is unknown and the calculated one is close to that of trans isomer, the

- stereoisomers could not be distinguished by only the coupling constant.
   R. M. Coates and R. L. Sowerby, J. Am. Chem. Soc., 93, 1027 (1971); G. Stork and J. Benaim, *ibid.*, 93, 5938 (1971), and references cited there-
- (12) L. Ruzicka and E. A. Rudolph, Helv. Chim. Acta, 9, 118 (1926); A. St. Pfau and P. A. Plattner, *ibid.*, **19**, 858 (1936); P. A. Plattner, *Angew. Chem.*, **55**, 154 (1942); D. H. R. Barton, "Chemistry of Carbon Compounds", Vol. IIB, E. H. Rodd, Ed., Elsevier, Amsterdam, 1953, p. 667. W. Keller-Schierlein and E. Heilbronner, "Non-Benzenoid Aromatic
- (13) W. Keller-Schlerlein and E. Heilbronner,
- W. Keller-Schlerlein and E. Heilbronner, "Non-Benzenoid Aromatic Compounds", D. Ginsburg, Ed., Interscience, New York, N.Y., 1959, pp 277-337; T. Nozoe and T. Asao, "Dal Yúki-Kagaku", Vol. 13, M. Kotake, Ed., Asakura, Tokyo, 1960, Chapters 16 and 17.
   For reviews, see R. A. Raphael, "Chemistry of Carbon Compounds", Vol. IIA, E. H. Rode, Ed., Elsevier, Amsterdam, 1953, pp. 298-307; N. A. J. Rogers, "Rodd's Chemistry of Carbon Compounds", Vol. IIC, 2nd ed, S. Coffey, Ed., Elsevier, Amsterdam, 1969, pp. 20-31; A. P. Krapcho, Syn-thecic 383 (1974). thesis, 383 (1974).
- (15) H. Takaya, S. Makino, Y. Hayakawa, and R. Novori, J. Am. Chem. Soc., 100, 1765 (1978).
- (16) R. Noyori, Y. Hayakawa, H. Takaya, S. Murai, R. Kobayashi, and N. Sonoda, J. Am. Chem. Soc., **100**, 1759 (1978).
- (17) G. H. Alt, "Enamines: Synthesis, Structure, and Reactions", A. G. Cook, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 4; V. B. Anderson, M.

N. Agnew, R. C. Allen, J. C. Wilker, H. B. Lassman, and W. J. Novick, J. Med. Chem., 19, 318 (1976); B. A. McAndrew and S. W. Russel, J. Chem. Soc., Perkin Trans. 1, 1172 (1975).

- R. B. King, Organomet. Synth., 1, 93 (1965).
   E. LeGoff, J. Org. Chem., 29, 2048 (1964).
   C. Rappe, Acta Chem. Scand., 16, 2467 (1962).

- (21) H. E. Hennis and W. B. Trapp, J. Org. Chem., 26, 4678 (1961).
   (22) N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling and W. S. Hammond, J. Am. Chem. Soc., 91, 2283 (1969).
- (23) G. Stork, A. Brizzolara, H. Landersman, J. Szmuszkovicz, and R. Terrell, J. Am. Chem. Soc., 85, 207 (1963).

- (24) The detailed procedure will appear in *Organic Syntheses*.
  (25) E. Benzing, *Angew. Chem.*, 71, 521 (1959).
  (26) Result from a homoallylic coupling that is very familiar in 2-cyclopentenone derivatives. The related long-range coupling was reported in W. v. E. Doering, M. R. Willcott, III, and M. Jones, Jr., J. Am. Chem. Soc., 84, 1224 (1962), and A. J. Fry and J. J. O'Dea, J. Org. Chem., 40, 3625 (1975).
  (27) G. Wittig, W. Böll, and K.-H. Krück, Chem. Ber., 95, 2514 (1962).
  (28) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 87, 1345 (1965).
  (29) P. A. Plattner, A. Fürst, and K. Jirasek, Helv. Chim. Acta, 30, 1320

- (1947).
- (30) W. Treibs, H.-J. Neupert, and J. Hiebsch, *Chem. Ber.*, **92**, 141 (1959).
   (31) H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Am. Chem. Soc.*,
- 94, 3940 (1972).

## Synthesis, Properties, and Reactions of Dispiro[2.2.2.2]deca-4,9-diene

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Abstract: Dispiro[2.2.2.2]deca-4,9-diene (1) was prepared in five steps from diethyl succinate. This particular cyclopropylethylene exhibits a relatively large bathochromic shift of the absorption maximum (222 nm) in UV and a marked lowering of the ionization potential (7.23 eV) compared to cis-1,2-dicyclopropylethylene (203.5 nm in UV and IP 7.70 eV). The chemical shift of the olefinic protons, however, does not suggest the existence of cyclic conjugation in 1. The spiro olefin 1 underwent interesting cycloadditions with a variety of unsaturated compounds. (1) It reacts with conjugated dienes at 160 °C to give [8]paracycloph-4-enes, 13 and 14. The two cyclopropane rings are cleaved and the central cyclohexadiene ring is aromatized. (2) It reacts with dimethyl maleate or dimethyl acetylenedicarboxylate at 160 °C to afford dispiro[2.2.4.2]dodecane derivatives, 22 and 23. One of the cyclopropanes is cleaved, to which the reacting olefin cycloadds. (3) It reacts with tetracyanoquinodimethane in o-dichlorobenzene to produce a [3.3] paracyclophane derivative, 30. The first two cycloadditions are proved to proceed via biradical intermediates, while the last reaction involves a zwitterionic intermediate which can be trapped by polar multiple bonds. Conformational equilibria of some cycloadducts are also discussed.

It is known that conjugative interaction between a cyclopropane ring and a double bond is maximized when a bisected conformation is attained.<sup>1</sup> Dispiro[2.2.2.2]deca-4,9-diene (1) where the double bonds and the cyclopropane rings are aligned alternately around the six-membered ring in the bisected conformation is, therefore, of considerable interest for a number of reasons including (1) the possibility of cyclic con-



jugation through the cyclopropane rings geminally substituted by the double bonds, (2) the  $\pi$ -base character due to the electron-donating property of a cyclopropane ring, and (3) the expected formation of the species, via the cleavage of the cyclopropane ring, whose spiro[2.5]octane moiety possesses the same structure as an intermediate (or a species in the transition state) postulated for 1,2-aryl migration.<sup>2</sup>

Herein we describe the preparation of 1, its properties, and some interesting reactions of 1 which proceed via homolysis as well as heterolysis of the cyclopropane ring and provide a convenient route to a variety of paracyclophane derivatives.

### **Results and Discussion**

Synthesis and Properties of Dispiro[2.2.2.2]deca-4,9diene. 2,5-Dimethylene-1,4-cyclohexanediol (2), prepared from diethyl succinate following the procedure of Murphy,<sup>3</sup> was cyclopropanated with methylene iodide and zinc-copper couple<sup>4</sup> to give the dispiro diol (3), which was subsequently oxidized with the Jones reagent to the diketone (4). Treatment of the bistosylhydrazone of 4 with n-butyllithium<sup>5</sup> afforded dispiro[2.2.2.2]deca-4,9-diene (1) in a 64% yield. The dispiro compound, 1, could be obtained as volatile, colorless plates melting at 121-122 °C. Proof of the structure of 1 was pro-



vided by its elemental analysis and spectral properties. Synthesis of 1 was also attempted by the pyrolysis of the bisxanthate of 3. When the temperature of the heating bath was slowly raised, the xanthate (5) isomerized almost quantitatively to the thermally more stable thiol carbonate (6).<sup>6</sup> When the flask containing **5** was immersed in a bath preheated to 300 °C, however, the elimination reaction took place and **1** was obtained together with **6**. The compounds obtained through the two different routes were identical in all respects.

It is known that a cyclopropyl substituent on an olefin brings about a bathochromic shift of the absorption maximum in the UV spectrum<sup>7</sup> and a lowering of the ionization potential,<sup>8</sup> owing to its conjugating ability and electron-donating property. A comparison of the UV spectrum of **1** with those of cyclopropylethylenes clearly indicated the presence of extended conjugation in **1**. The absorption maximum for **1** appears at 222 nm compared to 203.5 nm for *cis*-dicyclopropylethylene. The ionization potential (adiabatic) of **1** was found to be 7.23 eV,<sup>9</sup> which was lower than that of *cis*-dicyclopropylethylene by 0.47 eV and comparable with that of tetracyclopropylethylene.<sup>10</sup> These pronounced effects exerted by the cyclopropyl groups in **1** may be rationalized in terms of the conformational propriety of the cyclopropane rings for the conjugative interaction with the  $\pi$  system.

On the other hand, the NMR of 1 exhibits two singlets at  $\delta$  0.69 and 4.80, which indicates that no appreciable ring current is induced since the chemical shift of the olefinic protons is essentially the same as that of H-4 in spiro[2.5]oct-4-ene (7)



 $(\delta 4.90)$ .<sup>11</sup> In accord with the observations previously reported, <sup>12</sup> these results suggest that conjugation between the geminally substituted unsaturated moieties on the cyclopropane ring is not significant even in the system in which the cyclopropane ring and the double bonds are aligned in the bisected conformation.

The dispiro compound (1) is stable at ambient temperature indefinitely, but decomposes at 160 °C with a half-life of ca. 40 min in diglyme affording *p*-diethylbenzene as the major product. The first-order rate constants for the disappearance of 1 in triglyme were  $(3.04 \pm 0.08) \times 10^{-4} \, \text{s}^{-1}$  at 160.0 °C and  $(1.64 \pm 0.03) \times 10^{-3} \, \text{s}^{-1}$  at 179.9 °C. In the presence of *p*thiocresol, the disappearance of 1 was accelerated and the addition product (10) was formed along with *p*-diethylbenzene. Thus the thermal decomposition of 1 probably proceeds by way of the biradical intermediates, 8 and 9, resulting from the

Scheme I



homolytic cleavage of the cyclopropane rings. In the absence of a radical scavenger, that these intermediates are capable of recyclization and are in rapid equilibrium with 1 was demonstrated unambiguously by the CIDNP effect observed in 1 during thermolysis.<sup>13</sup> The photolysis of 1 proceeded analogously and the products isolated from the photolysate in ether were *p*-diethylbenzene and an adduct of the solvent, 11. Thus it appears that strain relief by the cleavage of the cyclopropane rings and the aromatization of the six-membered ring direct the thermal and photochemical reaction pathways of 1.

**Cycloaddition with Conjugated Dienes.**<sup>1</sup> The chemistry of paracyclophanes having a short bridge is of considerable interest,<sup>15,16</sup> but has so far not been well explored. The finding that the cyclopropane rings in 1 are cleaved thermally led us to an investigation of the cycloaddition reaction of 1 with conjugated dienes. The dispiro compound, 1, proved to be an excellent precursor of [8]paracyclophane derivatives bearing various functional groups on the bridge.

The reaction of 1 with 2 equiv of 1,3-butadiene in benzene at 160 °C produced a mixture of four products which were subsequently separated by preparative GLC. The major product was *trans*-[8]paracycloph-4-ene (13a), and the other three products were *cis*-[8]paracycloph-4-ene (14a) and the



two 1:2 cycloadducts represented by 15 and 16. This novel cycloaddition reaction was quite general and with various substituted 1,3-butadienes afforded [8]paracycloph-4-ene derivatives in 60-90% yields as shown in Table I. Proof of the structures of the cycloadducts was provided by their elemental analysis and spectral properties. In the <sup>1</sup>H NMR spectra, the olefinic proton signals characteristically appeared at an unusually high field reflecting the shielding effect by the underlying aromatic ring, i.e., at  $\delta$  3.7–4.3 in those of the *trans*-4-ene derivatives, 13, and at a somewhat lower field,  $\delta$  4.3-4.7, in those of the cis isomers, 14 (Table II). Molecular models indicate that in the trans-4-enes the planes of the double bond and the benzene ring are parallel to each other and the olefinic protons are located over the benzene ring whereas in the cis isomers the plane of the double bond is tilted against that of the benzene ring and the olefinic protons are at a greater distance from the center of the benzene ring. The UV spectra of the cycloadducts exhibited shifts of the absorption maxima to longer wavelengths relative to that of an open-chain analogue and the disappearance of the fine structure, which are characteristics of strained paracyclophanes. The cis-4-ene derivative invariably showed the absorption maximum at a longer wavelength by 5-7 nm than the corresponding trans isomer (Table III). This observation suggests the presence of a larger extent of deformation of the benzene ring from a planar configuration in the cis isomer than in the trans isomer.<sup>17</sup> An examination of molecular models of the two isomers indeed leaves little doubt that the cis isomer is more strained. The cis-4-ene derivatives (1) were obtained in the reactions with 1,3-butadiene, methyl pentadienoate, and 2,3-dimethyl-1,3-butadiene, but could not be isolated in the reactions with other dienes. In the case of the 1,4-disubstituted dienes, the high steric compression in the resulting 3,6-disubstituted cis-4-enes might hinder their formation.

**Conformation of Some [8]Paracycloph-4-enes.** In the reaction of 1 with the 1,4-disubstituted 1,3-diene, a mixture of two isomeric 1:1 cycloadducts was obtained. These compounds

Table I. Cycloaddition Products from the Reactions of Dispiro [2.2.2.2] deca-4,9-diene (1) with Conjugated Dienes,  $12^a$ 

							Products % yields <sup>b</sup>			
	Substituents				Concn, mol/L		13			
	R <sup>1</sup>	R <sup>2</sup>	<u>R<sup>3</sup></u>	Geometry of 12	1	12	Trans <sup>c</sup>		Cisc	14
a	н	Н	Н		0.19	0.38		74		10 <sup>d</sup>
b	Н	Н	$CH_3$		0.094	0.34		58e		
с	Н	Н	$CO_2CH_3$	Trans	0.19	0.38		65		5
d	Н	Н	CN	$Cis/trans \approx 1$	0.19	0.38		68		
e	CO <sub>2</sub> CH <sub>3</sub>	Н	CO <sub>2</sub> CH <sub>3</sub>	Trans, trans	0.38	0.75	54 <sup>f</sup>		<b>9</b> f	
				Cis,trans	0.38	0.75	39 <sup>f</sup>		32 <sup>f</sup>	
f	CO <sub>2</sub> CH <sub>3</sub>	Н	CN	Trans, trans	0.19	0.34	50 <sup>f</sup>		29 <i>f</i>	
g	CN	Н	CN	Cis,cis	0.38	0.72	58 <sup>f,g</sup>		31 <sup>f,g</sup>	
ĥ	C <sub>6</sub> H <sub>5</sub>	Н	C <sub>6</sub> H <sub>5</sub>	Trans, trans	0.38	0.75	30		$(5)^{h}$	
i	Н	CH3	Н		0.094	0.19		57		14
j	H	Cl	Н		0.094	0.16		30		

<sup>a</sup> The reactions were carried out in benzene at 160 °C. The reaction products were analyzed after 1 had been consumed unless otherwise noted. <sup>b</sup> Determined by GLC with internal standards unless otherwise indicated. <sup>c</sup> Configuration of two substituents,  $\mathbb{R}^1$  and  $\mathbb{R}^3$ , with respect to the paracyclophane ring. <sup>d</sup> In addition to the 1:1 adducts, two 1:2 cycloadducts, **15** (5%) and **16** (4%), were obtained. <sup>e</sup> In addition to **13b**, an open-chain adduct, **17** (13%), was isolated. <sup>f</sup> Isolated yields. <sup>g</sup> Determined after 86% of starting 1 had been consumed. Yields based on unrecovered 1. <sup>h</sup> Not isolated.

Table II. Absorption Maxima in the Ultraviolet Spectra of [8] Paracycloph-4-enes<sup>a</sup>

Compd		λ, nm	$(\log \epsilon)$	
13a <sup>b</sup>	224 (3.85)	265 (2.53) <sup>c</sup>	271 (2.63)	278 (2.59)
14a <sup>b</sup>	225 (3.88)	277 (2.56)	284.5 (2.51)	
13b	224 (3.84)	271 (2.63)	278 (2.58)	
13c	222 (3.86)	265.5 (2.51) <sup>c</sup>	270.5 (2.60)	278 (2.56)
14c	226 (3.79)	277 (2.57)	284 (2.52)	
13.1	223 (3.83)	270 (2.62)	277.5 (2.59)	
trans-13e	222 (3.91)	265 (2.46) <sup>c</sup>	271 (2.58)	278 (2.54)
cis-13e	221 (3.88)	270.5 (2.61)	277 (2.56)	
trans-13f	220 (3.86)	269.5 (2.57)	277 (2.54)	
trans-13g	223 (3.82)	269 (2.65)	276.5 (2.60)	
cis-13g	223 (3.83)	269 (2.62)	276.5 (2.57)	
trans-13h	262 (3.00)	269 (3.00)	279 (2.68)	
13i	222 (3.89)	273.5 (2.64)	281 (2.59)	
14i	231 (3.80)	278 (2.58)	285 (2.52)	
<u>13j</u>	221 (3.86)	265 (2.45) <sup>c</sup>	271 (2.53)	279 (2.48)

<sup>a</sup> Spectra taken in 95% ethanol unless otherwise indicated. <sup>b</sup> Taken in hexane. <sup>c</sup> Shoulder.

were identified as the *trans*-4-enes having two substituents in the cis and trans configurations at the C-3 and C-6 positions with respect to the paracyclophane ring primarily through the scrutiny of their NMR spectra. An examination of molecular models suggests that the *trans*-4-ene has the configuration shown below.<sup>17</sup> Therefore, the trans-disubstituted compound can possess two different conformations, **18** and **19**. The NMR



spectra of the trans-disubstituted derivatives were found to be essentially invariant with respect to temperature change and were consistent with either of the two conformers. The olefinic and allylic protons in the substance bearing the same substituents on the allylic positions form an AA'XX' system. The signal of the olefinic protons appears as a symmetrical quartet (doublet of doublets) in the spectra of *trans*-13e and *trans*-13h with the coupling constants |J| = 5.5 and 2.5 Hz in the former and |J| = 5.6 and 2.6 Hz in the latter. In contrast, in that of *trans*-13g the olefinic proton signal appears as a sharp singlet and thus the coupling constants must be less than 1 Hz. Molecular models show that the olefinic and the adjacent allylic C-H bonds are close to antiperiplanar to one another in the conformer, 18, whereas they are nearly orthogonal in the conformer, 19. Thus the coupling constants suggest that *trans*-13e and *trans*-13h possess essentially the conformation of 18 whereas in *trans*-13g the major conformer is 19.

The NMR spectra of the cis-3,6-disubstituted trans-[8]paracycloph-4-enes were found to be temperature dependent. For example, in acetone- $d_6$  the methyl groups of the cisdimethoxycarbonyl derivative, cis-13e, appear as a singlet at 23 °C, which broadens at -30 °C and splits into two sharp singlets at -60 °C. Concomitantly, the two singlets of the aromatic protons are replaced by two AB quartets of equal intensity and the quartet of the olefinic protons also by a doublet of doublets and a doublet of doublets of doublets. These results suggest that, accompanying the rotation of the double bond system with respect to the benzene ring, two isoenergetic conformers, 20e and 21e, are equilibrating rapidly on the NMR time scale at room temperature, but are frozen out at -60 °C. The spectrum of cis-13g exhibits analogous temperature dependence and, of the two singlets of the aromatic protons, the one at the higher field becomes an AB quartet while there is no apparent change in the lower field signal when the temperature was lowered, which is also consistent with the conformational equilibration between 20g and 21g. The barriers for the conformational interconversion for cis-13e and *cis*-13g were  $\Delta G^{\pm}_{238} = 12.3$  kcal/mol and  $\Delta G^{\pm}_{284} = 14.2$ kcal/mol, respectively, which were similar in magnitude with

<b>Table III.</b> Nuclear Magnetic Resonance Spectra of	8	Paracycloph-4-enes <sup>a</sup>
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	Temp,	δ, ppm (pattern)							
Compd	°C	Bridge alipha	tic protons	Olefinic protons	Aromatic protons	Other protons			
13a	69 <i><sup>b</sup></i>	1.3-1.8 (m. 8 H).	2.54 (t. 4H) <sup>c</sup>	3.78 (br s, 2 H)	6.80 (s, 4 H)				
	$-40^{d}$	0.8–1.7 (m, 4 H),	1.7-2.4 (m, 6 H)	3.80 (m, 2 H)	6.85 (AB q, 4 H) <sup>f</sup>				
		2.98 (d of d, 2 H) <sup>e</sup>							
14a	60 <i>b</i>	1.3-1.5 (m, 4 H),	1.5-1.8 (m, 4 H)	4.42 (t, 2 H) <sup>h</sup>	6.90 (s, 4 H)				
		$2.64 (t, 4 H)^{g}$							
	$-50^{d}$	1.0-1.8 (m, 6 H),	1.8-2.6 (m, 4 H)	4.5-4.7 (m, 2 H)	7.02 (s, 4 H)				
		2.8-3.2 (m, 2 H)							
13b	61 <i><sup>b</sup></i>	1.0-2.0 (m, 7 H),	2.0-2.5 (m, 2 H)	3.7-3.9 (m, 2 H)	6.7-7.0 (q, 4 H)	0.74 (d, 3 H)°			
		2.7-3.0 (m, 2 H)							
13c	23	1.0-1.8 (m, 3 H),	1.8–2.4 (m, 6 H)	3.7-4.2 (m, 2 H)	6.7-7.2 (m, 4 H)	3.45 (s, 3 H)			
		2.9-3.2 (m, 2 H)							
14c	23	1.1-1.6 (m, 4 H),	1.9-2.6 (m, 5 H)	4.4–4.8 (m, 2 H)	6.91 (s, 2 H)	3.44 (s, 3 H)			
		2.8-3.1 (m, 2 H)			6.96 (s, 2 H)				
13d	23	1.0-3.2 (m, 11 H)		3.76 (d of d, 1 H) <sup><math>i</math></sup>	6.7–7.1 (m, 4 H)				
				4.1-4.4 (m, 1 H)					
trans-13e	23 <i>ª</i>	1.6-2.5 (m, 8 H),	3.05 (q, 2 H)	4.12 (d of d, 2 H) <sup>j</sup>	6.98 (AB q, 4 H) <sup><i>j</i></sup>	3.53 (s, 6 H)			
cis-13e	23 <i>ª</i>	1.7-2.2 (m, 4 H),	2.4–3.0 (m, 6 H)	4.30 (d of d, 2 H)*	6.91 (s, 4 H)	3.60 (s, 6 H)			
	$-60^{7}$	1.6-3.2 (m, 10 H)		4.15 (d of d, 1 H) <sup><math>m</math></sup>	6.97 (AB q, 2 H) <sup>o</sup>	3.45 (s, 3 H)			
				4.46 (d of d of d, 1 H) <sup><math>n</math></sup>	7.00 (AB q, 2 H) <sup><math>p</math></sup>	3.57 (s, 3 H)			
trans-13f	23 <i>ª</i>	1.6-2.5 (m, 8 H),	2.9-3.2 (m, 2 H)	$4.07 (d \text{ of } d, 1 \text{ H})^q$	6.6–7.2 (m, 4 H)	3.60 (s, 3 H)			
	<b>a</b> a <i>d</i>			$4.25 (d \text{ of } d, 1 \text{ H})^{q}$	= 00 ( <b>/ / / /</b>				
trans-13g	23 <i>ª</i>	1.6-2.1 (m, 2 H),	2.1–2.4 (m, 2 H)	4.33 (s, 2 H)	7.03 (s, 4 H)				
	ech d	2.60 (d of t, 2 H) $^{\prime}$ ,	2.9–3.4 (m, 4 H)						
cis-13g	56 <i>0,4</i>	2.05 (m, 4 H),	2.5-3.0 (m, 6 H)	4.25 (d of d, 2 H) <sup>3</sup>	6.91 (s, 2 H)				
	201	1 ( 2 0 ( 7 11)	20.24( 211)		7.10(s, 2H)				
	-30*	1.6-2.8 (m, / H),	3.0-3.4 (m, 3 H)	$4.0-4.5 (m, 2 H)^{2}$	0.95 (AB q, 2 H)"				
4	22	16.21(m.4H)	21.2(	4.14 (d of d $2.11$ ) $i$	7.10(s, 2H)				
trans-13n	23	1.6-2.1 (m, 4 H),	2.1-2.0 (m, 4 H)	4.14 (d 01 d, 2 H) <sup>3</sup>	0.7 - 7.2 (m, 14 m)				
12;	72	2.7-3.2 (m, 2 H)	28.21(m.211)		670 (AP a 4 H)"	112 (6 6 11)			
131	23	1.3-2.3 (III, 10 H),	2.0-3.1 (III, 2 H) 2.52 (+ 4 H) (		$(AD q, 4 \Pi)^{\circ}$	$1.12(5,0\Pi)$ $1.26(0.6\Pi)$			
141	∠3 22d	$1.0-1.3$ (III, $\delta$ H), 1.7, 2.5 (m, $10$ H)	$2.32(1, 4 H)^{\circ}$		0.72 (5,4 M) 6 82 (AB a 4 M)W	1.20 (S, O H)			
10]	23=	1.7-2.5 (III, 10 H),	2.30 (DF U, 2 H)		0.02 (AD 4, 4 fl)"				

<sup>a</sup> Taken on a JEOL PS-100 spectrometer at 100 MHz with tetramethylsilane as internal standard in carbon tetrachloride unless otherwise indicated. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. <sup>b</sup> Fine structure broadens at room temperature. <sup>c</sup> J = 6 Hz. <sup>d</sup> Taken in deuteriochloroform. <sup>e</sup> J = 5 and 12 Hz. <sup>f</sup> J = 8 Hz,  $\Delta \nu = 22$  Hz. <sup>g</sup> J = 7 Hz. <sup>h</sup> J = 5 Hz. <sup>i</sup> J = 4 and 15 Hz. <sup>j</sup> J = 2.5 and 5.5 Hz. <sup>k</sup> J = 1.5 and 3.5 Hz. <sup>l</sup> Taken in hexadeuterioacetone. <sup>m</sup> J = 3.5 and 15 Hz. <sup>n</sup> J = 1.5, 9, and 15 Hz. <sup>o</sup> J = 8 Hz,  $\Delta \nu = 41$  Hz. <sup>p</sup> J = 8 Hz,  $\Delta \nu = 13$  Hz. <sup>q</sup> J = 8 and 15 Hz. <sup>r</sup> J = 5 and 13 Hz. <sup>s</sup> J = 1.5 and 3 Hz. <sup>l</sup> AB part of ABXY, J<sub>AB</sub> = 16 Hz. <sup>u</sup> J = 8 Hz,  $\Delta \nu = 23$  Hz. <sup>v</sup> J = 6.5 Hz. <sup>w</sup> J = 7.2 Hz,  $\Delta \nu = 8.6$  Hz.



that reported for deuterated [8]paracycloph-4-ene.<sup>18</sup> The AB quartets of the aromatic protons in 13i and 13j, in which the olefinic protons are substituted by methyl group and chlorine atom, respectively, remained without observable change up to 200 °C ( $\Delta G^{\ddagger} > 26$  kcal/mol). Apparently the repulsive interaction between those substituents and the benzene ring is large enough to make the rotamer equilibration slow on the NMR time scale. *cis*-[8]Paracycloph-4-ene also exhibits a temperature-dependent NMR spectrum, which may be explained by the conformational equilibration formulated below.



Reactions with Olefinic and Acetylenic Compounds. The reaction of 1 with dimethyl maleate was carried out as described for the conjugated dienes. GLC analysis of the reaction mixture indicated the presence of a major product, which was shown to be the dispiro cycloadduct, **22**.<sup>19</sup> Analogously, the



reaction with dimethyl acetylenedicarboxylate afforded 23 in good yield. In both reactions, no formation of either [6]- or [8]paracyclophane derivatives resulting from the 1:1 or 1:2 cycloaddition of 1 with the unsaturated compound was observed. The reaction of 1 with phenylalkenes resulted in the formation of [4.2]paracyclophanes,<sup>20</sup> full accounts of which were reported elsewhere.<sup>21</sup>

Mechanism of the Cycloaddition Reaction of 1 with Conjugated Dienes and Olefinic and Acetylenic Compounds. The present reaction may be explained by the pathway outlined in the following schematic diagram. As has been demonstrated previously, the cyclopropane ring in 1 cleaves homolytically at an appreciable rate above 150 °C. The biradical, 9, thus generated reversibly from 1 adds to 12 to give 24 and 25, which subsequently cyclize to 13 and 14, respectively. In fact, the



reaction of 1 with *trans,trans*-12e exhibited CIDNP in the cycloaddition products substantiating the radical pathway of the reaction. In the presence of *p*-thiocresol, the cycloaddition reaction was completely inhibited and *p*-diethylbenzene and the adduct of *p*-thiocresol to 1 (10) were the only isolable products. The formation of the 1:2 cycloadducts, 15 and 16, in the reaction of 1 with 12a also supports the above mechanism. The formation of the *cis*-4-ene derivatives (14) observed in some of the reactions would probably result from the addition of 9 (and/or 8) to the s-cis form of the dienes to give 25, while the *trans*-4-enes from the addition to the s-trans dienes. The rotational barrier for allyl radical ( $\geq 17$  kcal/mol)<sup>22</sup> is so high that the interconversion between 24 and 25 may be ruled out.

As shown in Table I, the reactions with *trans,trans*- and *cis,trans*-12e resulted in different compositions of *cis*- and *trans*-13e. This result implies that the biradical intermediate, 24e, collapsed to the paracyclophane before reaching the rotational equilibrium. In other words, the adducts partially retained the stable conformation of the dienes, i.e., 27 in



trans, trans-12e and 28 in cis, trans-12e. In the reaction of 1 with piperylene, the cycloadduct, 13b, was obtained rather surprisingly in a higher yield than the disproportionation product (17), which suggested, coupled with the partial retention of the stable conformation of the dienes, that the ring closure of the biradical (24) to the strained trans-[8] paracy-cloph-4-ene (13), was not hindered so much and proceeded efficiently.

The NMR spectrum recorded during the reaction of 1 with trans, trans-12e in biphenyl ether at 190 °C exhibited CIDNP and the characteristic signal of the olefinic protons in the cycloadducts, cis- and trans-13e, appeared as emission. The observed polarization in the olefinic protons could be due to S-T<sub>0</sub> mixing in 2e.<sup>23</sup> Alternatively, the biradical (9) in the triplet state which was generated through the S-T- transition in 9<sup>13</sup> might add to 12e to give triplet 24e, in which the polarization was induced through T\_-S transition. In the CIDNP spectrum, all the lines in the quartet signals of the olefinic protons in cis- and trans-13e appeared as emission and a multiplet effect was not observed. Therefore, if the former mechanism is operative, the g value of the odd electron on the  $\beta$ -arylethyl carbon in 24e must be substantially larger than that of the odd electron which delocalizes over the allylic system;<sup>24</sup> this appears rather implausible. The latter mechanism appears to be more consistent with the observation since all the CIDNP



signals occur in emission when a biradical is generated in a triplet state.<sup>25</sup>

**Reaction with TCNQ and Its Derivative.** The reaction of 1 with tetracyanoquinodimethane (TCNQ) proceeded smoothly at 60 °C in *o*-dichlorobenzene and 1 was consumed completely in 20 h. From the reaction mixture, 1,1,12,12-tetracyano[3.3]paracyclophane (30) was isolated in a 35% yield as colorless crystals melting at 260 °C. Proof of the structure of 30 was provided by its elemental analysis and spectral properties, and finally by reductive decyanation, which afforded the parent compound (31) in 76% yield. In acetonitrile, the reaction was complete within 60 h at room temperature. The sole product isolated was a solvent incorporated cycloadduct, 32 (65%). Analogously, the reaction in acetone resulted in the formation of 33. None of 30 was detected in those reactions.

As mentioned previously, 1 possesses an unusually low ionization potential. The reaction of 1 with TCNQ may be rationalized by the initial formation of the zwitterionic intermediate, 29. In o-dichlorobenzene, 29 collapses directly to 30. In acetonitrile and acetone, however, the interception of 29 by the solvent would be much faster than the ring closure to the strained 30 and hence 32 and 33 would result.<sup>26</sup> The formation of the solvent incorporated products strongly argues against the biradical mechanism.

Tetramethoxycarbonylquinodimethane (34), which possesses poorer electron-accepting ability as compared to TCNQ,<sup>27</sup> no longer underwent the donor-acceptor type cycloaddition with 1 and only its spontaneous polymerization took place when a mixture of 1 and 34 in acetonitrile was



stirred at room temperature. [3.3]Paracyclophane derivative (35) was, however, obtained in 10% yield when the mixture was heated at 170 °C for 5 h in benzene. Since the cyclopropane ring in 1 cleaves homolytically at the above temperature, 35 would probably be formed by way of the biradical intermediates as formulated for the reaction of 1 with conjugated dienes. The reaction with TCNQ in o-dichlorobenzene at 170 °C resulted in an increased yield of 30 (60%). It is noteworthy that the cycloaddition of TCNQ is rare<sup>28</sup> and, to our knowledge, paracyclophane formation in which TCNQ participates is not precedented. The cycloaddition-decyanation gives 31, which

can be prepared only after tedious synthetic procedures,<sup>29</sup> in a 46% overall yield in two steps.

Tetracyanoethylene (TCNE) undergoes a cycloaddition reaction with a variety of electron-rich olefins.<sup>30</sup> Treatment of 1 with TCNE in acetonitrile and ethyl acetate, however, led to the formation of amorphous polymeric material, but no product of definite structure was noted.

#### Conclusion

Dispiro[2.2.2.2]deca-4,9-diene (1) exhibited interesting chemical and physical properties and it also proved to be an excellent precursor of some paracyclophane derivatives. Owing to the bisected conformation of the cyclopropane ring in 1 which is most favorable for the conjugation between double bond and electron-donating cyclopropyl group, 1 possesses an unusually low ionization potential and shows a large bathochromic shift of the absorption maximum in the UV spectrum. The thermal cycloaddition with conjugated dienes proceeded by way of biradical intermediates and afforded [8]paracycloph-4-enes in yields higher than 60%. The dispiro compound, 1, also underwent the donor-acceptor type cycloaddition with TCNQ at ambient temperature.

#### **Experimental Section**

General. Melting points are uncorrected. NMR spectra were obtained with a JEOL PS-100 spectrometer at 100 MHz; temperature in the probe was maintained at 23 °C unless otherwise indicated. Chemical shifts are given in parts per million from Si(CH<sub>3</sub>)<sub>4</sub>. IR spectra were taken on a Hitachi Model 215 grating spectrometer. Mass spectra were recorded on a Hitachi Model RMU-6E spectrometer at an ionizing voltage of 80 eV; ions of each spectrum were normalized to the spectrum's most intense ion set equal to 100, and relative intensities are given in parentheses. UV spectra were taken on Cary Model 17 and Hitachi EPS-2 spectrophotometers. GLC work was done on Hitachi Type 063 and Yanaco G-8 gas chromatographs using helium as a carrier gas. The following columns were used: A, 20% Apiezon Grease L on Celite 545, 3 mm × 1 m; B, 20% Apiezon Grease L on Celite 545, 3 mm × 2.5 m; C, 15% Apiezon Grease L on Celite 545, 3 mm  $\times$  5 m; D, 5% Silicon SE-30 on Celite 545, 3 mm  $\times$ 70 cm.

**Materials.** Tetracyanoquinodimethane, tetracyanoethylene, *p*-thiocresol, dimethyl maleate, 1,3-butadiene, and piperylene were obtained from commercial sources and purified by recrystallization or fractional distillation before use. 2,5-Dimethylene-1,4-cyclohexanediol,<sup>3</sup> methyl *trans*-2,4-pentadienoate,<sup>31</sup> *cis*- and *trans*-2,4-pentadienenitriles,<sup>32</sup> dimethyl *cis*,*trans*-<sup>33</sup> and *trans*,*trans*-2,4-hexadiene-1,6-dioates,<sup>34</sup> *cis*,*cis*-2,4-hexadiene-1,6-dinitrile,<sup>35</sup> *trans*, *trans*-1,4-diphenyl-1,3-butadiene,<sup>36</sup> 2,3-dimethyl-1,3-butadiene,<sup>37</sup> 2,3-dichloro-1,3-butadiene,<sup>38</sup> dimethyl acetylenedicarboxylate,<sup>39</sup> and tetramethoxycarbonylquinodimethane<sup>27</sup> were prepared following the procedures reported previously. Solvents were purified by fractional distillations before use.

Dispiro[2.2.2.2]decane-4,9-diol (3). A mixture of 158 g of methylene iodide (0.59 mol) and 60 g of granular Zn-Cu couple<sup>40</sup> (0.92 mol) in 500 mL of dry ether was placed in a flask fitted with an efficient stirrer and heated under gentle reflux for 20 min. Fifteen grams of 2 (0.107 mol) pulverized in a mortar was added portionwise<sup>41</sup> and the resulting mixture was agitated under reflux for 20 h. Then ca. 200 mL of saturated aqueous NH4Cl solution was cautiously added to the cooled reaction mixture. The ether was evaporated in vacuo and the residue was filtered.42 The wet gray solid containing unreacted Zn granules was washed with water, air dried, and extracted with 750 mL of THF-CHCl<sub>3</sub> (1:1) solution. The dispiro diol (3) precipitated as fluffy, colorless crystals from the hot filtrate, yield 9.0 g (50%). Crystallization from THF-CHCl<sub>3</sub> afforded pure 3 melting at 219-220 °C: NMR (Me<sub>2</sub>SO-d<sub>6</sub>) δ 0.00-0.20 (m, 4 H), 0.50-0.70 (m, 4 H), 1.25 (d of d, J = 5 and 13 Hz, 2 H), 1.63 (d of d, J = 10 and 13 Hz, 2 H),3.58 (d of d, J = 5 and 10 Hz, 2 H), 4.1 (br s, 2 H); IR (Nujol) 3350, 3065, 1060 cm<sup>-1</sup>. Anal. (C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>) C, H.

**Dispiro**[2.2.2.2]decane-4,9-dione (4). To a suspension of 9.8 g of 3 (58.3 mmol) in 300 mL of purified acetone cooled in an ice bath was added slowly 35 mL of 8 N Jones reagent. After the addition, the mixture was stirred for 15 min and then the excess reagent was de-

stroyed with 15 mL of isopropyl alcohol. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The greenish-blue precipitate was dissolved in water and extracted with 300 mL of ether. The ethereal extract was combined with the concentrated acetone solution, washed with aqueous NaHCO<sub>3</sub>, and dried. Evaporation of the solvent afforded 7.2 g of crystalline 4 which was recrystallized from ether-petroleum ether to yield 6.6 g (70%) of 4 melting at 81–82 °C: NMR (CDCl<sub>3</sub>)  $\delta$  0.75–0.90 and 1.30–1.45 (AA'XX', 4 H each), 2.71 (s, 4 H); IR (Nujol) 1690 cm<sup>-1</sup>. Anal. (C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>) C, H.

**Bistosylhydrazone of 4.** A mixture of 5.0 g of 4 (30.8 mmol) and 12.0 g of tosylhydrazine (64.5 mmol) in 200 mL of ethanol was heated at 60-70 °C for 12 h. The bistosylhydrazone precipitated as fluffy crystals. The reaction mixture was cooled in an ice bath and filtered, yield 14.5 g (94%), mp 230 °C dec. Anal.  $(C_{24}H_{28}N_4O_4S_2)$  C, H, N.

Dispiro[2.2.2.2]deca-4,9-diene (1). A suspension of 27.4 g of the bistosylhydrazone (55 mmol) obtained above in 300 mL of dry ether was cooled to -20 °C in a dry ice-acetone bath and 250 mL of an ethereal 1 N n-BuLi solution was added slowly. After the addition, the mixture was stirred for 3 h at room temperature and then allowed to stand overnight. To the reddish brown mixture was added 250 mL of water and the ethereal layer was separated, washed with water, and dried. The solvent was removed through a 30-cm fractionating column and then with a rotary evaporator. The deep brown residue was dissolved in 50 mL of methanol and the solution was cooled in an ice-salt bath. The precipitated crystals were collected, washed with a small amount of chilled methanol, and dried over silica gel in a vial. (Because 1 is volatile, drying of 1 should not be carried out in an evacuated desiccator.) Sublimation at 100 °C under atmospheric pressure afforded colorless plates melting at 121-122 °C in a sealed capillary: yield 4.0 g (55%); NMR (CCl<sub>4</sub>)  $\delta$  0.69 (s, 8 H), 4.80 (s, 4 H); IR (Nujol) 3085, 1425, 1355, 1040, 975, 925, 845, 740, 730 cm<sup>-1;</sup> UV (hexane)  $\lambda_{max}(\epsilon)$  222 nm (2.0 × 10<sup>4</sup>); mass spectrum m/e 132 (M<sup>+</sup>. 36), 131 (15), 117 (100), 116 (24), 115 (53), 105 (29), 104 (22), 103 (30), 91 (74), 79 (21), 78 (41), 77 (57), 65 (20), 63 (24), 52 (44), 50 (27). Anal. (C10H12) C, H.

**Bisxanthate of 1 (5).** Sodium hydride (2.0 g, 50% mineral oil dispersion, 42 mmol) was freed of mineral oil by washings with pentane and the system was evacuated to remove the solvent. Dry Me<sub>2</sub>SO (75 mL) and 2.6 g of 3 (15.5 mmol) were added and the resulting mixture was stirred for 2 h at 40–50 °C. The gray, syrupy solution was cooled in an ice bath and 3.0 mL of CS<sub>2</sub> (50 mmol) was added. The reaction was slightly exothermic and the mixture immediately turned deep reddish brown. After standing overnight at room temperature, 3.2 mL of methyl iodide (51 mmol) was added. The reaction mixture was stirred for 8 h at room temperature, then poured onto ice, and the product was extracted with chloroform. Evaporation of the solvent and crystallization of the residue from chloroform-hexane afforded 3.8 g of the bisxanthate (5, 71%) decomposing at 146 °C: NMR (CDCl<sub>3</sub>)  $\delta$  0.3–0.7 (m, 8 H), 1.50 (d of d, J = 3 and 15 Hz, 2 H), 2.45–2.70 (d of d and s at 2.59, J = 2 and 15 Hz, 8 H), 5.15 (m, 2 H); IR (Nujol) 1205, 1030 cm<sup>-1</sup>. Anal. (C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>S<sub>4</sub>) C, H, S.

**Pyrolysis of the Bisxanthate 5.** When the bisxanthate was heated in an oil bath, the decomposition began at ca. 140 °C and was complete in 30 min at 150 °C. The viscous reaction mixture solidified on cooling. The IR spectrum of the crude crystalline product lacked completely the characteristic bands of the starting material. Crystallization from chloroform-methanol afforded the rearranged product (6) melting at 137-138 °C: NMR (CDCl<sub>3</sub>)  $\delta$  0.20-1.00 (complex m, 8 H), 1.22 (br d, J = 15 Hz, 2 H), 2.42 (s, 6 H), 2.55 (d of d, J = 3 and 15 Hz, 2 H), 3.50 (br s, 2 H); IR (Nujol) 1720, 1635, 840 cm<sup>-1</sup>.

A flask containing 2 g of the xanthate was immersed in a salt bath preheated at 300 °C and the pyrolysate was collected in a trap cooled in a dry ice-acetone bath. The IR spectrum of the condensate showed that it mainly consisted of 6. When the condensate was heated at 100 °C, colorless plates sublimed on the cold part of the glass wall. The sublimate (50 mg) showed no depression of the melting point on a mixture melting point measurement with 1 and its spectral properties were indistinguishable from those of 1.

**Rate of Disappearance of 1 in Triglyme.** A 0.15 M solution of 1 in triglyme containing phenyl isopropyl ketone as the internal standard was placed in a NMR tube, which was subsequently connected to a vacuum line. The solution was degassed by three freeze-thaw cycles. Then the tube was filled with argon and sealed off. The decomposition reaction was followed by measuring the relative intensity of the cy-

clopropane proton signal of 1 to the methyl proton signal of the standard material. The reaction was clean first order at least up to the 70% conversion.

**Reaction of 1 with 1,3-Butadiene.** A solution of 200 mg of 1 (1.51 mmol) in 8 mL of benzene was placed in a glass ampule and bubbled with argon for 30 min. Butadiene ( $260 \mu$ L, ca. 3.0 mmol) was added and the ampule was sealed off. After heating at 160 °C for 6 h, the reaction was almost complete and only a trace amount of 1 remained. The solvent was removed in vacuo and the residue was analyzed on GLC (column A, 200 °C). Three major peaks in a ratio of 64:4:5 (retention times of 9, 32, and 42 min) were separated by preparative GLC. The two minor products were shown to be 15 (5%) and 16 (4%). The first component was subjected again to GLC analysis (column C, 200 °C) and was found to be a mixture of two products in a ratio of 83:13. They were isolated and shown to be 13a (74%) and 14a (10%). 13a:<sup>15</sup> mass spectrum m/e 187 (5), 186 (M<sup>+</sup>, 38), 145 (22), 130 (23), 129 (27), 118 (63), 117 (59), 115 (22), 104 (100), 91 (43), 78 (24). Anal. (C<sub>14</sub>H<sub>18</sub>) C, H.

**14a:** mass spectrum m/e 187 (4), 186 (M<sup>+</sup>, 32), 145 (14), 129 (15), 118 (23), 117 (42), 105 (14), 104 (100), 91 (28). Anal. (C<sub>14</sub>H<sub>18</sub>) C, H.

**15:** NMR (CCl<sub>4</sub>)  $\delta$  1.2-2.2 (complex m, 12 H), 2.60 (m, 4 H), 4.4-5.7 (complex m, 4 H), 6.98 (s, 4 H); mass spectrum *m/e* 240 (M<sup>+</sup>, 8), 157 (34), 130 (42), 129 (61), 117 (80), 115 (30), 105 (27), 104 (100), 91 (72), 79 (26), 77 (25), 67 (31), 55 (27). Anal. (C<sub>18</sub>H<sub>24</sub>) C, H.

16: NMR (CCl<sub>4</sub>)  $\delta$  0.9–1.1 (m, 2 H), 1.2–2.1 (complex m, 9 H), 2.60 (q, 4 H), 4.50 (m, 2 H), 4.6–4.9 (two m, 2 H), 5.3–5.6 (complex m, 1 H), 6.93 (s, 4 H); mass spectrum *m/e* 240 (M<sup>+</sup>, 19), 211 (38), 171 (41), 157 (96), 129 (69), 117 (77), 104 (100), 91 (28). Anal. (C<sub>18</sub>H<sub>24</sub>) C, H.

**Reaction of 1 with Piperylene.** A solution of 200 mg of 1 (1.51 mmol) and 540  $\mu$ L of piperylene (ca. 5.4 mmol) in 16 mL of benzene prepared as described above was heated at 160 °C for 5 h. GLC analysis (column B, 200 °C) of the reaction mixture showed two peaks in a ratio of 19:81 (retention times of 18 and 23 min). They were isolated by preparative GLC and shown to be 17 (13%) and 13b (58%). 13b: mass spectrum *m/e* 201 (8), 200 (M<sup>+</sup>, 46), 185 (15), 157 (25), 129 (25), 118 (24), 117 (40), 104 (100), 91 (24). Anal. (C<sub>15</sub>H<sub>20</sub>) C, H.

**17**: NMR (CCl<sub>4</sub>)  $\delta$  1.22 (t, J = 7.5 Hz, 3 H), 1.5–1.9 (m, 2 H), 1.9–2.3 (m, 2 H), 2.4–2.7 (m, 4 H), 4.8–5.1 (m, 2 H), 5.4–6.4 (complex m, 3 H), 6.92 (s, 4 H). Anal. (C<sub>15</sub>H<sub>20</sub>) C, H.

**Reaction of 1 with Methyl trans-2,4-Pentadienoate.** A mixture of 400 mg of 1 (3.02 mmol) and 680 mg of trans-12c (6.1 mmol) in 16 mL of benzene was heated at 160 °C for 6 h in a glass ampule under argon. GLC analysis (column A, 220 °C) of the reaction mixture showed two major peaks in a ratio of 7:93. A fraction of bp 100–140 °C (3 mmHg) was collected on the distillation and subjected to preparative GLC to yield 13c (65%) and 14c (5%). 13c: mass spectrum m/e 245 (5), 244 (M<sup>+</sup>, 30), 212 (20), 185 (50), 184 (29), 157 (20), 143 (25), 129 (27), 118 (29), 117 (96), 115 (22), 105 (40), 104 (100), 91 (49), 79 (25). Anal. (C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>) C, H.

**14c:** mass spectrum m/e 245 (6), 244 (M<sup>+</sup>, 38), 185 (37), 184 (26), 143 (24), 118 (27), 117 (75), 105 (36), 104 (100), 91 (36). Anal. (C<sub>16</sub>H<sub>20</sub>O<sub>2</sub>) C, H.

**Reaction of 1 with** *cis-* **and** *trans-* **Pentadienenitriles.** A solution of 200 mg of 1 (1.51 mmol) and 240 mg of a ca. 1:1 mixture of *cis-* and *trans-* **12d** (3.04 mmol) in 8 mL of benzene was heated at 160 °C for 5 h under argon. The solution gradually became cloudy and at the end of the reaction fine oily droplets which appeared to be polymeric material separated. GLC analysis (column B, 230 °C) of the reaction mixture showed a single major peak. The product isolated by preparative GLC was shown to be **13d** (68%). Each of the cis and trans isomers of **12d** was isolated and subjected to the reaction with **1.** The results, however, did not differ appreciably and **13d** was obtained in 67% yield from cis isomer and in 69% yield from trans isomer. **13d:** mass spectrum *m*/*e* 212 (16), 211 (M<sup>+</sup>, 94), 143 (31), 131 (25), 129 (31), 118 (35), 117 (100), 115 (31), 106 (27), 105 (54), 104 (95), 93 (30), 91 (64), 77 (26). Anal. (C<sub>15</sub>H<sub>17</sub>N) C, H, N.

**Reaction of 1 with Dimethyl trans, trans-Hexadienedioate.** A mixture of 300 mg of 1 (2.26 mmol) and 770 mg of *trans, trans-* **12e** (4.52 mmol) in 6 mL of benzene was heated at 160 °C for 10 h. When the reaction mixture was cooled to room temperature, a small amount of the unreacted diene precipitated. The mixture was filtered and the filtrate was concentrated in vacuo. Chromatography of the residue on silica gel with benzene elution gave *trans,trans*-12e (total amount of the recovered ester was 130 mg). Further elution with benzene produced 60 mg of *cis*-13e (9%), which when recrystallized from petroleum ether-benzene had mp 90-90.5 °C, and then 372 mg of *trans*-13e (54%) which when recrystallized from methanol had mp 144-145 °C. *cis*-13e: IR (Nujol) 1740, 1730, 1205, 1160, 1150, 970, 800 cm<sup>-1</sup>; mass spectrum *m/e* 302 (M<sup>+</sup>, 4), 242 (53), 183 (61), 182 (31), 155 (31), 143 (31), 117 (93), 115 (32), 104 (100), 91 (52), 78 (31). Anal. (C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>) C, H.

*trans*-13e: IR (Nujol) 1730, 1275, 1150, 1020, 960, 815 cm<sup>-1</sup>; mass spectrum m/e 302 (M<sup>+</sup>, 7), 270 (33), 243 (35), 242 (95), 210 (30), 183 (86), 182 (36), 155 (32), 143 (32), 117 (99), 115 (31), 105 (31), 104 (100), 91 (51). Anal. (C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>) C, H.

**Reaction of 1 with Dimethyl** *cis,trans***-Hexadienedioate.** A mixture of 300 mg of **1** (2.26 mmol) and 770 mg of *cis,trans***- 12e** (4.52 mmol) in 6 mL of benzene was heated at 160 °C for 10 h and the resulting mixture was worked up as described for the reaction of the trans,trans isomer. Chromatography on silica gel with benzene elution produced 160 mg of the unreacted ester, 210 mg of *cis***- 13e** (32%), and 268 mg of *trans***- 13e** (39%).

Methyl 5-Cyano-*trans,trans*-2,4-pentadienoate. Methyl hydrogen *trans,trans*-2,4-hexadienedioate<sup>43</sup> was converted to the amide ester following the procedure of Roberts et al.<sup>44</sup> in 65% yield: mp 177–179 °C; IR (Nujol) 3440, 3170, 1712, 1680, 1615, 1320, 1240 cm<sup>-1</sup>. Anal. (C<sub>7</sub>H<sub>9</sub>NO<sub>3</sub>) C, H, N.

A mixture of 1.6 g of the amide ester (10 mmol) obtained above and 1.2 g of phosphorus pentoxide in 10 mL of tetrachloroethane was heated at 145 °C for 30 min. The supernatant organic layer was decanted and the residue was heated with another 10 mL of the solvent at the above temperature for 30 min. Concentration of the combined tetrachloroethane solution afforded light brown crystals which were purified by a column chromatography on silica gel with benzene elution: mp 93–94 °C; yield 1.0 g; IR (Nujol) 3090, 2230, 1720, 1640, 1600 cm<sup>-1</sup>.

**Reaction of 1 with Methyl 5-Cyano-2,4-pentadienoate.** A mixture of 200 mg of 1 (1.51 mmol) and 370 mg of *trans,trans*-12f (2.70 mmol) in 8 mL of benzene was heated at 160 °C for 6 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel. Elution with benzene produced successively 90 mg of 12f, 77 mg of oily *cis*-13f (29%), and then 135 mg of *trans*-13f (50%) which when recrystallized from benzene-petroleum ether had mp 129–130 °C. *cis*-13f: Anal. ( $C_{17}H_{19}NO_2$ ) C, H, N.

*trans*-13f: IR (Nujol) 2350, 1730, 1380, 1155, 995, 970, 805 cm<sup>-1</sup>; mass spectrum m/e 269 (M<sup>+</sup>, 16), 237 (24), 210 (44), 209 (60), 183 (21), 182 (23), 119 (21), 118 (27), 117 (100), 115 (27), 104 (62), 91 (56). Anal. (C<sub>17</sub>H<sub>19</sub>NO<sub>2</sub>) C, H, N.

**Reaction of 1 with** *cis,cis***-Hexadienedinitrile.** A mixture of 300 mg of 1 (2.26 mmol) and 452 mg of *cis,cis***-12g** (4.34 mmol) in 6 mL of benzene was heated at 160 °C under argon. The clear yellow solution gradually turned brown and became dark brown after 2 h. The reaction was discontinued then and the solvent was evaporated in vacuo. Chromatography of the residue on silica gel eluting with a benzene-petroleum ether (2:3) mixture gave 40 mg of unreacted **1.** Elution with benzene produced 258 mg of the unreacted nitrile. Further elution with benzene produced 270 mg of *trans***-13g** (58%), which when recrystallized from benzene-petroleum ether had mp 155-156 °C, followed by 146 mg of *cis***-13g** (31%) which when recrystallized from benzene-petroleum ether ng 134-135 °C. *trans***-13g** IR (Nujol) 2250, 1520, 1420, 965, 890, 810, 805 cm<sup>-1</sup>; mass spectrum *m/e* 236 (M<sup>+</sup>, 34), 183 (21), 182 (17), 130 (18), 117 (100), 115 (19), 105 (17), 104 (57), 91 (28), 77 (16). Anal. (C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>) C, H, N.

cis-13g: IR (Nujol) 2260, 2245, 1380, 980, 970, 895, 805; mass spectrum m/e 236 (M<sup>+</sup>, 21), 118 (13), 117 (100), 115 (13), 105 (14), 104 (33), 91 (23). Anal. (C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>) C, H, N.

**Reaction of 1 with** *trans,trans-1,4-Diphenyl-1,3-butadiene.* A mixture of 200 mg of 1 (1.51 mmol) and 620 mg of *trans,trans-12h* (3.00 mmol) in 4 mL of benzene was heated at 160 °C for 8 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel. Elution with petroleum ether produced 265 mg of the unreacted butadiene. Elution with benzene produced a yellow, viscous oil which was subjected to distillation. A fraction of up to 160 °C under  $10^{-2}$  mmHg was collected and dissolved in 5 mL of petroleum ether. The resulting solution was allowed to stand overnight, then filtered to remove yellow, amorphous precipitate and the filtrate was concentrated in vacuo. The NMR spectrum of the residue, which crystallized on standing, showed two olefinic proton peaks characteristic

of the [8]paracycloph-4-ene derivatives at  $\delta$  4.14 and 4.25 in a ratio of 6:1. Crystallization from methanol gave 77 mg of analytically pure *trans*-13h (15%) melting at 110.5-111.5 °C. The minor product appeared as a shoulder on the peak of the major one on GLC analysis (column A, 250 °C) and it was difficult to separate it by preparative GLC. The NMR spectrum of the mixture with *trans*-13h suggested that it was *cis*-13h. *trans*-13h: IR (Nujol) 3040, 1600, 1510, 1490, 955, 800, 745, 690 cm<sup>-1</sup>; mass spectrum *m/e* 339 (15), 338 (M<sup>+</sup>, 50), 234 (29), 207 (29), 129 (20), 118 (77), 117 (73), 105 (20), 104 (100), 91 (52). Anal. (C<sub>26</sub>H<sub>26</sub>) C, H.

**Reaction of 1 with 2,3-Dimethyl-1,3-butadiene.** A solution of 200 mg of 1 (1.51 mmol) and 248 mg of 12i (3.03 mmol) in 16 mL of benzene was heated at 160 °C for 6 h. GLC analysis (column B, 210 °C) of the reaction mixture showed two peaks in a ratio of 1:4. A fraction of bp 125-140 °C (2 mmHg) collected upon distillation was subjected to preparative GLC to give 13i (57%), which when recrystallized from methanol had mp 65-66 °C, and oily 14i (14%). 13i: mass spectrum m/e 215 (10), 214 (M<sup>+</sup>, 60), 173 (19), 143 (25), 131 (30), 130 (18), 129 (21), 118 (43), 117 (68), 104 (100), 91 (27), 55 (24). Anal. (C<sub>16</sub>H<sub>22</sub>) C, H.

14i: mass spectrum m/e 215 (8), 214 (M<sup>+</sup>, 47), 143 (17), 131 (23), 130 (17), 118 (40), 117 (54), 104 (100), 91 (20), 55 (25). Anal. (C<sub>16</sub>H<sub>22</sub>) C, H.

Reaction of 1 with 2,3-Dichloro-1,3-butadiene. A solution of 200 mg of 1 (1.51 mmol) and 250  $\mu$ L of 12j (ca. 2.5 mmol) in 16 mL of benzene was heated at 160 °C for 4 h. GLC analysis (column A, 200 °C) of the reaction mixture showed two peaks in a ratio of 9:1 (retention times 39 and 48 min). The mixture was distilled in vacuo and a fraction of bp 100-140 °C (2 mmHg) was collected. Recrystallization of the distillate from methanol gave 80 mg of 13j (21%) melting at 71-72 °C. The minor product was thought to be 14j, but was present in such small amount that it could not be isolated. 13j: Anal. (C<sub>14</sub>H<sub>16</sub>Cl<sub>2</sub>) C, H, Cl.

Reaction of 1 with 1,3-Butadiene in the Presence of *p*-Thiocresol. A mixture of 150 mg of 1 (1.13 mmol), 220  $\mu$ L of 12a (ca. 2.5 mmol), and 700 mg of *p*-thiocresol (5.64 mmol) in 6 mL of benzene was heated at 160 °C for 5 h under argon. The reaction mixture was poured into 75 mL of ether and the resulting solution was washed with 2 N NaOH to remove the unreacted thiocresol. The solvent was removed and the residue was analyzed by GLC (column A, 210 °C), which showed three peaks. They were separated by preparative GLC and shown to be *p*-diethylbenzene, di-*p*-tolyl disulfide, and 10. The cycloaddition products, 13a and 14a, were not detected on the GLC analysis.

**Reaction of 1 with Dimethyl Maleate.** A mixture of 132 mg of 1 (1.00 mmol) and 288 mg of dimethyl maleate (2.00 mmol) in 20 mL of *tert*-butyl alcohol was heated at 158 °C for 11 h under nitrogen. After solvent removal, the residue was subjected to vacuum distillation, which afforded 91 mg of the unreacted ester containing a trace amount of the trans isomer and 201 mg of colorless oil (bp ~170 °C (0.02 mmHg)) which solidified on standing. Crystallization of the latter from a petroleum ether-diethyl ether mixture afforded 115 mg of **22** (42%) melting at 66.0-67.2 °C. The yield of **22** determined by GLC with internal standard was 49%. NMR (CCl<sub>4</sub>)  $\delta$  0.72 (s, 4 H), 1.6-2.3 (complex m, 4 H), 2.84 (d, J = 9 Hz, 1 H), 3.3 (m, 1 H), 3.52 (s, 3 H), 3.60 (s, 3 H), 4.96 (m, 2 H), 5.40 (m, 2 H); IR (KBr) 1735 cm<sup>-1</sup>; mass spectrum m/e 276 (M<sup>+</sup>, trace), 216 (26), 157 (100), 156 (37), 129 (52), 128 (20), 117 (43), 115 (22), 91 (28). Anal. (C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>) C, H.

Reaction of 1 with Dimethyl Acetylenedicarboxylate (DMAD). A mixture of 132 mg of 1 (1.00 mmol) and 284 mg of DMAD (2.00 mmol) in 5 mL of tert-butyl alcohol was heated at 158 °C for 10.5 h under argon. After the reaction, a trace amount of 1 and ca. 20% of the starting DMAD remained. The GLC analysis (column D, 170 °C) of the reaction mixture showed a single major peak with some very minor peaks. The major product was isolated by preparative GLC and shown to be 23 (169 mg, 62%). Treatment with active charcoal and crystallization from an ether-methylene chloride mixture afforded analytically pure 23 melting at 75.8-77.3 °C: NMR (CCl<sub>4</sub>)  $\delta$  0.76 (s, 4 H), 2.00 (t, J = 8 Hz, 2 H), 2.66 (t, J = 8 Hz, 2 H), 3.64 (s, 3 H),3.68 (s, 3 H), 5.05 (d, J = 10 Hz, 2 H), 5.45 (d, J = 10 Hz, 2 H); IR(KBr) 1742, 1713, 1652 cm<sup>-1</sup>; mass spectrum *m/e* 274 (M<sup>+</sup>, 3.6), 243 (32), 242 (86), 227 (100), 214 (35), 184 (28), 183 (26), 156 (51), 155 (83), 141 (27), 128 (32), 107 (20), 105 (25). Anal. (C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>) C, H

Reaction of 1 with Tetracyanoquinodimethane (TCNQ) in o-Di-

chlorobenzene. A mixture of 200 mg of 1 (1.51 mmol) and 370 mg of TCNQ (1.82 mmol) in 40 mL of *o*-dichlorobenzene was stirred at 60 °C for 20 h. After the mixture was cooled to room temperature, insoluble amorphous material was filtered off and the filtrate was concentrated in vacuo. Chromatography of the brown residue on silica gel with ether elution gave a crystalline product which was crystallized from ethyl acetate to give 179 mg of 30 (35%) melting at 260-260.5 °C. When the mixture of 1 and TCNQ in *o*-dichlorobenzene was heated at 170 °C for 6 h, the yield of 30 was increased to 60%. NMR (CDCl<sub>3</sub>)  $\delta$  2.7-3.2 (m, 8 H), 6.72 (s, 4 H), 7.3 (s, 4 H); IR (Nujol) 2260 cm<sup>-1</sup>; UV (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}(\epsilon)$  262 nm (680), 267 (580), 297 (150); mass spectrum *m/e* 337 (27), 336 (M<sup>+</sup>, 97), 132 (49), 131 (33), 118 (22), 117 (100), 91 (27). Anal. (C<sub>2</sub>2H<sub>16</sub>N<sub>4</sub>) C, H, N.

Reductive Decyanation of 1,1,12,12-Tetracyano[3.3]paracyclophane. Under nitrogen, 1.7 g of sodium (74 mmol) was added to 160 mL of liquid ammonia and stirred until a dark blue color persisted; this was followed by portionwise addition of 800 mg of pulverized 30 (2.37 mmol). After 30 min of further stirring, the resulting reaction mixture was poured into 300 mL of ether cooled in an ice bath. Ice cubes were slowly added to the mixture until the blue color dissipated, and the ammonia was then allowed to boil off. The ether layer was separated from the aqueous residue, which was extracted with ether. The ethereal extracts were combined, dried with magnesium sulfate, filtered, and evaporated to give a white solid. Chromatography of the crude product on silica gel with 5% benzene in hexane elution followed by crystallization from acetone-methanol afforded 429 mg of 31 (76%) melting at 100.5-103.0 °C. When recrystallized from acetone-methanol, the product had a mp of 104.9-105.2 °C (lit.<sup>29a</sup> 105.0-105.5 °C). The spectral properties agreed well with those reported.29b

**Reaction of 1 with TCNQ in Acetonitrile.** Since the cycloaddition product, **32**, is highly susceptible to hydrolysis, all operations were carried out under anhydrous conditions. A mixture of 209 mg of **1** (1.58 mmol) and 308 mg of TCNQ (1.51 mmol) in 50 mL of dry acetonitrile was stirred at room temperature. The color of the reaction mixture changed from light green to brown during 5 days. The solvent was removed and the residue was crystallized from acetonitrile to yield 365 mg of pale yellow **32** (64%) decomposing above 110 °C.

The dispiro compound (1) and TCNQ were dissolved in acetonitrile- $d_3$  and the reaction was followed by its NMR spectrum, which showed that the reaction was complete in 60 h at room temperature. **32:** NMR (CD<sub>3</sub>CN)  $\delta$  1.90 (s, 3 H), 2.8–3.1 (m, 6 H), 3.80 (m, 2 H), 6.65 (s, 4 H), 7.25 (AB q, 4 H); IR (Nujol) 1680 cm<sup>-1</sup>; mass spectrum *m/e* 377 (M<sup>+</sup>, 24), 198 (48), 197 (78), 183 (52), 170 (89), 129 (80), 128 (100), 127 (50), 116 (34), 115 (89), 102 (24), 89 (31), 75 (28). Anal. (C<sub>24</sub>H<sub>19</sub>N<sub>5</sub>) C, H, N.

**Reaction of 1 with TCNQ in Acetone.** A mixture of 200 mg of 1 (1.51 mmol) and 320 mg of TCNQ (1.57 mmol) in 40 mL of dry acetone was stirred at room temperature. GLC analysis of the reaction mixture showed that 1 was consumed in 2 days. Evaporation of the solvent gave the crude crystalline product, which was washed well with methanol to remove reddish-brown oil and then crystallized from benzene to yield 166 mg of 33 (28%) decomposing at 153 °C. 33: NMR (CDCl<sub>3</sub>)  $\delta$  1.58 (s, 6 H), 2.80–2.95 (m, 4 H), 3.10–3.20 (m, 2 H), 3.75 (t, J = 5.5 Hz, 2 H), 6.72 (AB q, 4 H), 7.12 (s, 4 H); mass spectrum m/e 297 (31), 141 (23), 131 (21), 119 (100), 118 (28), 117 (83), 115 (26), 105 (40), 104 (47), 91 (74), 77 (28). Anal. (C<sub>25</sub>H<sub>22</sub>N<sub>4</sub>O) C, H, N.

**Reaction of 1 with Tetramethoxycarbonylquinodimethane.** A mixture of 128 mg of 1 (0.97 mmol) and 218 mg of 34 (0.65 mmol) in 20 mL of benzene was heated at 170 °C for 6 h and then filtered to remove amorphous precipitate. The filtrate was evaporated in vacuo and the residue was crystallized from methanol to give 30 mg of colorless 35 (10%) melting at 158.0–158.5 °C: NMR (CDCl<sub>3</sub>)  $\delta$  2.6–2.9 (m, 8 H), 3.78 (s, 12 H), 6.70 (s, 4 H), 7.05 (br s, 4 H); IR (Nujol) 1725 cm<sup>-1</sup>; mass spectrum *m/e* 469 (12), 468 (M<sup>+</sup>, 42), 306 (47), 274 (100), 117 (80), 104 (24). Anal. (C<sub>26</sub>H<sub>28</sub>O<sub>8</sub>) C, H.

#### **References and Notes**

 H. G. Richey, Jr., "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, p 1201; H. N. Volltrauer and R. H. Schwendeman, J. Chem. Phys., 54, 260, 268 (1971); W. J. Hehre, J. Am. Chem. Soc., 94, 6592 (1972); A. de Meijere and W. Lüttke, Tetrahedron, 25, 2047 (1969); M. J. Jorgenson and T. Leung, J. Am. Chem. Soc., 90, 3769 (1968); J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, 91, 1877, 1879 (1969); G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, 94, 146 (1972); P. v. R. Schleyer and V. Buss, Ibid., 91, 5880 (1969); B. R. Ree and J. C. Martin, ibid., 92, 1660 (1970)

- (2) For cetion rearrangement: C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer, "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, p. 1347. For free radical rearrangement: J. W. Wilt, "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 333; W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, p 266. For anion rearrangement: H. E. Zimmerman, "Molecular Rearrangements", Vol. I, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, p 345.
- J. G. Murphy, J. Med. Chem., 9, 157 (1966).
- (4) H. E. Simmons, T. L. Cairns, and S. A. Vladuchick, Org. React., 20, 1 (1973).
- R. H. Shapiro, Org. React., 23, 405 (1976).
- (6) C. G. Overberger and A. E. Borchert, J. Am. Chem. Soc., 82, 4896 (1960)
- (7) S. Nishida, I. Moritani, E. Tsuda, and T. Teraji, Chem. Commun., 781 (1969)
- (8) S. Nishida, I. Moritani, and T. Teraji, J. Chem. Soc., Chem. Commun., 1114 (1972). (9) Y. Harada, K. Ohno, K. Seki, and H. Inokuchi, Chem. Lett., 1081 (1974);
- P. Asmus, M. Klessinger, L.-U. Meyer, and A. de Meijere, Tetrahedron Lett., 381 (1975).
- (10) S. Nishida, I. Moritani, and T. Teraji, unpublished results
- (11) S. Nishida, I. Moritani, K. Ito, and K. Sakai, J. Org. Chem., 32, 939 (1967)
- (12) H. J. Reich and J. M. Renga, Tetrahedron Lett., 2747 (1974), and references cited therein
- (13)T. Tsuji and S. Nishida, Chem. Lett., 631 (1977); J. Am. Chem. Soc., 96, 3649 (1974); G. L. Closs and M. S. Czeropski, Chem. Phys. Lett., 45, 115 (1977)
- (14) For a preliminary report of this reaction, see T. Tsuji and S. Nishida, J. Am. Chem. Soc., 95, 7519 (1973).
- (15) D. J. Cram, C. S. Montgomery, and G. R. Knox, J. Am. Chem. Soc., 88, 515 (1966)
- (16) N. L. Allinger, T. J. Walter, and M. G. Newton, J. Am. Chem. Soc., 96, 4588 (1974); V. V. Kane, A. D. Wolf, and M. Jones, Jr., ibid., 96, 2643 (1974).
- (17) N. L. Allinger, J. T. Sprague, and T. Liljefors, J. Am. Chem. Soc., 96, 5100 (1974)
- (18) G. W. Whitesides, B. A. Pawson, and A. C. Cope, J. Am. Chem. Soc., 90, 639 (1968). The Arrhenius parameters for the conformational interconversion were reported to be  $E_a = 13.4 \pm 0.7$  kcal/mol and  $A = 10^{12.7\pm0.5}$
- (19) The cycloadduct was assigned tentatively as the trans isomer. The reaction with dimethyl fumarate also afforded 22 as the major product
- (20) T. Shibata, T. Tsuji, and S. Nishida, Tetrahedron Lett., 4095 (1976).

- (21) T. Shibata, T. Tsuji, and S. Nishida, Bull. Chem. Soc. Jpn., 50, 2039 (1977).
- (22) P. J. Krusic, P. Meakin, and B. E. Smart, J. Am. Chem. Soc., 96, 6211 (1974), and references cited therein. (23)T. Tsuji and S. Nishida, Chem. Lett., 1335 (1973).
- (24) H. R. Ward, Acc. Chem. Res., 5, 18 (1972); "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 239.
   (25) G. L. Closs, J. Am. Chem. Soc., 93, 1546 (1971); G. L. Closs and C. E.
- Doubleday, ibid., 94, 9248 (1972).
- (26) There are precedents of such trapping reactions of zwitterionic intermediates by polar multiple bonds. R. Schug and R. Huisgen, J. Chem. Soc., Chem. Commun., 60 (1975); R. Gompper and W.-R. Uirich, Angew. Chem., Int. Ed. Engl., 15, 299 (1976).
- (27) D. S. Acker and W. R. Hertler, J. Am. Chem. Soc., 84, 3370 (1962).

- (30) R. Huisgen, Acc. Chem. Res., 10, 117 (1977), and references cited therein.
- (31) E. Adlerová, L. Bláha, M. Borovička, I. Ernest, J. O. Jílek, B. Kakáč, L. Novác. M. Rajšner, and M. Protiva, Collect. Czech. Chem. Commun., 25, 221 (1960)
- (32) J. G. Grasselli, B. L. Ross, H. F. Huber, and J. M. Augl, Chem. Ind. (London), 162 (1963)
- (33) J. A. Elvidge, R. P. Linstead, B. A. Orkin, P. Sims, H. Baer, and D. B. Pattison, J. Chem. Soc., 2228 (1950).
- (34) P. C. Guha and D. K. Sankaran, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 623.
- (35) K. Nakagawa and H. Onoue, Chem. Commun., 396 (1965).
- (36) B. B. Corson, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 228. (37) C. F. H. Allen and A. Bell in ref 34, p 312.
- (38) H. von Brachel and U. Bahr, "Methoden der Organischen Chemie (Hou-ben-Weyl)", Vol. V/1c, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1970, p 282.
- (39) E. H. Huntress, T. E. Lesshe, and J. Barnstein, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 329.
- (40) E. LeGoff, J. Org. Chem., 29, 2048 (1964).
- (41) The diol (2) is not very soluble in ether
- (42) Since 3 is not soluble in ether, the extraction of 3 with ether does not work.
- (43) P. Karrer and M. Stoll, Helv. Chim. Acta, 14, 1189 (1931)
- (44) J. D. Roberts, W. T. Moreland, Jr., and W. Frager, J. Am. Chem. Soc., 75, 637 (1953).
- (45) P. G. Arapakos, M. K. Scott, and F. E. Huber, Jr., J. Am. Chem. Soc., 91, 2059 (1969).

# A Pulse Radiolysis Study of the Quenching of Aromatic Carbonyl Triplets by Norbornadienes and Quadricyclenes. The Mechanism of Interconversion

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Abstract: The technique of electron pulse radiolysis has been used to produce aromatic carbonyl triplet states in liquid benzene. Kinetic absorption spectrometry has allowed the determination of the rate constants for quenching of these states by norbornadiene (1), quadricyclene (2), and their ethoxycarbonyl analogues (3 and 4). Analysis of the rate constant data together with quantum yield measurements shows that norbornadienes quench high energy triplets such as that of acetophenone via an energy transfer mechanism and the free triplets of the diene thus produced decay mainly to the corresponding quadricyclene (2,  $\sim$  96%, and 4,  $\sim$  93%). With lower energy triplets the rate constant for quenching decreases as does the proportion of free triplets produced. The balance between energy transfer and decay to ground states then depends on the triplet energy and electron accepting properties of the triplet state involved. Quenching by quadricyclene involves charge transfer stabilization of the encounter complex and subsequent decay to ground states. Although attempted correlation with the function  $[{}^{3}\Delta E_{0,0} + E(A^{-}/A^{-})]$ A)] is inconclusive, there is a strong correlation with the quenching of the same triplet states by triethylamine.

### Introduction

A classical reaction of organic photochemistry involves the light-induced interconversion of norbornadiene (1) and quadricyclene (2) and their derivatives. On direct excitation

1 is converted to  $2^{2a}$  whereas triplet sensitization leads to the establishment of a photostationary state between these valence isomers.<sup>2b,3</sup> The strained hydrocarbon 2 has been shown to quench aromatic hydrocarbon fluorescence. It was originally