8.03 (2 H, t, J = 7.3 Hz), 4.41 (4 H, a, J = 7.1 Hz), 4.25 (4 H, s), 1.44 (6 H, t, J = 7.1 Hz); ^{13}C NMR δ 168.0, 131.9, 131.1, 129.3, 127.4, 126.0, 125.3, 123.8, 120.8, 61.5, 29.5, 14.2; IR (KBr) 1737, 1719 cm^{-1}. Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.79; H, 5.83.

Diels–Alder Reaction of 10 with Diethyl Maleate. Compound **10** (10.0 mg, 0.039 mmol) and diethyl maleate (96.6 mg, 0.56 mmol) in diethyl phthalate (0.60 mL) were treated by the same procedure as above at 180 °C for 1 h. Compound **21** was obtained in 96% yield (22.5 mg) as a mixture of endo and exo stereoisomers (1:1): ^{1}H NMR δ 8.34 (4 H, d, J = 7.9 Hz), 8.30 (4 H, d, J = 7.9 Hz), 8.03 (4 H, t, J = 7.9 Hz), 4.17 (16 H, m), 3.91 (4 H, m), 3.82 (4 H, m), 3.58 (4 H, m), 3.46 (12 H, m), 1.25 (12 H, t, J = 7.1 Hz), 1.24 (12 H, t, J = 7.1 Hz); ^{13}C NMR δ 173.0, 130.4, 128.2, 125.8, 120.4, 60.8, 40.1, 27.3, 14.1; IR (KBr), 1731 cm^{-1}. Anal. Calcd for $C_{36}H_{38}O_8$. C, 72.22; H, 6.40. Found: C, 71.92; H, 6.23.

Dimer 23. Compound **9** (49.7 mg, 0.22 mmol) in diethyl phthalate (0.34 mL) was treated by the same procedure as above at 180 °C for 1 h. Product **11** was obtained in 53% yield (26.3 mg): ^{1}H NMR δ 8.65 (1 H, dd, J = 7.8 and 1.1 Hz), 8.17 (4 H, m), 8.11 (2 H, s), 7.98 (1 H, t, J = 7.7 Hz), 7.88 (1 H, dd, J = 7.9 and 1.2 Hz), 7.79 (1 H, dd, J = 7.8 and 1.3 Hz), 7.79 (2 H, s), 7.75 (2 H, t, J = 7.6 Hz), 7.61 (1 H, t, J = 7.6 Hz), 7.47 (1 H, t, J = 7.7 Hz), 5.38 (1 H, s), 5.23 (1 H, s), 4.35 (1 H, d, J = 16.9 Hz), 4.18 (1 H, d, J = 16.9 Hz), 3.11 (2 H, m), 2.13 (2 H, m); ^{13}C NMR δ 149.2, 142.7, 134.7, 131.8, 131.4, 131.2, 130.7, 130.6, 130.5, 130.0, 129.9, 127.4, 127.1, 126.9, 126.7, 126.5, 126.5, 126.2, 125.9, 125.8, 124.9, 124.6, 123.9, 123.5, 123.2, 121.6, 120.9, 120.4, 113.5, 112.0, 43.2, 34.9, 32.6, 25.1; IR (KBr) 3046, 2920, 1626, 1602, 1587, 1425, 1299, 1179, 897, 825, 756, 732, 678 cm^{-1}; MS ($M^{\bullet+}$) m/z 456.

Acknowledgment. This work was supported in part by grants from the Ministry of Education, Culture, and Science, and the Torey Foundation. We are indebted to them.

Synthesis and Chemistry of Some Tricyclic Cyclopropenes. 3. Tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene[1,2]

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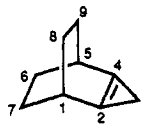
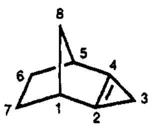
The title compound cyclopropene **2** has been synthesized in situ from dibromide **8** and diiodide **9** via dehalogenation of *tert*-butyllithium in THF at −78 °C. The dihalides were formed in six steps starting with cyclopentadiene and (chloromethyl)maleic anhydride. In the presence of diphenylisobenzofuran (DPIBF) **2** forms a Diels–Alder adduct, most probably **10**. Cyclopropene **2** and a previously synthesized cyclopropene **1** were decomposed under these same conditions, only without DPIBF present, to give complex mixtures of products, some of which were characterized as *tert*-butyl adducts and dimers via the ene reaction of the cyclopropenes.

Due to their unique structure and high reactivity, cyclopropenes continue to present a synthetic challenge to organic chemists. Incorporation of a cyclopropene ring into a bicyclic or tricyclic framework further increases the ring strain of a cyclopropene and makes for more challenging syntheses and trapping experiments. Most of the literature has been reviewed.[3]

We have undertaken the study of several different tricyclic systems in order to determine the effects of ring strain on the stability and ease of synthesis/trapping of these unusual compounds. Our previously published synthesis of tricyclo[3.2.2.0^{2,4}]non-2(4)-ene (**1**) and its Diels–Alder adduct with diphenylisobenzofuran (DPIBF) presented a pathway which has been used as a framework for the synthesis of similar tricyclic cyclopropenes. We report here the synthesis and trapping of tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene (**2**) as well as further studies performed on cyclopropene **1**. Recently Mühlebach and Neuenschwander have synthesized a dehydro analog of **2**, tricyclo[3.2.1.0^{2,4}]octa-2(4),6-diene, and have trapped it in a Diels–Alder reaction with DPIBF.[4]



1



2

Results and Discussion

Synthesis of the Precursor. To assess the effects of ring strain on the synthesis of **2** vs the previously reported **1**, differences between the pathway leading to the two compounds have been explored. Chloro anhydride **3** (Scheme I) can be easily synthesized by a room temperature reaction of (chloromethyl)maleic anhydride with cyclopentadiene. This is much more facile than the homologous reaction with cyclohexadiene, which took 26 h at 110 °C.[5] Ring opening of **4** to produce chloro diester **5** was achieved by a 48-h reflux in HCl-saturated ethanol. The subsequent addition of thionyl chloride and ethanol produced chloro diester **5** in about 35% yield. The product contained a large percentage of starting material. Ring closure by elimination of HCl was attempted by refluxing

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(1) Part 1: Chenier, P. J.; Southard, D. A., Jr. *J. Org. Chem.* **1989**, *54*, 3519. Part 2: Chenier, P. J.; Southard, D. A., Jr. **Ibid. 1990**, *55*, 4333.

(2) Preliminary accounts of this work have been presented: Chenier, P. J.; Balding, S. D.; Bauer, M. J.; Canard, G. M.; Hodge, C. L.; Southard, D. A., Jr. *Abstracts of Papers*; 4th Chemical Congress of North America and 202nd National Meeting of the American Chemical Society, New York, NY; American Chemical Society: Washington, DC, 1991; ORGN 232.

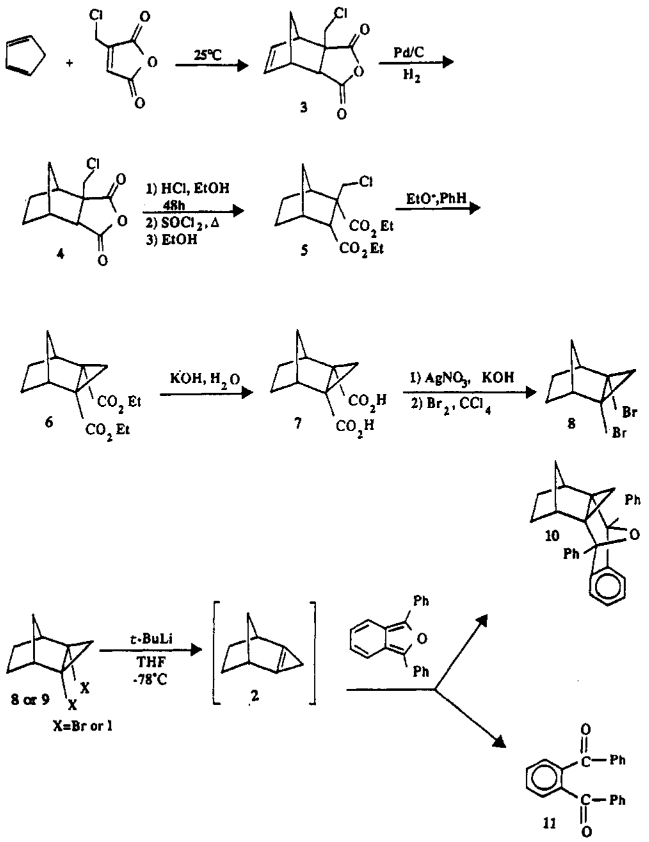
(3) For a list of pertinent review articles and references, see Part 2.[1] For a recent article of bicyclic cyclopropenes, see: Wiberg, K. B.; Artis, D. R.; Bonneville, G. *J. Am. Chem. Soc.* **1991**, *113*, 7969.

(4) Mühlebach, M.; Neuenschwander, M. *Chimia* **1991**, *45*, 24.

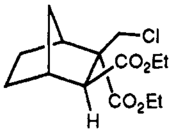
(5) Preliminary experiments with cycloheptadiene and (chloromethyl)maleic anhydride show that a 48-h reflux in toluene in a sealed vessel at 200 °C is necessary for a reasonable yield of the adduct. We thank D. A. Southard, Jr., University of Wisconsin—Eau Claire, for this study. Cyclooctadiene does not react with (chloromethyl)maleic anhydride even after 3 days at 200 °C.

0022-3263/92/1957-5959$03.00/0

Scheme I



chloro diester **5** in benzene with sodium ethoxide. One reaction yielded an 83% pure cyclopropyl diester, while another reaction under analogous conditions produced the cyclopropyl diester **6** and trans chloro diester **5t** after a 1-day reflux. Trans diester **5t** can be successfully ring closed by refluxing it in benzene with sodium ethoxide for 56 h.

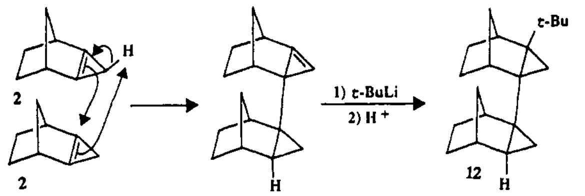


trans diester **5t**

Diacid **7** was used in the synthesis of dibromide **8** and diiodide **9**. The diiodide was produced by a decarboxylative iodination radical reaction involving *N*-hydroxy-2-thiopyridone and iodotrifluoroethane on the acid chloride.[6] The Hunsdiecker reaction[7] was found to produce acceptable yields of dibromide **8**. It should be noted that large-scale addition of bromine to the silver salt is quite exothermic. The Cristol–Firth modification[8] was not attempted because it had failed in the previous synthesis of the dibromide precursor for cyclopropene **1**.[1]

Trapping of Cyclopropene 2. Both dihalides can be reacted with *tert*-butyllithium in THF at −78 °C to produce intermediate cyclopropene **2**, which forms what we believe to be adduct **10** in the presence of DPIBF. HRMS confirmed the molecular formula of the adduct (376.1826 calcd, 376.1841 found), mp 269.3–270.5 °C. *o*-Benzoylbenzophenone (**11**) was isolated from the products of both the diiodide and dibromide reactions.[9] This product is of interest because it is an oxidized product, but the reaction is run under reducing conditions. To confirm that this product was formed in the reaction and not by starting material contamination, we observed the absence of the carbonyl in DPIBF by ^{13}C NMR. The DPIBF was allowed to sit open to the air for 2 weeks, at which time we reconfirmed the absence of any carbonyl groups by ^{13}C NMR. We concluded that the oxidation must be occurring in the reaction or workup. Further trapping experiments of cyclopropene **2** were attempted but were unsuccessful.

Scheme II



Decomposition of Cyclopropenes 1 and 2. Some attempts were made to answer the question of what happens to these tricyclic cyclopropenes when they are simply left to warm in the reaction mixture in which they are generated. Very complex mixtures result which could not be separated, and many of the products have not been determined. However, some have been partially characterized by GC–MS (see the supplementary material). The generation of cyclopropene **2** without DPIBF resulted in the production of no less than 12 products, four of which have been identified tentatively from their fragmentation patterns. Dimeric products such as **12** probably occur via the well-known "ene" reaction for cyclopropenes.[10] Two molecules of cyclopropene **2** (Scheme II) react with transfer of a proton to give a dimer, which then can undergo a reaction with *tert*-butyllithium to form compound **12**. These products, formed from known cyclopropene reactions, certainly lend further evidence to the formation of cyclopropene **2** as the reactive intermediate.

A decomposition of this type, with no DPIBF present, was also done on previously synthesized cyclopropene **1**. Of the nine products formed in this reaction, seven have been partially characterized by GC–MS (see the supplementary material).

In summary, we appear to be approaching the limit of strain where a cyclopropene can be placed in a rigid tricyclic cage and still be trapped easily, though Mühlebach and Neuenschwander have had success[4] with a similarly strained cyclopropene. Future studies will concentrate on the syntheses of less strained tricyclic-containing compounds, such as **13** and **14**. Hopefully the chemistry of these systems will be more easily studied.

13

14

Experimental Section

Melting and boiling points are uncorrected. NMR data are given in ppm relative to TMS. ^{1}H and ^{13}C NMR spectra were obtained at 80 and 20 MHz, respectively, unless noted otherwise. Elemental analyses were performed by Midwest Microlab, In-

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[6] (a) Barton, D. H. R.; Lacher, B.; Zard, S. Z. *Tetrahedron* **1987**, *43*, 4321. (b) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230. We thank Professor Eaton, University of Chicago, for details of his procedure with the diiodocubanes.

[7] Allen, C. F. H.; Wilson, C. V. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 578.

[8] Cristol, S. J.; Firth, W. C., Jr. *J. Org. Chem.* **1961**, *26*, 280.

[9] The observed mp was 146.1–148.1 °C as compared with the literature value of 145–148 °C. See: Zincke, *Chem. Ber.* *9*, 32.

[10] For a recent review, see: Baird, M. S. *Top. Curr. Chem.* **1988**, *144*, 137.

dianapolis, IN. Mass spectra were taken by the Department of Chemistry, University of Minnesota, Minneapolis, MN.

(Chloromethyl)maleic Anhydride. Prepared by the method of Schreiber et al.[11] from itaconic anhydride[12] via chlorination followed by dehydrochlorination.

Unsaturated Chloro Anhydride 3. (Chloromethyl)maleic anhydride (76.43 g, 0.522 mol) dissolved in ether (350 mL) and freshly cracked cyclopentadiene (34.45 g, 0.522 mol) in ether (100 mL) were stirred together at −10 °C. The reaction became exothermic upon warming to ambient temperature and refluxed by itself for 0.5 h. The mixture was stirred for 3 h. Rotary evaporation and drying in vacuo gave **3** as off-white solid (111.4 g, 0.524 mol, 100%). Three recrystallizations from hexane–ether gave a pure white solid: mp 70–72 °C; IR (KBr) 3072, 2994, 2967, 2890, 1856, 1784, 1321, 1236, 1209, 1047, 991, 934, 912, 723, 556; ^{1}H NMR ($CDCl_3$) δ 6.4 (m, 2 H, vinyl CH), 4.2 (d, 1 H, AB, CH_2Cl, J = 11.3 Hz), 3.6 (d, 1 H, AB, CH_2Cl, J = 11.3 Hz), 3.4–3.7 (m, 2 H, CHCO and bridgehead), 3.1 (m, 1 H, bridgehead), 1.9 (m, 2 H, bridge); ^{13}C NMR ($CDCl_3$) δ 172.3, 169.9, 136.7 (2 peaks), 62.5 (s), 51.2 (t), 50.5 (d), 50.3 (d), 46.6 (2 peaks, d and t); MS (EI, 30 eV, 70 °C) *m/e* (%) 212 (M^+, 1.6), 105 (25), 91 (23), 67 (21), 66 (100), 65 (30), 39 (40); HRMS calcd for $C_{10}H_9ClO_3$ 212.0239, found 212.0231. Anal. Calcd for $C_{10}H_9ClO_3$; C, 56.49; H, 4.27. Found: C, 56.55; H, 4.30.

Saturated Chloro Anhydride 4. Unsaturated chloro anhydride **3** (60 g, 0.280 mol) was dissolved in ethyl acetate (150 mL). The mixture was hydrogenated in a Parr apparatus with 10% palladium on carbon (1.0 g) at 30 psi for 2 h. An additional 3.0 g of catalyst was added over 6 h at 2-h intervals. Hydrogenation was allowed to continue overnight. Filtration of the catalyst, rotary evaporation, and vacuum drying gave a white solid (59.44 g, 0.277 mol, 98%). Two recrystallizations from ether gave a pure product: mp 101–104 °C; IR (KBr) 2967, 2917, 2890, 2847, 1856, 1764, 1215, 941, 907; ^{1}H NMR ($CDCl_3$) δ 4.1 (d, 1 H, AB, CH_2Cl, J = 11.2 Hz), 3.5 (d, 1 H, AB, CH_2Cl, J = 11.2 Hz), 3.4 (d, 1 H, J = 5.5 Hz), 2.9 (m, 1 H, bridgehead), 2.5 (m, 1 H, bridgehead), 1.2–1.8 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 173.1, 170.4, 62.6 (s), 52.5 (d), 46.5 (t), 45.0 (d), 40.8 (d), 40.5 (t), 25.7 (t), 24.4 (t); MS (EI, 30 eV, 70 °C) *m/e* (%) 142 (38), 116 (31), 114 (100), 79 (84). Anal. Calcd for $C_{10}H_{11}ClO_3$: C, 55.96; H, 5.17. Found: C, 56.20; H, 5.23.

Chloro Diester 5. Chloro anhydride **4** (165 g, 1.44 mol) was dissolved in ethanol (1300 mL). Hydrogen chloride was bubbled through the mixture for 1 h, aiding the dissolution of remaining solid. The solution was refluxed overnight. Rotary evaporation gave a brown oil. Thionyl chloride (430 g, 3.6 mol) was cautiously added dropwise with stirring at 0 °C. The solution was heated at 55–60 °C under nitrogen overnight. Rotary evaporation gave a brown slurry. Absolute ethanol (1000 mL) was added dropwise with stirring at 0 °C. The solution was allowed to come to ambient temperature. Rotary evaporation gave a brown oil. The approximate crude yield of chloro diester **5** was 30%. The oil was vacuum distilled, bp 150–154 °C (2 mm). This failed to give pure chloro diester **5**, but the product was pure enough to be identified and used in the next reaction: IR (KBr) 2980, 2889, 1848, 1792, 1735, 1462, 1377, 1307, 1258, 1208, 1074, 906; ^{1}H NMR ($CDCl_3$) δ 4.14 (2 q, 4 H, CH_2O's), 3.91 (AB, 1 H, CH_2Cl, J = 5.2 Hz), 3.66 (AB, 1 H, CH_2Cl, J = 5.2 Hz), 1.4–2.7 (m, 9 H), 1.25 (2 t, 6 H, CH_3CH_2O); ^{13}C NMR ($CDCl_3$) δ 171.6, 171.3, 60.9, 60.0, 57.9, 52.5, 50.7, 46.0, 40.6, 37.5, 25.8, 22.8, 14.1 (2C).

Cyclopropyl Diester 6. Chloro diester **5** (5.76 g, 0.0200 mol) was dissolved in dry benzene (10 mL) and added over 5 min to a stirred mixture of sodium ethoxide (2.72 g, 0.0400 mol) in dry benzene (100 mL). The mixture was refluxed with stirring under nitrogen for 24 h. The organic layer was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulfate. The filtrate was rotary evaporated and vacuum dried to give a yellow liquid: bp 136–138 °C (1.2 mm). Gas chromatography showed a peak of 97.7% purity. Samples sent in for MS and analysis were collected by preparative GC (QF-1, 250 °C, 85 mL/min): IR (KBr) 2980, 2882, 1722, 1488, 1370, 1329, 1265, 1152, 1111, 1040, 1019; ^{1}H NMR ($CDCl_3$) δ 4.1 (q, 4 H, CH_2O's), 2.5–2.6 (m, 2 H), 1.9–2.1 (m, 2 H), 1.1–1.6 (m, 11 H), 0.81 (d, 1 H, J = 11.2 Hz); ^{13}C NMR ($CDCl_3$) δ 171.2 (s), 60.5 (t), 39.2 (d), 35.9 (s), 30.3 (t), 26.0 (t), 14.9 (t), 14.2 (q); MS (EI, 30 eV, 100 °C) *m/e* (%) 252 (4.5), 207 (57), 206 (58), 180 (24), 179 (33), 178 (19), 133 (30), 132 (29), 123 (23), 105 (54), 79 (100); HRMS calcd for $C_{14}H_{20}O_4$ 252.1359, found 252.1363. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 65.67; H, 8.36.

Generation of *trans*-Chloro Diester 5t. Crude chloro diester **5** (211.5 g of 29% = 0.243 mol) was dissolved in dry benzene (300 mL). This was added dropwise over 1 h to a stirred mixture of sodium ethoxide (101 g, 1.55 mol) in dry benzene (1200 mL). The mixture was refluxed and stirred overnight. The organic layer was washed with water (4 × 400 mL). The combined aqueous layers were then extracted with ether (400 mL). The combined organic layers were dried over anhydrous magnesium sulfate, and the filtrate was rotary evaporated and vacuum dried to give a yellow solid. Upon standing at ambient temperature, the product partially liquefied to an oil. Gas chromatography showed a cyclopropyl diester peak of 40% and an unknown peak at 30%. The solid was isolated by two triturations with hexane and two recrystallizations from water–acetone. Two subsequent recrystallizations from hexane gave a pure white solid identified as *trans*-chloro diester **5t**: mp 93.6–96.6 °C; ^{1}H NMR ($CDCl_3$) δ 3.9–4.5 (m, 6 H, CH_2O's and CH_2Cl), 3.3 (d, 1 H, CHCO, J = 1.6 Hz), 2.2–2.4 (m, 3 H), 1.2–1.7 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 174.0, 172.4, 62.1, 61.4, 60.6, 49.9, 47.3, 45.7, 43.1, 37.0, 27.8, 26.4, 14.2, 14.0; HRMS calcd for $C_{14}H_{21}O_4Cl$ 288.1128, found 288.1124. Anal. Calcd for $C_{14}H_{21}O_4Cl$: C, 58.21; H, 7.33. Found: C, 58.01; H, 7.71. The *trans*-chloro diester can be converted to cyclopropyl diester **6** via a 56-h reflux with sodium ethoxide in dry benzene.

Cyclopropyl Diacid 7. Cyclopropyl diester **6** (58 g, 0.293 mol) was dissolved in ethanol–water (80:20, v/v, 500 mL), and potassium hydroxide (74 g of 87% = 1.32 mol) was added with stirring. The reaction was refluxed for 24 h. The solution was rotary evaporated, and the residue was dissolved in a minimum amount of water (70 mL). The solution was extracted with ether (200 mL), which was discarded. The aqueous layer was then acidified with concentrated hydrochloric acid at 0 °C. The solid was suction filtered and washed with water (20 mL). Vacuum drying gave a yellowish solid. The solid was dissolved in ethyl acetate (2 L) and refluxed for 2.5 h. Hot filtration removed all undissolved inorganic salts. The cooled filtrate was rotary evaporated to give a white solid. Three recrystallizations from acetone followed by sublimation at 190 °C (1 mm) gave the pure diacid: mp 235–236 °C; IR (KBr) 3451, 2980, 2903, 2656, 2586, 1707, 1420, 1329, 1300, 1271, 1194, 941; ^{1}H NMR (acetone-d_6) δ 7.1–8.7 (s, 2 H, CO_2H), 2.3–2.8 (m, 2 H, bridgehead), 1.2–2.3 (m, 7 H), 0.81 (dt, 1 H, J = 10.8 Hz, J = 1.3 Hz); ^{13}C NMR (acetone d-6) δ 174.7 (s), 39.5 (d), 37.5 (s), 29.1, 27.1, 18.2 (t); MS (EI, 30 eV, 180 °C) *m/e* (%) 196 (4.5), 178 (91), 151 (37), 150 (56), 133 (36), 123 (76), 105 (86), 79 (100), 77 (55); HRMS calcd for $C_{10}H_{12}O_4$ 196.0734, found 196.0732. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.18; H, 6.14.

Cyclopropyl Diiodide 9. Diacid **7** (4.90 g, 25.0 mmol) and thionyl chloride (29.75 g, 250 mmol) were added to dry benzene (75 mL) and heated with stirring at 55–60 °C under nitrogen for 2 h. The resulting mixture was rotary evaporated to give the intermediate acid chloride. The acid chloride was added dropwise over 30 min to a stirred boiling mixture of the following reagents in dry benzene (100 mL) under illumination of a 250-W bulb: *N*-hydroxypyridine-2-thione sodium salt (8.90 g, 60 mmol), 2-iodo-1,1,1-trifluoroethane (31.5 g, 150 mmol), and 4-(dimethylamino)pyridine (0.25 g, 2 mmol). The mixture was refluxed under close illumination for 2.5 h, resulting in a yellow solution containing a white precipitate. Hexane (250 mL) was added, and the mixture was washed with water (250 mL), dissolving the precipitate. This was followed by washes with concentrated hydrochloric acid (2 × 250 mL), 10% NaOH (250 mL), and brine. The organic layer was dried over anhydrous magnesium sulfate. The filtrate was rotary evaporated and vacuum dried to give a yellow-orange semisolid which crystallized after standing overnight. Ether (20 mL) was added to the solid, followed by an extraction with 10% NaOH. The organic layer was rotary evaporated and then stirred with 5% NaOH for 5 days to remove any anhydride formed during the reaction. The mixture was extracted with methylene chloride (2 × 20 mL), and the organic layer was dried over anhydrous magnesium sulfate. Rotary evaporation and vacuum drying gave

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[11] Schreiber, J.; Leimgruber, W.; Pesaro, M.; Schudel, P.; Threlfall, T.; Eschenmoser, A. *Helv. Chim. Acta* **1961**, *44*, 540.

[12] Aldrich Chemical Co., Milwaukee, WI.

a yellow solid. Four recrystallizations from hexane gave pure diiodide **9**: mp 48–49 °C; ^{1}H NMR (CDCl$_3$) δ 2.4 (m, 2 H, bridgehead), 1.95 (d, 1 H, J = 7.9 Hz), 1.2–1.8 (m, 5 H), 0.89 (d, 1 H, J = 7.9 Hz), 0.65 (dm, 1 H, J = 10.8 Hz); ^{13}C NMR (CDCl$_3$) δ 45.3 (d), 28.9 (2 peaks), 27.2, 21.6 (s); MS (EI, 30 eV, 0 °C) *m/e* (%) 360 (0.9), 233 (89), 205 (37), 106 (58), 79 (64), 78 (100); HRMS calcd for $C_8H_{10}I_2$ 359.8875, found 359.8889. Anal. Calcd for $C_8H_{10}I_2$: C, 26.69; H, 2.80. Found: C, 26.95; H, 2.76.

Cyclopropyl Dibromide 8. Diacid **7** (18.2 g, 96.5 mmol) was added to a stirred solution of potassium hydroxide (12.4 g of 87% = 193 mmol) and distilled water (300 mL). Silver nitrate solution (32.81 g, 193 mmol) in distilled water (100 mL) was added over 30 min with stirring. The precipitate, a brown solid, was suction filtered, washed with methanol, and vacuum dried for 3 h. It was subsequently vacuum dried in an oil bath at 105 °C (3 mm) for 36 h. For the following reaction, the silver salt was divided into two portions of approximately 20 g each. *Larger amounts were found to react violently with bromine.* Carbon tetrachloride (1300 mL) was added to each portion with stirring. Bromine (15.42 g, 193 mmol, dried via shaking with concentrated hydrochloric acid) was added to each portion in small quantities at 5-min intervals over 45 min at 0 °C. An exotherm occurred after approximately half of the bromine had been added. After the addition of bromine, the mixture was allowed to warm to ambient temperature and then refluxed overnight. The two mixtures were recombined and suction filtered, and the residue was washed with methylene chloride (20 mL). The filtrate was washed with sodium bisulfite, water, 10% sodium bicarbonate, and water (300 mL each). The organic layer was dried over anhydrous magnesium sulfate and the filtrate rotary evaporated. The resulting solid was stirred in 5% NaOH (200 mL) overnight to remove any anhydride. The mixture was extracted with methylene chloride (2 × 200 mL), and the organic layer was dried over anhydrous magnesium sulfate. The filtrate was rotary evaporated and vacuum dried to give dibromide **8** as an off-white semisolid (5.6 g, 21.0 mmol, 22%). This was vacuum distilled, bp 87–96 °C (1.2 mm) resulting in 86% purity by GC (SE-54, 160 °C). An analytical sample was prepared by four recrystallization from hexane followed by sublimation at 50–65 °C (21 mm): mp 69.0–70.1 °C; IR (KBr) 3079, 2973, 2882, 1813, 1728, 1851, 1482, 1300, 1172, 1111, 1082, 970, 885, 735; ^{1}H NMR (CDCl$_3$) δ 2.5 (m, 2 H, bridgehead), 1.89 (dd, 1 H, J = 8.2 Hz), 1.2–1.7 (m, 5 H), 1.1 (d, 1 H, J = 8.1 Hz), 0.87 (dt, 1 H, J = 10.8, 1.6 Hz); ^{13}C NMR (CDCl$_3$) δ 44.2 (d), 43.4 (s), 31.3 (t), 26.0 (t), 23.0 (t); MS (EI, 30 eV, 70 °C) *m/e* (%) 267 (8), 265 (16), 263 (8), 187 (53), 185 (52), 150 (98), 157 (100), 105 (43), 79 (54), 78 (52), 77 (84); HRMS calcd for $C_8H_9Br_2$ ($M^+ - 1$ H) 262.9068, found 262.9079. ; 23.0 (t); MS (EI, 30 eV, 70 °C) *m/e* (%) 267 (8), 265 (16), 263 (8), 187 (53), 185 (52), 159 (98), 157 (100), 105 (43), 79 (54), 78 (52), 77 (84); HRMS calcd for $C_8H_9Br_2$ ($M^+ - 1$ H) 262.9068, found 262.9079. Anal. Calcd for $C_9H_{10}Br_2$: Br, 60.09. Found: Br, 60.09.

Generation of Tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene (2) from Dibromide 8 and Trapping with DPIBF. To a solution of dibromide **8** (1.6 g, 6.00 mmol) and DPIBF (1.62 g, 6.00 mmol) in THF (90 mL, dried by distillation from sodium) at −78 °C was added *tert*-butyllithium (10.2 mmol) in pentane (1.7 M, 6 mL) over 30 min under nitrogen. A dark brown color occurred with each drop and remained at the end of the addition. The mixture was stirred for 0.5 h and quenched with methanol at which time it turned a fluorescent yellow color. The mixture was allowed to warm to ambient temperature for 1 h. Water (90 mL) was added, and the mixture was extracted with ether (2 × 110 mL). The ether layers were dried over anhydrous magnesium sulfate and filtered. The residue was washed with ether (50 mL), and the combined ether layers were rotary evaporated and vacuum dried to give a yellow solid (2.10 g). The ^{13}C NMR spectrum showed two peaks at δ 90–94 for the O–C–Ph region, indicating two stereoisomers of compound **10** (four are possible). TLC showed a mixture with possible starting DPIBF. Column chromatography on silica gel and elution with hexane–ethyl acetate gave partial separation of the mixture as indicated by TLC.

The major component of the mixture was identified to be an aromatic compound by NMR. In a subsequent, analogous reaction, it was isolated by recrystallization from hexane–ethyl acetate. Two recrystallizations gave pure *o*-benzoylbenzophenone (**11**) as pale yellow crystals: mp 146.1–148.1 °C (lit.[9] mp 145–148 °C; IR (KBr) 3445, 3318, 3085, 1887, 1672, 1603, 1454, 1321, 1279, 1160, 1151, 941, 773, 702, 653, 442; ^{1}H NMR (CDCl$_3$) δ 7.2–7.8 (m, 14 H); ^{13}C NMR (CDCl$_3$) δ 196.5, 140.1, 137.3, 132.9, 130.3, 129,8, 128.3, 122.6; HRMS calcd for $C_{20}H_{14}O_2$ 286.0994, found 286.0977.

Fractions shown by TLC to have very little aromatic compound **11** were combined and further separated in an analogous column chromatography procedure. GC–MS showed some fractions with two separated peaks, both having masses of 376 for compound **10**. NMR showed complete separation from aromatic compound **11**. Recrystallization from acetone–hexane gave 0.11 g of off-white crystals of **10**: mp 269.3–270.5 °C; MS (EI, 30 eV, 280 °C) *m/e* (%) 376 (100), 377 (26), 303 (20), 271 (32), 215 (18), 105 (21); HRMS calcd for $C_{28}H_{24}O$ 376.1826, found 376.1841. Compound **10** was not obtained as a pure stereoisomer to provide useful NMR spectra.

Generation of Tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene (2) from Diiodide 9 and Trapping with DPIBF. Generation and trapping of cyclopropene **2** was accomplished from diiodie **9** (0.35 g, 0.945 mmol) and DPIBF (0.25 g, 0.925 mmol) in THF (15 mL) with *tert*-butyllithium (1.70 mmol) in pentane by a similar procedure to that for dibromie **8** to give 0.40 g of a yellow oil. Interestingly, the ^{13}C NMR showed four absorptions at δ 90–94 for the O–C–Ph region. The mixture contained *o*-benzoylbenzophenone (**11**) and adduct **10** as shown by NMR and HRMS (HRMS calcd for $C_{28}H_{24}O$ 376.1826, found 376.1829).

Decomposition of Cyclopropene 2. To a solution of dibromide **8** (0.53 g, 2.00 mmol) in THF (30 mL) at −78 °C was added *tert*-butyllithium (3.4 mmol) in pentane (2 mL, 1.7 M) via the procedure and workup as described above only without DPIBF being present to give 0.24 g of crude product mixture. Gas chromatography (SE-54, 100–200 °C at 3 deg/min) showed 14% starting dibromide **8** and at least 12 products above 2.5% intensity ranging from 4.9- to 42.0-min retention times. GC–MS was used to identify some of the compounds (see the supplementary material).

Decomposition of Cyclopropene 1. The dibromide precursor (0.36 g) of cyclopropene **1** in THF (25 mL) at −78 °C was reacted with *tert*-butyllithium in pentane (2 mL, 1.7 M) in the absence of DPIBF as described above for dibromide **8**. Gas chromatography (SE-54, 100–200 °C at 3 deg/min) showed at least nine products above 0.6% intensity ranging from 10.5- to 47.3-min retention times. GC–MS results for seven of the products are given in the supplementary material.

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Supplementary Material Available: ^{13}C NMR spectral interpretation for **7**, **8**, and **9** and proposed structures, GC percentages, and MS fragmentation patterns for some of the products of the decompositions of **1** and **2** without DPIBF present (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.