

A CONVENIENT SYNTHESIS OF [2.4]PARACYCLOPHANES  
CYCLOADDITION OF DISPIRO[2.2.2.2]DECA-4,9-DIENE WITH STYRENES

Tohru Shibata, Takashi Tsuji, and Shinya Nishida

Department of Chemistry, Faculty of Science, Hokkaido University,  
Sapporo, Japan

(Received in Japan 12 August 1976; received in UK for publication 23 September 1976)

There has been much recent interest in the chemistry of cyclophanes.<sup>1)</sup> Previously we reported the cycloaddition reaction of dispiro[2.2.2.2]deca-4,9-diene 1 with 1,3-butadienes, which afforded [8]paracycloph-4-enes.<sup>2)</sup> In this report we describe the novel thermal cycloaddition of 1 with the styrene derivatives 2a-2e which gave [2.4]paracyclophanes in fair to good yields. Although a few methods have been reported so far for the preparation of [2.4]-paracyclophane, they are tedious and have not much generality.<sup>3)</sup> The present reaction is simple and provides a convenient route to [2.4]paracyclophanes functionalized at C-1 and C-2.

The tert-butanol solution of 1 and 1,1-diphenylethylene 2e ( 1:2 ) was heated at 150-155°C in a sealed glass ampoule under argon.<sup>4)</sup> The reaction completed in 12 hr. Separation of the products by column chromatography on silica gel afforded 1-phenyl[2.4]paracyclophane 3e ( 67 % ), whose structure was elucidated on the basis of elemental analysis and the spectral properties.<sup>5)</sup> Analogously, the reaction of 1 with the related styrene derivatives 2a-2d afforded 3a-3d. The results are summarized in Table I. The NMR and UV spectra of those products exhibited the characteristics observed in those of [2.4]paracyclophane ; appearance of the aromatic proton signals at the unusually high-field  $\delta$  6.2-6.6 in the NMR spectra and, in the UV spectra, bathochromic shift of  $\lambda_{max}$  to 282-283 nm<sup>3)</sup> and disappearance of fine structure were noted. The spectra of 3a also agreed very well with those reported.<sup>3b)</sup> In the mass spectrum ( 80-eV ) of 3e, the most intense peak occurred at m/e 180, while in those of 3a and 3d, m/e 104 fragment appeared as the most intense

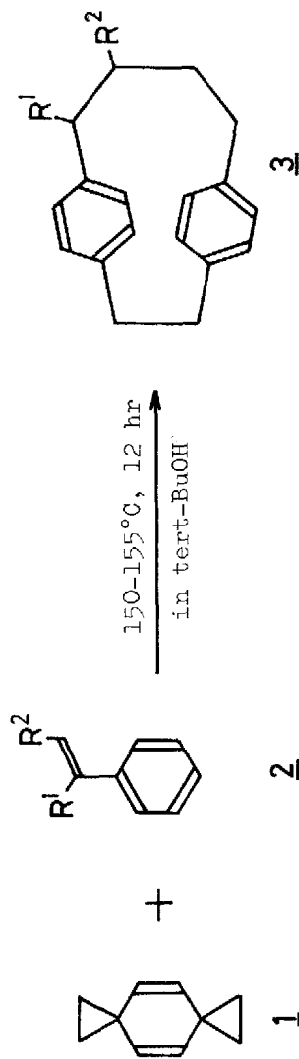


Table I. Products from the Reaction of Dispiro[2.2.2]deca-4,9-diene with Styrenes<sup>1</sup>,

	R <sup>1</sup>	R <sup>2</sup>	<u>1</u> (mol/l)	<u>2</u> (mol/l)	yield of <u>3</u> (%)	mp of <u>3</u> (°C)
a.	H	H	0.010	0.038	7.6 <sup>2</sup> , 4,	71.0-72.0
b.	H	COOCH <sub>3</sub>	0.082	0.20	28	85.2-86.9
c.	COOCH <sub>3</sub>	H	0.017	0.033	78 <sup>4</sup> ,	70.3-71.2
d.	H	C <sub>6</sub> H <sub>5</sub>	0.16	0.40	34 <sup>3</sup> ,	148.0-148.5
e.	C <sub>6</sub> H <sub>5</sub>	H	0.17	0.38	67	70.8-71.8

1. The reaction conditions were not optimized. 2. Besides the cycloadduct, there was obtained the open-chain hydrogen abstraction product 7a in 0.7 % yield. 3. Besides 3d, 7d was obtained in 7 % yield. 4. The reaction at higher concentration resulted in somewhat lower yield. When the reaction was carried out at the concentration of 0.15 mol/l in 1 and 0.3 mol/l in 2c, the yield of 3c was 59 %.

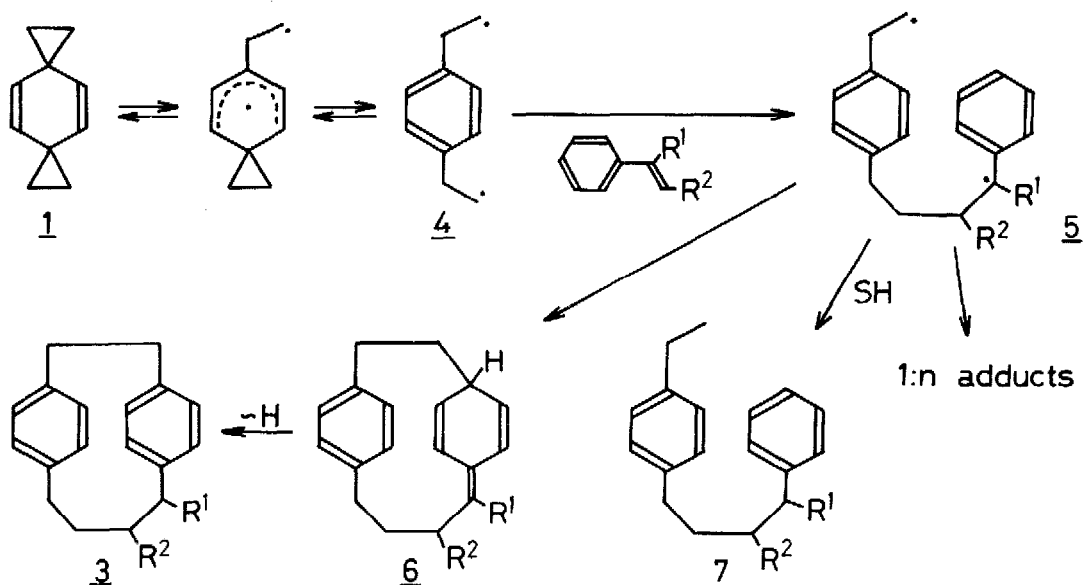
peak and  $m/e$  180 fragment was virtually absent.<sup>5)</sup>

These observations can be rationalized in terms of two  $\beta$ -cleavages and are in good accord with the assigned structures.

The present reaction may be accounted for by the pathway outlined in Scheme I. It has been demonstrated that the thermal homolytic cleavage of the cyclopropane ring in 1 takes place reversibly at 160°C.<sup>6)</sup> The biradical 4 thus formed added to the styrene derivative and the resulting biradical 5 would collapse to 6, which would isomerize to 3 under the reaction conditions. The thermal isomerization of 3-methylene-cyclohexa-1,4-diene to toluene is the known reaction and takes place at the boiling point of ether.<sup>7)</sup> The formation of the open-chain products 7 also supports the above scheme. The reaction with unsubstituted styrene 2a resulted in the low yield of 3a probably because of the high aptitude of 2a to polymerize.

To obtain further information on the reaction mechanism, the measurement of CIDNP spectrum was attempted. The NMR spectrum recorded during the reac-

Scheme I



tion of 1 and 2e in biphenyl at 190°C showed the polarization of signals and the characteristic spectrum of aromatic protons in 3e shifted up-field appeared as emission, thus confirming the radical pathway of the reaction. However, the attempts to detect the signal which could be ascribed to 6e were unsuccessful.

## REFERENCES AND NOTES

- 1) a) D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, 4, 204 (1971). b) F. Vögtle and P. Neumann, *Angew. Chem. internat. Ed.*, 11, 73 (1972). c) H. Irrgartinger, R.-D. Acker, W. Rebafka, and H. A. Staab, *ibid.*, 14, 674 (1975). d) R. Gray and V. Boekelheide, *ibid.*, 14, 107 (1975). e) H. Horita, N. Kannen, T. Otsubo, and S. Misumi, *Tetrahedron Lett.*, 1974, 501. f) R. C. Helgeson, J. M. Timko, and D. J. Cram, *J. Amer. Chem. Soc.*, 96, 7381 (1974). g) F. Vögtle and J. Grutze, *Angew. Chem. internat. Ed.*, 14, 559 (1975).
- 2) T. Tsuji and S. Nishida, *J. Amer. Chem. Soc.*, 95, 7519 (1973).
- 3) a) D. J. Cram and H. Steinberg, *ibid.*, 73, 5691 (1951). b) D. J. Cram and R. C. Helgeson, *ibid.*, 88, 3515 (1966). c) H. J. Reich and D. J. Cram, *ibid.*, 91, 3517 (1969).
- 4) The reaction could be carried out in other solvents such as benzene and n-hexane.
- 5) Satisfactory analytical results were obtained for the products. NMR and UV spectra were obtained in solutions of CCl<sub>4</sub> and n-hexane respectively. IR spectra were taken as KBr disks. Mass spectra were taken at ionizing voltage of 80-eV. Spectral data of the cycloadducts were as follows: 3a, NMR,  $\delta$  6.37 (s, 8H), 2.92 (s, 4H), 2.2 (br s, 4H), 1.4 (br s, 4H); UV,  $\lambda_{\max}$  ( $\epsilon \times 10^{-2}$ ), 271 (4.7), 283 (2.7); Mass (relative int.), 236 (M<sup>+</sup>, 35), 131 (22), 130 (23), 118 (32), 117 (32), 104 (100); 3b, NMR,  $\delta$  6.2-6.7 (m, 8H), 3.73 (s, 3H), 1.7-3.4 (complex m, 10H), 1.05 (t, J=13 Hz, 1H); UV,  $\lambda_{\max}$  ( $\epsilon \times 10^{-2}$ ), 271 (4.5), 283 (3.1); IR, 1731 cm<sup>-1</sup>: 3c, NMR,  $\delta$  6.4-6.8 (m, 8H), 3.59 (s, 3H), 0.8-3.2 (complex m, 11H); UV,  $\lambda_{\max}$  ( $\epsilon \times 10^{-2}$ ), 251 (3.9), 271 (3.9), 282 (2.7, shoulder), 292 (0.8, shoulder); IR, 1743 cm<sup>-1</sup>: 3d, NMR,  $\delta$  7.24 (s, 5H), 6.3-6.8 (m, 8H), 1.8-3.4 (m, 10H), 1.40 (t, J=12 Hz, 1H); UV,  $\lambda_{\max}$  ( $\epsilon \times 10^{-2}$ ), 255 (4.0), 262 (5.8), 268 (6.8), 283 (3.1); Mass (relative int.), 312 (M<sup>+</sup>, 13), 208 (13), 207 (17), 104 (100), 78 (12); 3e, NMR,  $\delta$  7.18 (s, 5H), 6.2-6.6 (m, 8H), 3.42 (d, J=10 Hz, 1H), 0.9-3.2 (complex m, 10H); UV,  $\lambda_{\max}$  ( $\epsilon \times 10^{-2}$ ), 254 (5.3), 263 (6.6), 270 (7.0), 283 (3.6); Mass (relative int.), 312 (M<sup>+</sup>, 30), 181 (19), 180 (100), 178 (16), 167 (20), 165 (30).
- 6) T. Tsuji and S. Nishida, *J. Amer. Chem. Soc.*, 96, 3649 (1974).
- 7) H. Plieninger and W. Maier-Bost, *Chem. Ber.*, 98, 2504 (1965).