offers a simple and useful approach to cyclopropyl carbonyl compounds.

We are currently investigating the application of the present reaction to the synthesis of natural products possessing cyclopropane rings.

Acknowledgment. This work was supported in parts by grants from the Ministry of Education (45148) of the Japanese Government and from the Kurata Foundation.

Registry No. 1 (R^1 = Ph; R^2 = H), 54533-00-5; **i** (R^1 = Ph; R^2 = CH_3), 70887-62-6; 1 (R^1 = C_2H_5O; R^2 = C_6H_5S), 73971-36-5; 1 (R^1, R^2 = $(CH_2)_{10}$), 73971-37-6; 1 (R^1 = $(CH_3)_3C$; R^2 = H), 70367-67-8; 1 (R^1, R^2 = $(CH_2)_4$), 56528-89-3; **1** (R^1 = $(CH_3)_2CH$; R^2 = H), 70367-68-9; **1** (R^1 = C_5H_{11}; R^2 = C_6H_5S), 73971-38-7; 1 (R^1 = C_2H_5O; R^2 = C_6H_5SO), 73971-39-8; 1 (R^1 = C_2H_5O; R^2 = $C_6H_5SO_2$), 73971-40-1; 1 (R^1 = C_2H_5O; R^2 = C_2H_5O-CO), 34727-00-9; **2** (R^3 = $C_{10}H_{21}$; Ar = Ph), 73971-41-2; **2** (R^3 = $C_{10}H_{21}$; Ar = *o*-$CH_3C_6H_4$), 73971-42-3; **2** (R^3 = $C_{10}H_{21}$; Ar = *m*-$CF_3C_6H_4$), 73971-43-4; **2** (R^3 = $C_{10}H_{21}$; Ar = *o*-$NO_2C_6H_4$), 73971-44-5; **2** (R^3 = H; Ar = *p*-ClC_6H_4), 73971-45-6; **2** (R^3 = $C_6H_5CH_2OCH_2$; Ar = *p*-ClC_6H_4), 73971-46-7; **2a**, 73971-47-8; **3** (R^1 = Ph; R^2 = H; R^3 = $C_{10}H_{21}$), 73985-89-4; **3** (R^1 = Ph; R^2 = H; R^3 = H), 3481-02-5; **3** (R^1 = Ph; R^2 = CH_3; R^3 = H), 26921-44-8; **3** (R^1 = C_2H_5O; R^2 = C_6H_5S; R^3 = H), 73971-48-9; **3** (R^1 = Ph; R^2 = H; R^3 = $C_6H_5CH_2OCH_2$), 73985-90-7; **3** (R^1 = Ph; R^2 = CH_3; R^3 = $C_6H_5CH_2OCH_2$), 73971-49-0; **3** (R^1 = C_2H_5O; R^2 = C_6H_5S; R^3 = $C_6H_5CH_2OCH_2$), 73971-50-3; **3** (R^1, R^2 = $(CH_2)_{10}$; R^3 = $C_6H_5CH_2OCH_2$), 73971-51-4; **3** (R^1 = Ph; R^2 = CH_3; R^3 = $C_{10}H_{21}$), 73971-52-5; **3** (R^1 = C_2H_5O; R^2 = C_6H_5S; R^3 = $C_{10}H_{21}$), 73971-53-6; **3** (R^1 = $(CH_3)_3C$; R^2 = H; R^3 = $C_{10}H_{21}$), 73971-54-7; **3** (R^1, R^2 = $(CH_2)_4$; R^3 = $C_{10}H_{21}$), 73971-55-8; **3** (R^1 = $(CH_3)_2CH$; R^2 = H; R^3 = $C_{10}H_{21}$), 73971-56-9; **3** (R^1 = C_5H_{11}; R^2 = C_6H_5S; R^3 = $C_{10}H_{21}$), 73971-57-0; **3** (R^1 = C_2H_5O; R^2 = C_6H_5SO; R^3 = $C_{10}H_{21}$), 73971-58-1; **3** (R^1 = C_5H_5O; R^2 = $C_6H_5SO_2$; R^3 = $C_{10}H_{21}$), 73971-59-2; **3** (R^1 = C_2H_5O; R^2 = C_2H_5OCO; R^3 = $C_{10}H_{21}$), 73971-60-5; **4**, 73971-61-6; camphor, 76-22-2; β-ionone, 14901-07-6; cyclohexenone, 930-68-7; 4,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,1′-cyclopropan]-3-one, 57761-38-3; 1-[2-[(phenylmethoxy)methyl]cyclopropyl]-3-(2,6,6-trimethyl-1-cyclohexen-1-yl-2-propen-1-one, 73971-62-7; 1-[(phenylmethoxy)methyl]spiro[2.5]oct-5-en-4-one, 73971-63-8.

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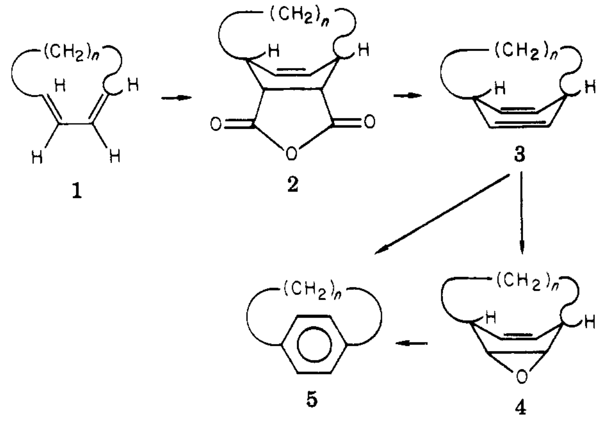
Received December 27, 1979

A General Approach to Small [*n*]Paracyclophanes

Summary: A general procedure has been developed for the synthesis of both substituted and unsubstituted [*n*]-paracyclophanes, where *n* equals 7 or 8.

Sir: There has been considerable recent interest in the synthesis[1] and properties[2] of [*n*]paracyclophanes where *n* equals 6,[1a] 7,[1b,c] and 8.[1d,2] Most of this interest has centered on the distortion of the aromatic ring and the effect of this distortion on both the physical and chemical properties of this ring. The currently available methods for the synthesis of the smaller of these systems do not readily lend themselves to the preparation of aryl-substituted versions of these compounds. We now report a general synthesis of both substituted and unsubstituted versions of [7]paracyclophane and [8]paracyclophane. Our synthetic process has its origin in our work on (i,o)-bicyclo[*n*.2.2]alkadienes.[3]

In analogy with our earlier work,[3] we added maleic anhydride to *cis,trans*-1,3-cyclododecadiene (**1a**) and to *cis,trans*-1,3-cycloundecadiene (**1b**) to give the corresponding Diels–Alder adducts, **2a** and **2b**, in 21% and 23% yields, respectively.[4] Refluxing of **2a** in 10% aqueous tetrahydrofuran gave a 98% yield of the corresponding diacid which was subjected to lead tetraacetate oxidation in toluene–pyridine to yield 22% **3a**.[5] The direct electrochemical decarboxylation of **2a** to **3a** was accomplished in 39% yield. Treatment of **3a** with 1 equiv of *m*-chloroperbenzoic acid gave an 80% yield of **4a** as a waxy solid, mp 39–41 °C. This epoxide was extremely labile and underwent slow conversion to **5a**, even in base-washed glassware. Exposure of **4a** to hydrochloric acid gave a 93% yield of [8]paracyclophane (**5a**), which was identical in all respects with the literature compound.[1d,6]



a, *n* = 8; **b**, *n* = 7

The observation that **5a** was present as an impurity in the oxidative decarboxylation of **2a** suggested that **3a** might be directly oxidized to give **5a**. Heating of **3a** with 1.5 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone at 95 °C for 12 days gave a 79% yield of **5a**.[7]

In a similar series of experiments, **2b** was hydrolyzed to the corresponding diacid in 98% yield. Lead tetraacetate decarboxylation gave 12% **3b**, while electrochemical oxidative decarboxylation produced 17% **3b**. Epoxidation of **3b** with *m*-chloroperbenzoic acid gave 98% **4b**, which on treatment with catalytic amounts of trifluoroacetic acid gave [7]paracyclophane (**5b**) in 88% yield. This material was spectroscopically identical with that previously reported.[1b]

We had previously reported the synthesis of both **6a** and **6b**[3] via the addition of perfluoro-2-butyne to the appro-

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[1] (a) V. V. Kane, A. D. Wolf, and M. Jones, Jr., *J. Am. Chem. Soc.*, **96**, 2643 (1974); (b) A. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *ibid.*, **95**, 1680 (1973); J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, *Recl. Trav. Chem. Pays-Bas*, **96**, 88 (1977); (c) N. L. Allinger and T. J. Walter, *J. Am. Chem. Soc.*, **94**, 9267 (1972); N. L. Allinger, T. J. Walter and M. G. Newton, *ibid.*, **96**, 4588 (1974); (d) D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961); N. L. Allinger and L. A. Freiberg, *J. Org. Chem.*, **27**, 1490 (1962); N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Am. Chem. Soc.*, **85**, 1171 (1963); D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966); T. Tsuji and S. Nishida, *ibid.*, **95**, 7519 (1973).

[2] M. G. Newton, T. J. Walter, and N. L. Allinger, *J. Am. Chem. Soc.*, **95**, 5652 (1973); N. L. Allinger, J. T. Sprague, and T. Liljefors, *ibid.*, **96**, 5100 (1974); S. L. Kammula, L. D. Iroff, M. Jones, Jr., J. W. van Straten, W. H. de Wolf, and F. Bickelhaupt, *ibid.*, **99**, 5815 (1977); H. Schmidt, A. Schweig, W. Thiel, and M. Jones, Jr., *Chem. Ber.*, **111**, 1958 (1978).

[3] P. G. Gassman, S. R. Korn, and R. P. Thummel, *J. Am. Chem. Soc.*, **96**, 6948 (1974); P. G. Gassman, S. R. Korn, T. F. Bailey, T. H. Johnson, J. Finer, and J. Clardy, *Tetrahedron Lett.*, 3401 (1979).

[4] Satisfactory elemental analysis and/or exact-mass molecular weights were obtained on all new compounds.

[5] In addition to **3a**, **5a** was formed as a 2% byproduct.

[6] Surprisingly, treatment of **4a** with *n*-butyllithium also produced **5a** (48% yield). The mechanism of this process is unknown.

[7] Tetracyanoethylene was also effective in converting **3a** into **5a** (49% yield).

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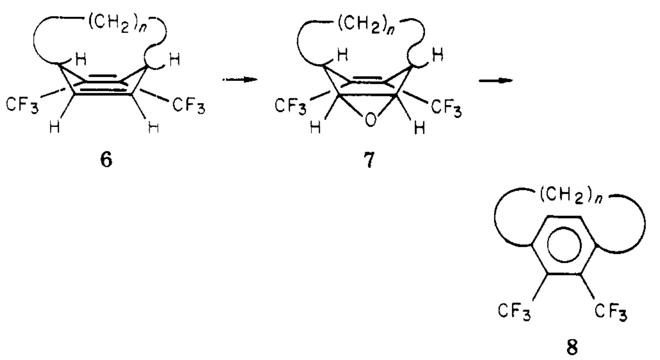
priate *cis,trans*-1,3-cycloalkadiene. Both **6a** and **6b** were resistant to direct oxidation to **8a** and **8b**, respectively. However, treatment of **6a** with *m*-chloroperbenzoic acid gave 72% purified **7a**. When **6a** was converted to **7a** and the crude reaction mixture was heated for 2 h at 140 °C in the presence of catalytic amounts of trifluoroacetic acid, **8a** was obtained in 59% overall yield from **6a**.

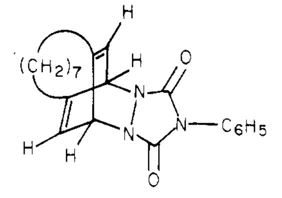


6 **7** **8**

a, $n = 8$; **b**, $n = 7$

When **6b** was treated with 1 equiv of *m*-chloroperbenzoic acid, we obtained 92% **7b**, mp 58–60 °C. Acid-catalyzed dehydration of **7b** with trifluoroacetic acid gave a 90% yield of **8b** as a colorless liquid. The NMR spectrum of **8b** was unique in that the proton which was most directly over the aromatic nucleus appeared at δ −2.4 as a doublet of triplets. This is to be contrasted with the proton NMR spectrum of **5b** which showed related signals at δ −0.4.[8]

The synthetic procedures outlined above provide ready access to a wide variety of [*n*]paracyclophanes where *n* is 7 or 8. In particular, substituted variants can be produced in substantial overall yields. We believe that our process will provide materials for a variety of studies on these intriguing molecules. For instance, we have found that [7]paracyclophane reacts readily with *N*-phenyl-1,2,4-triazoline-3,5-dione to give **9** in 84% yield after 6 h at 50 °C.[9] This colorless solid, mp 137–139 °C, showed ^{1}H NMR ($CDCl_3$) δ 7.70–7.75 (5 H), 6.32 (2 H, d, J = 6 Hz), 5.23 (2 H, d of d, J = 6, 3 Hz), 2.82–0.55 (14 H, m). On heating to 60 °C, **9** reverted to starting materials. We are continuing to explore the reactions of both strained (i,-o)-bicyclo[*n*.2.2]alkadienes and [*n*]paracyclophanes.



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Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation.

Registry No. 1a, 1129-92-6; **1b**, 73683-12-2; **2a**, 73926-66-6; **2b**, 73940-63-3; **3a**, 73926-67-7; **3b**, 73926-68-8; **4a**, 73926-69-9; **4b**, 73926-70-2; **5a**, 4685-74-9; **5b**, 3761-63-5; **6a**, 38772-94-0; **6b**, 73683-11-1; **7a**, 73926-71-3; **7b**, 73926-72-4; **8a**, 54108-99-5; **8b**, 73926-73-5; **9**, 73926-74-6; maleic anhydride, 108-31-6; bicyclo[8.2.2]tetradec-11-ene-13,14-dicarboxylic acid, 73926-75-7; bicyclo[7.2.2]tridec-10-ene-12,13-dicarboxylic acid, 73926-76-8.

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Received February 26, 1980

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[8] We are currently exploring the basis for this spectral difference.

[9] Diels–Alder additions to [*n*]paracyclophanes have been previously reported. For a recent example, see K.-L. Noble, H. Hopf, M. Jones, Jr., and S. L. Kammula, *Angew. Chem., Int. Ed. Engl.*, 17, 602 (1978).