Elimination Reactions of 1,3-Dihalo-1,3-dinitro-2,4-diphenylcyclobutanes and 1-Halo-1,3-dinitro-2,4-diphenylcyclobutanes. Chemistry of 1,3-Dinitro-2,4-diphenylcyclobutenes[1a,b]

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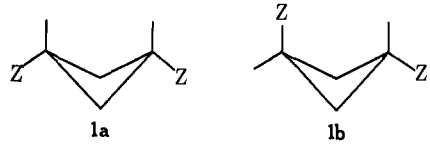
Abstract: *trans*-2,4-Diphenylcyclobutanes **2a**, **3a**, and **4a**, which have *cis*-1,3-dinitro and *cis*-1,3-dihalo (X = Br and/or Cl) groups, dehydrohalogenate exclusively anti to 3-halo-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutenes (**7a**, X = Br, and/or **8a**, X = Cl). *trans*-2,4-Diphenylcyclobutanes **2b**, **3b**, and **4b**, which have *trans*-1,3-dinitro and *trans*-1,3-dihalo (X = Br and/or Cl) groups, undergo competitive syn (25–74%) and anti dehydrohalogenation to **7a** and 3-bromo-1,*trans*-3-dinitro-2,*cis*-4-diphenylcyclobutene (**7b**) and/or **8a** and 3-chloro-1,*trans*-3-dinitro-2,*cis*-4-diphenylcyclobutene (**8b**). The anti dehydrohalogenations of **2a**, **3a**, and **4a** are attributed to the e,e conformations of the *cis*-nitro groups and the pronounced folding of the cyclobutane rings. Competitive syn and anti dehydrohalogenations of **2b**, **3b**, and **4b** presumably arise from offsetting a,e conformations of the *trans*-nitro groups which lead to relatively less-folded cyclobutane rings. Dehydrobromination of bromochloro dihalides **4a** and **4b** is five–seven times faster than dehydrochlorination. Bases dehydrohalogenate 1-halo-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutanes (**5a**, X = Br, and **6a**, X = Cl) and 1-halo-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutanes (**5b**, X = Br, and **6b**, X = Cl) to mixtures of 1,3-dinitro-2,*cis*-4-diphenylcyclobutene (**10a**) and 1,3-dinitro-2,*trans*-4-diphenylcyclobutene (**10b**). Acidification of the highly delocalized nitrocyclobutenenitronate salt **11** from **10a** and **10b** ($pK \sim 8.5$) results in preference for protonation trans to the 4-phenyl group to give a 2:1 mixture of **10a** and **10b**. In ethanol the equilibrium stability of **10b** is greater (~2:1) than that of **10a**. Bromination and chlorination of **11** occur mainly trans to the 4-phenyl groups to yield **7a** and **8a**. Debromination of **7a** by sodium iodide in acetic acid results in **10a** and **10b** in a 2:1 ratio. Bromocyclobutenes **7a** and **7b** interconvert in polar or basic environments presumably *via* nitronate **11**.

Cyclobutanes have been of interest with respect to their conformational properties[2] and their stereochemistry of elimination.[3] Such four-membered systems are nonplanar because of torsional effects; their folded rings (up to >40°) lead to pseudoaxial and pseudoequatorial positioning of their substituents.[2] For cyclobutanes containing substituents in 1,2 positions, trans isomers are the more stable.[2b] For 1,3 derivatives, cis (diequatorial; e,e) isomers, **1a**, are generally of lower energy,[2a] and the ring systems are possibly more folded than are the trans (axial, equatorial; a,e) isomers, **1b**.[2f] Hofmann elimination of *cis*-2d-cyclobutyl-*N*,*N*,*N*-trimethylammonium hydroxide at 50° occurs by a syn (90%) stereochemical process.[3a] On the other hand, anti elimination of *cis*-2-phenylcyclobutyl tosylate by potassium *tert*-butoxide occurs 2.5 times faster than does syn elimination of *trans*-2-phenylcyclobutyl tosylate.[3b] No other studies have been reported of the stereochemistry of elimination of cyclobutanes; however, the abilities for syn as compared to anti elimination in cyclic compounds increase as ring size decreases from six to five carbon atoms.[4]



1a **1b**

1,3-Dihalo-1,3-dinitro-2,4-diphenylcyclobutanes (**2a–4b**) and 1-halo-1,3-dinitro-2,4-diphenylcyclobutanes (**5a–6b**) of known stereochemistry are available from base-catalyzed halogenation of the photodimer of *trans*-β-nitrostyrene, 1-*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane.[5a] Reactions of bases with these halogenated derivatives have been presently investigated because they offer the possibility of study of competitive syn and anti dehydrohalogenations. The effects of structure and leaving groups on elimination reactions generally are studied by comparing the behavior of different stereoisomers and different stereoanalogs which give the same unsaturated elimination product.

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(1) (a) Initial observations in these systems are described in 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, and the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept, 1970, Abstracts, No. ORGN-69.

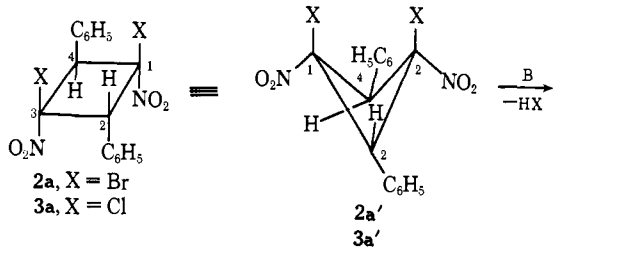
(2) For discussion and additional references concerning the conformational properties of cyclobutanes, see (a) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 389 (1965); (b) N. L. Allinger and L. A. Tushaus, *J. Org. Chem.*, **30**, 1945 (1965); (c) K. B. Wiberg and G. M. Lampman, *J. Amer. Chem. Soc.*, **88**, 4429 (1966); (d) T. N. Margulis and M. S. Fisher, *ibid.*, **89**, 223 (1967); (e) I. Lillien, *J. Org. Chem.*, **32**, 4152 (1967); (f) I. Lillien and R. A. Doughty, *J. Amer. Chem. Soc.*, **89**, 155 (1967); (g) I. Lillien and R. A. Doughty, *Tetrahedron*, **23**, 3321 (1967); and (h) I. Lillien and R. A. Doughty, *Tetrahedron Lett.*, 3953 (1967).

(3) (a) J. L. Coke, M. P. Cooke, Jr., and M. C. Mourning, *ibid.*, 2247 (1968); (b) C. H. DePuy, C. G. Naylor, and J. A. Beckman, *J. Org. Chem.*, **35**, 2750 (1970).

(4) (a) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Amer. Chem. Soc.*, **78**, 3468 (1956); (b) C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *ibid.*, **87**, 2421 (1965).

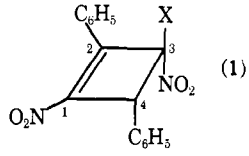
(5) (a) See accompanying manuscript: D. B. Miller, P. W. Flanagan, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 3912 (1972); (b) in the present manuscript the **a** series of cyclobutanes has *cis*-1,3-dinitro groups; the **b** series has *trans*-1,3-dinitro groups. The **a** series of cyclobutenes has their 3-nitro and 4-phenyl groups cis; the **b** series has *trans*-3-nitro and 4-phenyl groups. Compounds **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, and **10b** of the present manuscript correspond, respectively, to **8b**, **8a**, **9b**, **9a**, **10b**, **10a**, **4b**, **4a**, **5b**, **5a**, and **11** of ref 5a.

Scheme I



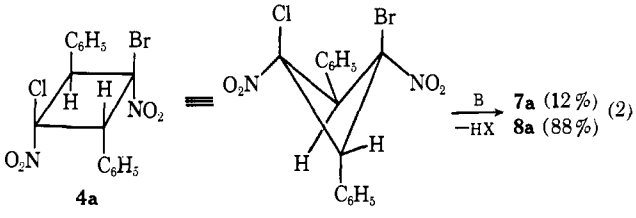
2a, X = Br
3a, X = Cl

2a′
3a′



(1)

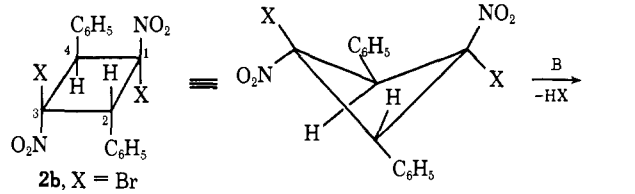
7a, X = Br
8a, X = Cl



4a

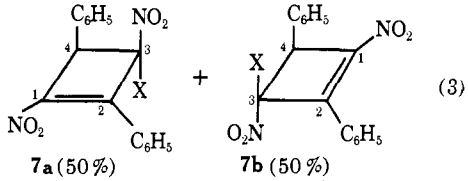
4a′

(2)



2b, X = Br
3b, X = Cl

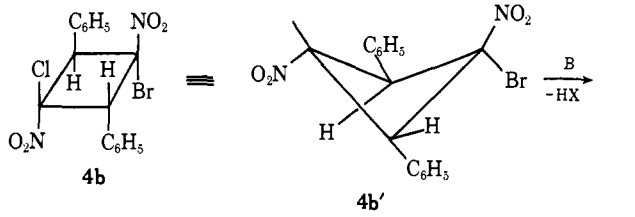
2b′
3b′



7a (50%)
8a (74%)

7b (50%)
8b (26%)

(3)



4b

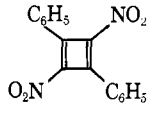
4b′

7a (12%), **7b** (5%)
8a (13%), **8b** (70%) (4)

Each of the dihalocyclobutanes of the present study can give two or more elimination products; the observed products reflect the relative preferences of the dihalo compounds for one or another mode of elimination and the relative elimination tendency of one or another halogen. Centrosymmetric compounds **2b** and **3b** are particularly noteworthy in that attack by base at either of the identical cyclobutyl hydrogens can result in either syn or anti elimination. In compound **4a** attack at one cyclobutyl hydrogen can result in syn dehydrobromination or dehydrochlorination while attack at the other hydrogen can result in anti dehydrobromination or dehydrochlorination. Eliminations of cyclobutanes **2a–6b** are also of interest in that synthesis and study of a variety of 1,3-dinitro-2,4-diphenylcyclobutenes (**7a–8b** and **10a–10b**) are allowed.

Results and Discussion

Bases dehydrohalogenate dihalides **2a–4b** rapidly and quantitatively to 3-bromo- (**7a–7b**) and 3-chloro-1,3-dinitro-2,4-diphenylcyclobutenes (**8a–8b**) (Scheme I). Reactions of dibromides **2a** and **2b** with pyridine in benzene at 25° are complete within 5 min; under comparable conditions dichlorides **3a** and **3b** dehydrohalogenate more slowly (>5, <20 min) than do **2a** and **2b**. The stereochemical assignments of the various 3-halocyclobutenes (**7a–8b**) will be discussed later.[6] 1,3-Dinitro-2,4-diphenylcyclobutadiene (**9**) was not isolated in any experiment.



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Conversion of **2a–4b** to cyclobutenes **7a–8b** reveals dramatic differences in the stereochemistry of dehydrohalogenation. Dihalides **2a**, **3a**, and **4a** have their nitro groups cis and dehydrohalogenate exclusively anti to cyclobutenes **7a** and **8a** (eq 1 and 2). On the other hand dibromide **2b** which has *trans*-nitro groups undergoes anti elimination (50%) to **7b** and syn elimination (50%) to **7a** at the same rates (eq 3). Dichloride **3b** (eq 3) has its nitro groups trans and eliminates primarily syn (74%) to **8a**; anti dehydrochlorination to **8b** is minor (26%). Bromochloro derivative **4b** contains *trans*-nitro groups and gives major (70%) anti dehydrobromination to **8b** (eq 4); syn dehydrobromination (13%) to **8a** and anti dehydrochlorination (5%) to **7b** occur slower than do their alternate stereochemical elinination processes. The results of the present study thus reveal that cyclobutanes having their 1,3-nitro groups cis undergo total anti elimination; the cyclobutanes with 1,3-nitro groups trans give competitive syn and anti elimination.

Although it has not been established whether **2a–4b** dehydrohalogenate by E2 and/or E1cB processes, it is highly likely that the dihedral angles between departing groups play important roles in the elimination reactions.[8] Coplanar transition states (dihedral angles of 180 and 0°) are the most favorable for dehydrohalogenation.[4b] As previously reported,[4b] when the di-

(6) The isomeric 3-halocyclobutenes (**7a–8b**) do not interconvert under the conditions of dehydrohalogenation. In preparative dehydrohalogenation experiments, the cyclobutenes are isomerized[7] in part to 1-halo-1,3-dinitro-2,4-diphenylbutadienes.

(7) (a) D. B. Miller, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract ORGN-106; (b) D. B. Miller, P. W. Flanagan, and H. Shechter, to be published.

(8) (a) Dehydrochlorination of (2-chloroethyl)benzene involves an E2 mechanism.[8b] (b) Reaction mechanisms of the E1cB type are extremely rare; for a review of E2 *cis-a-cis* E1cB mechanisms of elimination, see: D. J. McLennan, *Quart. Rev., Chem. Soc.*, **21**, 490 (1967). (c) The stereochemical proposals for the present results accommodate E1cB as well as E2 mechanisms. In E1cB processes favored dihedral angles for elimination between the p orbital of an intermediate carbanion (of sp^3 character)[8d] and the departing group should be analogous to those for E2 processes. (d) P. W. Flanagan, H. W. Amburn, H. Stone, J. G. Traynham, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 2797 (1969).

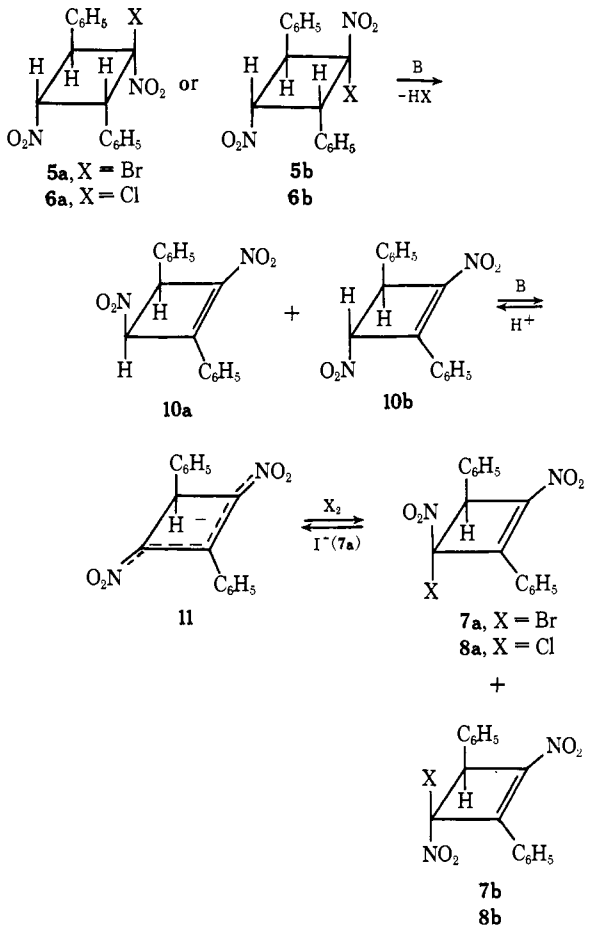
hedral angle of the leaving groups is 180°, anti elimination is strongly favored (the dihedral angle for the alternative syn process is ~60°). For systems in which the dihedral angle of the leaving groups is 0°, syn elimination is favored because the dihedral angle for the anti process is only ~120°. For intermediate dihedral angles, eliminations *via* pseudo syn and anti modes may occur at comparable rates.

As previously indicated, nitro groups have larger conformational energies than do halogens.[5,9] It is thus likely that dihalocyclobutanes **2a**, **3a**, and **4a**, which have nitro groups in cis 1,3 configurations, will assume conformations in which the nitro groups are e,e. To achieve this conformation entails pronounced folding of the cyclobutane ring. On the other hand, dihalocyclobutanes **2b**, **3b**, and **4b**, having their nitro groups trans, must assume conformations in which the nitro groups have one of two equivalent a,e conformations, or intermediate conformations which are relatively planar. Because of the offsetting effects of trans groups there is little advantage in having one or the other of the nitro groups in an equatorial position. It is therefore to be expected that trans compounds **2b**, **3b**, and **4b** will assume relatively planar conformations that are intermediate between the equivalent e,a–a,e conformations. Thus, cyclobutanes having cis 1,3 substituents should deviate more from planarity[2e-h] than cyclobutanes which are trans 1,3 disubstituted.[10]

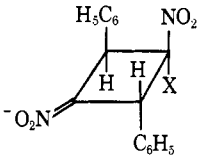
The more folded conformations proposed for cis-1,3 derivatives **2a**, **3a**, and **4a** and the relatively planar conformations proposed for *trans*-1,3-dinitro compounds **2b**, **3b**, and **4b** are depicted as **2a'**, **3a'**, and **4a'** (eq 1 and 2) and **2b'**, **3b'**, and **4b'** (eq 3 and 4), respectively. If these suppositions are correct the more folded cis compounds **2a**, **3a**, and **4a** permit nearly coplanar anti dehydrohalogenations, whereas the less folded trans structures **2b**, **3b**, and **4b**, for which syn or anti coplanar eliminations are excluded, undergo syn and anti dehydrohalogenations at comparable rates. In the elimination reactions of **4a** and **4b**, dehydrobromination occurs five–seven times faster than dehydrochlorination. This ratio is somewhat smaller than the values of ~35–60 reported for the relative rates of dehydrobromination and dehydrochlorination (E1 or E2) for various primary, secondary, and tertiary halides.[11]

Dehydrobromination of **5a** by triethylamine at 25° and dehydrochlorination of **6a** (in low yield) by aqueous sodium hydroxide–tetrahydrofuran occur sluggishly to give isomeric 1,3-dinitro-2,4-diphenylcyclobutenes (**10a** and **10b**, Scheme II). Similar results were obtained with **5b** and **6b** (Scheme II). Because these dehydrohalogenations occur much more slowly than does formation of nitronates **12** and **13**, and because of the rapid interconversion of **10a** and **10b** *via* nitronate

Scheme II



ion **11**, the compositions of the elimination products do not provide any information concerning the stereochemistry of dehydrohalogenation of **5a–6b**. In an



accompanying manuscript[5] it was reported that resolution of **5a** with brucine results in optically inactive **10b** along with other products. Although **10a** and **10b** are each dissymmetric and potentially resolvable, mesomeric anion **11** possesses a plane of symmetry through C-2 and C-4 and cannot be optically active. Base-catalyzed ionization of optically active **10a** and **10b** produced in the resolution of **5a** with brucine thus results in racemization of the dinitrocyclobutenes.[5]

The pK_a of **10a–10b**, determined by titration with sodium hydroxide in aqueous ethanol, is ~8.5. Since the pK_a values of nitrocyclobutane (33% methanol–water), 2-nitrobutane (50% aqueous ethanol),[12] and phenylnitromethane (50% aqueous ethanol) are 9.5, 9.4, and 8.2, respectively, it is evident that the enhanced acidity of **10a–10b** arises primarily from the stability of the delocalized symmetrical nitrocyclobutene nitronate

(9) J. A. Hirsch, *Top. Stereochem.*, 1, 202, 216 (1967).

(10) (a) Recent data[10b] based on dipole moments of 1,3-dihalocyclobutanes indicate that, as the substituents become larger, folding of the cis isomers increases whereas folding of the trans isomers decreases. Thus the fold angles of the *cis*-1,3-dichloro-, dibromo-, and diiodocyclobutanes are 32, 38, and ~48°, respectively, whereas those of the corresponding trans isomers are 37, 32, and 24°; for *trans*-1,3-dibromo-1,3-dimethylcyclobutane the fold angle is 14°. (b) G. R. Lampman, private communication, to be published.

(11) (a) E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937); (b) K. A. Cooper and E. D. Hughes, *ibid.*, 1183 (1937); (c) E. D. Hughes and B. J. MacNulty, *ibid.*, 1283 (1937); (d) H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.*, **76**, 455 (1954); (e) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957); (f) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2535 (1960).

(12) N. Kornblum, R. K. Blackwood and J. W. Power, *J. Amer. Chem. Soc.*, **79**, 2508 (1957).

ion, **11**.[13] The extensive conjugation in **11** is also indicated by its intense red color, a consequence of absorption at 500–560 mμ (ε 15,000–20,000).

Acidification of **11** instantly discharged the red color. Under conditions of kinetic control for protonation, the resulting mixture consisted of **10a** and **10b** in a ratio of ~2:1 (Scheme II). In the protonation of **11**, hydronium ion can attack the nitrocyclobutenenitronate ion cis or trans to the 4-phenyl group. The ratio of **10a** to **10b** found shows that there is moderate preference for protonation at the face of the planar four-membered ring opposite the 4-phenyl group. In ethanol at 25°, **10a** and **10b** equilibrate (Scheme II) in a ratio of ~1:2, the reverse of the kinetic ratio. The greater thermodynamic stability of **10b** than **10a** is in accord with the expectation that a compound containing phenyl vicinal to nitro experiences less steric strain when the groups are trans than when cis.

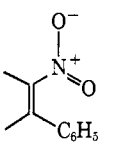
Structures were initially assigned to **10a** and **10b** on the basis of the composition of their equilibrium mixture and the composition of the protonation product of **11** as kinetically controlled. These assignments are confirmed by nmr methods. In cyclobutenes cis and trans vicinal allylic hydrogens have dihedral angles of about 0 and 120°, respectively, and thus the coupling constants for such cis hydrogens are greater than those for trans hydrogens.[14] The signals of the allylic hydrogens at C-3 and C-4 in **10a** and **10b** constitute the pairs of doublets expected for unlike vicinal hydrogens. The coupling constants are 5.4 and 1.2 Hz, respectively, and **10a** therefore has cis vinylic hydrogens.

Bromination of **11** (Scheme II) gave a mixture of bromodinitrodiphenylcyclobutenes **7a** and **7b** in which the former predominated (~70%).[15a] Similarly, chlorination of **11** resulted in a mixture of chloro compounds among which **8a** was the major product. Following the arguments applied to protonation of **11**, the predominant halogenation products (**7a** and **8a**) have the 3-nitro and 4-phenyl groups in cis configurations.[15b,c]

Bromocyclobutene **7a** was debrominated readily and in high conversion by sodium iodide in acetic acid at 20° (Scheme II) to give a mixture of **10a** and **10b** in approximately a 2:1 ratio. Since in this reaction **11** is generated in an acidic medium, the product mixture again is determined by the kinetically controlled protonation step. Chlorocyclobutene **8a**, unlike **7a**, was not dehalogenated by sodium iodide.

Bromocyclobutenes **7a** and **7b** undergo interconversion at 25° in acetone, dimethyl sulfoxide, or in benzene containing triethylamine by reactions analogous to those in Scheme II. These isomerizations apparently involve attack of the basic environment on bromine of **7a** and **7b** to form nitronate anion **11** which then reacts with the electrophilic brominating agents generated.[16,17] Accompanying this interconversion are valence isomerizations leading to butadienes;[6,15] therefore, determination of the equilibrium compositions of **7a** and **7b** was not attempted. Isomerization of chlorocyclobutene **8b** to **8a** was not appreciable in dimethyl sulfoxide.

Cyclobutenes **7a–8b**, **10a**, and **10b** have very similar ultraviolet spectra; the *cis*-β-nitrostyrene chromophores in these compounds absorb maximally at 329–332 mμ (ε 10,000–13,000 in EtOH).[18] For acyclic β-nitrostyrenes (*e.g.*, β-nitrostyrene and its α- and β-methyl derivatives) trans isomers have absorption maxima at 293–310 mμ (ε 12,000–17,000) whereas cis isomers absorb at shorter wavelengths (282–306 mμ) and/or have diminished intensities (ε 3000–6000).[7] The diminished absorptions of acyclic *cis*-β-nitrostyrenes are attributable to the inability of their nitro and phenyl groups to become coplanar. Incorporation of the ethylenic carbons of a β-nitrostyrene chromophore into a four-membered ring should spread the *cis*-nitro and phenyl groups apart (*cf.* **14** and **15**). The relatively long-wave-



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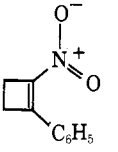

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length absorptions for cyclobutenes **7a–8b**, **10a**, and **10b** appear to result from the abilities of the conjugated nitro and phenyl groups to become (nearly) coplanar and from the steric strain in the conjugated chromophores.[19]

Experimental Section[20]

Dehydrobromination of 1,*trans*-3-Dibromo-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (2b) and 1,*cis*-3-Dibromo-*trans*-1,-

(13) Neutralization of **10a** and **10b** occurs very rapidly. The dinitrocyclobutenes are acids of considerable strength in spite of the cis steric interactions and the difficulty of solvation of the bulky ion **11**.

(14) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); (b) S. Masamune and F. Fukumoto, *Tetrahedron Lett.*, 4647 (1965); (c) E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967).

(15) (a) Since **7a** isomerizes in part to its 1,3-butadiene,[6] the diene was included in the yield of **7a**. (b) Bromination, chlorination, and protonation of the 3-nitro-*cis*-2,*trans*-4-diphenylcyclobutanenitronate, 3-bromo-*trans*-3-nitro-*cis*-2,*trans*-4-diphenylcyclobutanenitronate, and 3-chloro-*trans*-3-nitro-*cis*-2,*trans*-4-diphenylcyclobutanenitronate ions have been studied previously.[5a] From the structures of the major and minor products of each reaction,[5a] it is clear that the stereochemistry of halogenation is similar to that of protonation. (c) The nmr spectra of **7a**, **7b**, **8a**, and **8b** are so similar that structural assignments could not be confirmed by this method. Strongly supportive evidence for the structural assignments of **7a–8b** was provided by their thermal isomerization to 1,3-butadienes of established stereochemistry.[7a] Cyclobutenes **7a** and **8a** undergo quantitative conrotatory ring opening ($k_{56°} \sim 60 \times 10^{-6}$ sec^{-1} and 110×10^{-6} sec^{-1}, respectively) to the corresponding *cis*,*trans*-1-halo-1,3-dinitro-2,4-diphenylbutadienes. Thermal isomerization of **7b** occurs slowly ($k_{56°} \sim 0.1 \times 10^{-6}$ sec^{-1}), reversibly, and conrotatively to *cis*,*cis*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene. An insufficient sample prevented a detailed study of thermal isomerization of **8b**. The structures of the 3-halo-1,3-dinitro-2,4-diphenylbutadienes were assigned by comparing their nmr spectra with that of the model compounds: *cis*- and *trans*-β-nitrostyrenes, and the α-methyl, β-methyl, β-bromo, and β-chloro derivatives of *cis*- and *trans*-β-nitrostyrenes (cis and trans denote the relative geometries of the nitro and phenyl groups in the β-nitrostyrene moieties). Details of the valence isomerizations and of the preparation and characterization of the nitrostyrenes will be published separately.[7b]

(16) Cyclobutenes **10a** and **10b** may be prepared from 1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane *via* **5a** or *via* **2a** and **7a**. The latter sequence, though longer, is preferred because the reactions are cleaner and the products are easier to isolate.

(17) Bromocyclobutene **7b** may be obtained by (a) dehydrobromination of **2b**, (b) bromination of **11**, and (c) isomerization of **7a**. Unlike **2b** and **11**, **7a** is easily prepared in large quantity and method c is the preferred route to **7b**.

(18) The cyclobutenes exhibit maximum absorption at 322–327 mμ in cyclohexane.

(19) H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 197.

(20) (a) The general techniques used in this research are described in ref 5. For measuring uv spectra, the solvent was cyclohexane if not otherwise indicated. (b) To prevent interconversion of **10a** and **10b** during chromatography, adsorbents were treated with hydrogen chloride.

trans-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (2a). **Preparation of 3-Bromo-1,*trans*-3-dinitro-2,*cis*-4-diphenylcyclobutene (7b) and 3-Bromo-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutene (7a).** A mixture of **2b** (0.39 g, 0.85 mmol) and pyridine (0.3 g, 3.8 mmol) in benzene at 20° within a few seconds became yellow and deposited a white precipitate. After 10 min, the mixture was filtered and concentrated to dryness in a stream of air. Recrystallization gave fine yellow needles of **7a** (0.15 g): mp 130–132°; uv max 218, 326 mμ (ε 20,000 and 11,000); nmr δ 5.18 (s, allylic H) and 7.1–7.6, 8.1–8.3 ppm (m, C_6H_5). The supernatent liquid was chromatographed to give yellow prisms or columns of **7b** (0.10 g, 0.27 mmol, 31%) [mp 124–125° (α modification); uv max 218, 327 mμ (ε 18,000 and 10,000); nmr δ 5.09 (s, allylic H) and 7.1–7.6, 8.1–8.3 ppm (m, C_6H_5)], and 0.02 g of the more slowly eluted **7a** (total 0.16 g, 0.42 mmol, 49%). The original reaction mixture contained 50% **7b** and 50% **7a** (nmr analysis). Sometimes **7b** crystallized in a second (β) form that partly melted at 117–118°, with complete melting at 125°. The α and β forms of **7b**, as solids, gave differing ir spectra (Nujol mulls), but when dissolved, the two forms had identical ir spectra and identical nmr spectra. Detectable isomerization of **7b** in benzene containing pyridine did not occur in 15 min at 25° (chromatographic analysis).

Anal. Calcd for $C_{16}H_{11}BrN_2O_4$: C, 51.21; H, 2.96; Br, 21.30; N, 7.47. Found, **7a**: C, 51.36; H, 2.89; Br, 20.94; N, 7.13. Found, **7b**: C, 51.41; H, 2.88; Br, 21.09; N, 7.86.

Similarly, mixing pyridine (1.6 g, 20 mmol) and **2a** (7.60 g, 17 mmol) in benzene gave within a few seconds a yellow solution and a white precipitate. The products, isolated by fractional crystallization and by chromatography, were **7a** (4.47 g, 12 mmol, 73%), mp 129–131°, ir spectrum identical with **7a** obtained from **2b**, and *cis*,*trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene[7] (1.57 g, 4.3 mmol, 26%), mp 124–125°. Only **7a** was detectable in the original reaction mixture (nmr and chromatographic analyses).

Dehydrochlorination of 1,*trans*-3-Dichloro-*trans*-1,*cis*-3-dinitro-cis-2,*trans*-4-diphenylcyclobutane (3b) and 1,*cis*-3-Dichloro-*trans*-1,-*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (3a). Preparation of 3-Chloro-1,*trans*-3-dinitro-2,*cis*-4-diphenylcyclobutene (8b) and 3-Chloro-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutene (8a). Treating **3b** (0.367 g, 1.0 mmol) in benzene–hexane at 20° with pyridine (0.3 g, 3.8 mmol) gave within a few seconds a turbid yellow mixture which in about 1 min began depositing a white precipitate. After 1 hr the mixture was filtered and the filtrate was concentrated and crystallized, giving two crops of **8a** (0.21 g, 0.63 mmol, 63%) as fine yellow needles: mp 127–129°; uv max 217, 322 mμ (ε 18,000 and 11,000); nmr δ 5.10 (s, allylic H) and 7.1–7.7, 8.0–8.3 ppm (m, C_6H_5). From the filtrates were chromatographically separated **8b** (0.07 g, 0.21 mmol, 21%) as yellow prisms (mp 109–110°; uv max 218 sh, 324 mμ (ε 18,000 and 11,000); nmr δ 5.15 (s, allylic H), 7.1–7.7l, 8.0–8.2 ppm (C_6H_5)), and the more slowly eluted *cis*,*trans*-1-chloro-1,3-dinitro-2,4-diphenylbutadiene[7] (0.015 g, 0.04 mmol, 4%) as yellow pellets, mp 128–132°. The original reaction mixture contained 74% **8a** and 26% **8b**.

Anal. Calcd for $C_{16}H_{11}ClN_2O_4$: C, 58.10; H, 3.36; Cl, 10.72; N, 8.47. Found, **8a**: N, 8.02. Found, **8b**: C, 58.11; H, 3.38; Cl, 11.28; N, 8.10.

Similarly, a mixture of pyridine (0.3 g, 3.8 mmol) and **3a** (0.55 g, 1.5 mmol) in benzene–hexane at 0° gradually became turbid; precipitation began after about 15 min. After several hours at 30–40°, the mixture was filtered, concentrated, and recrystallized to give two crops (0.38 g), **8a**, mp 126–129°; not depressed by **8a** prepared from **3b**. From the supernatent liquid was chromatographically separated 0.02 g more of **8a** (total 0.40 g, 1.21 mmol, 81%) and *cis*,*trans*-1-chloro-1,3-dinitro-2,4-diphenylbutadiene[7] (0.04 g, 0.12 mmol, 8%) as yellow pellets, mp 133–136°. Only **8a** was present in the original dehydrochlorination product from **3a**.

Dehydrohalogenation of 1-Bromo-*trans*-3-chloro-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (4b) and 1-Bromo-*cis*-3-chloro-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (4a). After 0.5 hr at 15–20° the reaction mixture of pyridine (0.038 g) and **4b** (0.15 g) in benzene was filtered and concentrated to dryness. The product (0.15 g, mp 90–105°) contained approximately 12% **7a**, 5% **7b**, 13% **8a**, and 70% **8b** (nmr analysis). That **8b** was the principal product was also clearly evident from the ir spectrum. At similar conditions 0.25 g of pyridine and 1.0 g of **4a** gave 0.80 g of product containing predominantly **8a** (ir analysis); nmr analysis gave 12% **7a** and 88% **8a**.

Dehydrobromination of 1-Bromo-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (5a) and 1-Bromo-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (5b). A mixture of triethylamine (0.25 g, 2.5 mmol) and **5a** (0.75 g, 2.0 mmol) in benzene at 25° slowly became amber colored and deposited a needle-like precipitate. After 4 hr the mixture was filtered and chromatographed to give **10b** (0.30 g, 1.0 mmol, 50%) and the more slowly eluted **10a** (0.08 g, 0.27 mmol, 14%). Recrystallization of the former gave pure **10b** as yellow prisms: mp 111–113°; uv max 220, 319 mμ (ε 20,000 and 13,000); uv max (methanol) 222, 327 mμ (ε 19,000 and 12,000); nmr δ 4.77, 5.32 (two doublets, J = 1.2 Hz, hydrogens geminal to phenyl, C-4, and nitro, C-3) and 7.1–7.6, 7.9–8.1 ppm (m, C_6H_5). Pure **10a** crystallized as yellow needles: mp 127–129°; uv max 218, 319 mμ (ε 20,000 and 13,000); nmr δ 5.06, 5.92 (two doublets, J = 5.4 Hz, hydrogens geminal to phenyl, C-4, and nitro, C-3) and 7.1–7.6, 7.9–8.1 ppm (m, C_6H_5).

Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.85; H, 4.09; N, 9.47. Found, **10a**: C, 65.04; H, 4.23; N, 9.28. Found, **10b**: C, 64.98; H, 4.32; N, 9.07.

Dehydrobromination of mixed **5a** and **5b** also gave a mixture of **10a** and **10b**. Purification of **10a** was sometimes made difficult by the presence of *trans*,*trans*-1,3-dinitro-2,4-diphenylbutadiene,[7] an isomer of **10a** and **10b**.

Dehydrochlorination of 1-Chloro-*trans*-1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (6a) and 1-Chloro-*trans*-1,*cis*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane (6b). Although mixed **6a** and **6b** in benzene at 25° gave a precipitate within a few minutes, work-up of the reaction mixture after acidification with acetic acid gave recovered **6a** and **6b** rather than **10a** and **10b**. In another reaction, mixed **6a** and **6b** (1.0 g, 3.0 mmol) in tetrahydrofuran (75 ml) was treated at 0–10° with aqueous sodium hydroxide (75 ml, 0.1 N). Acidification after 10 min gave a product containing **10a** and **10b** (chromatographic analysis). Recrystallization gave **10a** (0.07 g, 0.2 mmol, 8%), mp 121–129°, identified by its ir spectrum.

Preparation of 1,3-Dinitro-2,*cis*-4-diphenylcyclobutene (10a) and 1,3-Dinitro-2-*trans*-4-diphenylcyclobutene (10b) by Reduction of 7a with Sodium Iodide–Acetic Acid. A mixture of sodium iodide (5.0 g, 33 mmol) and **7a** (1.5 g, 4.0 mmol) in 500 ml of acetic acid at 20° became deep red brown in 5–10 min. Addition (after 1 hr) of the mixture to ice water gave an emulsion that precipitated when treated with concentrated hydrochloric acid. One portion (25%) of the product was used for nmr analysis and contained 63% **10a** and 37% **10b**. The remainder of the product was recrystallized to give two crops (0.34 g) of **10a**, mp 127–129, 120–127°, identified by its ir spectrum. The uncrystallized material was chromatographed, giving 0.06 g more of **10a** (total 0.40 g, 1.4 mmol, 45%) and **10b** (0.23 g, 0.78 mmol, 26%), mp 110–112°, also identified by its ir spectrum. In subsequent preparations, both **10a** and **10b** were isolated by fractional crystallization of their mixtures.

When **10b** was the preferred product, the reaction products from **7a** (12.5 g, 33 mmol) and sodium iodide (15 g, 100 mmol) were equilibrated (see following paragraph) for 24 hr at 5° in acetone containing 1% pyridine and then recovered by precipitation with water. Fractional crystallization gave 3.4 g of **10b** and 1.3 g of **10a**. The uncrystallized material was again equilibrated in acetone–pyridine, recovered, and fractionally crystallized. The **10b** was retained; the uncrystallized material and unneeded **10a** were again equilibrated, recovered, and fractionally crystallized. This procedure gave in all **10b** (6.09 g, 20.6 mmol, 62%), **10a** (1.65 g, 5.6 mmol, 17%), and *trans*,*trans*-1,3-dinitro-2,4-diphenylbutadiene[7] (0.62 g, 2.1 mmol, 6.3%).

Interconversion of 10a and 10b. Sodium 1-Nitro-2,4-diphenylcyclobutene-3-nitronate (11). Attempts to equilibrate **10a** and **10b** in ethanol at 50–60° were complicated by the formation of *trans*,-*trans*-1,3-dinitro-2,4-diphenylbutadiene.[7] It was clear, however, that **10b** was the principal component of the **10a**–**10b** mixture. After 3 days at 25°, a solution of **10a** in ethanol was precipitated by addition to dilute hydrochloric acid. The recovered material contained 32% **10a** and 59% **10b** (ir analysis).

Titration of **10b** (0.06 g, 0.2 mmol) in 95% ethanol (21 ml) required 21 ml of 0.01 N sodium hydroxide (0.21 mmol); the pH at the half-neutralization point was 8.6. This solution was in turn titrated with 0.02 N hydrochloric acid; at the half-neutralization point the pH was 8.3. Salt **11**, which was not isolated, has a brilliant red color: uv max (90% water–10% ethanol) 360, 500 mμ (ε 6000 and 15,000); (95% ethanol) 342, 557 mμ (ε 8000 and 20,000); acidification caused immediate decolorization.

A solution of **11**, prepared from **10b** (1.5 g, 5.0 mmol) in 90 ml of tetrahydrofuran and 65 ml of sodium hydroxide (0.089 N, 5.9 mmol) at 10°, was diluted with ice water to 500 ml. Part (100 ml) of the red solution was added to a dilute aqueous solution of acetic acid and urea. The resulting precipitate contained 65% **10a** and 30% **10b** (ir analysis). Another part (300 ml) of the solution of **11** was

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

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

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

Cyclopropanols. IX. Cyclopropoxy Radicals from Cyclopropyl Nitrites

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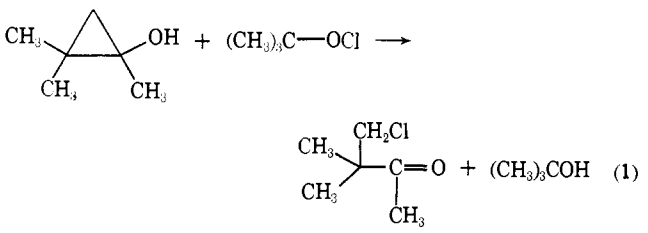
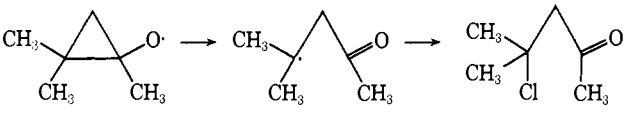
Abstract: Cyclopropyl nitrite esters decompose homolytically at very low temperatures (−80 to +20°) compared to ordinary aliphatic nitrite esters. The relative stability of the esters and the direction of ring opening are dependent upon the substitution pattern of the cyclopropanol. Those nitrite esters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

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

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



(1)



(2)

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

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

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

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

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