

ORGANIC REACTIONS AT HIGH PRESSURE. DIELS-ALDER REACTIONS OF [2.2]PARACYCLOPHANE<sup>1)</sup>

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[2.2]Paracyclophane which is totally inert to maleic anhydride and maleimides even at 180 °C and 1 bar does undergo Diels-Alder reactions with these dienophiles in kirobar region around 70 °C giving the 1:2 adducts in moderate yields.

Non-annelated arenes normally do not participate as diene components in Diels-Alder reactions.<sup>2)</sup> To surmount this lack of reactivity, considerable improvements have been realized and still challenged via recourse to chemical modification of dienes and dienophiles, catalysis by Lewis acids, and high temperature and high pressure as well.<sup>3)</sup> From the diene side, for example, this may be achieved by the incorporation of bridging structural units into the arenes. Specifically, when simple aromatic 6 $\pi$ -electron systems, which are extremely sluggish in Diels-Alder additions, are incorporated into a [2<sub>n</sub>]cyclophane system, e.g. [2.2]paracyclophane (1) which is a formal dimer of p-xylene, a dramatic increase in the rate of addition is observed in certain cases.<sup>4)</sup> However, [2.2]paracyclophane (1) only adds to such "superdienophiles" as 4-N-phenyl-1,2,4-triazoline-3,5-dione (at 20 °C)<sup>5)</sup> and dicyanoacetylene (120 °C)<sup>6)</sup>; 1 is totally inert towards other dienophiles like maleic anhydride (180 °C, 37 h).<sup>5)</sup>

We now report that, by performing the title reaction at kirobar region and by using maleic anhydride (2a) and maleimides (2b-e) as the dienophile, 1 produces the 1:2 cycloadducts (3) in moderate yields.<sup>7,8)</sup> The results are summarized in Table 1. The <sup>13</sup>C-NMR spectra of these adducts<sup>8)</sup> indicate non-equivalence of olefinic and methylene carbons suggesting a highly hindered and congested structure of 3; especially, 3c and 3d which are soluble in CDCl<sub>3</sub> show four separate

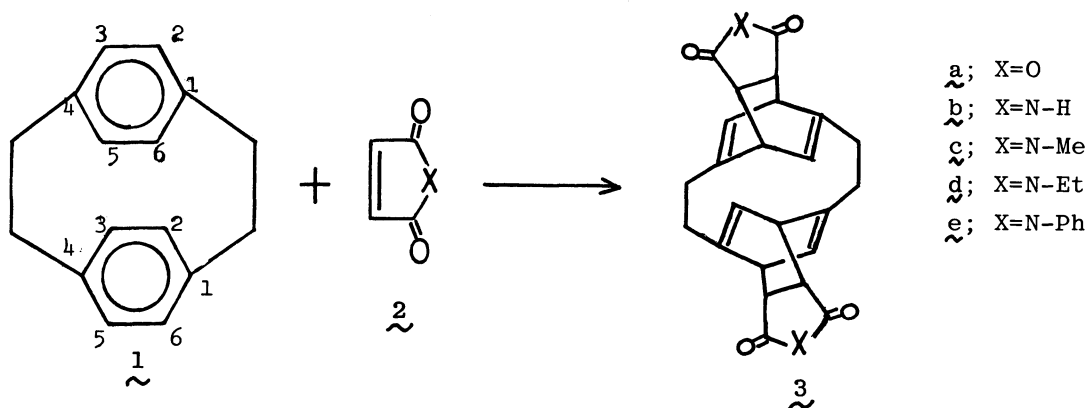


Table 1. Formation of the 1:2 Adducts (3) from 1 and 2 under High Pressure

1:2 Adduct (3)	Pressure/kbar	Temperature/°C	Time/d	Yield/% <sup>a)</sup>
3a	6	70	21	53
3b	8	80	14	35
3c	8	70	14	28
3d	8	70	14	22
3e	6	70	21	26

a) Yield of isolated pure product. Reaction conditions were not optimized.

peaks for the olefinic carbons.<sup>9)</sup> The adducts (3) are of interest for photoisomerization studies, since the related compound, barrelene, may be photorearranged to semibullvalene and cyclooctatetraene.<sup>10)</sup>

In conclusion, with appropriate methods for preparing a wide variety of cyclophanes, the potential for preparing highly intriguing bridged systems appears to be unlimited when performed at high pressures.

#### References

- 1) Dedicated to Prof. Dr. Rolf Huisgen on the occasion of his 65th birthday.
- 2) Review: J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 221 (1966); S. Seltzer, *Adv. Alicycl. Chem.*, **2**, 1 (1968).
- 3) Review on organic synthesis under high pressure including apparatus used and recent improvements for the Diels-Alder reactions: K. Matsumoto and A. Sera, *Synthesis*, **1985**, December issue.
- 4) Review on [2<sub>n</sub>]cyclophanes: J. Kleinschroth and H. Hopf, *Angew. Chem., Int. Ed. Engl.*, **21**, 469 (1982).
- 5) A. F. Murad, J. Kleinschroth, and H. Hopf, *Angew. Chem., Int. Ed. Engl.*, **19**, 389 (1980).
- 6) E. Ciganek, *Tetrahedron Lett.*, **1967**, 3321.
- 7) Satisfactory CHN analyses were obtained. The structure of adducts is assumed to be of the same type as that reported.<sup>5,6)</sup> At present, the alternative structure arising from 2,5- and 3,6-additions, can not be ruled out. This is a subject of future communications.
- 8) Typical examples of data of 3: 3a: mp 246-248 °C; IR(KBr) 1860, 1770 cm<sup>-1</sup>; <sup>13</sup>C-NMR(DMSO-d<sub>6</sub>, 50 °C) δ 29.8, 30.9(t, CH<sub>2</sub>), 39.7, 40.2(d, bridgehead carbon), 46.7, 46.9(d, COCH), 128.6, 130.6(d, CH=), 146.7, 146.9(s, C=), 171.5, 171.9 (s, C=O). 3c: mp 273-274 °C; IR(KBr) 1765, 1690 cm<sup>-1</sup>; <sup>13</sup>C-NMR(CDCl<sub>3</sub>, 40 °C) δ 24.4(q, CH<sub>3</sub>), 30.7, 30.8(t, CH<sub>2</sub>), 31.6, 39.9(d, bridgehead C), 46.0(d, COCH), 127.8, 127.9, 130.9, 131.1(d, CH=), 146.2, 146.5, 147.2, 147.6(s, C=), 177.6, 178.1(s, C=O).
- 9) 3a, 3b, and 3e are insoluble in CDCl<sub>3</sub>.
- 10) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M.-A. Sherwin, *J. Am. Chem. Soc.*, **91**, 3316 (1969).

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