with Zinc. To **1b** (1.0 g, 3.3 mmol) in 50 ml of acetic acid at 70° was gradually added 8 g of zinc dust during 0.5 hr. The reaction mixture was filtered, made strongly alkaline with sodium hydroxide, and extracted with ether. The resulting solution of diamine **12b** was used for derivatizations. As zinc–acetic acid reductions gave erratic results, catalytic reductions were usually used.

After drying over sodium hydroxide, an ether solution of **12a** was warmed several hours with acetic anhydride. Removal of the solvents and crystallization of the residue from ethanol–water gave a colorless diacetyl derivative **13a** (undetermined yield), mp 246–248° (lit.[22] mp 251–252°). The ir spectrum of **13a**, prepared from **1a**, was identical with the ir spectra of **13a** prepared from α-truxillic acid *via* the Curtius reaction.[33] An ethereal solution of **12b** (from the zinc–acetic acid reduction of **1b** (0.5 g, 1.67 mmol) was warmed 1 hr with excess acetic anhydride and pyridine. Several recrystallizations of the nonvolatile product from ethanol–water gave colorless diacetyl derivative **13b** (0.13 g, 0.42 mmol, 25%), mp 314–315°.

Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.52; H, 6.84; N, 8.70. Found, **13a**: C, 74.31; H, 6.88; N, 8.62. Found, **13b**: C, 74.23; H, 7.02; N, 8.51.

An ethereal solution of **12a** (from the catalytic reduction of **1a** (1.50 g, 5.0 mmol)) was stirred 1 hr at 25° with sodium hydroxide (70 ml, 0.2 *N*) and benzoyl chloride (1.5 g, 11 mmol). Recrystallization of the product from dimethylformamide–ethanol gave colorless dibenzoyl derivative **14a** (0.92 g, 2.1 mmol, 41%), mp 310–311°. Similarly, reaction of **12b** (from the catalytic reduction of **1b** (0.24 g, 0.82 mmol)) with benzoyl chloride gave colorless **14b** (0.15 g, 0.34 mmol, 42%), mp, α form, 244–245° (slow crystallization from dimethylformamide–ethanol). Rapid crystallization from solution gave a second β form of **14b** which ostensibly melted at 244–245° if the temperature was raised very slowly. When rapidly heated the β form melted at 200° or below, then resolidified and finally melted at 244–245°. By comparison of ir spectra, which differed slightly for the two forms, the thermal conversion of the β to the α form was confirmed.

Anal. Calcd for $C_{30}H_{26}N_2O_4$: C, 80.70; H, 5.83; N, 6.28. Found, **14a**: C, 80.78; H, 5.93; N, 6.42. Found, **14b**: C, 80.66; H, 5.81; N, 6.13.

Reaction of **12a** (from 5 mmol of **1a**) with tosyl(*p*-toluenesulfonyl) chloride by the same procedure as for benzoyl chloride gave ditosyl derivative **15a** (1.1 g, 2.0 mmol, 40%), mp, α form, 245–247° (slow crystallization from dimethylformamide–ethanol). Rapid crystallization gave a second β form of **15a**, mp 243–246°, having a slightly different ir spectrum. Resolidification of the melt gave the α form. Mixed **12a** and **12b** (from 16 mmol of mixed **1a** and **1b**) was allowed to react with tosyl chloride as before. Two recrystallizations from dimethylformamide–ethanol gave colorless ditosyl derivative **15b** (2.2 g), mp 293–295°. The filtrates were concentrated, washed with benzene to remove tars, and twice recrystallized from ethanol to give **15a** (1.2 g), mp 243–246° (total yield of **15a** and **15b**, 6.2 mmol, 39%).

Anal. Calcd for $C_{30}H_{30}N_2O_4S_2$: C, 65.92; H, 5.53; N, 5.12; S, 11.73. Found, **15a**:[34] C, 65.92; H, 5.41; N, 5.09; S, 11.71. Found, **15b**: N, 5.14.

Mixed **14a** and **14b** were also cleanly separable by fraction crystallization. The high melting **14a** crystallized first from dimethylformamide–ethanol; the more soluble **14b** then was crystallized from ethanol.

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(33) Independently prepared samples of **13a**, synthesized from α-truxillic acid, were kindly provided by Dr. H. C. Dunathan and Dr. F. Kennedy.

(34) Analyzed by Stanford University Microanalytical Laboratory.