(t, 1 H, J = 8 Hz, C_7=CHR), 5.17 (br s, 1 H, bridgehead), 3.78 (s, 3 H, CO_2CH_3), 2.13 (2 H, γ to ester), 1.90 (d, 2 H, J = 8 Hz, $HC_8CH_2C(CH_3)_2$), 1.2 (m, 4 H, ethano bridge), 0.92 (s, 6 H, $(CH_3)_2C$); for **2h** δ 6.8 (s, 1 H, vinyl), 5.53 (m, 1 H, bridgehead), 5.2 (m, 1 H, bridgehead), 2.13 (s, 3 H, CH_3), 1.7 (br m, 4 H, ethano bridge).

Acknowledgment. We are very grateful to Professor Arthur Hubbard and Dr. Ross Lane of UCSB for sharing with us their expertise in electrochemistry. We also acknowledge the encouragement of Professor Hubbard and Dr. M. Baizer during the early stages of our work. Professor H. Offen (UCSB) gratiously allowed us to use his X-Y recorder for our cyclic voltammetry studies.

This investigation was supported by Grant No. CA21144-02 awarded by the National Cancer Institute, DHEW; we are most grateful for their support.

Registry No. **2a**, 71807-24-4; **2b**, 31689-32-4; **2c**, 66322-88-1; **2d**, 70713-02-9; **2e**, 66322-90-5; **2f**, 71807-25-5; **2g**, 71807-26-6; **2h**, 71807-27-7; **3a**, 71807-16-4; **3b**, 71807-17-5; **3c**, 71807-18-6; **3d**, 71807-19-7; **3e**, 71807-20-0; **3f**, 71807-21-1; **3g**, 71807-22-2; **3h**, 71807-23-3.

Decomposition of 5-Aryl-5-(*tert*-butylperoxy)-3,4-diphenyl-2(5*H*)-furanones

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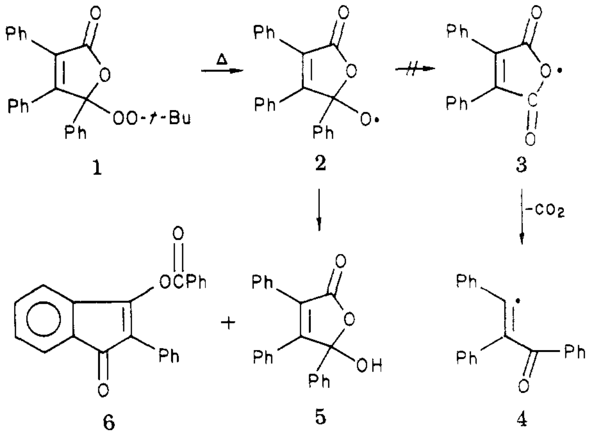
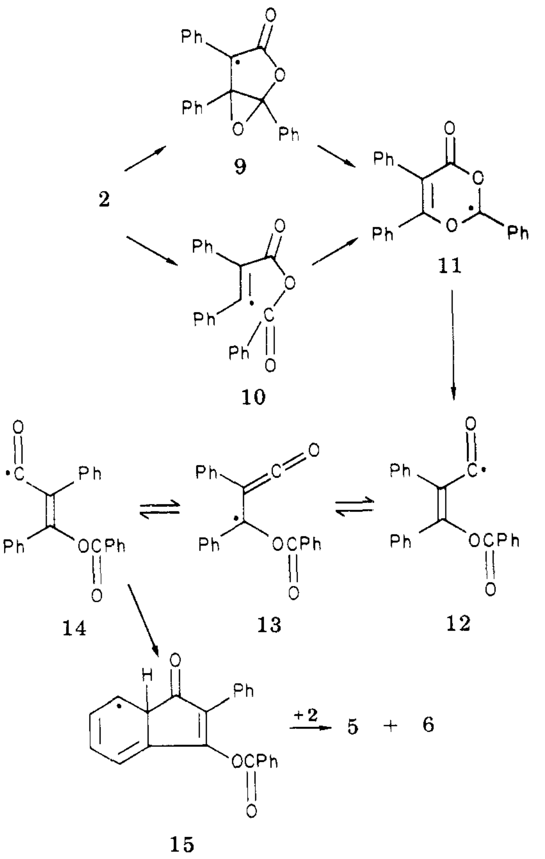
In light of recent interest in γ-lactone systems, namely, Padwa's investigation of migratory aptitude in the photochemical rearrangement of 2(5*H*)-furanone[1] and Tidwell's work on cyclization by radical displacement on ester groups and conversion of acetals to lactones,[2] we wish to report the radical rearrangement of the lactone, 5-(*tert*-butylperoxy)-3,4,5-triphenyl-2(5*H*)-furanone (**1**). In the course of seeking a route to β-aroylvinyl radicals,[3] we presumed that the decomposition of **1** under nitrogen in bromobenzene would lead to the oxy-2(5*H*)-furanone radical **2**. This intermediate might then be expected to open to the carboxy radical **3** and, upon decarboxylation, generate the β-benzoylvinyl radical **4** (see Scheme I). However, when compound **1** was heated, neither β-benzoylvinyl radical nor any product of decarboxylation was detected. Instead, the reaction gave 48% of the reduced 5-hydroxy-3,4,5-triphenyl-2(5*H*)-furanone (**5**) and 42% of rearranged oxidized product, 3-(benzoyloxy)-2-phenyl-1-indenone (**6**).

Scheme I



Scheme II



Results and Discussion

Compound **1** was prepared from the known 5-chloro-3,4,5-triphenyl-2(5*H*)-furanone (**7**), utilizing *tert*-butyl hydroperoxide in pyridine–benzene, a modification of Bartlett and Hiatt's procedure.[4] The stable perester, mp 102.5–104.5 °C, had spectra and an elemental analysis in agreement with its structure. Synthesis of the precursors to **7** was straightforward (see Experimental Section).

The initial reaction conditions for the thermal decomposition of compound **1** involved a 0.01 M solution of **1** in bromobenzene which was degassed and heated in a sealed tube at 110–120 °C for 24 h. The reaction afforded **5** and **6** in approximately equal amounts. Compound **6** was identified by degradation in base to 2-phenyl-1*H*-indene-1,3(3*H*)-dione (**8**) and benzoic acid. Compounds **5**, **6**, and **8** were unequivocally identified by comparison with authentic samples.

A plausible mechanism for the decomposition of **1** is depicted in Scheme II.[5] The oxygen–oxygen bond of peroxide **1** is initially homolyzed to give oxyfuranone radical **2** which could either epoxidize to form radical **9** or ring open to yield vinyl radical **10**. Rearrangement of either **9** or **10** would lead to the six-membered heterocyclic radical **11** which is stabilized by the adjacent phenyl group and oxygen atoms. A fragmentation of radical **11** between the carbonyl–oxygen bond of the ester would lead to

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(1) A. Padwa, T. Brookhart, D. Dehm, and G. Wubbels, *J. Am. Chem. Soc.*, **100**, 8247 (1978).

(2) C. Rynard, C. Thankachan, and T. Tidwell, *J. Am. Chem. Soc.*, **101**, 1196 (1979).

(3) James Weinberg, Ph.D. Thesis, University of Connecticut, 1978.

(4) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(5) Of course, subtle variations of some of the steps are also possible.

0022-3263/79/1944-4722$01.00/0

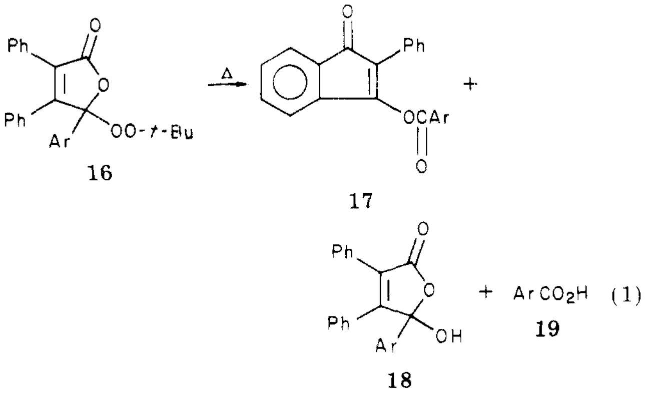
Table I. Attempted Trapping of an Intermediate

run	solvent[a]	conditions	amt identified prod,[b] % 5	amt identified prod,[b] % 6
1	toluene	sealed tube 115 °C 24 h	68	22
2	cumene	sealed tube 117–125 °C 24 h	67	24[c]
3	methanol	reflux under N_2 23 h	no reaction	
4	*n*-butyl alcohol	reflux under N_2 13.5 h	68[d]	
5	*t*-BuOH in bromobenzene	sealed tube 115 °C 24 h	32	58

[a] All solutions were 0.01 M in 1. [b] Yield based on weight of compound from preparative TLC. [c] A small amount of bicumyl was also isolated. [d] Recrystallized yield.

(*Z*)-acyl radical **12**. The radical **12** is free to isomerize to the (*E*)-acyl radical **14** via a ketene radical intermediate **13**. Radical **14** is able to react with the 4-phenyl group forming **15** which upon loss of a hydrogen atom to another oxyfuranone radical **2** would yield the two observed products **5** and **6** in equal amounts.

In order to provide some support for this mechanistic hypothesis, we synthesized 5-(*tert*-butylperoxy)-5-(*p*-chlorophenyl)-3,4-diphenyl-2(5*H*)-furanone (**16**) and allowed it to decompose under the reaction conditions. As expected, the thermolysis of **16** yielded only 3-(*p*-chlorobenzoyloxy)-2-phenyl-1-indenone (**17**) (55%), 5-(*p*-chlorophenyl)-3,4-diphenyl-5-hydroxy-2(5*H*)-furanone (**18**), and *p*-chlorobenzoic acid (**19**) (eq 1).



Ar = *p*-chlorophenyl

We attempted to trap an intermediate on the reaction pathway from **1** to **6** by changing the solvent. The results of these experiments are given in Table I. In general the reactions in toluene and cumene led to higher yields of the reduced product **5** and lower yields of the oxidized product **6**. This is presumably due to the ability of the oxyfuranone radical **2** to readily abstract a hydrogen from the solvent. It was hoped that an alcohol as solvent would trap the ketene intermediate **13**. However, in no case could the corresponding ester be isolated.

Experimental Section

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 137 or 283 spectrophotometer. The UV spectra were recorded with a Cary Model 14, Cary Model 17, or a Beckman DB spectrophotometer. The NMR spectra were measured on a Varian A60A or an EM-360A at 60 Hz. Mass spectra were taken on at AEI MS-902 double-focusing high-resolution spectrometer. Thick-layer chromatography plates were prepared according to Stahl with silica gel GF (1 mm thick). The plates were developed in benzene–hexane, 2:1.

Diphenylmaleic Anhydride. By modification of a literature method,[6] α-bromo-α-phenylacetonitrile[7] (from 1 mol of benzyl cyanide) was converted to the anhydride. To the crude nitrile was added 200 mL of 95% EtOH. A 270-g (4.8 mol) sample of KOH dissolved in 700 mL of EtOH was then added slowly with cooling and swirling in an ice bath. After the reaction mixture stood at room temperature for 3 h, 350 mL of water was added, and the mixture was refluxed for 4 days. It was cooled, poured into 2 L of water, and extracted twice with 300-mL portions of ether. To the aqueous layer was added 6 N HCl until it was quite acidic. A brown oil formed which slowly solidified. The solid was collected, washed with water, and allowed to dry in the air. Two recrystallizations (EtOH) gave 30 g of orange-yellow crystals, mp 155.5–157 °C, and a second crop of 3 g of tan crystals, mp 154–156 °C (lit.[6] mp 155 °C); total yield 33 g (26% based upon benzyl cyanide).

5-Hydroxy-3,4,5-triphenyl-2(5*H*)-furanone (5). The Friedel–Crafts procedure previously reported[8] was unsatisfactory, so an organocadmium reagent was used. The methods of deBenneville[9] and Cason[10] were followed.

The reaction was carried out under a stream of nitrogen. In a 200-mL three-necked round-bottomed flask equipped with a magnetic stirrer, pressure-equalizing dropping funnel, condenser with drying tube, and Claisen adapter with septums and a nitrogen inlet, phenylmagnesium bromide was prepared. To 0.445 g (1.8×10^{-2} mol) of magnesium was added, with stirring, a solution of 2.5 mL (2.4×10^{-2} mol) of freshly distilled bromobenzene and 15 mL of ether. After completion of the addition, the mixture was stirred and heated in a bath at 43–50 °C for 1 h and cooled to 17 °C. The diphenylcadmium was then prepared. The nitrogen flow was increased, and an Erlenmeyer flask containing 2.424 g (9.5×10^{-3} mol) of anhydrous cadmium chloride, freshly dried to constant weight, was attached to the three-necked flask through a piece of tubing. To the stirred, cooled solution was added the cadmium chloride over 10 min. The mixture turned gray-blue. The reaction was heated in a bath at 49 °C for 10 min. The nitrogen flow was then increased, and the condenser was turned off. The mixture thickened as the ether evaporated. As the temperature of the bath was increased to 56 °C during the next 5 min, 200 mL of dried benzene was injected into the stirring mixture. When the temperature reached 63 °C, the nitrogen flow was lowered, and the condenser was turned on. The temperature was raised to 89–92 °C, and the stirred gray-white mixture was heated to reflux for 75 min. After the mixture was cooled, the dropping funnel was replaced by a new pressure-equalizing dropping funnel, containing a yellow solution of 2.009 g (7.9×10^{-3} mol) of diphenylmaleic anhydride dissolved in 25 mL of benzene and stoppered with a rubber septum. This solution was added over 13 min to the stirred reaction mixture as the bath was warmed to 18 °C. The reaction mixture was green. Over the next 45 min, the reaction mixture was heated to 80 °C, and the cloudy green-yellow solution began to reflux. The reaction mixture was heated to reflux for an additional 3 h, cooled, and hydrolyzed with 50 mL of 10% H_2SO_4. The orange organic layer was separated and saved. The aqueous layer was extracted three times with 20-mL portions of ether. All organic layers were combined and extracted five times with 20-mL portions of 1 N NaOH. The combined basic layers were filtered through a fritted-disk funnel. The filtrate was chilled in an ice bath and acidified with approximately 18 mL of concentrated HCl. A yellow-white precipitate formed that was collected upon filtration, rinsed with distilled H_2O, and air-dried. Recrystallization from 1:2 benz-

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(6) C. L. Reimer, *Chem. Ber.*, **13**, 742 (1880).

(7) E. C. Horning, Ed., "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 347.

(8) G. Rio and J. C. Hardy, *Bull. Soc. Chim. Fr.*, 3572 (1970).

(9) P. deBenneville, *J. Org. Chem.*, **6**, 462 (1941).

(10) J. Cason, *J. Am. Chem. Soc.*, **68**, 2078 (1946).

ene–hexane yielded 1.960 g (76%) of white **5**: mp 175.5–177 °C (lit.[8] mp 177–178 °C; from EtOH); IR (KBr) 3300 (OH), 1730 (C=O), 1640 cm^{-1} (C=C).

5-(*tert*-Butylperoxy)-3,4,5-triphenyl-2(5*H*)-furanone (1). In a three-necked round-bottomed flask equipped with a magnetic stirrer, addition funnel, and reflux condenser, 2.82 g (8.12 × 10^{-3} mol) of **7**[8] dissolved in 15 mL of dried benzene and 1.65 mL of dried pyridine was stirred and chilled in an ice bath. To the above yellow chilled solution was added, through the dropping funnel, a chilled solution of 13 mL (1.29 × 10^{-1} mol) of *tert*-butyl hydroperoxide in 15 mL of benzene. The funnel was then rinsed with an additional 3 mL of chilled benzene. The chilled turbid white reaction mixture was stirred for an additional hour and slowly allowed to warm to room temperature. The mixture was hydrolyzed with ice-cold water and the organic layer was washed with 10% H_2SO_4, 10% Na_2CO_3, and then H_2O. The organic layer was dried ($MgSO_4$), passed through 3 cm of Florisil, and rinsed with small portions of benzene totaling 100 mL. Evaporation of the solvent in vacuo left white crystals; recrystallization (cyclohexane) gave 1.65 g (50%) of **1**, mp 96–97 °C. A sample of **1** was prepared for analysis by dissolving it in toluene at room temperature followed by the addition of a large amount of pentane (1:10). The solution was then placed in the freezer and yielded, upon filtration, white crystals, mp 102.5–104.5 °C. The sample was stored in a freezer or away from light in a vacuum desiccator: IR (KBr) 3090, 3070, 1365, 1250, 1190, 1180, 1150, 968, 692 cm^{-1}; UV max (95% EtOH) 287 nm (log ε 4.01); NMR ($CDCl_3$) δ 8.4–7.35 (m, 15, aromatic), 1.35 (s, 9, $(CH_3)_3C$); mass spectrum, *m/e* 327 (P − O-*t*-Bu), 283 (327 − CO_2), 105 (283 − PhC≡CPh).

Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04. Found: C, 77.81; H, 5.97.

Thermal Decomposition of 1. In general, the reaction mixtures for the thermal decomposition of peroxy lactone **1** were prepared with approximately 4.0 × 10^{-3} mol of compound dissolved in 40 mL of distilled bromobenzene (a 0.01 M solution) in a Pyrex tube. The dimensions of the tubes were 30 cm long, 30 mm o.d., and 26 mm i.d. The tubes were approximately one-fourth filled with the reaction mixture. They were degassed three times and sealed on the fourth. The tubes were heated in a furnace at 115–120 °C for 24 h. The tubes were opened, and the bromobenzene was removed at reduced pressure [28–29 °C (1 mm)], with care being taken not to overheat the remaining residues. The residues were separated by preparative TLC, followed by stripping with ether and rotary evaporation of the solvent. The products remaining were placed in a vacuum desiccator. Yields were based on the dry weight of these products.

From a run utilizing 0.160 g (4.0 × 10^{-4} mol) of **1**, two products were obtained. From the base line 0.057 g (43%) of crude **5** and from the middle of the layer 0.068 g (52%) of orange crystalline **6**, dec 156–164 °C, were isolated. Compound **5** upon crystallization from benzene–hexane yielded a white product, mp 170–173 °C. A mixture melting point with an authentic sample of **5** gave a melting point of 172–173 °C. The IR spectrum was identical with that of the authentic sample.

Recrystallization of compound **6** (benzene–hexane) gave yellow needles: mp 167.5–168.5 °C (lit.[11] mp 168 °C); mixture melting point with authentic sample, 168–168.5 °C; IR (KBr) 1745 (C=O), 1735, 1719, 1640, 1600, 1255, 1340 cm^{-1} (C—O); mass spectrum, *m/e* calcd for $C_{22}H_{14}O_3$ 326.0940, found 326.0945.

Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 81.16; H, 4.55.

Basic Hydrolysis of 3-(Benzoyloxy)-2-phenyl-1-indenone (6). To 0.327 g of compound **6** was added 65 mL of 2 N KOH in MeOH. After 15 min of refluxing, the reaction mixture was cooled and added to 250 mL of water. The aqueous layer was extracted with CH_2Cl_2 and then acidified with concentrated HCl, which gave a white precipitate. The acid solution was extracted with CH_2Cl_2 which was washed (H_2O), dried ($MgSO_4$), and removed in vacuo. Recrystallization of the product from ethanol–water gave 0.198 g (89%) of white crystals of 2-phenyl-1*H*-indene-1,3(2*H*)-dione: mp 148–149 °C (lit.[12] mp 149–151 °C); mixture melting point with an authentic sample (Pfaltz and Bauer, mp 149–150 °C) 148–150 °C. The IR and NMR spectra were identical with those of the authentic sample.

5-(*p*-Chlorophenyl)-3,4-diphenyl-5-hydroxy-2(5*H*)-furanone (18). The organocadmium method for the preparation of analogue **1** was modified for the preparation of compound **18**. The Grignard reagent was prepared in the same manner from 0.454 g (1.87 × 10^{-2} mol) of magnesium and 5.169 g (2.41 × 10^{-2} mol) of *p*-bromochlorobenzene (Eastman) dissolved in 28 mL of ether and stirred. Upon completion of the addition the mixture was heated in a bath at 45–50 °C for 30 min and then cooled to 10 °C. To the cooled yellow solution of *p*-chlorophenylmagnesium bromide was added 2.327 g (1.28 × 10^{-2} mol) of anhydrous $CdCl_2$ over a 15-min period. The reaction mixture darkened and over the next 25 min was heated in a bath to 55 °C. During this time, the ether evaporated, the reaction mixture thickened, and 20 mL of benzene was injected over a 5-min period. The mixture was heated to reflux for 90 min and cooled in a 5 °C ice–water bath. A solution of 2.005 g (7.89 × 10^{-3} mol) of diphenylmaleic anhydride dissolved in 25 mL of benzene was added through a dropping funnel over a 15-min period, and then the funnel was rinsed with 5 mL of benzene. The mixture turned yellow. Over the next 20 min it was heated to reflux, maintained at reflux for 90 min, and then cooled. The mixture was hydrolyzed in 50 mL of 10% H_2SO_4. The organic layer was separated and saved. The aqueous layer was extracted three times with 20-mL portions of ether. The combined organic layers were extracted seven times with 1 N NaOH. In the basic layer was a large amount of yellow-orange precipitate. The basic layer was chilled in ice and the crude open salt of compound **18** was collected upon filtration (the salt was insoluble in base and ether): IR 1585 (CO_2),[13] 1380 (CO_2),[13] 1660 cm^{-1} (s, C=O).

In a beaker, the salt of **18** was mixed with 100 mL of 5% HCl and 50 mL of ether. The yellow organic layer was separated and saved. The aqueous layer was extracted three times with 20-mL portions of ether. The ether layers were combined, washed (H_2O), dried ($MgSO_4$), and removed in vacuo, yielding 2.516 g (87%) of crude **18**. The product was crystallized (benzene–hexane), yielding 1.521 g (53%) of white crystals: mp 147–148 °C, analytical sample (benzene–hexane) mp 148–149 °C; IR (KBr) 3420 (br, OH), 1740 (C=O), 1640 (C=C), 1600 cm^{-1} (C=C); mass spectrum, *m/e* calcd for $C_{22}H_{15}O_3Cl$ 362.0708, found 362.0718.

Anal. Calcd for $C_{22}H_{15}O_3Cl$: C, 72.83; H, 4.18; Cl, 9.77. Found: C, 73.08; H, 4.48; Cl, 9.41.

5-Chloro-5-(*p*-chlorophenyl)-3,4-diphenyl-2(5*H*)-furanone (20). Following the method for the preparation of analogue **7**, we mixed 2.77 g (7.44 × 10^{-3} mol) of **18** and 27 mL of pyridine in 270 mL of ether with 13.95 mL of thionyl chloride, and the reaction mixture was stirred for 2 days. The reaction mixture was then hydrolyzed and worked up (in the same manner as in the preparation of **7**) to yield an oil, which was placed in a vacuum desiccator for 2 days. The oil swelled into 2.655 g (94%) of white crystalline product, which softened at 96 °C and melted at 103–106 °C. The product **20** was stored in a vacuum desiccator and utilized without further purification. The analytical sample was recrystallized in cyclohexane and melted at 107–108.5 °C: IR (KBr) 1785 (C=O), 1647 cm^{-1} (C=C); mass spectrum, *m/e* calcd for $C_{22}H_{14}O_2Cl$ (minus a Cl fragment) 345.0679, found 345.0684.

Anal. Calcd for $C_{22}H_{14}O_2Cl_2$: C, 69.31; H, 3.67; Cl, 18.60. Found: C, 69.54; H, 3.96; Cl, 18.19.

5-(*tert*-Butylperoxy)-5-(*p*-chlorophenyl)-3,4-diphenyl-2-(5*H*)-furanone (16) was prepared by the same procedure used to synthesize **1**. From 2.66 g of **20** was obtained after recrystallization from benzene–pentane 1.36 g (50%) of **16**: mp 133–135 °C; IR (KBr) 1770 (C=O), 1640 (C=C); NMR ($CDCl_3$) δ 7.4–7.1 (s, 14, aromatic), 1.35 (s, 9, $(CH_3)_3C$); mass spectrum *m/e* calcd for $C_{22}H_{14}O_3Cl$ (minus *t*-BuO fragment) 361.0627, found 361.0618.

Anal. Calcd for $C_{26}H_{23}O_4Cl$: C, 71.80; H, 5.33; Cl, 8.15. Found: C, 71.52, 71.49; H, 5.49, 5.58; Cl, 8.40, 8.54.

Thermal Decomposition of 16. Compound **16** was thermally decomposed in the same manner as **1**. From 0.215 g (4.9 × 10^{-4}

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[11] E. Braun, *Chem. Ber.*, **28**, 1388 (1895).

[12] "Merck Index", 9th ed., Merck and Co., Inc., Rahway, NJ, 1976, compound 7027.

[13] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3rd ed., Wiley, New York, 1974, pp 101–2.

[14] Prepared by the general method of W. Hinkinbottom, "Reactions of Organic Compounds", 3rd ed., Wiley, New York, 1962, p 291.

mol) of **16** were obtained from thick-layer chromatography one minor and two major products. From the middle of the plate, 0.125 g (70%) of an orange solid, compound **17**, was isolated; mp 139–160 °C (softening at 55 °C). From the base of the plate was isolated 0.063 g of a yellow solid, which appeared by IR to be a mixture of compound **18** and *p*-chlorobenzoic acid **19**. Between the two previously discussed bands, 0.023 g of a red-orange oily substance was obtained, which had a broad carbonyl absorption at 1739–1668 cm^{-1} in the IR spectrum.

Compound **17** upon recrystallization (EtOH) yielded 0.054 g of fluffy orange crystals: mp 169–172 °C; mixture melting point with an authentic sample (mp 173–174 °C, see below) melted at 173–174 °C. Its IR spectrum was identical with that of the authentic sample.

The products from the base of the plate were fractionally crystallized (EtOH). Their IR spectrum was identical, peak for peak, with that obtained by superimposing those of authentic samples of **18** and **19**; mass spectrum, *m/e* calcd for $C_{22}H_{15}O_3Cl$ (**18**) 362.0708, found 362.0713; *m/e* calcd for $C_7H_5O_2Cl$ (**21**) 155.9978, found 155.9964. [This is outside the standard error limits. The large deviation (9.03 ppm) of the measured mass may have been due to an unresolved doublet.]

3-(*p*-Chlorobenzoyloxy)-2-phenyl-1-indenone (17). Compound **17** was prepared by a modification of the procedure for the preparation of the authentic sample of compound **6**. In a round-bottomed flask equipped with a condenser and drying tube, 3.959 g (1.78×10^{-2} mol) of 2-benzoyl-2-phenyl-1*H*-indene-1,3-(2*H*)-dione was heated to reflux with 6.8 mL (5.35×10^{-2} mol) of *p*-chlorobenzoyl chloride for 30 min. The reaction mixture was cooled, and an orange precipitate formed. The precipitate was collected by filtration and the excess acid chloride rinsed off with chilled pentane, yielding 7.276 g of orange product, mp 109–238 °C. The product was recrystallized (EtOH) and yielded 3.519 g (53%) of fluffy orange product, mp 170–171 °C (softening at 160 °C). A sample was prepared for analysis (EtOH) and melted at 173–174 °C: IR (KBr) 1741 (C=O), 1719 (C=O), 1617 cm^{-1} (C=C); mass spectrum, *m/e* calcd for $C_{22}H_{13}O_3Cl$ 360.0549, found 360.0544.

Anal. Calcd for $C_{22}H_{13}O_3Cl$: C, 73.24; H, 3.63; Cl, 9.83. Found: C, 73.02; H, 3.84; C, 10.22.

Acknowledgment. We wish to thank the University of Connecticut Research Foundation and the American Cyanamid Co. for stipends to J.S.W.

Registry No. **1**, 71627-60-6; **5**, 30336-09-5; **6**, 25098-00-4; **7**, 31590-00-8; **8**, 83-12-5; **16**, 71749-99-0; **17**, 71785-22-3; **18**, 71750-00-0; **19**, 74-11-3; **20**, 71750-01-1; diphenylmaleic anhydride, 4808-48-4; α-bromo-α-phenylacetonitrile, 5798-79-8; bromobenzene, 108-86-1; *tert*-butyl hydroperoxide, 75-91-2; *p*-bromochlorobenzene, 106-39-8; 2-benzyl-2-phenyl-1*H*-indene-1,3(2*H*)-dione, 69808-15-7; *p*-chlorobenzoyl chloride, 122-01-0.

Hindered Bis(*cis*-alkenyl)durene and Bis(*cis*-alkenyl)mesitylene: Preparation by Selective Photosensitized Isomerization and Hindered Rotation by Dynamic Nuclear Magnetic Resonance

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Recently we demonstrated that selective photosensitization is a useful method for preparation of hindered cis olefins, particularly those with a chromophore in a much more skewed conformation than the corresponding trans olefin.[1] In many cases, the conversion from trans to cis can be forced into one direction, thus giving quantitatively the cis isomer.

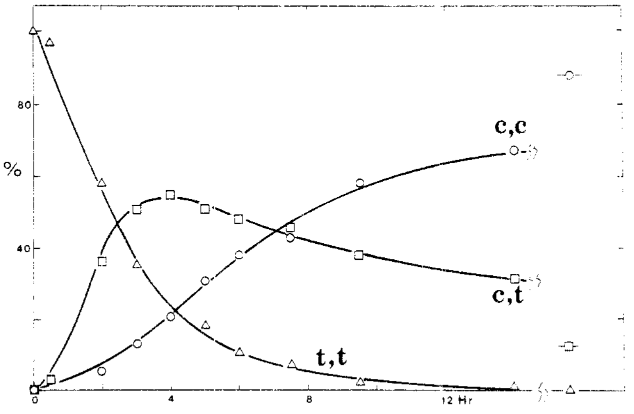
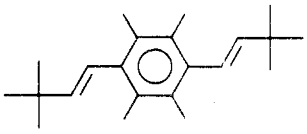


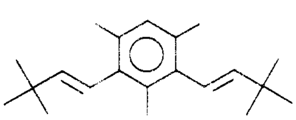
Figure 1. Time plot of triphenylene-photosensitized isomerization of the t,t isomer (Δ) of compound 1. The point corresponding to the longest period of irradiation was obtained after 23 h of exposure.

When applied to the aromatic series we showed that the method is useful for preparation of a series of homologous hindered styrenes.[2] As demonstrated by Adams and coworkers many years ago,[3] steric hindrance in such styrenes results in slow interconversion of enantiomeric conformers which we were also able to demonstrate with the aid of a chiral shift reagent. We now would like to report results of studies on two hindered bis(alkenyl) aromatic compounds, both on their photochemical and conformational properties.

Results and Discussion

Two compounds were prepared in this study: bis(3,3-dimethyl-1-butenyl)durene (**1**) and bis(3,3-dimethyl-1-butenyl)mesitylene (**2**). The trans,trans (t,t) isomers of both compounds were obtained via identical reaction sequences of bis acylation of the parent aromatic hydrocarbons and reduction by $LiAlH_4$ followed by acid-catalyzed dehydration. The only step that presented some difficulties was the reduction step. Due to severe steric crowding, the reaction proceeded very slowly. Only after rather long reaction times were good yields of diols possible.


1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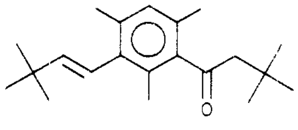

3

Photosensitized Isomerization. Upon sensitized irradiation of either **1** or **2**, the formation of two products, one dominant during early stages of irradiation, was detected by GLC analyses of the reaction mixtures. In the case of triphenylene-sensitized reactions, the processes during early stages were followed closely. The resultant time plots are shown in Figures 1 and 2. The buildup of the first photoproduct is particularly evident in the case of **2**. But, in both cases, this early product as well as the

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[1] Ramamurthy, V.; Butt, Y.; Yang, C.; Yang, P.; Liu, R. S. H. *J. Org. Chem.* **1973**, *38*, 1247–1249.

[2] Yang, C. S. C.; Liu, R. S. H. *Tetrahedron Lett.* **1973**, 4811–4814.

[3] Adams, R.; Mecorney, J. W. *J. Am. Chem. Soc.* **1945**, *67*, 798–802 and previous papers in the series.