Isolation of Keto-*S*-phenylthioxime of [2³]Cyclophane-1,2-dione. Re-visited Contraction of 1,2,5-Thiadiazole Ring Incorporated in a [2³]Cyclophane Bridge by Phenylmagnesium Bromide.

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[2³]Paracyclophane derivative **3** of keto-*S*-phenylthioxime which is the hydrolyzed product of the hypothetical intermediate in the reaction of 1,2,5-thiadiazole with organometallic reagents, was obtained, together with diketone **1**, in the reaction of 1,2,5-thiadiazolo[2³]paracyclophane **2** with two equivalents of phenylmagnesium bromide. Contrary, [2³]metacyclophane **7** gave only diketone **12** in the reaction with phenylmagnesium bromide under the same conditions.

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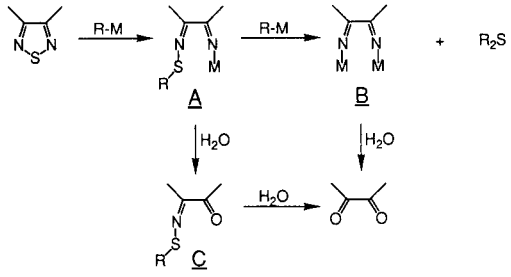
Contraction of 1,2,5-thiadiazoles with organometallic reagents was reported to give the corresponding 1,2-diketones [1]. The reaction is considered to proceed *via* imine **A** and/or diimine **B** as an intermediate (Scheme 1) [1]. The intermediate **A** might give ketothioxime ether **C** by hydrolysis under the conditions of the usual work-up, but, to the best of our knowledge, isolation of **C** has not been reported up to the present time.

Scheme 1

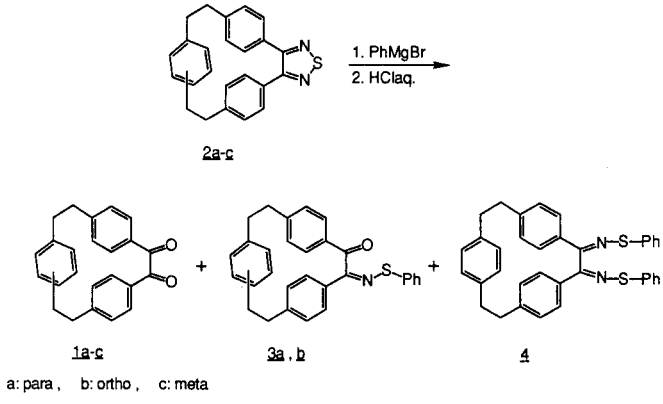


Previously, we reported the preparation of [2³]cyclophane-1,2-dione **1** by the reaction of thiadiazolocyclophane **2** with phenylmagnesium bromide [2]. During the detailed investigation on the above reactions, we succeeded in the isolation of keto-*S*-phenylthioxime **3**, which is described in the present paper.

Results and Discussion.

As earlier reported [2], **2a-c** gave the corresponding diketones **1a-c** when treated with seven equivalents of phenylmagnesium bromide at room temperature for 1.5 ~ 3 hours. The reaction was re-investigated under various conditions and the results are given in Table 1 and Scheme 2.

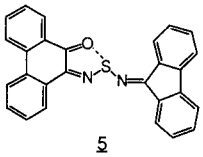
Scheme 2



During the reaction the development of a yellow color was noticed in the reaction mixture. The reaction of **2a** with two equivalents of phenylmagnesium bromide for a short period (15 minutes) gave keto-*S*-phenylthioxime **3a** and bis(*S*-phenylthioxime) **4** in 12% and 5% yields, respectively, both as yellow crystals. Unchanged **2a** was recovered in 65% yield and diketone **1a** was obtained in 15% yield. When the reaction was carried out for 5 hours, **3a** and **1a** were obtained in 26% and 31% yields, respectively, and unchanged **2a** in 14% yield. The reaction of **2b**

for 5 hours gave imine **3b** in 31% yield, with recovered **2b** in 31% yield.

The structures of **3** and **4** were elucidated by elemental analysis and spectral data. The presence of partial bonding between sulfur and oxygen atom in phenylsulfenylimine **5** and **6** was reported as evidenced by the weak carbonyl absorption at a low wave number (around 1600 cm^{-1}) in ir spectra [3].



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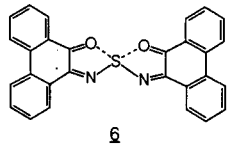

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Figure 1. Partial bonding between S---O atoms.

In the spectra of **3a** and **3b**, carbonyl absorption was observed at 1680 and 1675 cm^{-1}, respectively, suggesting the absence of the partial bond in **3**.

In order to study the effect of the cyclophane skeleton on the reaction of the 1,2,5-thiadiazole ring with phenylmagnesium bromide, we prepared a series of [2³]metacyclophanes **7** according to Scheme 3.

Di-*m*-tolylacetylene was prepared by a sequence of reactions (Wittig reaction [4], bromination [5], and dehydrobromination [5]). Reaction with tetrasulfur tetranitride (N_4S_4) gave 3,4-di(*m*-tolyl)-1,2,5-thiadiazole (**8**). Bromination with *N*-bromosuccinimide in methylene chloride in the presence of V-65 [6] afforded the desired dibromide **9**. Dithiacyclophanes **10a-c** were prepared by condensation of **9** with 1,x-bis(mercaptomethyl)benzene under highly dilute conditions. Oxidation with hydrogen peroxide and pyrolysis of disulfones **11a-c** at 600° under reduced pressure (0.5-1.0 mmHg) yielded **7a-c**.

The results of the reaction of **7a-c** with phenylmagnesium bromide are summarized in Table 2 and Scheme 4.

When eight and a half equivalents of phenylmagnesium bromide were used, diketones **12a-c** were obtained, as expected. The reaction of **7a** proceeded, as is the case of the reaction of *para*-derivative **2**, with yellow-colorization of the reaction mixture when two equivalents of phenylmagnesium bromide were employed. Unchanged **7a** and the corresponding diketone **12a** were obtained in 74% and 5% yields, respectively, however, the corresponding keto-*S*-phenylthioxime derivative was not obtained. The reaction of **7c** gave the similar results: **12c** was obtained in 24% yield with a recovery of **7c** in 47% yield. These results are in a sharp contrast with the reaction of the more strained **2**.

Scheme 4

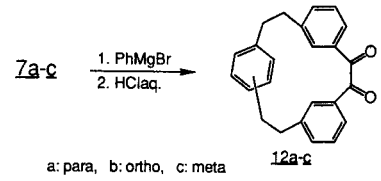


Table 1
Reaction of **2a-c** with Phenylmagnesium Bromide

2	2/phenylmagnesium bromide [a]	Time [b]	Products, Yields (%)
2a	2	0.25	**1a** (15), **3a** (12), **4** (5), **2a** (65)
2a	2	5	**1a** (31), **3a** (26), **2a** (14)
2a	7	1.5	**1a** (66)
2b	2	0.25	**1b** (+), **3b** (8), **2b** (60)
2b	2	5	**1b** (+), **3b** (31), **2b** (31)
2b	7	1.5	**1b** (81)
2c	7	3	**1c** (58)

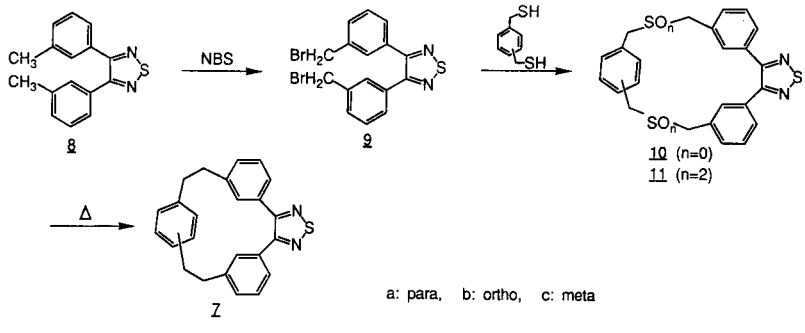
[a] Molar ratio. [b] Hours.

Table 2
Reaction of **7a-c** with Phenylmagnesium Bromide

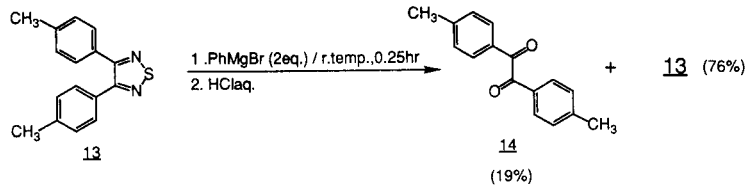
7	7/phenylmagnesium bromide [a]	Time [b]	Products, Yields (%)
7a	2	5	**12a** (5), **7a** (74)
7a	8.5	1.5	**12a** (50)
7b	8.5	1.5	**12b** (38)
7c	2	5	**12c** (24), **7c** (47)
7c	8.5	1.5	**12c** (41)

[a] Molar ratio. [b] Hours.

Scheme 3



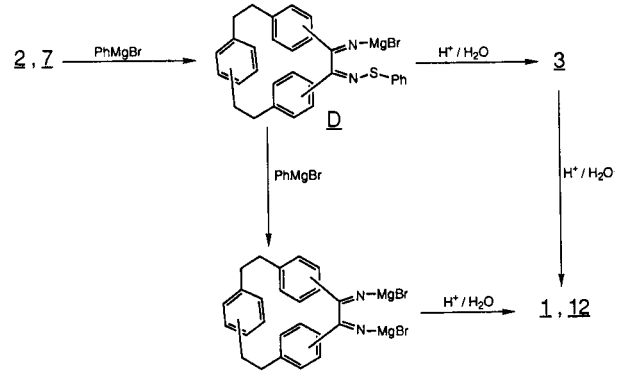
Scheme 5



For comparison, we carried out the reaction of **13**, using two equivalents of phenylmagnesium bromide for 15 minutes. During the reaction, though weak, a yellow color developed in the mixture. After the usual work-up, diketone **14** [7] was obtained in 19% yield, together with unchanged **13** in 76% yield, but none of the expected keto-*S*-phenylthioxime was obtained (Scheme 5).

The above results seem parallel with the strain of the cyclophane-structure; because of the release of the cyclophane-ring strain, the first attack of phenylmagnesium bromide on the 1,2,5-thiadiazole ring in **2** is faster than the second attack on the ring-opened intermediate **A** and thus allows the isolation of **3**, while the attack of two molecules of phenylmagnesium bromide on the 1,2,5-thiadiazole ring of flexible **7**, gave diketone **12** after work-up.

Scheme 6



EXPERIMENTAL

All melting points are uncorrected. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct inlet system. The ^{1}H-nmr spectra were recorded on a Nippon Denshi JEOL FT-100 NMR spectrometer using tetramethylsilane as an internal standard in deuteriochloroform unless otherwise stated. The ir spectra were measured on a Nippon-bunko A-102 spectrophotometer as potassium bromide pellets. Column chromatography was carried out on silica gel (Wako gel, C-300). Preparative thin-layer chromatography was accomplished on 2 mm precoated plates of silica gel (Merck Kieselgel 60F_{254}S, 20 x 20 cm) with concentrating zone (4 x 20 cm).

Preparation of 3,4-Di(*m*-tolyl)-1,2,5-thiadiazole (**8**).

A mixture of di-*m*-tolylacetylene (12.4 g) and tetrasulfur tetranitride (N_4S_4) (12.2 g) in toluene (200 ml) was refluxed for 50 hours. Insoluble materials were filtered and the filtrate was evaporated *in vacuo* to leave the residue which was washed with ether (50 ml). The washings were condensed and chromatographed using a 1:1-mixture of hexane and benzene as an eluent to give **8**. This compound was obtained as colorless prisms (95% methanol) (8.30 g, 50%), mp 72-73°; ^{1}H-nmr: δ 2.32 (s, 6H), 7.18 (s, 6H), 7.37 (s, 2H); ms: m/e 266 (M^+).

Anal. Calcd. for $C_{16}H_{14}N_2S$: C, 72.15; H, 5.30; N, 10.52. Found: C, 71.96; H, 5.34; N, 10.32.

Preparation of 3,4-Di(3-bromomethylphenyl)-1,2,5-thiadiazole (**9**).

After a mixture of **8** (5.00 g), *N*-bromosuccinimide (8.40 g), and V-65 [6] (35 mg) in dry methylene chloride (300 ml) was gently refluxed for 8 hours, the solvent was evaporated *in vacuo* and, to the residue was added carbon tetrachloride and the insoluble materials were filtered off. The filtrate was condensed *in vacuo* and extracted with hot light petroleum (bp 40-60°). The extract was evaporated *in vacuo*, giving a yellow oil, which, on column chromatography using a 7:3-mixture of hexane and benzene as an eluent, gave **9** (5.40 g, 68%). This compound was obtained as colorless prisms (hexane), mp 110-111°; ^{1}H-nmr: δ 4.41 (s, 4H), 7.23-7.53 (m, 8H); ms: m/e 426 (M^+), 424 (M^+), 422 (M^+).

Anal. Calcd. for $C_{16}H_{12}Br_2N_2S$: C, 45.31; H, 2.85; N, 6.60. Found: C, 45.18; H, 2.98; N, 6.64.

Preparation of Dithia-1,2,5-thiadiazolocyclophane **10a**.

To a mixture of sodium borohydride (0.55 g) and cesium hydroxide monohydrate (1.90 g) in degassed ethanol (1.5 l) at reflux was added dropwise a solution of **9** (2.00 g) and 1,4-bis(mercaptomethyl)benzene (0.80 g) in benzene (80 ml) for 14 hours and the mixture was refluxed for 2 hours. After solvents were evaporated *in vacuo*, water (500 ml) was added to the residue. The water layer was acidified with 10% hydrochloric acid and the whole mixture was extracted with methylene chloride (800 ml). The extract was washed with saturated aqueous sodium chloride dried over magnesium sulfate, and evaporated *in vacuo*, giving a yellow tar, which, on chromatography with chloroform as an eluent, gave pale yellow crystals. Recrystallization from ethyl acetate gave **10a** as colorless prisms (1.10 g 54%).

2,16-Dithia-4,6-12,14-1,3-dibenzo[6.6](3,4)-1,2,5-thiadiazoloparacyclophane (**10a**).

This compound had mp 175-177°; ^{1}H-nmr: δ 3.51 (s, 4H), 3.61 (s, 4H), 7.00-7.43 (m, 12H); ms: m/e 432 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2S_3$: C, 66.63; H, 4.66; N, 6.47. Found: C, 66.38; H, 4.73; N, 6.31.

Preparation of Dithia-1,2,5-thiadiazolocyclophanes **10b** and **10c**.

To a mixture of sodium borohydride (1.96 g) and cesium hydroxide monohydrate (7.49 g) in degassed ethanol (4 l) at reflux

was added dropwise a solution of **9** (7.00 g) and 1,2-bis(mercaptomethyl)benzene (2.81 g) in benzene (300 ml) for 10 hours and the mixture was refluxed for 7 hours. The reaction mixture was worked up as described above, to give yellow solid, which, on chromatography with benzene as an eluent, afforded pale yellow solid. Recrystallization from a mixture of hexane and benzene gave **10b** as colorless prisms (4.68 g, 65%).

Compound **10c** was similarly prepared.

2,16-Dithia-4,6-12,14-1,3-dibenzo[6.6](3,4)-1,2,5-thiadiazoloorthocyclophane (**10b**).

This compound had mp 134-135°; ^{1}H-nmr: δ 3.23 (s, 4H), 3.48 (s, 4H), 6.92-7.86 (m, 12H); ms: m/e 432 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2S_3$: C, 66.63; H, 4.66; N, 6.47. Found: C, 66.54; H, 4.72; N, 6.36.

2,16-Dithia-4,6-12,14-1,3-dibenzo[6.6](3.4)-1,2,5-thiadiazolometacyclophane (**10c**).

This compound was obtained as colorless prisms (ethyl acetate) from **9** (7.00 g) and 1,3-bis(mercaptomethyl)benzene (2.81 g) in 57% yield (4.07 g), mp 161-163°; ^{1}H-nmr: δ 3.46 (s, 4H), 3.52 (s, 4H), 5.91 (br s, 1H), 6.92-7.60 (m, 11H); ms: m/e 432 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2S_3$: C, 66.63; H, 4.66; N, 6.47. Found: C, 66.69; H, 4.70; N, 6.60.

Oxidation of **10**. Typical Procedure.

After a mixture of **10a** (4.00 g) and 30% aqueous hydrogen peroxide (14 ml) in acetic acid (150 ml) was heated in oil bath at 60-70° for 4 hours, it was diluted with water (150 ml) and cooled in ice bath for 2 hours. The precipitate was filtered and washed with ethanol and hexane, giving **11a** as colorless prisms (4.19 g, 92%).

Compounds **11b** and **11c** were similarly prepared.

2,16-Dithia-4,6-12,14-1,3-dibenzo[6.6](3,4)-1,2,5-thiadiazoloparacyclophane-2,2,16,16-tetraoxide (**11a**).

This compound had mp 342-346° dec; ir: 1319, 1117 cm^{-1}; ^{1}H-nmr: δ 4.17 (s, 4H), 4.23 (s, 4H), 7.17-7.60 (m, 12H); ms: m/e 496 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2O_4S_3$: C, 58.05; H, 4.06; N, 5.64. Found: C, 57.94; H, 4.02; N, 5.59.

2,16-Dithia-4,6-12,14-1,3-dibenzo[6.6](3.4)-1,2,5-thiadiazoloorthocyclophane-2,2,16,16-tetraoxide (**11b**).

This compound was obtained in 86% yield (4.45 g) from **10b** (4.50 g) as colorless prisms, mp 310-315° dec; ir: 1319, 1117 cm^{-1}; ^{1}H-nmr: δ 4.12 (s, 4H), 4.19 (s, 4H), 7.12-8.00 (m, 12H); ms: m/e 368 ($M^+ - 2SO_2$).

Anal. Calcd. for $C_{24}H_{20}N_2O_4S_3$: C, 58.05; H, 4.06; N, 5.64. Found: C, 57.98; H, 4.09; N, 5.40.

2,16-Dithia-4,6-12,14-1,3-dibenzo[6.6](3,4)-1,2,5-thiadiazolometacyclophane-2,2,16,16-tetraoxide (**11c**).

This compound was obtained in 92% yield (4.47 g) from **10c** (4.21 g) as pale green prisms, mp 290-298° dec; ir: 1318, 1113 cm^{-1}; ^{1}H-nmr: δ 4.12 (s, 4H), 4.16 (s, 4H), 5.96 (br s, 1H), 7.24-7.80 (m, 11H); ms: m/e 496 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2O_4S_3$: C, 58.05; H, 4.06; N, 5.64. Found: C, 58.06; H, 4.09; N, 5.44.

Preparation of 1,2,5-Thiadiazolocyclophane **7**.

Pyrolysis was conducted under reduced pressure (0.5-1.0 mm Hg) in an apparatus described previously [8]. A typical procedure is as follows: After **11a** (1.40 g) was pyrolyzed at 600° for 10 minutes, the pyrolysate was extracted with methylene chloride (80 ml). The extract was evaporated *in vacuo*, leaving a residue which, on chromatography with 1:2-mixture of hexane and benzene as an eluent, gave crude **7a**. Washing with hot hexane and recrystallization from ethanol gave **7a** in 51% yield (0.53 g) as pale yellow prisms in 51% yield (0.52 g).

Compounds **7b** and **7c** were similarly prepared.

3,5-11,13-Di-1,3-benzo[5.5](3,4)-1,2,5-thiadiazoloparacyclophane (**7a**).

This compound had mp 211-213°; ^{1}H-nmr: δ 2.66-3.00 (m, 8H), 6.31 (s, 2H), 6.61 (s, 4H), 7.26-7.54 (m, 6H); ms: m/e 368 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2S$: C, 78.23; H, 5.47; N, 7.60. Found: C, 78.07; H, 5.61; N, 7.43.

3,5-11,13-Di-1,3-benzo[5.5](3,4)-1,2,5-thiadiazoloorthocyclophane (**7b**).

This compound was obtained in 53% yield (0.544 g) from **11b** (1.40 g) as pale yellow prisms (a mixture of hexane and benzene), mp 176-178°; ^{1}H-nmr: δ 2.48-3.12 (m, 8H), 6.73 (m, 2H), 7.02 (s, 4H), 7.12-7.60 (m, 6H); ms: m/e 368 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2S$: C, 78.23; H, 5.47; N, 7.60. Found: C, 78.16; H, 5.49; N, 7.53.

3,5-11,13-Di-1,3-benzo[5.5](3,4)-1,2,5-thiadiazolometacyclophane (**7c**).

This compound was obtained in 62% yield (0.615 g) from **11c** (1.40 g) as pale yellow prisms [light petroleum (bp 40-60°)], mp 120-121°; ^{1}H-nmr: δ 2.82 (s, 8H), 6.26-6.48 (m, 3H), 6.52-7.05 (m, 3H), 7.05-7.52 (m, 6H); ms: m/e 368 (M^+).

Anal. Calcd. for $C_{24}H_{20}N_2S$: C, 78.23; H, 5.47; N, 7.60. Found: C, 78.06; H, 5.47; N, 7.47.

Reaction of Cyclophanes **2** and **7** with Phenylmagnesium Bromide. (i) With Two equivalents of phenylmagnesium Bromide. Typical procedure.

An ether solution (2 ml) of phenylmagnesium bromide (prepared from 104 mg of bromobenzene and 13 mg of magnesium turnings) was added dropwise to an ether solution (20 ml) of **2a** (100 mg) at room temperature for 5 minutes under nitrogen stream and the mixture was stirred for 10 minutes at this temperature. It was poured into ice-cold 5% hydrochloric acid (10 ml), stirred for 15 minutes, and extracted with methylene chloride (30 ml). The combined extract was washed with water, dried over magnesium sulfate and evaporated *in vacuo* to leave the residue which was subjected to ptlc with a 9:1 mixture of hexane and ethyl acetate as an eluent, giving **1a** (Rf = 0.17, 14 mg, 15%), **3a** (Rf = 0.30, 15 mg, 12%), **4** (Rf = 0.40, 8 mg, 5%) and **2a** (Rf = 0.40, 65 mg, 65%).

The physical and spectral data of **3** and **4** are given below.

[2^3](1,4)(1,4)(1,4)Cyclophane-1,2-dione *S*-Phenylthioxime (**3a**).

This compound was obtained as a ⅓ hydrate of yellow prisms (cyclohexane), mp 112-118° dec; ir: 1675 cm^{-1}; ^{1}H-nmr: δ 2.76-3.12 (m, 8H), 6.56-7.67 (m, 17H); ms: m/e 447 (M^+).

Anal. Calcd. for ($C_{30}H_{25}NOS$ + ⅓ H_2O): C, 79.45; H, 5.70; N, 3.09. Found: C, 79.70; H, 5.77; N, 3.02.

[2^3](1,4)(1,2)(1,4)Cyclophane-1,2-dione *S*-phenylthioxime (**3b**).

This compound was obtained as yellow prisms (hexane), mp

162-167° dec; ir: 1680 cm^{-1}; ^1H-nmr: δ 2.44-3.17 (m, 8H), 6.32-7.76 (m, 17H); ms: m/e 447 (M^+).

Anal. Calcd. for $C_{30}H_{25}NOS$: C, 80.50; H, 5.63; N, 3.13. Found: C, 80.43; H, 5.65; N, 3.17.

[2³](1,4)(1,4)(1,4)Cyclophane-1,2-dione Bis(*S*-phenylthioxime) (**4**).

This compound was obtained as yellow needles (hexane), mp 211-216° dec; ^1H-nmr: δ 2.84-3.18 (m, 8H), 6.42-7.85 (m, 22H); ms: m/e 554 (M^+).

Anal. Calcd. for $C_{36}H_{30}N_2S_2$: C, 77.94; H, 5.45; N, 5.05. Found: C, 78.01; H, 5.48; N, 4.69.

(ii) With a Large Excess of Phenylmagnesium Bromide. Typical Procedure.

To a stirred ether solution (4.4 ml) of phenylmagnesium bromide (prepared from 650 mg of bromobenzene and 84 mg of magnesium turnings) was added dropwise an ether solution of **7a** (150 mg) at room temperature for 15 minutes under nitrogen stream and the mixture was stirred for 1.5 hours at this temperature. It was poured into ice-cold 5% hydrochloric acid (30 ml), stirred for 15 minutes, and extracted with ether (20 ml) and methylene chloride (50 ml). The combined extract was washed with water, dried over magnesium sulfate and evaporated *in vacuo* to leave the residue, which, on washing with benzene, afforded **12a** (69 mg, 50%) as pale yellow prisms.

Physical and spectral properties of **12** are given below.

[2³](1,3)(1,4)(1,3)Cyclophane-1,2-dione (**12a**).

This compound had mp 223-224°; ir: 1673, 1662 cm^{-1}; ^1H-nmr: δ 2.08-3.80 (m, 8H), 5.94-7.16 (m, 6H), 7.20-7.64 (m, 4H), 7.76-8.02 (m, 2H); ms: m/e 340 (M^+).

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.68; H, 5.73.

[2³](1,3)(1,2)(1,3)Cyclophane-1,2-dione (**12b**).

This compound was obtained in 38% yield (52 mg) from **7b** (150 mg) as pale yellow prisms (degassed cyclohexane), mp 171-173°; ir: 1690 cm^{-1}; ^1H-nmr: δ 2.56-3.20 (m, 8H), 6.80 (br s, 2H), 7.12 (s, 4H), 7.18-7.66 (m, 6H); ms: m/e 340 (M^+).

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.74; H, 5.79.

[2³](1,3)(1,3)(1,3)Cyclophane-1,2-dione (**12c**).

This compound was obtained in 41% yield (56 mg) from **7c** (150 mg) as pale yellow prisms (cyclohexane), mp 178-180°; ir: 1674 cm^{-1}; ^1H-nmr: δ 2.64-3.10 (m, 8H), 6.12 (br s, 1H), 6.68-7.58 (m, 9H), 7.74-8.02 (m, 2H); ms: m/e 340 (M^+).

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.55; H, 5.84.

REFERENCES AND NOTES

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