Stereochemistry of Thermal Isomerization of 1,3-Dinitro-2,4-diphenylcyclobutenes and 1,3-Dinitro-2,4-diphenylbutadienes. Cis,Trans Isomerism of β-Nitrostyrenes[1]

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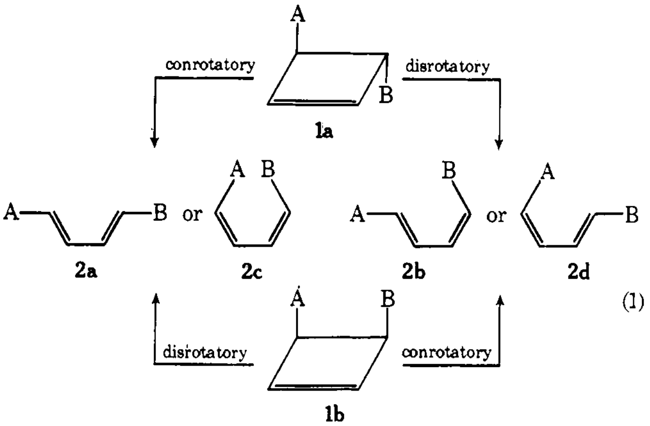
Thermal isomerization of 1,3-dinitro-2,*trans*-4-diphenylcyclobutene (**3a**) results initially in reversible outward conrotation of its *trans*-3-nitro and 4-phenyl groups to give *cis,cis*-1,3-dinitro-2,4-diphenylbutadiene (**6a**). *cis,trans*-1,3-Dinitro-2,4-diphenylbutadiene (**6b**) and *trans,trans*-1,3-dinitro-2,4-diphenylbutadiene (**6c**) are formed more slowly. 1,3-Dinitro-2,*cis*-4-diphenylcyclobutene (**3b**) isomerizes by an apparently disrotatory process to **6c**. The expected conrotatory product, diene **6b**, is excluded as an initial intermediate in conversion of **3b** to **6c**. The alternate product of conrotatory isomerization of **3b**, *trans,cis*-1,3-dinitro-2,4-diphenylbutadiene (**6d**), was not found. The rates of ring opening of **3a** and **3b** are similar. 3-Bromo-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutene (**4b**) and 3-chloro-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutene (**5b**) undergo quantitative conrotatory ring opening at similar rates in which the 3-nitro groups rotate outward and the 4-phenyl groups rotate inward to yield *cis,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene (**7b**) and *cis,trans*-1-chloro-1,3-dinitro-2,4-diphenylbutadiene (**8b**), respectively. Higher temperatures and/or polar solvents reversibly isomerize **7b** and **8b** to *trans,trans*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene (**7c**) and *trans,trans*-1-chloro-1,3-dinitro-2,4-diphenylbutadiene (**8c**), respectively. 3-Bromo-1,*trans*-3-dinitro-2,*cis*-4-diphenylcyclobutene (**4a**) reversibly and conrotatively isomerizes with outward rotation of its nitro group to *cis,cis*-1-bromo-1,3-dinitro-2,4-diphenylbutadiene (**7a**). Bromine at the 3 position of a cyclobutene enhances its stability relative to its isomeric diene. The structures of the present butadienes were assigned by comparison of their NMR spectra with those of *trans*- and *cis*-β-nitrostyrenes and their α-methyl, β-methyl, β-bromo, and β-chloro derivatives. The syntheses and characterizations of previously unreported *cis*-β-nitrostyrenes and their interconversions with their trans isomers are described.

Thermolysis of cyclobutenes to conjugated butadienes (sequence 1) is one of the simplest valence isomerization reactions.[2a-c] The reverse process, thermal cyclization of a butadiene to a cyclobutene, is relatively rare,[2d-h] however, because butadienes are usually much more stable thermodynamically.[2i] As presently known, thermal valence isomerizations of cyclobutenes to open-chain butadienes are invariably conrotatory.[3-5] This specificity has been rationalized on the basis of orbital symmetry.[3]



(1)

Four isomeric 1,3-butadienes are derivable from valence isomerizations of the 3,4-disubstituted cyclobutenes **1a** and **1b** (sequence 1).[6] Trans 3,4-disubstituted cyclobutenes **1a** generally isomerize more rapidly than do their cis isomers **1b** and give the conrotatory products **2a** rather than **2c** (sequence 1). Conrotatory isomerization of **1a** thus appears to be controlled by steric interactions in the alternative transition states.[7] Cis 3,4-disubstituted dienes **1b** may isomerize thermally via conrotatory routes to dienes **2b** and **2d** (sequence 1); detailed knowledge of steric and electronic effects on the stereochemistry of isomerization of such systems is limited, however.

Although the principles of concerted isomerization of simple cyclobutenes have been established,[3,4] it has been proposed that bulk, polar, or/and conjugative substituent effects may alter the control mechanism or the stereochemistry of ring opening of highly substituted cyclobutenes.[8] In an effort to obtain additional information with respect to various factors involved in isomerizations of cyclobutenes, a study has been made of the isomerization of various 1,3-dinitro-2,4-diphenylcyclobutenes (**3a**–**5b**).

Results and Discussion

Isomerization of 1,3-Dinitro-2,4-diphenylcyclobutenes (3a–5b). In the present study the stereochemistry and rates of thermal isomerizations of stereoisomeric 1,3-dinitro-2,4-diphenylcyclobutenes (**3a**, **3b**), 3-bromo-1,3-dinitro-2,4-diphenylcyclobutenes (**4a**, **4b**), and 3-chloro-1,3-dinitro-2,4-diphenylcyclobutenes (**5a**, **5b**) have been investigated.[9] The products are 1,3-dinitro-2,4-diphenylbutadienes and 1-halo-1,3-dinitro-2,4-diphenylbutadienes and the structures are assigned primarily upon NMR comparison with model compounds as explained later in this paper. Significant among our findings are (1) cyclobutenes **3a**, **4a**, **4b**, and **5b** undergo kinetically controlled conrotatory isomerizations in which the 3-nitro groups rotate outward, (2) cyclobutene **3b** isomerizes thermally by an ostensibly disrotatory process, and (3) 1,3-dinitro-2,4-diphenylbutadienes **6a** and **7a** reversibly cyclize extensively or nearly completely to cyclobutenes.

In chloroform at 56 °C, trans 3,4-disubstituted cyclobutene **3a** isomerizes ($k_1 = 8 \times 10^{-6}$ s^{-1}; see Table I) reversibly to *cis,cis*-1,3-dinitro-2,4-diphenylbutadiene (**6a**),[10] the product of conrotatory isomerization (sequence 2). Subsequently, **3a** or **6a** at 56 °C gives a mixture containing **3a** and **6a** in a 35:65 ratio. Cis,trans diene **6b** and trans,trans diene **6c** then form as heating is continued (sequence 2; cf. Table I and Figure 1). Prolonged heating gives **6c**, the thermodynamically stable

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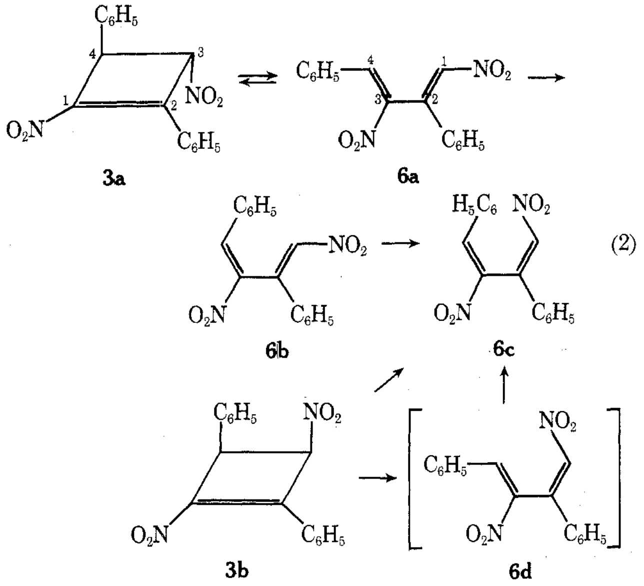
Table I. Kinetic and Equilibrium Data for Isomerization of 3a, 3b, 6a, 6b, and 6c [a]

				Product composition,[d] %						
Compd	Solvent[b]	Temp, °C	Time,[c] h	3a	3b	6a	6b	6c	Unk	$k_1 \times 10^6$, s^{-1}
3a	C	56	15	69		31				7.8
		56	40	49		51		Tr		6.9
		56	140	25		39	4	33		
3a	C–H	56	15	63		21	11	5		
		56	40	44		21	Tr	27	8	
3a	C–H	56	24.5	53		47				9.5
3a	B–H	56	24.5	54		46				8.9
3a	A–H	56	24.5	21				79		18
6a	C	56	14.8	19		81				5.2
		51–55	38	30		70		Tr		
		56	93	31		53	Tr	16		
		56	219				Tr	100		
6a	C–H	56	14.8	12		51	20	16		
		51–55	38	15		22	7	45	12	
		56	93	Tr		Tr	Tr	66	34	
3b	C	56	50		59			41		3.0
			294				Tr	100		
3b	C	56	61.5		36		Tr	64		4.6
3b	C–H	56	61.5		34			43	23	4.9
3b	C–H	56	24.5		64			36		5.0
3b	B–H	56	24.5		77			22		2.7
3b	A–H	56	24.5		73			27		3.5
6b	C	56	61.5				100			
6b	C–H	56	300				13	61	26	
6c	C	80	119					100		

[a] Data from representative kinetic and equilibration experiments are presented in Table I. The data given are only a small part of the total obtained. The rate constants reported in the Discussion are average values based on all of the data, and therefore may differ from the rate constants in Table I, which are calculated from an individual experiment. [b] Solvents: C, chloroform-*d*; C–H, chloroform-*d* + hydrogen chloride; B–H, benzene-d_6 + hydrogen chloride; A–H, acetonitrile + hydrogen chloride. Omission of a solvent symbol indicates that the experiment is a continuation of the one listed immediately above. [c] Time is given cumulatively for an experiment at a single temperature. If an experiment was continued at different temperatures, the time listed for the continued experiment is for that temperature only. [d] Unk, unknown compounds; Tr, trace amounts.



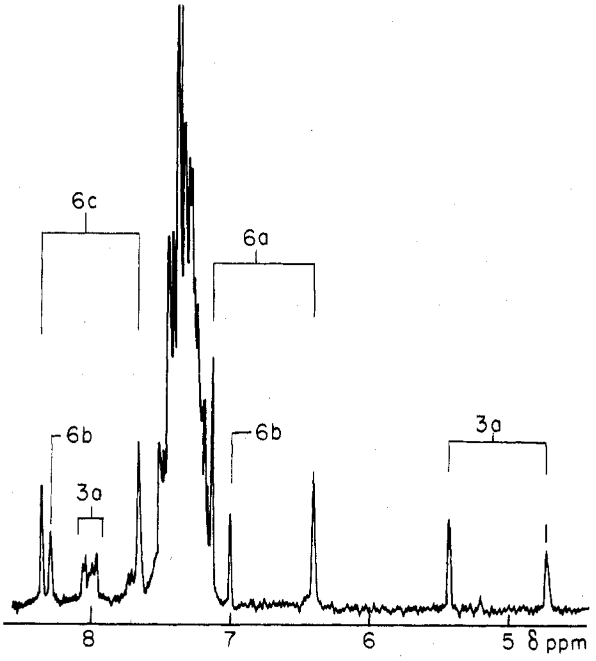


Figure 1. NMR spectrum (100 MHz) of reaction mixture from **6a** after 250 h at 56 °C ($CDCl_3$ + HCl); approximate composition **3a**, 20%; **6a**, 37%; **6b**, 16%; and **6c**, 27%.

product, in increasing proportions.[11] The rapid quantitative conversions of **6a** and **6b** to **6c** in warm ethanol or in the presence of triethylamine provide further evidence that **6c** is the most stable diene of the present system.

Of particular interest with respect to **3a** is that its conrotatory isomerization could give either **6a** or **6c** (sequence 2). Initial formation of the thermodynamically less stable **6a** thus constitutes a clear example of kinetic control in electrocyclic isomerization of the cyclobutene. Although **6c** is more stable than **6a** because of the thermodynamic preference of β-nitrostyrene moieties for trans geometry, the reaction path for decomposition of **3a** apparently reflects the structure of the reactant and thus the transition state in which the *trans*-3-nitro and 4-phenyl groups conrotate outward leading to **6a** is favored. In the transition state leading to **6c** there will be se-

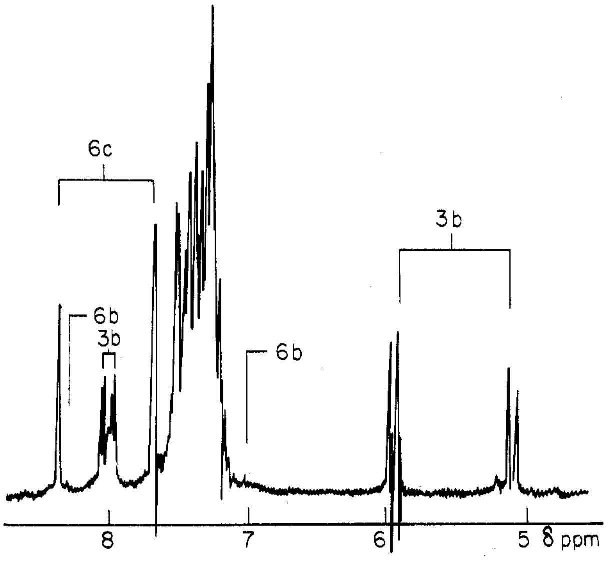


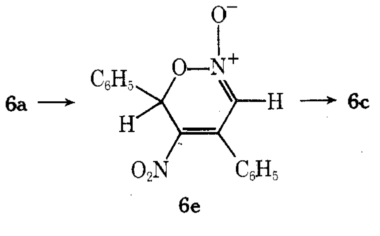
Figure 2. NMR spectrum (100 MHz) of reaction mixture from **3b** after 1160 h at ~30 °C ($CDCl_3$ + HCl); approximate composition **3b**, 54%; **6b**, trace; and **6c**, 46%.

vere intramolecular crowding as both the 3-nitro and 4-phenyl groups rotate inward.

In chloroform at 56 °C cis 3,4-disubstituted cyclobutene **3b** isomerizes ($k_1 = 4.7 \times 10^{-6}\ s^{-1}$; $t_{1/2}$ ~40 h) to trans,trans butadiene **6c**, the thermodynamically most stable butadiene that can be formed in this system (sequence 2 and Table I). Conversion of **3b** to **6c** is formally a disrotatory process.[5] Of further note is that the rate constant for ring opening of **3b** at 56 °C is similar to that of **3a**. Cis,trans diene **6b** is never observed among the products of the isomerization of **3b** in more than trace amounts (cf. Figure 2). Moreover, **6b** is unchanged after more than 60 h in chloroform at 56 °C. Thus diene **6b**, the conrotatory product expected if the 3-nitro group of **3b** rotates outward and the 4-phenyl group rotates inward, is excluded as an unstable intermediate in isomerization of **3b** to **6c**. The alternative conrotatory product, *trans,cis*-1,3-dinitro-2,4-diphenylbutadiene (**6d**, sequence 2), derived from inward rotation of the 3-nitro group and outward rotation of the 4-phenyl group, could not be found though intensively sought.[12–14]

The rate of isomerization of **3b** is as anomalous as the stereochemistry of its ring opening. Commonly cis 3,4-disubstituted cyclobutenes isomerize more slowly than the corresponding trans 3,4-disubstituted cyclobutenes by factors of 20 to 100 or more.[2a–b,15] When, as in bicyclic structures, conrotatory isomerization of cyclobutenes is prevented by steric constraints, the rates of disrotatory isomerization may be orders of magnitude slower than for the analogous nonbicyclic conrotatory reactions.[3b] However, **3b**, a cis-disubstituted cyclobutene, isomerizes slower than the trans-disubstituted cyclobutene **3a** by a factor of only 2 or less.

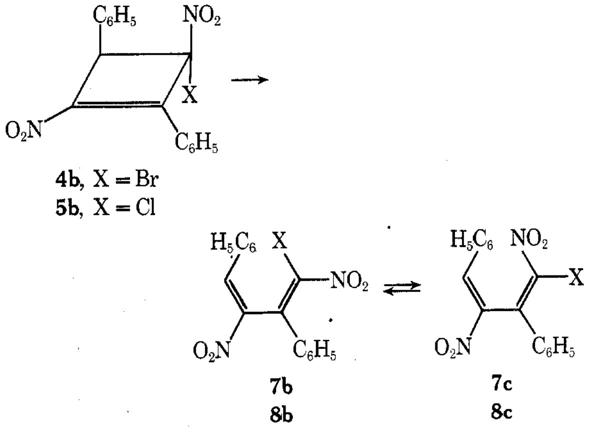
There is as yet no definitive explanation for the isomerization of **3b** to **6c**. An immediate question that can be raised is that the structure of **6c** is in error and that **6c** is **6d**, a product of conrotatory ring opening of **3b**. As will be indicated in subsequent discussion, an incorrect stereochemical assignment for **6c** is unlikely.[16] One of the possible interpretations of the results for isomerization of **3b** is that **6d** is indeed formed initially and that the "allowed" diene undergoes rapid isomerization to **6c** by the sterically favorable heterocyclic route as illustrated in sequence 3. Ring closure and isomerization to **6c** via **6e** is much more accessible sterically for **6d** than for its diene isomers. An alternate possibility for the difference in the stereochemical control for ring opening of **3a** and **3b** is that the cyclobutenes react by different mechanisms. Preservation of orbital symmetry in ring opening of **3a** and **3b** will only be required if the cyclobutenes collapse via concerted processes. As has been noted **3b** undergoes isomerization more rapidly, when compared to **3a**, than might be expected. Study of solvent effects on the rates of ring opening of **3a** and **3b** (Table I) reveals that there is but little acceleration of isomerization of the cyclobutenes in acetonitrile, a polar solvent, as compared to benzene and chloroform. The limited kinetic responses of **3a** and **3b** to solvent polarity during isomerization thus indicate that there is no great difference in the polar character of the transition states for the two ring-opening reactions. The facts that **3b** collapses almost as rapidly as does **3a** to dienes and that the solvent response for these two processes is similar leave open the possibility that isomerization of **3a** to **6a** is an electrocyclic process whereas **3b**, the more strained isomer, undergoes ring rupture by a homolytic mechanism with subsequent reorganization to **6c**.



(3)

6e

A study was then made of thermal isomerization of cyclobutenes **4a–5b**, stereochemical analogues of **3a–3b** containing bromine or chlorine at the 3 positions of the cyclobutene rings. Bromocyclobutene **4b** and chlorocyclobutene **5b**, which have *cis*-3-nitro and 4-phenyl groups, quantitatively undergo conrotatory ring opening (sequence 4, Tables II and III) to cis,trans bromodiene **7b** and cis,trans chlorodiene **8b**, respectively. In the isomerizations of **4b** and **5b**, the 3-nitro groups rotate outward and the 4-phenyl groups rotate inward. There was no evidence for formation of alternative conrotatory or disrotatory products. The rate constants (k_1) for decomposition of **4b** and **5b** in chloroform at 56 °C are 70×10^{-6} and $120 \times 10^{-6}\ s^{-1}$, respectively. Cyclobutenes **4b** and **5b** thus isomerize considerably more rapidly than do **3a** or **3b**. Dienes **7b** and **8b** are initially stable in chloroform at 56 °C and thus are conrotatory products of kinetic control from **4b** and **5b**. At higher temperature (80 °C) and/or in polar solvents, **7b** and **8b** isomerize and give equilibrium mixtures containing trans,trans bromo- and chlorodienes **7c** and **8c**, respectively; **7b** and **7c** equilibrate in near-equal amounts.[17]



4b, X = Br
5b, X = Cl

7b
8b

7c
8c

(4)

The valence isomerizations of **4b** and **5b** are noteworthy in that the observed stereochemistries are not predictable from the relative sizes of the substituents on carbon atoms 3 and 4. When ranked according to their conformational energies in monosubstituted cyclohexanes the relative sizes are C_6H_5

Table II. Kinetic and Equilibrium Data for Isomerization of 4a, 4b, 7a, 7b, and 7c [a]

				Product composition,[d] %							
Compd	Solvent[b]	Temp, °C	Time,[c] h	4a	4b	7a	7b	7c	7e	Unk	$k_1 \times 10^6$, s^{-1}
4a	C–H	56	95	100		Tr					
		56	335	21			14	7	58		
4a	C[e]	56	104	>85		Tr		~5			
		56	340	86		4		10	Tr		
		56	990	14			12	13	35	26	
7a	C	56	20	11		65	14	10			2
		56	63	23		22	33	22			
7a	C	56	236	50		11	16	23			
		80	60	15			35	29	22		
4b	C	56	3.9		32		68				81
4b	C	67	72				100				
7b	C	56	23				100				
		56	84.4				100	Tr			
7b	C–H	56	23				100	Tr			
		56	84.4				86	14			
7b	C	67	72				100				
7b	D[f]	56	240				49	51		g	
7c	D	56	240				51	49		g	
7c	C	56	176					100			
7c	C	80	380				44	56			

[a–d] These footnotes are explained in Table I. [e] A 30% solution of **4a** in C. [f] Solvent: D, dimethyl sulfoxide-d_6. [g] Unknowns present in undetermined amounts.

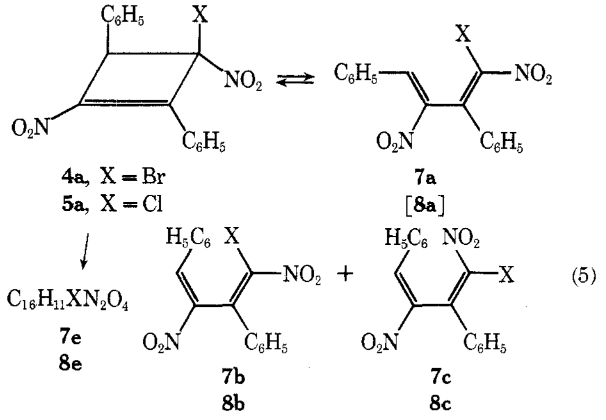
Table III. Kinetic and Equilibrium Data for Isomerization of 5a, 5b, and 8b [a]

				Product composition, %					
Compd	Solvent[b]	Temp, °C	Time,[c] h	5a	5b	8b	8c	8e	$k_1 \times 10^6$, s^{-1}
5a	C	56	25	100					
		56	236	90		10	Tr		
		56	610	22		15	Tr	63	
		80	60	11		23	8	59	
5b	C	56	3.9		17	83			127
5b	C	67	72			100			
8b	C	100	108			63	37		

[a–c] These footnotes are explained in Table I.

(3.0) > NO_2 (1.1) > Br (0.4) ~ Cl (0.4).[18] Thus in the expected conrotatory isomerizations of **4b** and **5b**, phenyl and halogen would rotate outward, and nitro would rotate inward. However, in the observed reactions of **4b** and **5b** the nitro group rotates outward and the phenyl and halogen rotate inward. The reason for the strong preference of the nitro group for outward rotation is not yet clear but may be related to its strong conjugating properties. The influence of substituents on cyclobutene carbons 1 and 2 on the stereochemistry of conrotatory isomerization of cis 3,4-disubstituted cyclobutenes may be significant but is not presently assessable.

The thermolysis of **4a** (sequence 5, Table II) is notably more complicated than that of its epimer **4b** and yields three bromobutadienes (**7a–c**) and an unidentified isomer **7e** which on the basis of its chemical and physical (especially spectral) properties is neither a cyclobutene nor a butadiene.[19,20] Heating either **4a** or **7a** gives mixtures containing **4a**, **7a**, and varying proportions of **7b** and **7c**. Since **7b** and **7c** do not cyclize detectably to **4a**, conversion of cyclobutene **4a** to cis,cis diene **7a** constitutes a reversible conrotatory isomerization in which the nitro group moves outward. The relative slowness of ring opening of **4a**, the small proportion (~4%) of **7a** in the equilibrium, and the side reaction leading to **7e** prevented direct measurement of the rate of isomerization of **4a** to **7a**. The rate constant (k_1, 56 °C) for reversible ring opening of **4a** as estimated from the rate constant of cyclization of **7a** to **4a** and the proportion of **4a** and **7a** present at equilibrium is of the magnitude 0.1×10^{-6} s^{-1}.[21] Isomer **4a** thus undergoes ring opening slower by a factor of at least 200 than does **4b**. The cyclobutene–butadiene equilibrium for bromocyclobutene **4a** contains predominantly cyclobutene **4a** whereas the corresponding equilibrium for cyclobutene **3a**, which lacks bromine, consists predominantly of butadiene **6a**. The presence of halogen at the 3 position of a cyclobutene appears to favor the cyclic form of a cyclobutene–butadiene equilibrium, a trend observed by others.[2e–g]



4a, X = Br
5a, X = Cl

7a
[**8a**]

$C_{16}H_{11}XN_2O_4$
7e
8e

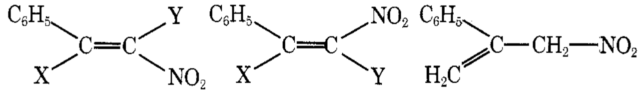
7b
8b

7c
8c

(5)

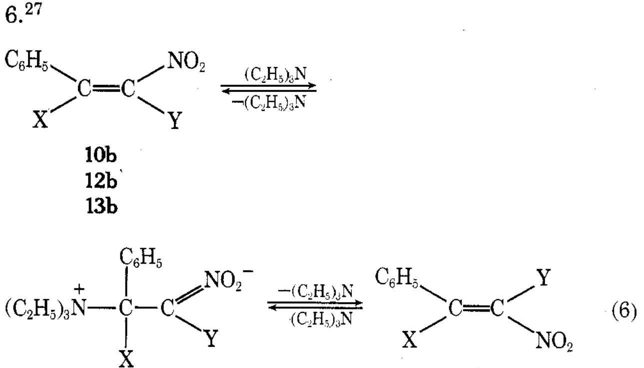
The fact that cyclobutene **4b** undergoes ring opening more rapidly than do **3a**, **3b**, and **4a** is of considerable interest. It might be expected that collapse of **4b** would occur slowest since movement of phenyl at C-4 toward bromine at C-3 is involved. The greater reactivity of **4b** than of **3a** or **3b** may result from weakening of the C-3 and C-4 bond of a dinitrodiphenylcyclobutene upon substitution of bromine at C-3. The greater ease of ring opening of **4b** than **4a** might also arise from greater weakening of the C-3 and C-4 bond in the cyclobutenes when phenyl at C-4 is cis rather than trans to the nitro group at C-3.

Synthesis and Interconversions of *cis*- and *trans*-β-Nitrostyrenes. Implicit in the preceding discussion are reliable structural assignments for butadienes **6a–8c**. In the present work the structures of the dienes were deduced principally from their NMR spectra upon comparison with the model compounds: *trans*- and *cis*-β-nitrostyrenes (**9a, 9b**) and their β-methyl (**10a, 10b**), α-methyl (**11a, 11b**), β-chloro (**12a, 12b**), and β-bromo (**13a, 13b**) derivatives, respectively.



9a, X = Y = H	**9b**	**11c**
10a, X = H; Y = CH_3	**10b**	
11a, X = CH_3; Y = H	**11b**	
12a, X = H; Y = Cl	**12b**	
13a, X = H; Y = Br	**13b**	

Cis–trans isomerism and photoisomerizations of β-nitrostyrene and its simple derivatives have been described only fragmentarily.[1b,22] The known isomers of β-nitrostyrene and 2-nitro-1-phenylpropene were assigned trans structures (**9a, 10a**) from their dipole moments;[23] isolation of *trans*- and *cis*-α-methyl-β-nitrostyrenes (**11a, 11b**) was independently reported by us[1b] and others.[22b,c,24] We prepared **11a** by treating the product of α-methylstyrene and dinitrogen tetroxide with triethylamine;[25] **11a** was isolated chromatographically from coproducts **11b** and **11c**. Solar irradiation of the individual trans isomers **9a**,[26] **10a, 11a**, and **12a** in hydrocarbon solvents yielded photostationary mixtures containing 60–80% of the corresponding cis isomers **9b, 10b, 11b**, and **12b**, respectively; irradiation of **13a**, however, gave mixtures having only 10–20% **13b**. The cis isomers were isolated by chromatography and evaporative distillation or recrystallization. In the presence of iodine, **9b, 10b**, and **12b** revert completely to their respective trans isomers **9a, 10a**, and **12a**. Isomerization of **11b** by iodine gives an equilibrium mixture of ~98% **11a** and 2% **11b**. The fact that **11b** is not completely isomerized to **11a** is indicative of the steric interaction of the nitro and the methyl groups in **11a**. Triethylamine is an effective catalyst for trans isomerizations of **10b, 12b**, and **13b** presumably by addition–elimination processes as in sequence 6.[27]



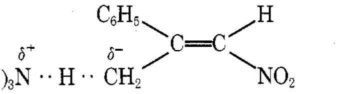
10b
12b
13b

X = H; Y = CH_3
X = H; Y = Cl
X = H; Y = Br

10a
12a
13a

(6)

Reaction of **11a** with basic methanol and acidification of the resulting 2-phenyl-2-propenenitronate ion with acetic acid yields a mixture of methylnitrostyrenes of near-kinetic control in which the principal product (84%) is the isomer (**11c**) in which the olefinic center is not conjugated with the nitro group.[28] This result parallels that for acidification of other conjugated alkenenitronate ions[29a–c] and agrees with the expectation that proton transfer to a stabilized ambident ion will give the product of kinetic control that is derived from minimum reorganization of the reactants.[29d] It is of note that **11a** is isomerized more rapidly to **11c** by triethylamine than is **11b**. Isomerizations of **11a** and **11b** to **11c** by triethylamine occur primarily by proton transfer processes involving triethylamine rather than by addition–elimination (as in sequence 6). Nitropropene **11a** may be more reactive because its transition state for proton removal is of preferred cis-allylic structure[30] and will allow more effective conjugation of its nitro and phenyl groups.



11d

NMR Properties of β-Nitrostyrenes. NMR Properties and Structural Assignments of 1,3-Dinitro-2,4-diphenylbutadienes. The NMR spectra and the geometries of model compounds **9a–13b** (Table IV) are correlatable in that the signals from H or CH_3 in either the α or β position appear at lower field in the trans isomers than in the corresponding cis isomers.[31] In the compounds having *trans*-β-nitrostyrene moieties, resonance of the α-vinyl hydrogens occurs at 7.84–8.60 ppm; the α-vinyl hydrogen signals of *cis*-β-nitrostyrene moieties, however, are in the 6.34–7.02-ppm region. The signals for β-vinyl hydrogen of the β-nitrostyrene moieties are less strongly influenced by geometry and occur at 7.16–7.41 ppm for the trans compounds and at 6.91–6.96 ppm for the cis compounds.

The NMR properties of the 1,3-dinitro-2,4-diphenylbutadienes (**6a–c**) and the 1-halo-1,3-dinitro-2,4-diphenylbutadienes (**7a–8c**) are summarized in Table IV. Butadienes **6b, 6c, 7b, 7c, 8b**, and **8c** all have singlet signals at 8.2–8.4 ppm; clearly this demonstrates the presence of α-vinyl hydrogen of *trans*-β-nitrostyrene moieties in these dienes. Diene **6c** has a second signal for vinyl hydrogen at 7.73 ppm. Since β hydrogen of a *cis*-nitrostyrene would resonate much further upfield, the 7.73-ppm signal can reasonably be only that of β hydrogen of a second *trans*-β-nitrostyrene moiety and thus **6c** has the trans,trans structure. The second vinyl hydrogen signal for **6b** at 7.06 ppm is in the range for β-vinyl hydrogen of a *cis*-β-nitrostyrene and thus **6b** is a cis,trans diene. Diene **6a** has vinyl hydrogen signals at 7.18 and 6.45 ppm. The latter signal unambiguously demonstrates α hydrogen of a *cis*-β-nitrostyrene moiety. On comparison with the model compounds (Table IV), the 7.18-ppm signal of β hydrogen is compatible with either *cis*- or *trans*-β-nitrostyrene geometry. In **6c** however, the β-hydrogen signal of the *trans*-β-nitrostyrene moiety was much farther downfield, near 7.7 ppm. Therefore, the 7.18 ppm signal of **6a** most probably represents β-vinyl hydrogen of a *cis*-β-nitrostyrene moiety and thus **6a** has a cis,cis structure. The stereochemical assignment for **6a** is consistent with its reversible conrotatory isomerization to **3a**.

Halodienes **7a–8c** lack β-vinyl hydrogens but the geometries of the β-halo-β-nitrostyrene moieties of these dienes could be assigned by comparing the NMR spectra of their phenyl hydrogens with the spectra of the model compounds, *cis*- and *trans*-β-halo-β-nitrostyrenes. *trans*-β-Halo-β-nitrostyrenes **12a** and **13a** exhibit phenyl hydrogen signals that consist of two distinctive multiplets at relatively low field. The phenyl hydrogen signals of the cis isomers **12b** and **13b** differ diag-

Table IV. Nuclear Magnetic Resonance of 1,3-Dinitro-2,4-diphenylbutadienes 6a–8c and Nitrostyrenes 9a–13b [a]

Compd	αH	βH	CH_3	C_6H_5
6a	6.45 s	7.18 s		7.1–7.5 m
6b	8.33 s (1)	7.06 s (1)		7.35–7.55 m (8); 7.65–7.8 m (2)
6c	8.39 s	7.73 s		7.2–7.6 m
7a	7.04 s (1)			7.3–7.5 m (10)
7b	8.18 s			7.3–7.6 m
7c	8.31 s (1)			7.32 s (5); 7.45–7.60 m (3); 7.65–7.80 m (2)
8b	8.22 s			7.3–7.6 m
8c	8.33 s (1)			7.31 s (5); 7.45–7.60 m (3); 7.70–7.82 m (2)
9a [b,c]	7.84 d	7.41 d		7.49 s
9b [b,c]	6.71 d	6.91 d		7.4 m
10a [c]	8.00 d		2.40 d	7.35 s
10b [c]	6.34 d		2.30 d	7.24 s
11a [c]		7.16 d	2.58 d	7.37 s
11b [c]		6.96 d	2.13 d	7.0–7.4 m
11c	[5.41 s, vinyl H]	[5.69 s, vinyl H]	[5.20 s, CH_2NO_2]	7.26 s
12a	8.33 s (1)			7.4–7.6 m (3); 7.75–7.95 m (2)
12b	6.90 s			7.2–7.4 m
13a	8.60 s (1)			7.4–7.6 m (3); 7.75–7.95 m (2)
13b	7.02 s			7.2–7.4 m

[a] Chemical shifts are δ values relative to tetramethylsilane; the NMR solvent was chloroform-*d*. Singlet, doublet, and multiplet signals are designated by s, d, and m. Relative signal areas, if obtained, are given in parentheses. [b] These assignments were confirmed by deuteration experiments. [c] Coupling constants are for *vicinal* vinyl hydrogens or vinyl hydrogens and the hydrogens of *vicinal* methyl groups and are **9a,** $J = 13.7$; **9b,** $J = 9.6$; **10a, 10b, 11a, 11b,** $J \leqslant 1.5$ Hz.

Table V. Ultraviolet Absorption Maxima of Nitrostyrenes 9a–13b in Ethanol

Compd	λ_{max}, nm	$\epsilon \times 10^{-4}$	λ_{max}, nm	$\epsilon \times 10^{-4}$
9a [a]	226	0.9	310	1.7
9b	223	1.0	306	0.6
10a	226	1.0	305	1.2
10b	225	1.4	282	0.3
11a	226	1.1	293	1.3
11b	223 [b]	1.1	270 [b]	0.4
11c	237	1.1		
12a	226	1.3	320	1.9
12b	223	1.3	320	0.4
13a	226	0.9	324	1.2
13b	246	1.2	327	0.19

[a] Data from ref 32a. [b] Inflection.

nostically in form and occur at higher field (Table IV). Since the phenyl hydrogen signals of *cis*- and *trans*-β-bromostyrenes exhibit similar qualitative differences[31d] while the NMR signals of nonhalogenated *cis*- and *trans*-β-nitrostyrenes lack these specific differences, the differences appear to reflect the cis and trans geometries of the β-halo groups.

The phenyl hydrogen signals of halodienes **7c** and **8c** each contain two distinctive multiplets indicative of their *trans*-β-halo-β-nitrostyrene moieties (Table IV); **7c** and **8c** are therefore assigned trans,trans structures. The phenyl hydrogen signals of **7b** and **8b** resemble those of *cis*-β-halo-β-nitrostyrenes **12b** and **13b**; therefore **7b** and **8b** have cis,trans structures. Bromodiene **7a** has a NMR signal at 7.04 ppm that represents α-vinyl hydrogen of a *cis*-β-nitrostyrene moiety. Diene **7a** is assigned as cis,cis rather than as trans,cis on the basis that its phenyl hydrogen signals are at 7.31–7.41 ppm as simple multiplets and correspond to those of *cis*- rather than *trans*-β-halo-β-nitrostyrenes (Table IV). The structure for **7a** is also consistent with reversible conrotatory isomerization of **4a** involving outward rotation of the trans 3-nitro and 4-phenyl groups.

Ultraviolet Absorption of *trans*- and *cis*-β-Nitrostyrenes. The β-nitrostyrenes studied previously show strong ultraviolet absorption maxima in the 300-nm region[32] and are presumably of trans stereochemistry. α-Nitrostilbenes containing the *cis*-nitrostyrene moiety lack this 300-nm maximum. As seen in Table V, the ultraviolet spectra of the simpler *trans*- and *cis*-nitrostyrenes (**9a–13b**) of the present study also show such a contrast. Whereas the trans isomers exhibit strong maxima in the 300-nm region, the cis isomers usually absorb at shorter wavelengths and have greatly reduced maxima or show end absorption. The reduced long wavelength absorption of the *cis*-β-nitrostyrenes may be related to the inability of these isomers to assume the planar configuration which is necessary for effective conjugation. Derivatives of 1-nitro-2-phenylcyclobutene, although containing the *cis*-β-nitrostyrene moiety, exhibit absorption maxima near 330 nm ($\epsilon \sim 10^4$).[9] Incorporation of a *cis*-β-nitrostyrene moiety into a four-membered ring should allow the phenyl and nitro groups to approach coplanarity and in conjunction with the ground-state strains lead to the bathochromic effects exhibited by **3a–5b**.[9]

Experimental Section

General Techniques. Analysis, separation, and purification of reaction products by column and thin layer chromatographic methods were effected as described previously.[9] The uv spectra of **6a–8c** in cyclohexane were determined on a Cary 14M spectrometer. The uv spectra of **9b–13b** in ethanol were recorded as a separate group with Bausch and Lomb Spectronic 505 and Cary 14M spectrometers. Varian Associates HR 60 and HR 100 spectrometers were used to determine the nuclear magnetic resonance of the nitro compounds in chloroform-*d* or carbon tetrachloride containing tetramethylsilane.[33]

Isomerization of 1,3-Dinitro-2,*trans*-4-diphenylcyclobutene (3a) to *cis,cis*-1,3-Dinitro-2,4-diphenylbutadiene (6a), *cis,-trans*-1,3-Dinitro-2,4-diphenylbutadiene (6b), and *trans,-trans*-1,3-Dinitro-2,4-diphenylbutadiene (6c). After exposure to hydrogen chloride, a solution of **3a** (1.5 g) in toluene was kept for 75 h at 56 °C and then concentrated in vacuo. Fractional crystallization gave recovered **3a,** then two crops that contained predominantly **6a** (0.72 g) along with **3a** (0.17 g). Prisms of **3a** and **6a** could be manually separated because of their different crystal habits and the deeper yellow color of **6a.** Further crystallization yielded **3a** (0.05 g; total 0.38 g, 25%), **6a** (0.06 g; total 0.78 g, 52%), yellow dendrites of **6b** (0.01 g, 0.7%), and yellow plates of **6c** (<0.01 g) that became green-yellow in light. Recrystallization gave pure **6a**, mp 105–106 °C, uv λ_{max} (cyclohexane) (ϵ) 232 nm (sh, 1.2×10^4), 322 (1.8×10^4); **6b**, mp 120–128 °C, uv λ_{max} (cyclohexane) (ϵ) 228 nm (2.0×10^4), 308 (1.6×10^4); and **6c**, mp 144–145 °C, uv D_{max} (cyclohexane) (ϵ) 226 nm (1.5×10^4), 307 (2.4×10^4). In chromatographic separation, the order of elution (benzene–hexane) for the isomers is **3a** > **6a** > **6b** > **3b** ~ **6c**.

Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.85; H, 4.09; N, 9.47. Found for **6a**: C, 64.94; H, 4.21; N, 9.47. Found for **6c**: C, 64.96; H, 4.00; N, 9.32.

When **6a** (0.1 g) in ethanol was kept for 10 min at 75 °C, **6c** (0.08 g, 80%), mp 144–145 °C, was obtained. Heating **3a** (0.1 g) at 70 °C for 4 days in ethanol gave **6c** (0.09 g, 90%), mp 144–145 °C. After **6b** was kept for 15 h in methanol at 65 °C, only **6c** was detectable (TLC analysis). Treating a mixture of 10% **3a**, 17% **6a**, 18% **6b**, and 55% **6c** (total 0.04 g) in chloroform (0.5 ml) with triethylamine (1 drop) caused gradual deepening red coloration. After 20 min, the mixture contained ~5% **3a** and ~95% **6c**; **6a** and **6b** were no longer detectable. In addition to the chemical characterization of **6b** by its isomerization to **6c** (see also Table I), **6b** was identified by its NMR (no detectable impurities), ir, and uv spectra. Because so little **6b** was isolated, elemental analysis was not performed.

Isomerization of 1,3-Dinitro-2,*cis*-4-diphenylcyclobutene (3b) to *trans,trans*-1,3-Dinitro-2,4-diphenylbutadiene (6c). Heating **3b** in various solvents (e.g., ethanol, chloroform, benzene, and toluene) gave **6c** in nearly quantitative yield. The very low solubility of **6c** in hexane greatly facilitated its isolation.

Isomerization of 3-Bromo-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutene (4b) to *cis,trans*-1-Bromo-1,3-dinitro-2,4-diphenylbutadiene (7b). A toluene solution of **4b** (0.50 g) was heated for 36 h at 65 °C. Concentration and recrystallization gave **7b** (0.40 g, 80%) as clumps of spiraled yellow fibers, mp 125–127 °C, mol wt calcd 375, found 389 (vapor phase osmometer). In chloroform at 67 °C for 72 h, the conversion of **4b** to **7b** was quantitative.

Anal. Calcd for $C_{16}H_{11}BrN_2O_4$: C, 51.21; H, 2.96; Br, 21.30; N, 7.47. Found: C, 51.00; H, 2.82; Br, 21.32; N, 7.26.

Isomerization of 3-Bromo-1,*trans*-3-dinitro-2,*cis*-4-diphenylcyclobutene (4a) to *cis,cis*-1-Bromo-1,3-dinitro-2,4-diphenylbutadiene (7a), *cis,trans*-1-Bromo-1,3-dinitro-2,4-diphenylbutadiene (7b), *trans,trans*-1-Bromo-1,3-dinitro-2,4-diphenylbutadiene (7c), and Compound 7e. A chloroform solution of **4a** (0.52 g) was exposed to hydrogen chloride, sealed in a bottle, and heated at 80 °C for 58 h. After concentration of the mixture, the product was first crystallized to **4a** (three crops, 0.16 g, identified by ir). After filtration through silicic acid (previously exposed to hydrogen chloride), the product was crystallized further to yellow clumps of **7b** (0.02 g), mp 124–127 °C, uv λ_{max} (cyclohexane) (ϵ) 225 nm (1.6×10^4), 308 (1.6×10^4), and yellow prisms of **7c**, mp 150–151 °C, mol wt calcd 375, found 331 (cryoscopic method in benzene), uv λ_{max} (cyclohexane) (ϵ) 228 nm (1.8×10^4), 310 (1.5×10^4). The next crystallization gave yellow plates of **4a** (0.02 g) and small, oblong, yellow prisms of **7a** (0.01 g, 2%), mp 126–129 °C. The remaining material, when chromatographed on silicic acid with 20% benzene–hexane as eluent, gave colorless columns or prisms of **7e** (0.002 g, 0.4%), mp 132–134 °C, mol wt calcd 375, found 395 (vapor phase osmometer), uv max 261 nm (ϵ 20 000), NMR δ 5.48 (singlet, area 1, nonaromatic H) and 7.2–7.6, 7.7–7.9 (multiplets, areas 8 and 2, respectively, C_6H_5), additional **4a** (total 0.21 g, 40%), **7b** (total 0.08 g, 15%), and **7c** (total 0.13 g, 25%). In thin layer or column chromatography, the order of elution (benzene–hexane) is **7e** > **4a** ~ **4b** > **7a** ~ **7c** > **7b**. Diene **7a** was also isolated in ~1% yield by fractional crystallization of the mixture resulting from refluxing **4a** in 1-octene for 30 min; uv λ_{max} (cyclohexane) (ϵ) 231 nm (1.5×10^4), 291 (0.9×10^4).

Anal. Calcd for $C_{16}H_{11}BrN_2O_4$: C, 51.21; H, 2.96; Br, 21.30; N, 7.47. Found for **7c**: C, 51.30; H, 3.16; Br, 21.55; N, 7.46. Found for **7e**: C, 51.01; H, 3.05; Br, 21.87; N, 7.30.

Because very little **7a** was isolated, it was not analyzed. Chemical characterization of **7a** was provided by its isomerization to **4a**, **7b**, and **7c** (Table II). Refluxing **7b** (0.2 g) in ethanol for 2 days gave unchanged **7b** (0.07 g) and **7c** (0.09 g, 45%; identified by ir spectra). Refluxing **7c** (0.40 g) for 2 days in ethanol yielded unchanged **7c** (0.14 g) and **7b** (0.10 g, 25%). Dienes **7b** and **7c** also interconvert in dimethyl sulfoxide and, under more drastic conditions, in chloroform (see Table II).

Conversion of 7b by Sodium Iodide–Acetic Acid to 6c. A mixture of sodium iodide (4.0 g, 27 mmol) and **7b** (1.0 g, 2.7 mmol) in acetic acid (75 ml) was heated for 3 days at 65 °C. Addition of the solution to ice water gave a gummy solid. Chromatographic separation and crystallization from benzene–hexane yielded yellow plates of **6c** (0.42 g, 1.4 mmol, 52%), mp 143–145 °C, identified by its ir spectrum.

Isomerization of 3-Chloro-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutene (5b) to *cis,trans*-1-Chloro-1,3-dinitro-2,4-diphenylbutadiene (8b). A toluene solution of **5b** (1.0 g) was heated for 26 h at 65 °C. After concentration, the product crystallized to spiraled yellow fibers of **8b** (0.95 g, 95%), mp 132–134 °C, uv λ_{max} (cyclohexane) (ϵ) 226 nm (1.6×10^4), 309 (1.5×10^4). In chloroform at 67 °C for 72 h, the conversion of **5b** to **8b** was quantitative.

Anal. Calcd for $C_{16}H_{11}ClN_2O_4$: C, 58.10; H, 3.36; Cl, 10.72; N, 8.47. Found: C, 58.25; H, 3.36; Cl, 10.40; N, 8.25.

Interconversion of *cis,trans*-1-Chloro-1,3-dinitro-2,4-diphenylbutadiene (8b) and *trans,trans*-1-Chloro-1,3-dinitro-2,4-diphenylbutadiene (8c). An ethanolic solution of **8b** (1.0 g) was heated for 24 h at 65 °C. After removal of the ethanol, crystallization of the product gave unchanged **8b** (0.5 g) which in turn was heated for 24 h in ethanol. The mixture was concentrated and combined with the previous filtrate. Fractional crystallization yielded **8b** (0.37 g, 37%) as clumps of spiraled yellow fibers, mp 132–133 °C, which were manually separated from yellow prisms of **8c** (0.13 g, 13%), mp 132–134 °C (mmp with **8b**, 105–120 °C), uv λ_{max} (cyclohexane) (ϵ) 227 nm (1.9×10^4), 309 (1.5×10^4). The NMR spectra of **7c** and **8c** are nearly indistinguishable.

Anal. Calcd for $C_{16}H_{11}ClN_2O_4$: N, 8.47. Found: N, 8.02.

After an ethanolic solution of **8c** (0.10 g) had been heated for 24 h at 65 °C, removal of ethanol and fractional crystallization of the product from benzene–cyclohexane resulted in **8b** (0.06 g, 60%) as fibrous clumps, mp 120–128 °C, identified by its ir spectrum, and **8c** (0.01 g, 10%), mp 131–134 °C, yellow prisms. In chloroform, the isomerization of **6b** to **6c** required more drastic conditions (Table III).

Isomerization of 3-Chloro-1,*trans*-3-dinitro-2,*cis*-4-diphenylcyclobutene (5a) to 8b, 8c, and Compound 8e. A solution of **5a** in chloroform, after 610 h at 56 °C, contained 22% **5a**, 15% **8b**, a trace of **8c**, and 63% **8e**. After more intensive heating (300 h at 80 °C followed by 108 h at 100–105 °C), the mixture contained no **5a**, 25% **8b**, 9% **8c**, 48% **8e**, and 18% unidentified compound(s) with singlet NMR signals at δ 5.82 and 6.37 ppm. Although not isolated, **8e**, which is believed to be the chloro analogue of **7e**, was identified and characterized by NMR signals at δ 5.46 (singlet) and 7.2–7.6, 7.7–7.85 ppm (multiplets).

Kinetic and Equilibration Experiments. Isomerization reactions were conducted in chloroform-*d* or other solvents in NMR sample tubes. Constant-temperature baths were maintained at 56 °C. The concentration of the reactants usually was 3–10%. Because some early experiments were complicated by base-catalyzed interconversion of **3a** and **3b**, reaction mixtures were usually flushed with hydrogen chloride. Later studies showed that, although the valence isomerizations of **3a** and **3b** were not affected by hydrogen chloride, hydrogen chloride does catalyze the conversion of **6a** to **6b** and **6c**, and the isomerization of **6b** to **6c**.

The compositions of reaction mixtures were determined by comparison of the intensities of the NMR signals of the nonaromatic hydrogens. Figures 1 and 2 show representative spectra of reaction mixtures formed by thermal isomerization of **6a** and **3b**, respectively. Frequently faint signals (δ 7.06, 8.33 ppm) in the NMR spectra of isomerization mixtures of **3b** indicated that **6b** was present in trace amounts. That **3a** and **3b** isomerize by first-order processes was demonstrated by the constancy of the calculated first-order rate constants at different extents of reaction. For other compounds, for which there was less kinetic data available, rate constants were calculated by assuming that the isomerizations were first order.

Determination of the rates of valence isomerization of cyclobutenes **3a** and **3b**, the most intensively investigated of the present compounds, was straightforward. Although temperature variation and analytical difficulties cause minor uncertainties in their absolute values, the rate constants for **3a** and **3b** are reproducible (±10–20%) and are believed reliable.

The relative slowness of the ring opening of bromocyclobutene **4a**, the small proportion of diene **7a** in the equilibrium mixture, and the side reaction leading to **7e** prevented direct measurement of the rate of isomerization of **4a**. The rate constant for valence isomerization of **4a** was therefore estimated from the rate constant for the cyclization of **7a** and the proportions of **7a** and **4a** in the equilibrium mixture. Analytical difficulties prevented precise determination of these values, but meaningful estimates were obtainable.

Cyclization of diene **7a** is accompanied by formation of dienes **7b** and **7c**. Since **7b** and **7c** do not interconvert under the conditions studied, they were assumed to be products of unimolecular isomerization of **7a** and the rate of cyclization was calculated from the rate of disappearance of **7a** and the proportion of **4a** in the products. The calculated rate constant for cyclization of **7a** is not sensitive to the assumptions regarding **7b** and **7c** or to the exact composition of the equilibrium of **7a**–**4a**. Various limiting assumptions gave *k* (cyclization of **7a**) = 1.5×10^{-6} to 3×10^{-6} s^{-1} with 2×10^{-6} s^{-1} as a preferred value.

The value of the rate constant for ring opening of **4a**, as calculated from the rate of cyclization of **7a**, is sensitive to the proportion of **7a** present at equilibrium. Isolation experiments reveal that the proportion of **7a** in equilibrium with **4a** is at least 1%, and NMR analyses indicate that the equilibrium proportion of **4a** is less than 10%, since **7a** usually was not detectable in mixtures resulting from long heating of **4a** or **7a**. However, upon heating a 30% solution of **4a** for 340 h at 56 °C, diene **7a** constituted ~4% of the mixture of **4a–7a**. Thus, 4% was taken as a preferred value for the equilibrium concentration of **7a**, from which is calculated a preferred value for k (ring opening of **4a**) of $\sim 0.1 \times 10^{-6}$ s^{-1}. Assuming that the proportion of **7a** at equilibrium lies within 1% and 10%, the limiting values for the rate constant for valence isomerization of **4a** are 0.015×10^{-6} and 0.33×10^{-6} s^{-1}.

***trans-β*-Nitrostyrene (9a), *trans*-2-Nitro-1-phenylpropene (10a), *trans-β*-Chloro-*β*-nitrostyrene (12a), and *trans-β*-Bromo-*β*-nitrostyrene (13a).** Nitro derivatives **9a**,[34] **10a**,[35] **12a**,[36] and **13a**[36] were prepared according to previous procedures. When reaction of benzaldehyde and nitromethane catalyzed by sodium hydroxide was conducted in $CH_3OD–D_2O$, addition of the nitronate ion solution to hydrochloric acid (HCl) gave **9a**, 70% deuterated at the β position.

***trans*-1-Nitro-2-phenylpropene (11a).** Treatment of the reaction product of α-methylstyrene and dinitrogen tetroxide with triethylamine gave a product believed to consist largely of acetophenone. The oil was extracted several times with hexane, and the hexane-immiscible portion was chromatographed using cyclohexane containing increasing concentrations of benzene as eluent. Initial fractions chromatographed consisted of a slightly impure single component identified as **11a**. Later fractions contained mixed nitromethylstyrenes. Chromatography followed by evaporative distillation gave **11a**, a yellow liquid, n^{20}D 1.6014, which solidified (mp 15–20 °C) when stored at 5–10 °C.

Anal. Calcd for $C_9H_9NO_2$: N, 8.57. Found: N, 8.69.

***cis-β*-Nitrostyrene (9b), *cis*-2-Nitro-1-phenylpropene (10b), *cis*-1-Nitro-2-phenylpropene (11b), *cis-β*-Chloro-*β*-nitrostyrene (12b), and *cis-β*-Bromo-*β*-nitrostyrene (13b).** Experiments on small scale showed that solutions of **9a**, **10a** (in cyclohexane), **11a** (in heptane), **12a**, and **13a** (in cyclohexane), when exposed in Pyrex vessels (soft glass for **13a**) to sunlight, gave within 20–40 h mixtures containing ~63, 74, 80, 64, and 15%, respectively, of cis isomers **9b**, **10b**, **11b**, **12b**, and **13b**. Further irradiation of **9a–12a** did not alter the proportions of the isomers, but continued irradiation soon destroyed **13a–13b**. In preparative experiments cis isomers **9b**, **10b**, and **11b** were isolated chromatographically as the more slowly eluted isomers; **12b** and **13b** were the more rapidly eluted isomers, however. Evaporative distillation (40–60 °C, 1–5 Torr) yielded pure **9b**, a yellow liquid, mp ~0 °C (hexane); pure **11b**, a yellow liquid, n^{20}D 1.5690; and pure **12b**, a yellow liquid, mp 22–30 °C. Recrystallization of **10b** from hexane resulted in yellow needles, mp 43–44 °C. To obviate reversion of **13b** to its trans isomer (**13a**), the irradiated mixture was chromatographed with cyclohexane on 100% silicic acid; removal of cyclohexane by freeze drying gave **13b**, yellow solid, mp 22–27 °C.

Anal. Calcd for $C_8H_7NO_2$: N, 9.40. Found for **9b**: N, 9.40. Calcd for $C_9H_9NO_2$: N, 8.57. Found for **10b**: N, 8.42. Found for **11b**: N, 8.68. Calcd for $C_8H_6ClNO_2$: N, 7.64. Found for **12b**: N, 7.63. Calcd for $C_8H_6BrNO_2$: C, 42.13; H, 2.65; N, 6.14. Found for **13b**: C, 42.09; H, 2.82; N, 6.09.

Isomerization of 11a to 3-Nitro-2-phenylpropene (11c). Solutions of **11a** (0.8 g, 5 mmol) in methanol (50 ml) and sodium hydroxide (0.4 g, 10 mmol) in water (20 ml) were mixed for 10 min at 0–10 °C and then added to excess dilute acetic acid. Extraction with hexane, concentration, and chromatographic separation gave a little **11a** (not isolated) and a slower moving major component whose chromatographic properties resembled those of **11b**. Evaporative distillation of this major component gave faintly yellow **11c** (0.4 g, 50%, n^{20}D 1.554), uncontaminated by **11a** or **11b**, but containing ~10% unidentified impurities. Isomer **11c** constituted 84% of the nitromethylstyrenes in the crude hexane extract.

Isomerization of Cis Isomers 9b, 10b, 12b, and 13b to Their Respective Trans Isomers, 9a, 10a, 12a, and 13a. A solution of **9b** (0.035 g) and a few crystals of iodine in benzene (30 ml) was left at 25 °C for 2 days and then concentrated and chromatographed to give **9a** (0.02 g), mp 56–57 °C, identified by its ir spectrum. A mixture of 22% **9a** and 78% **9b** in carbon tetrachloride containing iodine was stored at 25 °C. Within 16 h, most of the **9b** had isomerized to **9a**; after 5 days, only **9a** was detectable.

A mixture of **10b** (10 mg) and iodine crystals in benzene (3 ml), after storage for 3 days, concentration, and chromatography, yielded **10a** (4 mg), mp 60–63 °C, undepressed mixture melting point with authentic **10a**. A solution of 24% **10a** and 76% **10b** in carbon tetrachloride was divided into two parts which were treated with iodine and triethylamine, respectively. After 6 days at 25 °C, only **10a** was in the iodine containing solution; both **10a** and **10b** were in the solution containing triethylamine but **10b** was present in only small percentage.

A solution of **12b** in carbon tetrachloride containing iodine did not change composition in 2 days at 25 °C, changed only slightly after 3 days at 50 °C, but contained only **12a** after 7 days at 70 °C. Treatment of a cyclohexane solution of **12b** with triethylamine caused some isomerization within 5 min; after 1 h at 25 °C only **12a** was present.

After 15 days in chloroform at 25 °C, bromonitrostyrene **13b** was 40% isomerized to trans isomer **13a**. Treatment of a mixture of 15% **13a** and 85% **13b** in chloroform with triethylamine caused complete isomerization to **13a** in 30 min.

Nonphotochemical Interconversions of 11a, 11b, and 11c. Reactions of **11a–c** (0.05–0.1 g) in carbon tetrachloride (0.5 ml) were conducted in NMR tubes. Treatment of **11a** or **11c** with triethylamine (1–2 drops) gave within 30 min an equilibrated mixture containing 74% **11a** and 26% **11c**. Within 1 day equilibrium containing 73% **11a**, 2% **11b**, and 25% **11c** was attained. The composition of the mixture did not change in 12 days. Treatment of **11b** with a small crystal of iodine gave after 12 days a mixture containing 98% **11a** and 2% **11b**. A mixture of 61% **11c**, 16% **11b**, trace **11a**, and ~23% unidentified materials was treated with triethylamine (3 drops). Within 30 min, equilibrium of **11a–c** was established but the proportion of **11b** was only slightly diminished. The concentration of **11b** became very small (~2% of that of **11a**) within 1 day; no significant changes occurred in 12 additional days.

Registry No.—**3a**, 38779-62-3; **3b**, 38779-61-2; **4a**, 38779-58-7; **4b**, 38779-57-6; **5a**, 38779-60-1; **5b**, 38779-59-8; **6a**, 58502-60-6; **6b**, 58502-61-7; **6c**, 58502-62-8; **7a**, 58502-63-9; **7b**, 58502-64-0; **7c**, 58502-65-1; **8b**, 58502-66-2; **8c**, 58502-67-3; **9a**, 5153-67-3; **9b**, 15241-23-3; **10a**, 18315-84-9; **10b**, 58321-79-2; **11a**, 15241-24-4; **11b**, 5670-65-5; **11c**, 58502-68-4; **12a**, 58502-69-5; **12b**, 58502-70-8; **13a**, 18315-81-6; **13b**, 39674-40-3; α-methylstyrene, 98-83-9; dinitrogen tetroxide, 10544-72-6.

References and Notes

(1) Initial portions of this work were presented at (a) the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract No. ORGN-106, and (b) the 11th Oklahoma Tetrasectional Meeting of the American Chemical Society, Bartlesville, Okla., March 1965.

(2) (a) R. Criegee, D. Seebach, R. E. K. Winter, B. Borretzen, and H. A. Brune, *Chem. Ber.*, **98**, 2339 (1965); (b) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **7**, 559 (1968); (c) H. M. Frey, *Adv. Phys. Org. Chem.*, **4**, 183 (1966); (d) R. Breslow in "Molecular Rearrangements", P. de Mayo, Ed., Interscience, New York, N.Y., 1963, Chapter 4; (e) R. Breslow, D. Kivelevich, M. J. Mitchell, W. Fabian, and K. Wendel, *J. Am. Chem. Soc.*, **87**, 5132 (1965); (f) G. A. Doorakian and H. H. Freedman, *ibid.*, **90**, 3582 (1968); (g) H. A. Brune and W. Schwalb, *Tetrahedron*, **25**, 4375 (1969); (h) D. L. Dalrymple and W. B. Russo, *J. Org. Chem.*, **40**, 492 (1975); (i) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

(3) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (c) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).

(4) (a) J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968); (b) J. I. Brauman and W. C. Archie, Jr., *ibid.*, **94**, 4262 (1972); (c) M. Pomerantz, R. N. Wilke, G. W. Bruber, and V. Roy, *ibid.*, **94**, 2752 (1972); (d) E. Müller and A. Huth, *Tetrahedron Lett.*, 1035, 4359 (1972).

(5) Disrotation has been previously observed for decomposition of cyclobutenes in which one or more rings are fused to the cis 3,4 bonds of the cyclobutene.[3] In these cases relatively strainless transition states and reaction products can come only from disrotatory processes.

(6) The conrotatory valence isomerization products from cyclobutenes **1a** and **1b** are designated (sequence 1) as **2a** and **2b**, respectively, to conform with the letter system subsequently used in this paper to denote the conrotatory relationship of various cyclobutenes and their dienes.

(7) It is to be noted that **2c**, a possible product of kinetic control in conrotatory ring opening of **1a**, may isomerize to the alternate conrotatory product **2a** because of the greater thermodynamic stability of the latter.

(8) (a) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *J. Am. Chem. Soc.*, **93**, 5005 (1971); (b) N. D. Epiotis, *ibid.*, **95**, 1200 (1973).

(9) The syntheses and characterizations of **3a–5b** are described by D. B. Miller, P. W. Flanagan, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 3912, 3919 (1972).

(10) In this paper cis and trans designate the relative geometries of the nitro and phenyl groups of β-nitrostyrene moieties.

(11) Initial thermal isomerization experiments in chloroform were complicated by the interconversion of **3a** and **3b** apparently caused by adventitious base. This epimerization was suppressed by flushing the reaction vessels with hydrogen chloride. Hydrogen chlorides does not affect the rates of ring opening of **3a** or **3b**, but does catalyze the conversion of **6a** to **6b** to **6c**. That the concentration of hydrogen chloride was uncontrolled probably accounts for the variability of the acid-catalyzed isomerizations of **6a** and

6b; in any event the reactions were slow relative to ring openings of **3a** and **3b**. *In pure chloroform*, **3a** *and* **3b** *do not interconvert.*

(12) Dienes **6a**, **6b**, and **6c** are easily recognized in mixtures by the distinctive vinyl hydrogen signals in their NMR spectra (Figures 1 and 2). From the chemical shifts of the vinyl hydrogens of **6a**, **6b**, **6c**, and the *cis*- and *trans*-nitrostyrenes used as model compounds, the vinyl hydrogen signals of **6d** are expected at 6.4–6.9 and 7.5–8.0 ppm (see the discussion of NMR spectra later in this paper). Signals attributable to **6d** are not observed.

(13) Although sensitive to bases, dienes **6a** and **6b** are easily isolated and are stable during chromatography, recrystallization, etc. It thus might be expected that missing diene **6d** should have stability comparable to that of **6a** and **6b**.

(14) Attempts to generate **6d** by photoisomerization were unsuccessful. Ultraviolet irradiation of **6a** in chloroform or benzene gives **6b** and **6c**. Photolysis of **6c** in various solvents yields 2-nitro-3-phenylnaphthalene (15–30%), *trans*-2,3-diphenylacrylonitrile (5–15%), *cis*-2,3-diphenylacrylonitrile (<3%), and tar. Irradiation of solid **6c** gives tar, 2-nitro-3-phenylnaphthalene (<5%), *trans*-2,3-diphenylacrylonitrile (15–30%), and *cis*-2,3-diphenylacrylonitrile (5–10%). Cf. D. B. Miller, Abstracts of Papers, XXIII IUPAC Congress, Boston, Mass., July 1971, p 101.

(15) (a) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.*, **87**, 3019 (1965); (b) in the present study **4b** has been found to isomerize at least 200 times faster than **4a**.

(16) Samples of **6a** and **6c** are available for determination of their structures by crystallographic methods.

(17) Bromodiene **7b** was reduced to diene **6c** by sodium iodide in acetic acid. While this reaction has no stereochemical significance, it provides further evidence that the overall common structures of the butadienes are correct.

(18) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(19) (a) Product **7e** forms erratically when **4a** is heated and is sometimes the major product. Since in the presence of bromine, **4a** isomerizes to **7e** at 25 °C, formation of **7e** appears to result from a bromine-catalyzed process which is independent of the thermal ring opening reactions of **4a**. (b) Bromine is a possible decomposition product of **4a** and its isomers. (c) The structure and chemistry of **7e** are under investigation.

(20) Preliminary study (see Experimental Section) indicates that isomerization of chlorocyclobutene **5a** proceeds similarly to that of its structural analogue, bromocyclobutene **4a**. Lack of sample prevented detailed study of **5a**.

(21) Limiting estimates as to the proportion of **7a** in equilibrium with **4a** and the rate of cyclization of **7a** give rate constants for ring opening of **4a** between 0.015 × 10^{-6} and 0.33 × 10^{-6} s^{-1}; see Experimental Section for details.

(22) (a) A. A. Dudinskaya, G. A. Shvekhgeimer, S. S. Novikov, and V. I. Slovetskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 168 (1961); *Chem. Abstr.*, **55**, 18559 (1961); (b) A. L. Bluhm and J. Weinstein, *J. Am. Chem. Soc.*, **87**, 5511 (1965); (c) J. A. Sousa, J. Weinstein, and A. L. Bluhm, *J. Org. Chem.*, **34**, 3320 (1969).

(23) H. L. Goebel and H. H. Wenzke, *J. Am. Chem. Soc.*, **60**, 697 (1938); G. Drefahl and G. Heublein, *Chem. Ber.*, **93**, 497 (1960); V. N. Vasil'eva, V. V. Perekalin, and V. G. Vasil'eva, *J. Gen. Chem. USSR (Engl. Transl.)*, **31**, 2027, 2031 (1960).

(24) (a) A formula given in *Chem. Abstr.*, **55**, 14580 (1961), as $C_6H_5C(R')=CHNO_2$ (R' = methyl and other groups) should be $C_6H_5CH=C(R')NO_2$; (b) K. A. Oglobin and V. P. Semenov, *Zh. Obshch. Khim.*, **29**, 2660 (1959) [*Chem. Abstr.*, **54**, 8679 (1960)], report an **11a** with n^{20}D 1.5803; (c) C. A. Burkhard and J. F. Brown, Jr., U.S. Patent 2 867 669 (Jan 6, 1959), describe a mixture, n^{20}D 1.5831, containing 60% **11a** and 40% **11c**.

(25) W. K. Seifert, *J. Org. Chem.*, **28**, 125 (1963).

(26) Solid **9a** is photodimerized by sunlight to 1,*trans*-3-dinitro-*cis*-2,*trans*-4-diphenylcyclobutane.[9]

(27) Nitro olefins **12b** and **13b** are isomerized more rapidly than is **10b** by triethylamine.

(28) (a) In carbon tetrachloride at 25 °C, the equilibrium proportions of **11a**, **11b**, and **11c** are 73, 2, and 25%, respectively. (b) Comparison of indices of refraction suggests that the nitromethylstyrenes of ref 24b and 24c are mixtures of isomers. Cf. values of n^{20}D for **11a**, **11b**, and **11c** reported in the Experimental Section of the present paper.

(29) (a) H. Shechter and J. W. Shepherd, *J. Am. Chem. Soc.*, **76**, 3617 (1954); (b) L. V. Phillips and D. M. Coyne, *J. Org. Chem.*, **29**, 1937 (1964); (c) see also L. Bouveault and A. Wahl, *Bull. Soc. Chim. Fr.*, **25**, 808 (1901); H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934); (d) M. J. S. Dewar, *Discuss. Faraday Soc.*, **2**, 261 (1947).

(30) S. Bank, A. Schriesheim, and C. A. Rowe, Jr. [*J. Am. Chem. Soc.*, **87**, 3244 (1965)], S. Bank [*ibid.*, **87**, 3245 (1965)], and R. Hoffmann and R. A. Olofson [*ibid.*, **88**, 943 (1966)] have discussed allylic anions which are thermodynamically more stable in cis than in trans forms.

(31) (a) Similar correlations have been reported for α,β-dialkylstyrenes,[31b] β-bromo-α-methylstyrenes,[31c] β-bromostyrenes,[31d] and β-acetoxystyrenes.[31d] The changes in chemical shift as a result of cis–trans isomerism in β-nitrostyrene are considerably larger, however, presumably because of the magnetic anisotropy of the nitro group. (b) M. Barbieux, N. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belg.*, **73**, 716 (1964). (c) D. R. Davis and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2252 (1962). (d) D. T. Witiak and B. B. Chaudhari, *J. Org. Chem.*, **30**, 1467 (1965).

(32) (a) E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1104 (1947); (b) M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **77**, 5696 (1955).

(33) We thank F. M. Evans and B. J. Taylor, Continental Oil Co., Ponca City, Okla., for determining some of the uv spectra and L. D. Stietzel and H. C. Barrett, Stanford Research Institute, Menlo Park, Calif., for recording many of the NMR spectra.

(34) D. E. Worrall, *Org. Synth.*, **9**, 66 (1929).

(35) H. B. Hass, A. G. Susie, and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

(36) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **73**, 4664 (1951).

Carbenic Processes in Decomposition of Spiro[fluorene-9,3'-indazole]. A Simple Route to the Fluoradene System

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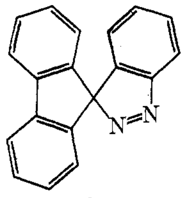
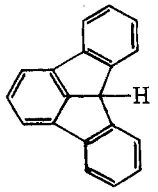
Spiro[fluorene-9,3'-indazole] (1), obtained along with 9-fluorenyl anthranilate (6) by aprotic diazotization of anthranilic acid in the presence of 9-diazofluorene (3), thermolyzes to fluoradene (2), 12,12'-bifluoradene (8), and 9-phenylfluorene (9). Thermolysis and photolysis of 1 in solution are interpretable on the basis of formation of triplet 2-(9-fluorenylidene)-3,5-cyclohexadienylidene (13), isomerization of 13 to 2, and hydrogen abstraction by 13 to yield the fluoradenyl (15) and the 9-phenylfluorenyl (16) radicals and their subsequent products. Irradiation of 1 in 2-methyltetrahydrofuran at 77 °C gives intense ESR absorption for 13. Decomposition of 1 occurs photolytically in *N*-phenylmaleimide with loss of nitrogen to form the adduct 20, $C_{29}H_{19}NO_2$. In benzene 1 photolyzes in the presence of oxygen to 2 and 8 along with 9,9-diphenylfluorene (23), 9-phenylfluorenyl peroxide (25), and biphenyl (28). Photolysis of 1 in ethyl ether and exposure of the reaction mixture to oxygen results in near-quantitative formation of 25.

Synthesis of 3-substituted 3*H*-indazoles and determination of the products and the mechanisms of their isomerization and decomposition are being studied in this laboratory.[1,2] We now describe the preparation and the thermolysis and photolysis reactions of spiro[fluorene-9,3'-indazole] (1). Decomposition of 1 is significant in that its intramolecular and intermolecular reactions take place by triplet carbenic processes. Thermolysis and photolysis of 1 are also of value in that the interesting hydrocarbon, fluoradene (2), is formed efficiently.[3]



1



2

Spiroindazole 1 is prepared in 70–80% yields by cycloaddition (eq 1) of 9-diazofluorene (3) to benzyne (4) as gener-