Ring-Opening Reactions of Anionic Cyclopropyl Compounds. 3

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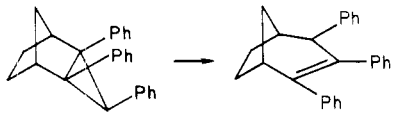
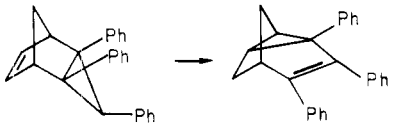
The reaction of KO-*t*-Bu in Me_2SO with the tricyclocyclopropyl carbonyl compounds **3a,b** was shown to result in the formation of cyclopentadienes and cinnamic acid derivatives **4a,b** and **5a,b** which were shown to be preceded by intermediates **6a,b**. It is suggested that **6a,b** rearrange to **4a,b** and **5a,b** via an unusual electrocyclization followed by a fragmentation. An example of an apparent conrotatory ring opening of a cyclopropyl carbanion or anion radical is presented in the conversion of **8** to **9**.

It was recently demonstrated that the tricyclic compounds **1** and **2** undergo a disrotatory ring opening of a



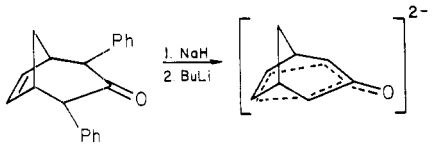
1



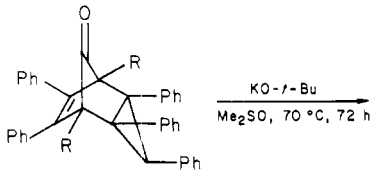
2

cyclopropyl anion when treated with KO-*t*-Bu in Me_2SO.[1,2a] It was shown that the transformation of **2** does not proceed via a bishomocyclopentadienyl carbanion.[1,2a]

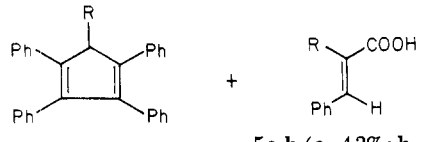
It was of interest to determine the effect of a bridging carbonyl group on the course of reaction. It has been shown by Trimitsis and co-workers,[2b] for example, that the bicyclooctenone is converted to a bishomocyclopentadienyl dianion as shown below.



Therefore, **3a**[3] and **3b**[4] were treated with KO-*t*-Bu in Me_2SO. These reactions resulted in rearrangement and fragmentation reactions as shown. Authentic samples of



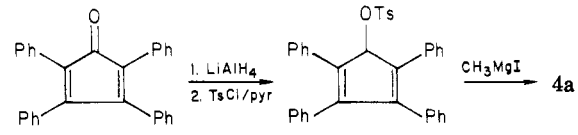
3a,b



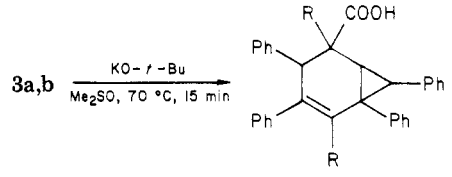
4a,b (a, 75%; b, 78%) **5a,b** (a, 43%; b, 20%)

a, R = CH_3; b, R = Ph

4b, **5a**, and **5b** were synthesized via literature procedures and found to be identical with the reaction products shown above. Compound **4a** was unequivocally synthesized as shown.

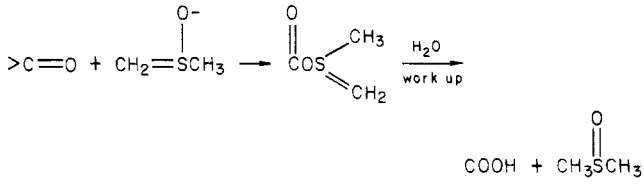


When the reaction of **3a,b** with KO-*t*-Bu in Me_2SO was terminated after only 15 min, **6a,b** were isolated in ~90%

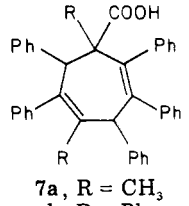


6a, R = CH_3
b, R = Ph

yield and identified by spectral and analytical data (see Experimental Section). Compounds **6a,b** can readily arise by a Haller–Bauer-type cleavage of the nonenolizable ketones **3a,b**. The fact that **6a,b** are obtained as the free carboxylic acids rather than the *tert*-butyl esters is consistent with other observations[3] concerning the cleavage of ketones in KO-*t*-Bu/Me_2SO. It has been suggested that the dimsyl anion adds to the carbonyl group followed by rapid hydrolysis of the ester intermediate.[3]



Finally, if the reaction of **3a,b** with KO-*t*-Bu/Me_2SO is terminated after 3–4 h, rather than 15 min, the ring-opened compounds **7a,b** are isolated and their structures assigned on the basis of analytical and spectral data (see Experimental Section). Of particular significance is the fact that in the NMR spectra, the benzylic protons of **7a** and **7b**



7a, R = CH_3
b, R = Ph

appear as singlets with different chemical shifts. Any other arrangement of the double bonds in the ring would result in multiplicity or equivalence.

(1) M. E. Londrigan and J. E. Mulvaney, *J. Org. Chem.*, **37**, 2823 (1972). For recent evidence suggesting that the reaction may proceed via a radical anion, see M. Newcomb, T. Seidel, and M. B. McPherson, *J. Am. Chem. Soc.*, **101**, 777 (1979).

(2) (a) H. D. Martin, *Chem. Ber.*, **107**, 477 (1974). (b) G. B. Trimitsis, E. W. Crowe, G. Slomp, and T. L. Helle, *J. Am. Chem. Soc.*, **95**, 4333 (1973).

(3) P. G. Gassman and F. V. Zalar, *Tetrahedron Lett.*, 3251 (1964).

(4) B. Halton, M. A. Battiste, R. Rahberg, C. L. Deyrup, and M. E. Brennan, *J. Am. Chem. Soc.*, **89**, 5964 (1967).

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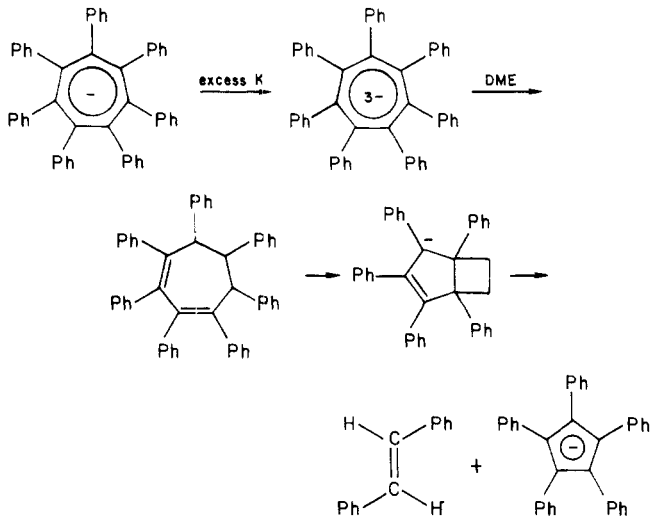
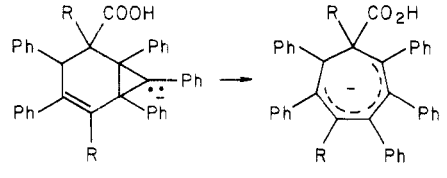
Scheme I



As a control, **3a,b** were heated in Me_2SO at 70 °C for 72 h in the absence of KO-*t*-Bu. Compound **3a** was recovered unchanged whereas **3b** yielded heptaphenyltropylidene in 95% yield in accord with earlier studies carried out in benzene as solvent.[4]

From the results described above it is clear that the reaction proceeds in at least three stages: (1) Haller–Bauer cleavage of **3a,b** to produce an anion which on protonation yields **6a,b**; (2) deprotonation of **6a,b** to give a product in which the cyclopropyl ring has opened to provide **7a,b**; (3) rearrangement and fragmentation of an anion derived from **7a,b** to produce the final products, **4a,b** and **5a,b**.

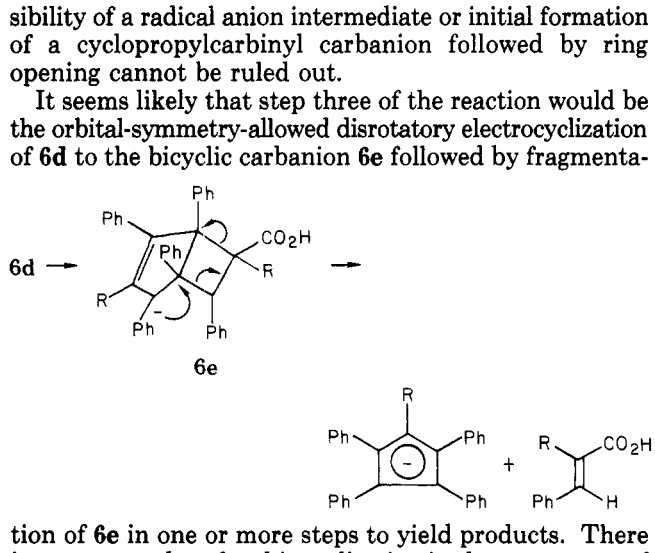
With regard to the second step, **6a,b** may react via an orbital-symmetry-forbidden disrotatory opening of a cyclopropyl anion, **6c** → **6d**. On the other hand, the pos-



6c **6d**

sibility of a radical anion intermediate or initial formation of a cyclopropylcarbinyl carbanion followed by ring opening cannot be ruled out.

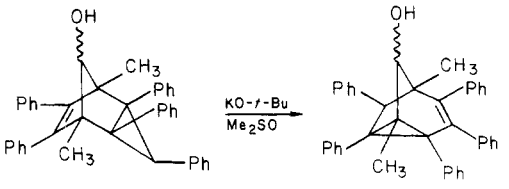
It seems likely that step three of the reaction would be the orbital-symmetry-allowed disrotatory electrocyclization of **6d** to the bicyclic carbanion **6e** followed by fragmenta-



6e

tion of **6e** in one or more steps to yield products. There is some precedent for this cyclization in that treatment of 1,4-cycloheptadiene with strong base gives a small amount of bicyclo[3.2.0]hept-2-ene.[5] In addition, Breslow and Chang[6] treated the hexaphenyltropylium ion with excess potassium in the hope of generating **7**, a potentially 10-π-electron aromatic system.[7] Although **7** was not isolated, the products from the reaction were the pentaphenylcyclopentadienyl anion and *trans*-stilbene, the vinylic protons of the latter having come from the solvent dimethoxyethane. Although a mechanism was not suggested, in accord with the results presented here a possible mechanism is that shown in Scheme I.

Compound **3a** was reduced with $LiAlH_4$ to the corresponding alcohol **8**. The reaction of **8** with KO-*t*-Bu in Me_2SO led to the isolation of **9** in 44% yield, another reaction involving disrotatory opening of a cyclopropyl intermediate.



8 **9**

Experimental Section

General Methods. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were determined on a Varian A-60 spectrometer at 60 MHz using tetramethylsilane as an internal standard. Either a Perkin-Elmer Infracord or a Perkin-Elmer Model 337 was used to determine the infrared spectra. Ultraviolet spectra were obtained from a Cary 14 spectrometer.

Carbon and hydrogen microanalyses were performed by Huffman Laboratories, Inc. Molecular weight data were obtained by using a Hitachi Perkin-Elmer RHU-6E mass spectrometer.

Mallinckrodt anhydrous reagent-grade ether was used without further purification. Reagent-grade benzene and toluene were refluxed over sodium metal 24 h prior to final distillation and stored over 4A molecular sieves. Reagent-grade dimethyl sulfoxide (Me_2SO) was refluxed over calcium hydride 3 h prior to final distillation at reduced pressure and stored over 4A molecular sieves.

Matheson Coleman and Bell practical-grade potassium *tert*-butoxide was used without further purification.

Deuterium oxide (99.8 atom % deuterium) and dimethyl-d_6 sulfoxide (99.5 atom % deuterium) were obtained from Stohler Isotope Chemicals.

All other solvents or reagents were used without further purification.

1,2,3-Triphenylcyclopropene. This compound was prepared in 45% yield according to the procedure of Breslow and Dowd[8] with the exception that elution chromatography of the crude 1,2,3-triphenylcyclopropene was not necessary. The compound was identified by its NMR, and mass spectra and melting point.

2,5-Dimethyl-3,4-diphenylcyclopentadienone Dimer. This compound was prepared in 12% yield according to the procedure of Allen and Van Allen[9] and identified by its NMR and IR spectra and melting point.

2,3,4,5-Tetraphenylcyclopentadienone (Tetracyclone). This compound was prepared in 85% yield according to the procedure of Allen and Van Allen[9] and identified by its IR spectrum and melting point.

6,6-Diphenylfulvene. This compound was prepared in 65% yield according to the procedure of Wagner and Hunt[10] and

(5) Private communication from S. Winstein to R. Bates cited by R. Bates et al. [*J. Am. Chem. Soc.*, 91, 4608 (1969)].

(6) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, 87, 2200 (1965).

(7) The parent cycloheptatrienyl trianion has recently been reported by Bates and co-workers. J. J. Bahl, R. B. Bates, W. A. Beavers, and C. R. Launer, *J. Am. Chem. Soc.*, 99, 6126 (1977).

(8) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, 85, 2729 (1963).

(9) C. F. H. Allen and J. A. Van Allen, *J. Am. Chem. Soc.*, 72, 5165 (1950).

(10) E. C. Wagner and W. C. Hunt, *J. Chem. Educ.*, 28, 309 (1951).

identified by its IR spectrum and melting point.

***endo*-1,5-Dimethyl-2,3,4,6,7-pentaphenyltricyclo[3.2.1.0^{2,4}]-6-octen-8-one (3a).** This compound was prepared in 95% yield according to the procedure of Anderson and Hassner[11] and identified by its IR, NMR, and mass spectra and melting point.

***endo*-1,2,3,4,5,6,7-Heptaphenyltricyclo[3.2.1.0^{2,4}]-6-octen-8-one (3b).** This compound was prepared in 85% yield according to the procedure of Battiste[12] and identified by its IR, NMR, and mass spectra.

***endo*-1,5-Dimethyl-2,3,4,6,7-pentaphenyltricyclo[3.2.1.0^{2,4}]-6-octen-8-one (3a) and Potassium *tert*-Butoxide in Me_2SO.** Potassium *tert*-butoxide (0.500 g, 0.0046 mol) was added to a solution of **3a** (0.528 g, 0.0010 mol) in Me_2SO (15 mL) with stirring under nitrogen. The deep blue reaction mixture was stirred for 72 h at 70 °C. The reaction mixture was then poured into 100 mL of water and extracted three times with ether. The aqueous solution was acidified with dilute hydrochloric acid and extracted three more times with ether. The first set of ether extracts were combined and dried over sodium sulfate. Removal of the solvent and recrystallization of the resulting solid from 95% ethanol afforded 0.288 g (75%) of 5-methyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**4a**), mp 182–183 °C. The product's IR and NMR spectra were identical with those of an authentic sample, and a mixture melting point gave no depression. The second set of ether extracts were also combined and dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol afforded 0.069 g (43%) of *cis*-2-methyl-3-phenylacrylic acid (**5a**), mp 81–82 °C. The product's IR and NMR spectra were identical with those of an authentic sample, and a mixture melting point gave no depression.

***endo*-1,2,3,4,5,6,7-Heptaphenyltricyclo[3.2.1.0^{2,4}]-6-octen-8-one (3b) and Potassium *tert*-Butoxide in Me_2SO.** Potassium *tert*-butoxide (0.510 g 0.0046 mol) was added to a solution of **3b** (0.652 g, 0.0010 mol) in Me_2SO (15 mL) with stirring under nitrogen. The deep blue reaction mixture was stirred at 70 °C for 72 h. The reaction mixture was poured into 100 mL of water and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol/benzene afforded 0.348 g (78%) of 1,2,3,4,5-pentaphenylcyclopentadiene (**4b**), mp 253–255 °C. The product's IR and NMR spectra were identical with those of an authentic sample, and a mixture melting point gave no depression. The aqueous mixture was acidified with dilute hydrochloric acid and extracted three times with ether. The combined extracts were dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol afforded 0.043 g (20%) of *cis*-2,3-diphenylacrylic acid (**5b**), mp 172–173 °C. The product's IR and NMR spectra were identical with those of an authentic sample, and a mixture melting point gave no depression.

5-Methyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene (4a). To 2.00 g (0.0052 mol) of tetracyclone in 80 mL of ether was added 1.00 g (0.0264 mol) of lithium aluminum hydride with stirring under nitrogen. The solution was stirred for 24 h at room temperature. The reaction mixture was worked up successively with ethyl acetate, absolute ethanol, and finally excess water. Dilute hydrochloric acid was added to acidify the solution. The mixture was extracted two times with ether, and the combined extracts were dried over sodium sulfate. The solvent was removed and the resulting alcohol recrystallized from benzene/hexane, yielding 1.80 g (90%) of 1-hydroxy-2,3,4,5-tetraphenyl-2,4-cyclopentadiene, mp 150–151 °C.

To 1.10 g (0.002 85 mol) of 1-hydroxy-2,3,4,5-tetraphenyl-2,4-cyclopentadiene in 25 mL of benzene was added 0.540 g (0.002 85 mol) of *p*-toluenesulfonyl chloride. The mixture was stirred at room temperature and 3 mL (0.0373 mol) of pyridine added slowly. The reaction mixture was stirred for 1 h, and then the solvent was removed. The resulting solid tosylate ester was recrystallized from cyclohexane, yielding 1.20 g (75%) of 2,3,4,5-tetraphenyl-2,4-cyclopentadienyl 1-tosylate, mp 164–165 °C.

To 0.24 g (0.010 mol) of magnesium turnings in 20 mL of ether was added 1.41 g of methyl iodide (0.010 mol) with stirring under nitrogen. The exothermic Grignard reaction proceeded smoothly until almost all of the magnesium was consumed. At this point, 0.25 g (0.0048 mol) of 2,3,4,5-tetraphenyl-2,4-cyclopentadienyl 1-tosylate in 20 mL of ether was added slowly and allowed to react for 1 h after completion of the addition. The reaction mixture was worked up with dilute hydrochloric acid and extracted two times with ether. The combined ether extracts were dried over sodium sulfate. Evaporation of the solvent left a brown solid that was recrystallized from 95% ethanol/benzene and yielded 0.030 g (16%, 0.000 78 mol) of 5-methyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**4a**), mp 183.5–184 °C.

***trans*-2-Methyl-3-phenylacrylic Acid (5a).** This compound was prepared in 52% yield according to the procedure of Cohen and Whiteley[13] and identified by its NMR spectrum and melting point.

1,2,3,4,5-Pentaphenylcyclopentadiene (4b). This compound was prepared in 61% yield according to the procedure of Rio and Sang[14] and identified by its NMR spectrum and melting point.

***cis*-2,3-Diphenylacrylic Acid (5b).** This compound was prepared in 52% yield according to the procedure of Burkles and Bremmer[15] and identified by its NMR spectrum and melting point.

1,2,3,4,5,6,7-Heptaphenylbicyclo[4.1.0]-4-heptene-2-carboxylic Acid (6b). To 0.510 g (4.56 mmol) of potassium *tert*-butoxide in 15 mL of Me_2SO was added 0.652 g (1.00 mmol) of **3b** under nitrogen with stirring. The dark blue reaction solution was heated at 70 °C for 15 min, and the reaction mixture was poured into 100 mL of water. The aqueous solution was acidified with dilute hydrochloric acid and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. The solvent was removed and the resulting solid recrystallized from 100% ethanol, yielding 0.295 g (44%) of 1,2,3,4,5,6,7-heptaphenylbicyclo[4.1.0]-4-heptene-2-carboxylic acid (**6b**), mp 370 °C (sublimes). The ultraviolet spectrum (THF) had λ_{max} at 245 nm (ϵ 20 400) and 275 (sh, ϵ 7440). The NMR spectrum ($CDCl_3$) showed peaks centered at τ 3.00 (m, 35 H, assigned to the aromatic protons), 6.17 (s, 1 H, assigned to the benzyl proton), 6.43 (assigned to the cyclopropyl proton), and −2.00 (s, 1 H, assigned to the carboxylic acid proton). The IR spectrum (KBr pellet) showed a carboxylic acid carbonyl stretch at 1710 cm^{-1} and a broad OH stretch at 3500 cm^{-1}.

Anal. Calcd for $C_{50}H_{38}O_2$: C, 89.54; H, 5.68; O, 4.78; mol wt 670. Found: C, 89.72; H, 5.90; mol wt (mass spectrum) 670.

When the reaction was carried out under the same conditions in Me_2SO-d_6, there was obtained 0.605 g (90%) of product, and the low-field signal at τ 6.17 due to the benzylic proton at C-3 was absent in the NMR spectrum.

2,5-Dimethyl-1,3,4,6,7-pentaphenylbicyclo[4.1.0]-4-heptene-2-carboxylic Acid (6a). To 0.510 g (4.56 mmol) of potassium *tert*-butoxide in 15 mL of Me_2SO was added 0.528 g (1.00 mmol) of **3a** under nitrogen with stirring. The dark blue solution was heated at 70 °C for 15 min, and the reaction mixture was poured into 100 mL of water. The aqueous solution was acidified with dilute hydrochloric acid and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. The solvent was removed and the resulting solid recrystallized from chloroform, yielding 0.490 g (90%) of colorless needles of 2,5-dimethyl-1,3,4,6,7-pentaphenylbicyclo[4.1.0]-4-heptene-2-carboxylic acid (**6a**), mp 278–280 °C. The ultraviolet spectrum (dioxane) had λ_{max} at 217 nm (ϵ 9200) and 254 (sh, ϵ 1950). The NMR spectrum ($CDCl_3$) showed peaks centered at τ 3.00 (m, 25 H, assigned to the aromatic protons), 4.82 (s, 1 H, assigned to the benzyl proton), 5.30 (s, 1 H, assigned to the cyclopropyl proton), 8.46 (s, 3 H, assigned to the allylic methyl protons), 9.27 (s, 3 H, assigned to the tertiary methyl protons), and −2.10 (s, 1 H, assigned to the carboxylic acid proton). The IR spectrum (KBr pellet) showed a carboxylic acid carbonyl stretch at 1700 cm^{-1} and a broad OH stretch at 3500 cm^{-1}.

Anal. Calcd for $C_{40}H_{34}O_2$: C, 87.90; H, 6.23; mol wt 546. Found: C, 87.84; H, 6.27; mol wt (mass spectrum) 546.

When the reaction was carried out under the same conditions

(11) D. J. Anderson and A. Hassner, *J. Am. Chem. Soc.*, **93**, 4339 (1971).
(12) M. A. Battiste, *Chem. Ind. (London)*, 550 (1961).
(13) J. B. Cohen and C. E. Whiteley, *J. Chem. Soc.*, 1312 (1901).
(14) G. Rio and G. Sang, *Bull. Soc. Chim. Fr.*, 3775 (1966).
(15) R. E. Burkles and K. Bremmer, "Organic Syntheses", Collect. Vol IV, Wiley, New York, 1963, p 777.

in Me_2SO-d_6, there was obtained 0.480 g (88%) of product, and the low-field signal at τ 4.82 due to the benzylic proton at C-3 was absent in the NMR spectrum.

Lithium Aluminum Hydride Reduction of *endo*-1,5-Dimethyl-2,3,4,6,7-pentaphenyltricyclo[3.2.1.$0^{2,4}$]-6-octen-8-one (3a) in Ether. To 1.056 g (2.00 mmol) of **3a** in 10 mL of ether was added 0.050 g (1.50 mmol) of lithium aluminum hydride under nitrogen with stirring. The reaction mixture was stirred at room temperature for 24 h and worked up successively with ethyl acetate, 100% ethanol, and water. The resulting solution was extracted three times with ether, and the combined ether extracts were dried over sodium sulfate. The solvent was removed, and the solid residue was recrystallized from ethanol/benzene, yielding 0.610 g (60%) of *endo*-1,5-dimethyl-2,3,4,6,7-pentaphenyltricyclo[3.2.1.$0^{2,4}$]-6-octen-8-ol (8), mp 234–235 °C. The NMR spectrum (CCl_4) showed peaks centered at τ 3.00 (m, 25 H, assigned to the aromatic protons), 6.27 (d, 1 H, assigned to the bridged proton), 6.90 (s, 1 H, assigned to the cyclopropyl proton), 7.80 (d, 1 H assigned to the hydroxyl proton), and 9.20 (s, 6 H, assigned to the tertiary methyl protons). The IR spectrum (KBr pellet) showed a broad OH stretching at 3500 cm^{-1} and no carbonyl absorption. The ultraviolet spectrum gave a shoulder at 275 nm (ϵ 10 100).

Anal. Calcd for $C_{40}H_{34}O$: C, 90.58; H, 6.42; mol wt 530. Found: C, 90.69; H, 6.66; mol wt (mass spectrum) 530.

***endo*-1,5-Dimethyl-2,3,4,6,7-pentaphenyltricyclo-[3.2.1.$0^{2,4}$]-6-octen-9-ol (8) and Potassium *tert*-Butoxide in Me_2SO.** To 0.510 g (4.56 mmol) of potassium *tert*-butoxide in 15 mL of Me_2SO was added 0.530 g (1.00 mmol) of **8** with stirring under nitrogen. The deep red reaction mixture was heated to 70 °C for 2 h and poured into 100 mL of water. The solution was acidified with saturated ammonium chloride solution and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. The solvent was removed and the solid recrystallized from 100% ethanol, yielding 0.23 g (44%) of 1,5-dimethyl-2,3,4,6,7-pentaphenyltricyclo[3.2.1.$0^{4,6}$]-2-octen-8-ol (**9**), mp 285–287 °C. The NMR spectrum ($CDCl_3$) showed peaks centered at τ 5.90 (s, 1 H, assigned to the bridge proton), 7.87 (s, 1 H, assigned to the hydroxyl proton), 6.73 (s, 1 H, assigned to the benzyl proton), 8.40 (s, 3 H, assigned to the cyclopropyl methyl protons), and 8.91 (s, 3 H, assigned to the tertiary methyl protons). The IR spectrum (KBr pellet) showed a broad OH stretching at 3500 cm^{-1} and an overall pattern different from the starting material. The ultraviolet spectrum showed a shoulder at 270 nm (ϵ 4100).

Anal. Calcd for $C_{40}H_{34}O$: C, 90.58; H, 6.42; mol wt 530. Found: C, 90.62; H, 6.63; mol wt (mass spectrum) 530.

1,4-Dimethyl-2,3,5,6,7-pentaphenyl-3,5-cycloheptadiene-1-carboxylic Acid (7a). To 0.510 g (4.56 mmol) of potassium *tert*-butoxide in 15 mL of Me_2SO was added 0.528 g (1.00 mmol) of **3a** under nitrogen with stirring. The dark reddish blue solution was heated at 70 °C for 3 h and the reaction mixture poured into 100 mL of water. The aqueous solution was acidified with dilute hydrochloric acid and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. The solvent was removed and the resulting solid recrystallized twice from benzene, yielding 0.099 g (18%) of 1,4-dimethyl-2,3,5,6,7-pentaphenyl-3,5-cycloheptadiene-1-carboxylic acid (**7a**), mp 294–296 °C. The ultraviolet spectrum (THF) had λ_{max} at 273 nm (ϵ 14 700). The NMR spectrum ($CDCl_3$) showed peaks centered at τ 3.00 (m, 25 H, assigned to the aromatic protons), 4.57 (s, 1 H, assigned to a benzyl proton), 6.50 (s, 1 H, assigned to the other benzyl proton), 8.06 (s, 3 H, assigned to the allylic methyl protons), and 9.48 (s, 3 H, assigned to the tertiary methyl protons). The IR spectrum showed a broad OH stretch at 3500 cm^{-1} and a carboxylic acid carbonyl stretch at 1700 cm^{-1}. No strained carbonyl stretch was detected.

Anal. Calcd for $C_{40}H_{34}O_2$: C, 87.90; H, 6.23; mol wt 546. Found: C, 87.79; H, 6.39; mol wt (mass spectrum) 546.

1,2,3,4,5,6,7-Heptaphenyl-3,5-cycloheptadiene-1-carboxylic Acid (7b). To 0.510 g (4.56 mmol) of potassium *tert*-butoxide in 15 mL of Me_2SO was added 0.652 g (1.00 mmol) of *endo*-1,2,3,4,5,6,7-heptaphenyltricyclo[3.2.1.$0^{2,4}$]-6-octen-8-one (**3b**) with stirring under nitrogen. The deep blue reaction mixture was stirred at 70 °C for 3 h. The reaction mixture was poured into 100 mL of water. The solution was acidified with dilute hydrochloric acid and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. The solvent was removed and the resulting solid recrystallized twice from 100% ethanol, yielding 0.140 g (22%) of 1,2,3,4,5,6,7-heptaphenyl-3,5-cyclohexadiene-1-carboxylic acid (**7b**), mp 381–384 °C. The ultraviolet spectrum (THF) had λ_{max} at 270 (sh, ϵ 18 800). The NMR spectrum ($CDCl_3$) showed peaks centered at τ 3.10 (m, 35 H, assigned to the aromatic protons), 4.97 (s, 1 H, assigned to a benzyl proton), and 5.60 (s, 1 H, assigned to the other benzyl proton). The IR spectrum (KBr pellet) showed a broad OH stretch at 3500 cm^{-1} and a carboxylic acid carbonyl stretch at 1700 cm^{-1}. No strained carbonyl stretch was detected.

Anal. Calcd for $C_{50}H_{38}O_2$: C, 89.54; H, 5.68; mol wt 670. Found: C, 89.31; H, 5.82; mol wt (mass spectrum) 670.

Thermal Reaction of *endo*-1,5-Dimethyl-2,3,4,6,7-pentaphenyltricyclo[3.2.1.$0^{2,4}$]-6-octen-8-one (3a) in Me_2SO. A solution of **3a** (0.0528 g, 0.10 mmol) in 3 mL of Me_2SO was stirred for 72 h under nitrogen at 70 °C. Only unreacted starting material was recovered.

Thermal Reaction of *endo*-1,2,3,4,5,6,7-Heptaphenyltricyclo[3.2.1.$0^{2,4}$]-6-octen-8-one (3b) in Me_2SO. A solution of **3b** (0.0652 g, 0.10 mmol) in 3 mL of Me_2SO was stirred for 72 h under nitrogen at 70 °C. The solution was poured into water and the precipitate collected. Recrystallization from benzene yielded (96%) of 1,2,3,4,5,6,7-heptaphenyltropylidene. A mixture melting point with an authentic sample gave no depression. A small amount (2%) of tetracyclone was identified by its visible spectrum.

Registry No. **3a**, 39934-05-9; **3b**, 17875-72-8; **4a**, 72318-01-5; **4b**, 2519-10-0; **5a**, 1895-97-2; **5b**, 91-48-5; **6a**, 72331-00-1; **6b**, 72318-02-6; **7a**, 72331-01-2; **7b**, 72318-03-7; **8**, 72318-04-8; **9**, 72318-05-9; tetracyclone, 479-33-4; 1-hydroxy-2,3,4,5-tetraphenyl-2,4-cyclopentadiene, 42220-67-7; 2,3,4,5-tetraphenyl-2,4-cyclopentadienyl 1-tosylate, 72318-06-0; 1,2,3,4,5,6,7-heptaphenyltropylidene, 1835-56-9.