Decomposition of [2.2.2]Cyclophane-1,2-dione Mono- and Bis(tosylhydrazone)s

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Synopsis. Monotosylhydrazone (**2**) of [2.2.2]cyclophane-1,2-dione (**1**) decomposed on silica gel, giving the ring-contracted [2.2.1]cyclophane-17-carboxylic acid (**4**). The electronic spectrum of **4** showed a red shift of the λ_{max} and a broadening of the peak shape in comparison with that of di-*p*-tolylacetic acid, due to a through-space π–π interaction. Thermolysis of bis(tosylhydrazone) (**3**) afforded [2.2.2]cyclophan-1-en-1-yl *p*-toluenesulfonate (**6**). An intermediate formation of the corresponding [2.2.2]cyclophan-1-yne is suggested.

It is well-known that the monohydrazone of a cyclic 1,2-diketone gives a ring-contracted ketene via an α-diazo ketone (Wolff rearrangement), and that its bishydrazone gives a cyclic acetylene via a 1,2-bis(diazo) compound.[1)]

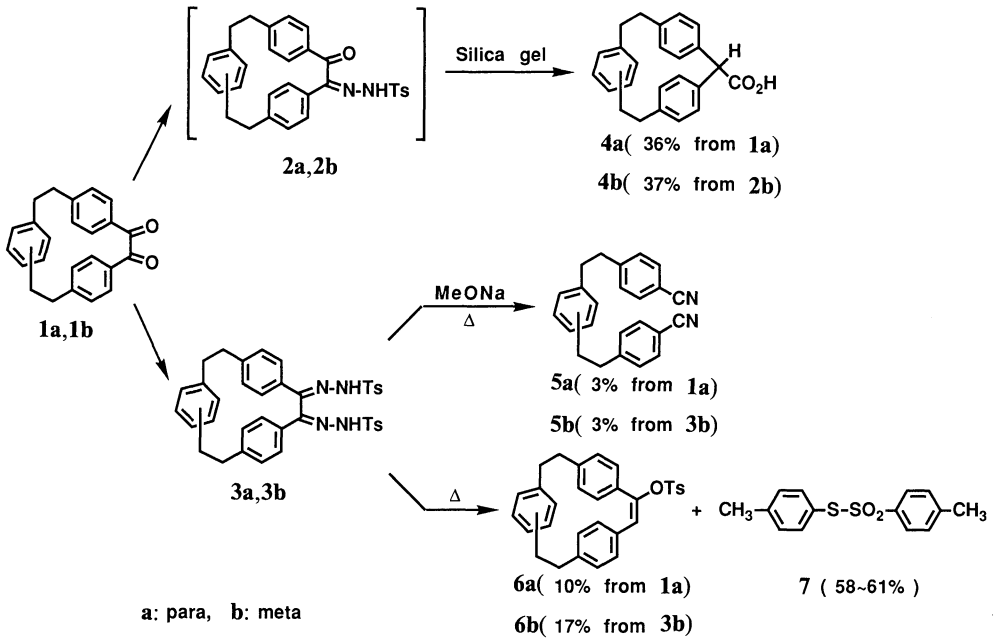
We recently prepared [2.2.2]cyclophane-1,2-diones (**1**) by cleaving the 1,2,5-thiadiazole ring in [2.2.2]cyclophanes using phenylmagnesium bromide.[2)] We now describe the degradation reaction of mono- (**2**) and bis(tosylhydrazone)s (**3**) of **1**.

Results and Discussion

Degradation. The results of the decomposition of [2.2.2]cyclophane-1,2-dione mono- (**2**) and bis(tosylhydrazone)s (**3**) are given in Scheme 1.

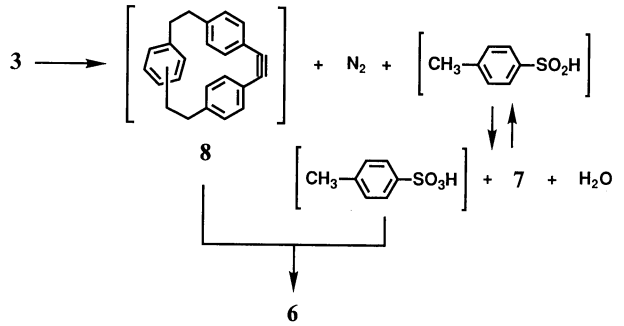
Tosylhydrazone (**2a**) of **1a** was too labile to be purified. A work-up of the reaction mixture of **1a** and one equivalent of tosylhydrazine on a silica-gel plate afforded ring-contracted [2.2.1]cyclophane-17-carboxylic acid (**4a**) in a total yield of 36% from **1a**, accompanied by unchanged **1a** in 15% yield. It should be noted that the contraction of [2.2.2]paracyclophane (**2a**) gave more strained [2.2.1]paracyclophane (**4a**). Although the metaparacyclophane analog **2b** is more stable than **2a**, similarly, **2b** decomposed on silica gel while producing **4b** in 37% yield.

Bis(tosylhydrazone) (**3a**) was also unstable and could not be purified as well as **2**; metaparacyclophane analog **3b**, however, was obtained in a pure form by recrystallization from ethanol. The addition of sodium methoxide to a solution of **3** in absolute ethanol caused



Scheme 1.

the development of a deep color, indicating the formation of a sodium salt of **3**. Neutralization of the mixture with concentrated hydrochloric acid recovered **3**. When the colored mixture was heated at reflux for 4 h, the cyclophane ring was cleaved, giving α,ω-dinitrile **5** in poor yield, together with a complex mixture of unidentified products. On the other hand, thermolysis of **3** in *m*-xylene under reflux gave [2.2.2]cyclophan-1-en-1-yl sulfonate (**6**) in low yield, together with thiol sulfonate (**7**). Since sulfinic acid disproportionates into sulfonic acid and thiol sulfonate,[3] **6** might be formed via the strained cyclophan-1-yne (**8**), as is shown in Scheme 2.



Scheme 2.

Spectra. The H_a-protons of [2.2.2]cyclophanes **1b**,[2] **3b**, and **6b**, which take a folded conformation, are shielded by the two para-substituted benzene rings; in the ^1H NMR spectrum, their signals were observed around 6.1—6.2 ppm. When one ethano bridge was substituted with a short methano bridge in [2.2.1]cyclophane **4b**, the H_a-proton of **4b** was shielded more effectively and showed a signal at 5.77 ppm in the spectrum (Fig. 1). The ^{13}C NMR of **4** showed more peaks than one would naively predict based on symmetry. This indicates a hindered rotation of the two para-substituted benzene rings in **4**.

It was reported that the electronic spectra of [2.2.2]cyclophane **9**, which is a higher homolog of [2.2.1]cyclophane, are very similar to that of 1,2-ditolylethane and that the three benzene rings of **9** are normal.[4] On the other hand, the λ_{max} of **4a** and **4b** in the spectra (Fig. 2) showed a red shift; further, the peak shapes are broadened in comparison with those of di-*p*-tolylacetic acid.[5] These features are characteristic of cyclophanes having an intramolecular through-space π–π interaction.

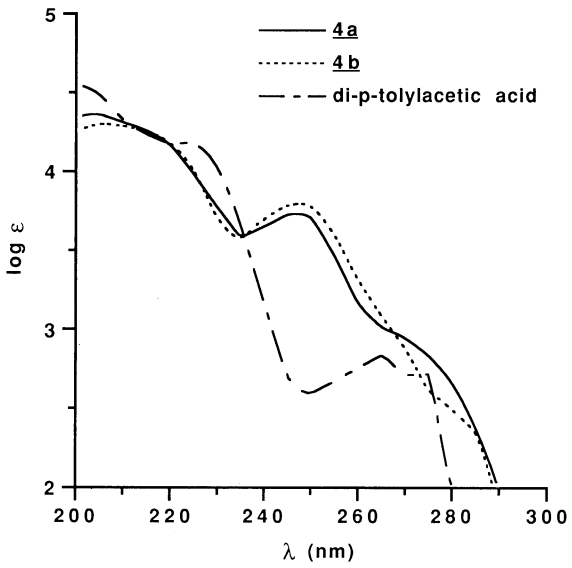


Fig. 2. Electronic spectra of **4a**, **4b**, and di-*p*-tolylacetic acid in cyclohexane.

Experimental

General. All of the melting points were determined on a Mitamura-riken MELT THERMO and are uncorrected. The IR spectra were measured as KBr pellets on a Nippon-Bunko A-102. ^1H and ^{13}C NMR were recorded with a JEOL GSX-270 using TMS as an internal standard. The mass spectra were obtained on a JEOL JMS-O1SG-2 mass spectrometer at 75 eV using a direct inlet system. PLC was carried out on 2 mm precoated plates of silica gel (Merck Kieselgel $60F_{254}S$, 20×20 cm) with a concentrating zone (4×20 cm).

[2.2.1](1,4)(1,4)(1,4)Cyclophane-17-carboxylic Acid (4a). To a mixture of **1a** (80 mg, 0.24 mmol) in ethanol (5 cm^3) was added tosylhydrazine (48 mg, 0.26 mmol) at room temperature. This mixture was stirred for 8 h. Insoluble materials were filtered, and the filtrate was evaporated in vacuo, leaving a residue which was subjected to preparative TLC using a 8 : 1-mixture of benzene and ethyl acetate, giving **1a** (12 mg, 15%) and **4a** (29 mg, 36% from **1a**): Colorless needles (cyclohexane); mp 216—218 °C (decomp); IR 3400—2400, 1700, 1510, 1440, 1410, 1220, 920, 800, 740, and 720 cm^{-1}; ^1H NMR (DMSO-d_6) δ=2.70—3.00 (m, 8H), 4.70 (s, 1H), 6.45 (s, 2H), 6.56 (s, 2H), 6.65—6.86 (m, 6H), 6.97—7.10 (m, 2H), and 12.56 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ=32.9, 34.4, 56.3, 125.4, 127.1, 128.3, 129.3, 129.9, 135.8, 138.6, 138.7, and 177.2; MS *m*/*z* 342 (M^+). Found; C, 84.25; H, 6.64. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48.

[2.2.1](1,4)(1,3)(1,4)Cyclophane-17-carboxylic Acid (4b). To a mixture of **1b** (80 mg, 0.24 mmol) in ethanol (5 cm^3) was

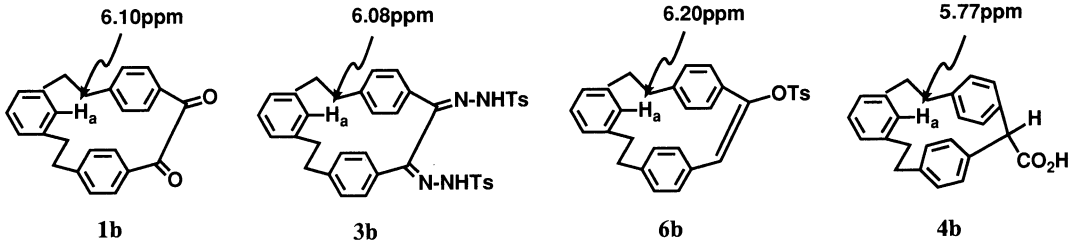


Fig. 1. Chemical shifts of H_a-proton of **1b**, **3b**, **4b**, and **6b** (δ: $CDCl_3$).

added tosylhydrazine (48 mg, 0.26 mmol) at room temperature. This mixture was then stirred for 1 h. The solvent was evaporated in vacuo, leaving a residue, which upon washing with hexane, gave **2b** (118 mg) as a white solid. Crude **2b** (100 mg) was dissolved in CH_2Cl_2 (100 cm^3); to the solution was added silica gel (Wako gel, C-300) (50 g). The mixture was stirred at room temperature for 27 h and filtered. The filtrate was evaporated in vacuo and the residue was triturated with hexane, giving a white solid, which, upon chromatography using a 5 : 1-mixture of chloroform and acetonitrile, afforded **4b**. Recrystallization from a mixture of hexane and ethyl acetate gave **4b** (25 mg, 37% from **2b**) as colorless needles; mp 202—203 °C; IR 3400—2400, 1700, 1510, 1440, 1410, 1310, 1240, 1210, 930, 800, 750, and 710 cm^{-1}; ^1H NMR (DMSO-d_6) δ=2.45—2.64 (m, 4H), 2.70—2.90 (m, 4H), 4.78 (s, 1H), 5.70 (s, 1H), 6.67 (d, 4H, J=8.4 Hz), 6.79—6.95 (m, 4H), 6.99—7.08 (m, 3H), and 12.60 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ=35.3, 37.5, 56.4, 125.0, 126.0, 127.5, 127.7, 128.6, 129.3, 132.2, 139.0, 139.5, 139.8, and 177.1; MS m/z 342 (M^+). Found: C, 83.91; H, 6.35. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48.

[2.2.2](1,4)(1,3)(1,4)Cyclophane-1,2-dione Bis(tosylhydrazone) (3b). A mixture of **1b** (100 mg, 0.29 mmol) and tosylhydrazine (220 mg, 1.18 mmol) in ethanol (5 cm^3) was stirred at room temperature for 24 h. The precipitates were collected by filtration and recrystallized, giving **3b** (140 mg, 70%) as colorless prisms (ethanol); mp 169—179 °C (decomp); IR 3182, 29922, 1598, 1443, 1346, 1168, 1093, 1044, 1018, 973, 855, 813, 778, 703, 671 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.41 (s, 3H), 2.48 (s, 3H), 2.74—2.94 (m, 8H), 6.08 (s, 1H), 6.57—6.68 (m, 6H), 6.80—7.03 (m, 4H), 7.16—7.30 (m, 3H), 7.44 (d, J=8.1 Hz, 2H), 7.83—7.92 (m, 4H), 8.04 (s, 1H), and 11.81 (s, 1H). Found: C, 67.65; H, 5.51; N, 7.98. Calcd for $C_{38}H_{36}N_4O_4S_2$: C, 67.43; H, 5.36; N, 8.28.

1,4-Bis[2-(4-cyanophenyl)ethyl]benzene (5a). Crude **3a** (122 mg) was prepared by stirring a mixture of **1a** (100 mg, 0.29 mmol) and tosylhydrazine (220 mg, 1.18 mmol) in ethanol (5 cm^3) at room temperature for 24 h. A mixture of crude **3a** (168 mg) and MeONa (34 mg, 0.63 mmol) in benzene (5 cm^3) was heated under reflux for 6 h. After it was cooled to room temperature, it was poured into water and extracted with CH_2Cl_2. The extract was washed with water, dried over $MgSO_4$, and evaporated in vacuo, leaving a residue, which, upon trituration with ethanol, afforded **5a** (4 mg, total 3% yield from **1a**): Colorless needles (benzene); mp 221.5—223.5 °C; IR 2916, 2224, 1607, 1506, 1455, 1177, 1020, and 833 cm^{-1}; MS m/z 336 (M^+). Found: C, 85.33; H, 6.18; N, 8.11. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33.

1,3-Bis[2-(4-cyanophenyl)ethyl]benzene (5b). A mixture of **3b** (128 mg, 0.19 mmol) and MeONa (23 mg, 0.42 mmol) in ethanol (5 cm^3) was heated under reflux for 4 h and worked up as described above. The residue obtained was subjected to preparative TLC using a 10 : 1-mixture of hexane and ethyl acetate as an eluent, giving **5b** (2 mg, 3%): Colorless needles (hexane); mp 150—153.5 °C; IR 2922, 2222, 1606, 1507, 1177, and 826 cm^{-1}; MS m/z 336 (M^+). Found: C, 85.08; H, 5.99; N, 8.11. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33.

[2.2.2](1,4)(1,4)(1,4)Cyclophan-1-en-1-yl *p*-Toluenesulfonate (6a). A solution of crude **3a** (130 mg) in *m*-xylene (5 cm^3) was heated under reflux for 15 h. The solvent was evaporated in vacuo. The residue was then subjected to preparative TLC using a 10 : 1-mixture of hexane and ethyl acetate as an eluent, giving **7** (32 mg, 58%) and **6a** (16 mg, total 10% yield from **1a**): Pale yellow prisms (hexane); mp 135—138 °C; IR 2918, 1598, 1511, 1440, 1371, 1192, 1179, 1096, 1006, 883, 773, and 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.41 (s, 3H), 2.88—2.99 (m, 8H), 6.56 (d, J=1.7 Hz, 2H), 6.58—6.70 (m, 11H), 7.24 (dd, J=7.8 and 2.1 Hz, 2H), and 7.75 (dd, J=8.4 and 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=21.7, 33.6, 33.8, 33.9, 34.0, 122.7, 128.3, 128.4, 128.5, 129.5, 130.0, 131.5, 133.7, 136.3, 136.5, 138.6, 140.6, 144.9, and 150.1; MS m/z 480 (M^+). Found: C, 77.95; H, 5.99. Calcd for $C_{31}H_{28}O_3S$: C, 77.47; H, 5.87.

[2.2.2](1,4)(1,3)(1,4)Cyclophan-1-en-1-yl *p*-Toluenesulfonate (6b). A solution of **3b** (123 mg, 0.18 mmol) in *m*-xylene (5 cm^3) was heated under reflux for 3 h and worked up as described above, giving **7** (31 mg, 61%) and **6b** (15 mg, 17%) as pale yellow prisms (hexane); mp 134—137 °C; IR 2930, 1602, 1446, 1369, 1219, 1176, 1029, 1009, 883, 859, 817, 774, 730, and 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.42 (s, 3H), 2.75—2.92 (m, 8H), 6.20 (s, 1H), 6.53—6.72 (m, 9H), 7.02 (dd, J=8.0 and 0.9 Hz, 2H), 7.17—7.28 (m, 3H), and 7.77 (dd, J=8.4 and 1.8 Hz, 2H); MS m/z 480 (M^+). Found: C, 78.02; H, 5.95. Calcd for $C_{31}H_{28}O_3S$: C, 77.47; H, 5.87.

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