Acknowledgment. We would like to thank Dr. A. Frimer for helpful duscussions. The support of this research by the Bar-Ilan Research Committee under Grant No. 161-84-15-8 is also gratefully acknowledged.

Registry No.—**2E,** 28764-49-0; **2Z,** 28764-48-9; **3,** 37939-96-1; **4E,** 69257-81-4; **4Z,** 69257-82-5; **5,** 694-98-4; **6E,** 69257-78-9; **6Z,** 69257-79-0; **7,** 37939-83-6; **8,** 37939-98-3; **9E,** 69257-83-6; **9Z,** 69257-80-3; benzylidenetriphenylphosphorane, 16721-45-2; benzyltriphenylphosphonium bromide, 1449-46-3; benzyl diethylphosphonate, 1080-32-6.

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(31) Dienes **3** and **4** were prepared by Ipaktschi, who was the first to show that **3** undergoes an efficient DPM rearrangement.[14]
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Photoextrusion of Sulfur Dioxide: General Route to [2.2]Cyclophanes[1]

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The synthesis of cyclophanes **1–5** by the photoextrusion of SO_2 from bis sulfones **12–17** is detailed. Yields vary from 32 to 100% and are comparable to the current methods available. The ease of synthesis of the sulfones and the convenience of the cyclophane isolation method suggest that photoextrusion is a useful alternative to other methods. Sensitization with acetophenone is effective for the naphthyl sulfones **15** and **16** while acetone sensitization is ineffective for **12.** Thus, the excited-state precursor is probably a singlet for **1** and a triplet for (±)-**4** and **5.** The reactions occur stepwise going through the monosulfone by loss of the first SO_2, followed by photochemical loss of the second molecule of SO_2. The intermediate (**24**) can be trapped as a methanol addition product, **23.**

Recent interest in "stacked" π systems[3] and in strained molecules[4] has provided an added stimulus to the search for effective methods for the synthesis of cyclophanes and their analogues[5] and the chemistry of the cyclophanes continues to be a very fruitful area of study.[6] We wish to report the details of our study of the photoextrusion of sulfur dioxide from bis sulfones as a relatively mild, efficient entry into the [2.2]cyclophanes, a subset of this intriguing class of compounds.

Photoextrusion of sulfur dioxide as a route to carbon–carbon single bonds is not a new reaction, having been reported by Cava, Schlessinger, and Van Meter in 1964.[7] However, the method has not found wide application in synthesis[8] and only recently reports by Staab[3c-h] and Boekelheide[4d] have appeared in which substituted cyclophanes have been made by this method.

In conjunction with our studies on the mechanism and scope of the photoextrusion reactions of sulfones,[9a] esters,[9b] and ketones,[9c] the usefulness and application of these reactions to the synthesis of strained molecules was developed. Cyclophanes were chosen as synthetic targets because (1) a wealth of potential applications is available as evidenced by the number of cyclophane analogues known,[3,4,5] (2) the sulfones are readily synthesized, i.e., the sulfide precursors or the sul-

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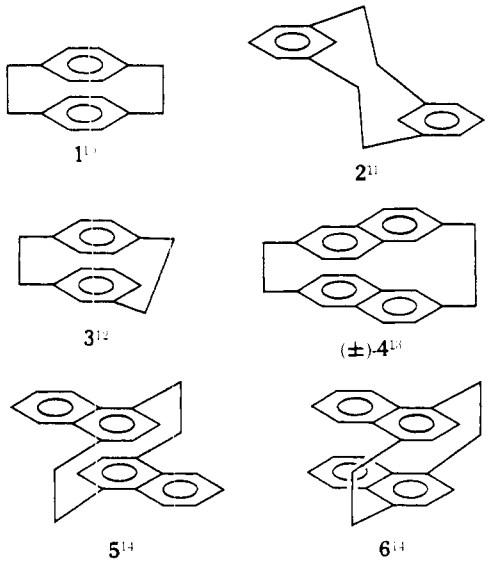
fones themselves are available using established synthetic methods,[3,4,10] (3) the inherent strain in [2.2]cyclophanes provides a relatively sensitive test of the limits of the photoextrusion process in forming strained carbon–carbon bonds and (4) the established methods for [2.2]cyclophane synthesis are often low yield routes or are not generally applicable to a wide range of cyclophane analogues. Thus, a general, high yield route was sought.

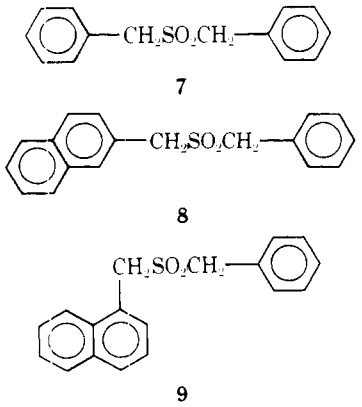
Results and Discussion

A. General Synthetic Approach. We have selected the six cyclophanes listed below (1–6) for our initial targets. In addition to the four reasons listed above, the selection of these cyclophanes was based on the structural similarities of the sulfone precursors to those of the acyclic benzyl and naphthylmethyl sulfones 7, 8, and 9, which we had examined previously,[9a] thus affording us the additional possibility of a mechanistic comparison of these two groups of compounds. Furthermore, all of the cyclophanes are known. The general route for the synthesis of the sulfones is given in Scheme I. The only low-yield step in the sequence to the sulfones was the coupling reaction giving the dithiacyclophane, where the yields varied from 55 to 76% for the benzene derivatives. These yields could be improved by using high dilution techniques.[6c] The other steps could be accomplished in from 90% to nearly quantitative yields.



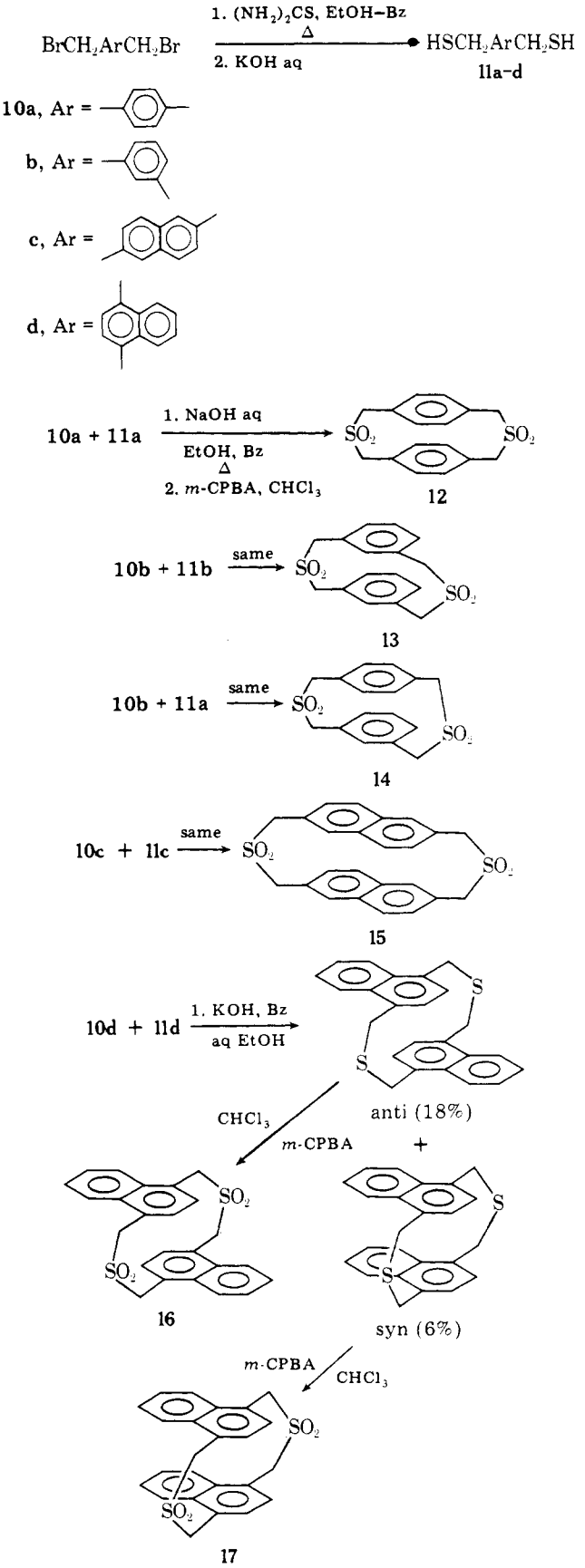
1[11] 2[11] 3[12] (±)-4[13] 5[14] 6[14]

The key step in the cyclophane synthesis, the photoextrusion of SO_2, was examined next. Due to the low solubility of the sulfones in most organic solvents, the irradiations were carried out with a suspension of the sulfone in benzene employing a Hanovia 450-W immersion well apparatus. Constant nitrogen purging was useful for removing the SO_2 and for stirring the suspension. Generally, Vycor filters were used ($\lambda > 230$ nm); for those runs employing acetone or acetophenone as a sensitizer, Pyrex filters ($\lambda > 310$ nm) were employed. Table I lists the results for each sulfone.



7 8 9

Scheme I. General Method for Sulfone Synthesis



As is evident from Table I, the yields of cyclophanes from the sulfones are generally 30–60%, which compares favorably with the current known routes to these hydrocarbons (vide infra). For the cyclophane series, there is a qualitative corre-

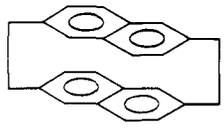
Table I. Conditions and Yields from the Photoextrusion of SO_2 to Cyclophanes 1–6

sulfone	registry no.	cyclophane produced	registry no.	irradiation conditions: sensitizer	filter[a]	time, h	% conversion[b]	% yield[b]
12	67263-07-4	1	1633-22-3	none	V	56	30	54
12		1		acetone	P	8	15	~10
13	34284-20-3	2	51744-98-0	none	V	21	43	100
14	69309-12-2	3	5385-36-4	none	V	13	28	65
15	43012-10-8	4	67374-99-6	none	V	12	80	61
15		4		acetophenone	P	4.5	97	64
16	69309-13-3	5	14724-91-5	none	V	2	85	35
16		5		acetophenone	P	0.5	62	32
17	69351-07-1	5		none	V	2	62	~32
		6[c]	23284-44-8	none	V	2	62	~5

[a] V = Vycor (>230 nm), P = Pyrex (>310 nm). [b] Based on recovered sulfone. [c] Estimated from the NMR spectrum of the crude reaction mixture.

lation between the percent yield and the amount of strain energy of the cyclophane. For example, the yields increase in the order **1** < **3** < **2**, the same order as that for decreasing strain energy (31, 23, and 13 kcal/mol, respectively[15,16]). It is noteworthy that even with the high strain energy of [2.2]paracyclophane, the yield is still quite good (54%). Any recovered sulfone can be recycled without further purification, thus allowing higher overall conversions than the 30–40% for the single irradiation that are illustrated in Table I.

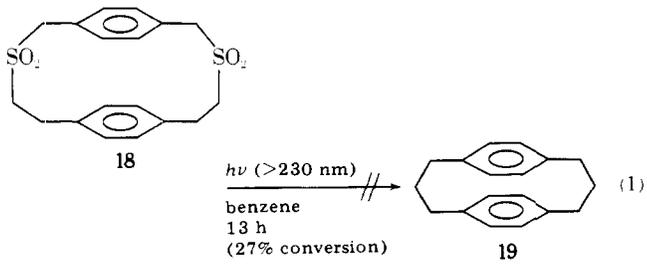
For the naphthalenophanes **4** and **5**, the yields are somewhat lower; yet again these yields are representative of the yields from current known routes. The limitation for the method is evident from the product study of these naphthalenophanes in that the thermodynamically more stable product is formed preferentially. Thus, of the two possible diastereomers of **4** only (±)-**4** is obtained. The unknown meso diastereomer (*meso*-**4**) in which the two naphthyl rings are aligned parallel to each other is probably highly strained and has so far eluded detection. Even in large scale runs it was absent from the reaction mixture. Likewise, the only product observed in the irradiation of sulfone **13** was the *anti*-[2.2]-metacyclophane; again the unknown *syn*-[2.2]metacyclophane was not detected.



meso-4

More convincing evidence is the observation that irradiation of either the syn or anti sulfones **16** or **17** gave *anti*-[2.2]-1,4-naphthalenophane (**5**) as the major product. The syn isomer **6** was observed in trace quantities and only from the syn sulfone **17**; the *syn*- to *anti*-[2.2]-1,4-naphthalenophane ratio was 1:7.

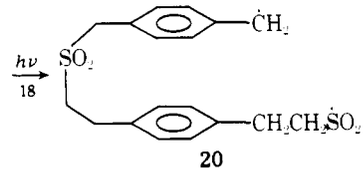
A second limitation on the photoextrusion route was discovered when the method was applied to the synthesis of [3.3]paracyclophane. Sulfone **18**[17] was irradiated as a benzene suspension under identical conditions used for sulfones **12–14.** After 13 h, 27% of the sulfone had been consumed but no trace of the expected [3.3]paracyclophane (**19**) was obtained (eq 1).



(1)

It is probable that the initial homolytic benzyl carbon–sulfur bond cleavage occurs (eq 2), but that loss of SO_2 from **20** requires a greater activation than is required for the intermediates generated in photolysis of sulfones **12–17.**[18] Recombination or disproportionation reactions dominate.

Within the above restrictions, the usefulness of this approach to cyclophanes is evident from the ease of synthesis



(2)

and photoreaction workup as well as the cyclophane yields. Isolation of the product involves (1) removal of the benzene solvent, (2) trituration of the residue with chloroform, (3) concentration of the chloroform solution of the cyclophane, and (4) either recrystallization or chromatography of the residue to give pure cyclophane. The solid, residual sulfone obtained from step 2 is usually of sufficient purity that it can be immediately reirradiated and carried through the three-stage process again.

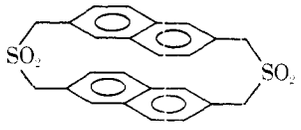
The sequence outlined above is simple and fast. Although the yields were not optimized, they are sufficiently high that the method compares favorably with other methods reported for the synthesis of cyclophanes **1**,[10a-c,22,25] **2**,[11,19-21] **3**,[12,24] (±)-**4**,[13] and **5**.[14,22,23] The fact that these bis sulfones are available in good yields by standard synthetic routes is an additional attractive feature.

B. Mechanistic Considerations. Although this study was intended primarily as a synthetic application of the photoextrusion reactions for sulfones,[26] several mechanistic features were examined. These include (1) a study of the multiplicity of the extrusion process, (2) a study of the sequential loss of SO_2 from the bis sulfones, and (3) a cursory study of changes in the reaction conditions on the extrusion reaction.

(1) Multiplicity Studies. Our current investigations of the multiplicity of SO_2 photoextrusion from sulfones **7**, **8**, and **9** have shown that both singlet and triplet excited states are reactive.[7] For **7** and **8** the extrusions were shown to proceed primarily from the singlet excited states, while for **9** the extrusion was essentially a triplet-state reaction. In comparison, as shown in Table I, the corresponding bis sulfone **12** parallels the multiplicity requirement of the monosulfone **9**. Thus, sensitization with acetone was ineffective for sulfone **12** as other reactions (e.g., polymer formation) dominate. In contrast, the bis sulfones **15** and **16** were effectively sensitized by acetophenone and gave comparable yields of the cyclophanes for a much shorter period of irradiation. The crude reaction mixtures were less colored and the workup gave a cleaner

initial product under these conditions also. (The acetophenone was readily removed by vacuum transfer.) Although quantum efficiencies could not be obtained due to the nature of this two-phase suspension, the qualitative evidence suggest that the reactive excited states are triplets for the naphthalenophane precursors **15** and **16** (also **17**) while a singlet-state precursor is the reactive excited state for the cyclophane precursor **12** (and probably for **13** and **14** also).

(2) Sequential Loss of SO_2. Irradiation of bis sulfone **15** for shorter reaction times (4.5 h, 72% conversion) using a Pyrex filter followed by a chromatography of the crude reaction mixture gave a 50% yield of (±)-**4** and a 15% yield of a second cyclophane product (eq 3). The new product was identified as monosulfone **21** by the following spectroscopic data: IR ($CHCl_3$) 1110 and 1315 cm^{-1} ($-SO_2-$); NMR ($CDCl_3$) δ 3.1 (m, 4 H), 4.3 (m, 4 H), and 6.3–8.2 (m, ~12 H); mass spectrum (*m/e*) 372 (M^+, 6%, $C_{24}H_{20}SO_2$), 338 (5%), 308 (33%, $C_{24}H^+_{20}$), 168 (22%, $C_{13}H^+_{12}$), and 154 (100%, $C_{12}H^+_{10}$). That this was the monosulfone precursor to (±)-**4** was further established by a 254-nm irradiation of a 5 mg sample of **21** in benzene,



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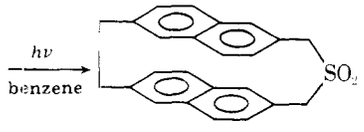

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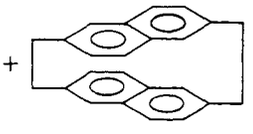
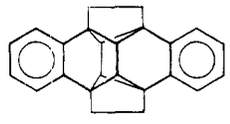


(±)-**4**[13] (3)

which gave (±)-[2.2]-2,6-naphthalenophane [(±)-**4**] as the major product. Although the other sulfones were not examined in this detail, it is reasonable to expect that the loss of both sulfur dioxides from the bis sulfones was sequential also.[26]

(3) Changes in Reaction Conditions. Two additional studies were conducted which tested the nature of the reaction conditions. The first was an attempt to detect dibenzoequinine (**22**) from extended irradiations of bis sulfones **16** and **17**.



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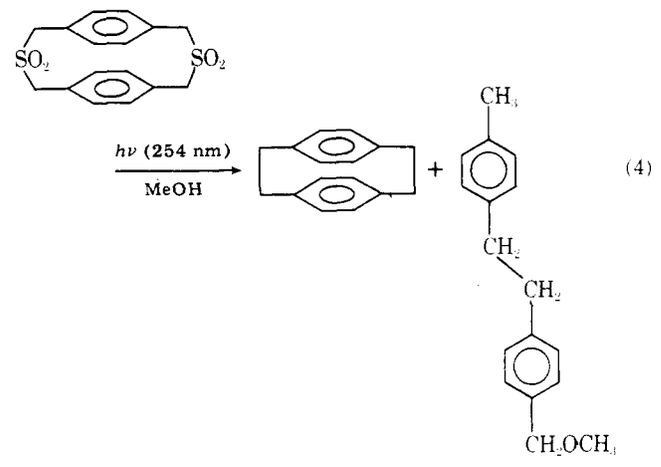
Under the longest irradiation times employed, no dibenzoequinine[14a] could be detected, illustrating the fact that the photoextrusion process is much more efficient than cycloaddition of the two naphthyl chromophores. This is in keeping with our earlier report that SO_2 photoextrusion occurs with high efficiency (Φ = 0.59, 0.03, and 0.003 for **7**, **8**, and **9**, respectively).[7] Dibenzoequinine forms with a much lower efficiency, requiring a 10-day irradiation of **5** in benzene.[14b]

Finally, because of the limited solubility of the sulfones, a complete solvent effect study was not possible. However, the solubility of sulfone **12** in methanol was sufficient to allow a product study of irradiations in this hydroxylic solvent. Irradiation at 254 nm of **12** for 6 h in absolute methanol gave, in addition to a small amount of [2.2]paracyclophane, methanol addition product **23** (eq 4). This was shown to be the same methanol addition product obtained when [2.2]paracyclophane is irradiated in methanol for 5 days under otherwise similar conditions.[6d] Thus, it is likely that the same intermediate (**24**) is formed from the sulfone and from direct ir-



(4)

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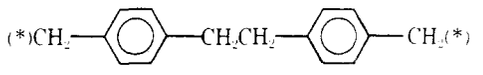

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radiation of **1**. The photolysis is much more efficient from the sulfone, however.

Conclusions

Photoextrusion of SO_2 from bis sulfones **12–17** provides an efficient, convenient route to unsubstituted cyclophanes. Our studies together with those of Staab,[3e-h] and more recently those of Boekelheide,[4d] provide evidence that this method is quite general. The yields obtained from photoextrusion of SO_2 are comparable to those obtained from the currently established methods. Therefore, the method is a useful alternative to the synthesis of known cyclophanes and should find application in the synthesis of newer members of this class of compounds.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. The following spectrometers were used: NMR, Varian A-60A or EM-360; IR, Beckman Acculab 3; mass, Varian MAT CH-5.

Mallinckrodt analytical reagent benzene was stored over 4A molecular sieves prior to use. Fisher spectrograde acetone and certified grade acetophenone were used as received.

Preparation of Bis Sulfones. Approximately 1 g of the bis sulfide[27] was dissolved in chloroform and the stirred solution was cooled to 0 °C. *m*-Chloroperoxybenzoic acid (4 equiv) was added. The solution was allowed to warm to room temperature and stirring was continued for 48–72 h. At the end of this time, the product was collected by suction filtration and washed several times with chloroform. The following results were obtained for the bis sulfides (sulfone: mmol of bis sulfide; reaction volume; reaction time; yield; melting point; spectral data (new compounds, only); analysis).

12: 9.2 mmol; 165 mL; 48 h; 97%; mp >250 °C dec; NMR (DF_3CO_2H) δ 4.68 (s, 8 H) and 7.42 (s, 8 H); IR (KBr) 892, 1110, 1212, 1316, 1340, 1307, 1426, 1522, 2898, 2922, 2955 and 2985 cm^{-1}; mass spectrum (*m/e*) 336 (M^+, 1), 208 (16), 105 (12), 104 (100), 103 (9), and 78 (8). Anal. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.80. Found: C, 57.08; H, 4.86.

14:[5b] 4.0 mmol; 150 mL; 72 h; 92%; mp >300 °C. Anal. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.80. Found: C, 57.39; H, 4.86.

13:[19] 2.7 mmol; 165 mL; 48 h; 88%; mp >350 °C. Anal. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.80. Found: C, 57.00; H, 4.60.

18:[17] 1.0 mmol; 50 mL; 48 h; 83%; mp > 300 °C. Anal. Calcd for $C_{18}H_{20}O_4S_2$: C, 59.31; H, 5.54. Found: C. 59.01; H, 5.41.

15:[13] 4.0 mmol; 200 mL; 48 h; 95%; mp >350 °C. Anal. Calcd for $C_{24}H_{20}O_4S_2$ by peak matching: *m/e* 436.08018. Found: *m/e* 436.07559.

17: 0.45 mmol; 50 mL; 72 h; 65%; mp >300 °C; NMR (CF_3CO_2H) δ 4.84 (s), 6.9–7.2 (m), and 7.4–7.8 (m); IR (KBr) 745, 1110, 1180, 1260,

and 1320 cm^{-1}; mass spectrum (*m/e*) 436 (M^+, 3), 309 (3), 308 (12), 155 (14), 154 (100), and 153 (16). Anal. Calcd for $C_{24}H_{20}O_4S_2$ by peak matching: *m/e* 436.08018 Found: *m/e* 436.08163

16: 1.2 mmol; 200 mL; 72 h; 92%; mp >300 °C; IR (KBr) 750, 880, 1020, 1110, and 1315 cm^{-1}; mass spectrum (*m/e*) 436 (M^+, 2), 309 (3), 308 (10), 202 (2), 185 (2), 155 (16), 154 (100), 153 (19), 152 (10), and 151 (3). Anal. Calcd for $C_{24}H_{20}O_4S_2$: *m/e* 436.08018 Found: *m/e* 436.07344.

Preparative Irradiations. The bis sulfones were suspended in benzene, purged with nitrogen, and then irradiated using a 450-W Hanovia medium-pressure lamp fitted with either a Vycor or Pyrex filter. The suspensions were continuously purged with nitrogen to remove the SO_2 which formed.

After the irradiations, the solvent was evaporated and the acetophenone, if present, was removed by vacuum distillation. The product was separated from unchanged starting material by chloroform extraction (trituration). Purification of the cyclophane was completed by a chromatography on silica gel (Mallinckrodt CC-7). The following results were obtained.

Irradiation of Bis Sulfone 12. A suspension of 500 mg of **12** in 800 mL of benzene was irradiated for 56 h using a Vycor filter. Workup yielded 351 mg of unchanged starting material. Chromatography of the remaining chloroform-soluble material on silica gel eluting with 1% ether in hexane afforded 50 mg (54%) of [2.2]paracyclophane (**1**). Spectral and physical properties were identical with those of an authentic sample.[10c]

Irradiation of Bis Sulfone 13. A suspension of 278 mg of **13** in 800 mL of benzene was irradiated for 13 h using a Vycor filter. Workup yielded 201 mg of unchanged starting material. Chromatography of the chloroform-soluble material on silica gel eluting with 5% benzene in hexane afforded 31 mg (65%) of [2.2]metaparacyclophane (**3**).[28]

Irradiation of Bis Sulfone 14. A suspension of 250 mg of **14** in 800 mL of benzene was irradiated for 21 h using a Vycor filter. Workup yielded 140 mg of unchanged starting material. Chromatography of the chloroform-soluble material on silica gel eluting with 0.5% ether in hexane afforded 69.5 mg (100%) of [2.2]metacyclophane (**2**).[29]

Irradiation of bis sulfone 18. A suspension of 154 mg of **18** in 800 mL of benzene was irradiated for 13 h using a Vycor filter. Workup yielded 113 mg of unchanged starting material. NMR analysis of the remaining crude reaction mixture gave no evidence of [3.3]paracyclophane.

Irradiation of Bis Sulfone 15. A suspension of 250 mg of **15** in 800 mL of benzene was irradiated for 11 h using a Vycor filter. Workup yielded 52 mg of unchanged starting material. Chromatography on silica gel eluting with 50% benzene in hexane afforded 108 mg (61%) of (±)-[2.2]2,6-naphthalenophane (**4**).[13]

Isolation of Monosulfone 21. A suspension of 109 mg of bis sulfone **15** in 800 mL of benzene was irradiated for 4.5 h using a Pyrex filter. Workup (vide supra) yielded 30 mg of unchanged starting material. The chloroform-soluble photomixture was chromatographed on a 1.5 × 23 cm silica gel column (benzene eluent, 25-mL fractions) giving the following results: fractions 1–4, 28 mg (50%) of [2.2]2,6-naphthalenophane; fractions 5–6, nil; fractions 7–13, 10 mg (15%) of monosulfone **21**; NMR ($CDCl_3$) δ 3.1 (m, 4 H), 4.3 (m, 4 H), and 6.3–8.2 (m, ~12 H); IR ($CHCl_3$) 1110 and 1315 cm^{-1}; mass spectrum (*m/e*) 372 (M^+, 6), 338 (5), 308 (33), 168 (22), and 154 (100).

Photolysis of Monosulfone 21. A solution of 5.0 mg of monosulfone **21** in 0.5 mL of benzene-d_6 was irradiated in a quartz tube for 2 h using nine 254-nm lamps in a Rayonet RPR-100 reactor. TLC analysis of the photolysate clearly showed the presence of [2.2]2,6-naphthalenophane.

Irradiation of Anti Bis Sulfone 16. A suspension of 208 mg of **16** in 800 mL of benzene was irradiated for 2 h using a Vycor filter. Workup yielded 31 mg of unchanged starting material. Chromatography of the remaining material on silica gel eluting with 50% benzene in hexane afforded 44 mg (35%) of *anti*-[2.2]1,4-naphthalenophane (**5**).[14b]

Irradiation of Syn Bis Sulfone 17. A suspension of 102 mg of **17** in 800 mL of benzene was irradiated for 2 h using a Vycor filter. Workup yielded 39 mg of unchanged starting material. Chromatography of the remaining material on silica gel eluting with 50% benzene in hexane afforded 14 mg (32%) of mainly *anti*-[2.2]1,4-naphthalenophane (**5**). The NMR spectrum of the product contained a singlet at 6.63 ppm and a multiplet at 6.8 ppm, indicating the presence of a small amount of *syn*-[2.2]1,4-naphthalenophane (**6**).[14b] The ratio of products was estimated to be anti/syn = 7 by comparison of the singlets at 5.69 and 6.63 ppm.

Acetone-Sensitized Irradiation of 12. A suspension of 130 mg of **12** in 800 mL of benzene/acetone (15:1) was irradiated for 8 h using a Pyrex filter. Workup yielded 110 mg of unchanged starting material. Chromatography of the chloroform-soluble material on silica gel eluting with hexane afforded ~1 mg (~10%) of [2.2]paracyclophane (**1**).

Acetophenone-Sensitized Irradiation of 15. A suspension of 210 mg of **15** in 800 mL of a solution of 64 mL of acetophenone in benzene was irradiated for 4.5 h using a Pyrex filter. Workup yielded 7 mg of unchanged starting material. Chromatography on silica gel eluting with hexane afforded 92 mg (64%) of (±)-[2.2]2,6-naphthalenophane (**4**).

Acetophenone-Sensitized Irradiation of 16. A suspension of 65 mg of **16** in 600 mL of a solution of 25 mL of acetophenone in benzene was irradiated for 0.5 h using a Pyrex filter. Workup yielded 25 mg of unchanged starting material. Chromatography on silica gel eluting with hexane afforded 9 mg (32%) of *anti*-[2.2]1,4-naphthalenophane (**5**).

Irradiation of 12 in Methanol. A solid suspension of **12** (150 mg) in 300 mL of absolute methanol was placed in a 5 × 34 cm quartz irradiation vessel centered in a Rayonet reactor of 14 2537-Å lamps. The solution was degassed (N_2 bubbling), irradiated under a nitrogen atmosphere for 6 h, and evaporated leaving a yellow residue having NMR peaks which were correct for [2.2]paracyclophane[10] and *p*-methyl-*p'*-methoxymethylbibenzyl.[6d] No attempt was made to isolate the photoproducts.

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Mild, Selective, General Method of Ketone Synthesis from Acid Chlorides and Organotin Compounds Catalyzed by Palladium

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Benzylchlorobis(triphenylphosphine)palladium(II) catalyzes the reaction of acid chlorides with tetraorganotin compounds to give ketones in quantitative yields. The reaction is general with respect to both reactants, and a wide variety of substituent groups on the acid chloride, including an aldehyde function, is tolerated, thus making this reaction one of the most general methods for ketone synthesis. The reaction is accelerated by oxygen, deactivated by triphenylphosphine, and shows an abnormal dependence on catalyst concentration. Benzoylchlorobis(triphenylphosphine)palladium(II), a key intermediate in the catalytic cycle, has been shown to react with tetramethyltin to afford acetophenone. The mechanism of the catalytic reaction is discussed.

Syntheses of a number of ketones using organometallic reagents suffer from a variety of unwanted side reactions, the major one of which is the addition of the organometallic reagent to the product ketone. Transition-metal catalyzed coupling reactions of acid halides with organometallic reagents have received considerable attention recently;[1-3] we have discovered a general and selective method for the quantitative synthesis of ketones from acid chlorides and organotin compounds[4] (eq 1).

$$\mathrm{RCOCl} + \mathrm{R'_4Sn} \xrightarrow[\text{HMPA, 65 °C}]{\mathrm{PhCH_2Pd(PPh_3)_2Cl\ (1)}} \mathrm{RCOR'} + \mathrm{R'_3SnCl} \qquad (1)$$

Results and Discussion

Reaction 1 is general both with respect to the organotin compound and the acid chloride (Table I). Aromatic, aliphatic, and heterocyclic acid chlorides have been utilized (section 1, Table I). Sterically hindered acid chlorides react normally (entries 1f and 2f), and α,β-unsaturated acid chlorides (entries 1c and 1g) do not undergo conjugate addition. Diacid chlorides can also be utilized (entries 1h and 1i), with the exception of oxalyl chloride, which reacts with tetramethyltin in the presence of 1 to yield small amounts (10%) of acetone instead of the expected diacetyl. Acetone is probably formed in this reaction by decarbonylation of the intermediate monoacid chloride (eq 2). The liberated carbon monoxide can react with the intermediate Pd(0) complex to form unreactive palladium carbonyl complexes.

$$\mathrm{ClC(=O)C(=O)Cl} \xrightarrow{\mathrm{Me_4Sn}} \mathrm{CH_3C(=O)C(=O)Cl} \xrightarrow{-\mathrm{CO}} \mathrm{ClCCH_3} \longrightarrow \mathrm{CH_3CCH_3} \qquad (2)$$

There is no further addition to the product ketone, while this is the major side reaction when other organometallic reagents (cadmium, zinc, magnesium) are utilized; low temperatures are generally required to avoid this reaction when organocopper compounds are used.[5] Reaction 1 can be carried out in the presence of a wide variety of functional groups. Nitro, nitrile, arylhalo, methoxy, ester, and *even aldehyde functions are tolerated.* This feature, combined with the fact that the reaction is performed under neutral conditions, made the synthesis of *p*-acetylbenzaldehyde possible. Difficulties are encountered in the preparation of this compound by other methods due to the propensity for self-condensation under conditions which are not strictly neutral.[6,7] However, bromine substituents in a position affected by electron-withdrawing groups compete with the acyl chloride for the tin compound (entry 2d).

Since in most cases there are virtually no side reactions that complicate isolation and purification, the yields are high and the workup is simple. The solvent and trimethyltin chloride are removed by water extraction, and the product is purified by distillation or crystallization. In cases where water-insoluble triorganotin chlorides are formed, the product can be separated from the tin compound by distillation or alternatively the triorganotin chlorides can be converted into the highly insoluble triorganotin fluorides by addition of an alcoholic solution of potassium fluoride to the ethereal solution of the product. The end of the reaction is clearly visualized since palladium metal precipitates as soon as all of the acid chloride is consumed and the clear yellow solution turns black. The manipulation is very simple, and there is no need for an inert atmosphere; on the contrary, oxygen has an accelerating effect on the reaction (vide infra).

Almost any tetraorganotin compound can be utilized for reaction 1 (Table I, section 3). Triorganotin chlorides also react (entry 3h), or alternatively a second organic group can also be transfered from tetraorganotin compounds. However, this transfer is much slower than transfer of the first organic

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