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SYNTHESES OF [3.3]CYCLOPHANES[1)]

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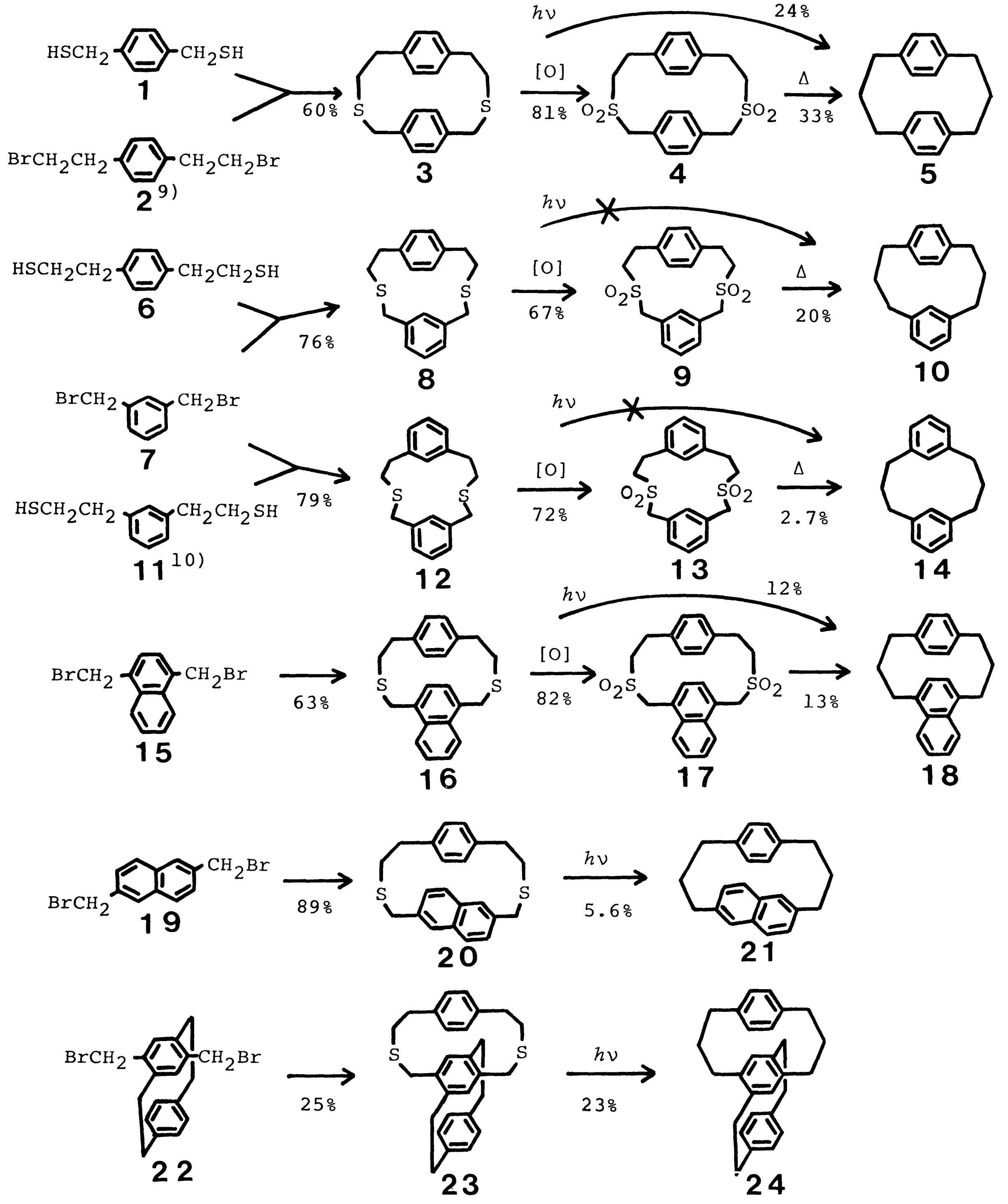
Two synthetic methods of [3.3]cyclophanes via dithia[4.4]-cyclophanes are presented. Direct photodesulfurization method is generally successful except in the cases of metapara- and meta-cyclophanes which are prepared by pyrolytic method of bissulfone.

Cram and coworkers reported the first synthesis of [3.3]paracyclophane 5 and its unique properties associated with the transannular electronic interaction.[2)] However, the extensive study of [3.3]cyclophane system has been limited because of difficulty in the synthesis,[3)] in contrast to the well-known chemistry of highly strained [2.2]cyclophanes. In recent years we have searched a general and easy synthesis of [3.3]cyclophane system. Now we wish to report on the new synthetic methods via cyclic dithia compounds and on the application to a variety of [3.3]cyclophanes 5, 10, 14,[4)] 18, 21, and 24.

The precursor, dithia[4.4]cyclophanes 3, 8, 12, 16, 20, and 23, were obtained in good yields by coupling reactions between the corresponding dibromide and dimercaptan.[5)] Direct photodesulfurization of the dithia compounds to [3.3]cyclophanes is successful as in the case of [2.2]cyclophanes.[6)] Thus, irradiation of 3 in triethylphosphite with a high pressure mercury lamp for one week under a nitrogen atmosphere led to the desired [3.3]paracyclophane 5 in 24% yield. The use of a low pressure mercury lamp brought about a considerable reduction of the reaction time. The yield reached a maximum 20% after 15 hours of the irradiation, and the prolonged irradiations decreased the yield due to the decomposition of the product. In the cases of paracyclonaphthalenophanes 18 and 21 and triple-layered [3.3][2.2]paracyclophane 24, the photodesulfurizations with a high pressure mercury lamp proceeded smoothly and completed within 6 hours.

As an alternative route, the pyrolytic method[7)] of bissulfone turned out to be useful. [3.3]Paracyclophane 5 was obtained in 33% yield by pyrolysis of bissulfone 4 which was derived in 81% yield by oxidation of 3 with *m*-chloroperbenzoic acid in dichloromethane.[8)] In the cases of [3.3]metaparacyclophane 10 and [3.3]metacyclophane 14, direct photodesulfurizations of dithia cyclophanes 8



and **12** were unsuccessful. However, the pyrolytic reactions of bissulfones **9** and **13** gave the desired cyclophanes **10** and **14**, respectively. The metacyclophane case showed an unexpected poor yield (2.7%) as compared to 33% for the paracyclophane and 20% for the metaparacyclophane. The pyrolytic method is also applicable to preparation of [3.3]paracyclonaphthalenophane **18**.

All the new cyclophanes were characterized by NMR and MS spectra and elemental analyses. The crystal forms, melting points, and NMR data are summarized in Table 1. The spectral properties concerning the transannular π-electronic interactions will be reported elsewhere.

Table 1. Properties of [3.3]cyclophanes NMR data were taken in CDCl$_3$(δ ppm).

3	Colorless plates from benzene-hexane, mp 183-185°C. NMR 2.75(A$_2$B$_2$m, 8H, CH$_2$), 3.39 (s, 4H, CH$_2$), 6.80(s, 8H, ArH).
5	Colorless plates from methanol, mp 103-104°C(104.3-105.3°C).[2] NMR 2.03 (m, 4H, CH$_2$), 2.72(t, 8H, CH$_2$), 6.66(s, 8H, ArH).
8	Colorless needles from benzene-hexane, mp 81-82°C. NMR 2.83(bs, 8H, CH$_2$), 3.46(s, 4H, CH$_2$), 6.40(bs, 1H, meta ArH), 6.88(s, 4H, para ArH), 6.98(bs, 3H, meta ArH).
10	Colorless plates from hexane, mp 90-91°C. NMR 1.9-2.9(m, 8H, CH$_2$), 2.71 (t, J=6Hz, 4H, CH$_2$), 5.55(bs, 1H, meta ArH), 6.63(s, 4H, para ArH), 6.7-7.2 (A$_2$B$_2$m, 3H, meta ArH).
12	Colorless prisms from benzene-hexane, mp 109-109.5°C. NMR 2.74(A$_2$B$_2$m, 8H, CH$_2$), 3.65(s, 4H, CH$_2$), 6.67(bs, 1H, ArH), 7.0-7.2(m, 3H, ArH), 7.39(bs, 4H, ArH).
14	Colorless plates from ethanol, mp 81-82°C(79-80°C).[4] NMR 1.9-2.9(m, 12H, CH$_2$), 6.7-7.1(m, 8H, ArH).
16	Colorless columns from benzene-hexane, mp 187-188°C. NMR 2.3-3.1(A$_2$B$_2$m, 8H, CH$_2$), 3.86(s, 4H, CH$_2$), 6.45(s, 4H, ArH), 6.72(s, 2H, ArH), 7.53 (A$_2$B$_2$dd, J=7 and 3Hz, 2H, ArH), 8.02(A$_2$B$_2$dd, J=7 and 3Hz, 2H, ArH).
18	Colorless fine crystals from pentane, mp 106-107°C. NMR 2.0-3.0(m, 10H, CH$_2$), 3.4-3.8(m, 2H, CH$_2$), 5.95(bs, 2H, ArH), 6.70(s, 2H, ArH), 6.76(bs, 2H, ArH), 7.43(A$_2$B$_2$dd, J=7 and 3Hz, 2H, ArH), 7.94(A$_2$B$_2$dd, J=7 and 3Hz, 2H, ArH).
20	Colorless plates from benzene-hexane, mp 198-200°C. NMR 2.2-2.8(m, 8H, CH$_2$), 3.77(s, 4H, CH$_2$), 6.41(s, 4H, ArH), 7.26(ABd, J=8Hz, 2H, ArH), 7.36 (bs, 2H, ArH), 7.53(ABd, J=8Hz, 2H, ArH).
21	Colorless plates from benzene-hexane, mp 160-161°C. NMR 1.8-3.0(m, 12H, CH$_2$), 6.04(s, 4H, ArH), 7.01(bs, 2H, ArH), 7.13(bs, 4H, ArH).
23	Colorless plates from benzene, mp 162-164°C. NMR 2.3-3.1(m, 16H, CH$_2$), 3.07 (ABd, J=14Hz, 2H, CH$_2$), 3.51(ABd, J=14Hz, 2H, CH$_2$), 5.80(s, 2H, ArH), 6.37 (A$_2$B$_2$m, 4H, ArH), 6.67(s, 4H, ArH).
24	Colorless prisms from hexane, mp 161-162.5°C. NMR 1.7-3.4(m, 20H, CH$_2$), 5.57(s, 2H, ArH), 6.14(A$_2$B$_2$dd, J=7Hz, 2H, ArH), 6.35(A$_2$B$_2$dd, J=7Hz, 2H, ArH), 6.46(s, 4H, ArH).

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10) 1,3-Bis(2-mercaptoethyl)benzene 11 was prepared in 53% overall yield from α,α′-dibromo-*m*-xylene in a similar manner as the para analogue 6.

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