washed with brine, dried ($MgSO_4$), and freed of solvent. The residual oil, when subjected to flash chromatography on silica gel with 3:1 hexane/ethyl acetate for elution, afforded 1.32 g (81%) of **9** as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.40 (s, 3), 1.83–2.33 (m, 2), 2.17 (s, 3), 2.53 (t, J = 8 Hz, 2), 3.21, 3.23 (s, 6), 3.70 (s, 3), 3.88 (t, J = 8 Hz, 1).

A solution of 534 mg (2.0 mmol) of **9**, 1 mL of H_2O, and 100 mg of TsOH in 300 mL of toluene was heated at reflux for 12 h. Upon cooling, it was diluted with ether, washed with diluted $NaHCO_3$ and brine; dried ($MgSO_4$) and concentrated to 5 – 10 mL volume. Flash chromatography on silica after elution with 6:1 hexane:ethyl acetate afforded 106 mg (37%) of **10** as a light yellow oil: IR ($CHCl_3$) ν_{max} 1707, 1689, 1675, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (t, J = 2 Hz, 3), 2.45–2.76 (m, 2), 2.48 (s, 3), 2.67–2.90 (m, 2); mass spectrum, m/e 138.0703 (calcd for $C_8H_{10}O_2$, 138.0680 (parent)). Continued elution with 4:1 hexane/ethyl acetate afforded 25 mg (6%) of **12** whose spectral characteristics are described in the next experiment.

Methyl 2-Acetyl-4-oxo-2-cyclohexene-1-carboxylate (12). To a solution of 914 mg (48 mmol) of methyl 4,4-dimethoxy-3-oxopentanoate (**5**) and 608 mg (8.7 mmol) of methyl vinyl ketone at 0 °C was added, in rapid dropwise fashion, 3 mL of methanol containing 1.2 mmol of sodium methoxide. The reaction mixture was maintained at 4 °C overnight and was poured into 200 mL of ether and 100 mL of saturated NH_4Cl. The organic layer was washed with brine, dried ($MgSO_4$), and freed of solvent. Flash chromatography of the residual oil on silica gel and elution with 3:1 hexane/ethyl acetate afforded 42 mg (3.3%) of **9**. Further elution with 2:1 hexane/ethyl acetate afforded 934 mg (74%) of the β-ketol epimers **11** as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.4 (s), 1.9–2.6 (m) 3.28 (s), 3.32 (s), 3.40–3.65 (m), 3.97–4.24 (m).

A solution of 195 mg of the ketol **11**, 0.1 mL of H_2O, and 43 mg of TsOH in 50 mL of toluene was heated at reflux for 2.5 h. Upon cooling, the reaction mixture was diluted with ether, washed with diluted $NaHCO_3$ and brine, dried ($MgSO_4$), and freed of solvent to afford 107 mg (73%) of **12**: IR ($CHCl_3$) 1733, 1684, 1602 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0–2.7 (m, 4), 2.44 (s, 3), 3.73 (s, 3) 3.7–3.9 (m, 1), 6.63 (s, 1); mass spectrum, m/e 196.0747 (calcd for $C_{10}H_{12}O_4$, 196.0734 (parent)).

Acknowledgment. This research was supported by a grant from the National Institutes of Health (CA 28824).

Registry No. **5**, 62759-83-5; **7a** (isomer 1), 83220-21-7; **7a** (isomer 2), 83220-22-8; **7b** (isomer 1), 83220-23-9; **7b** (isomer 2), 83220-24-0; **7c** (isomer 1), 83220-25-1; **7c** (isomer 2), 83220-26-2; **8a**, 83220-27-3; **8b**, 83220-28-4; **8c**, 83220-29-5; **9**, 83220-30-8; **10**, 83220-31-9; *cis*-**11**, 83220-32-0; *trans*-**11**, 83232-00-2; **12**, 83220-33-1; methyl vinyl ketone, 78-94-4; Δ^2-cycloheptanone, 1121-66-0; Δ^2-cyclohexenone, 930-68-7; Δ^2-cyclopentenone, 930-30-3; coriolin, 33404-85-2.

1-Phenyl-3,4:5,6-dibenzocycloheptatrienyl Anion. A Stable Antiaromatic Carbanion

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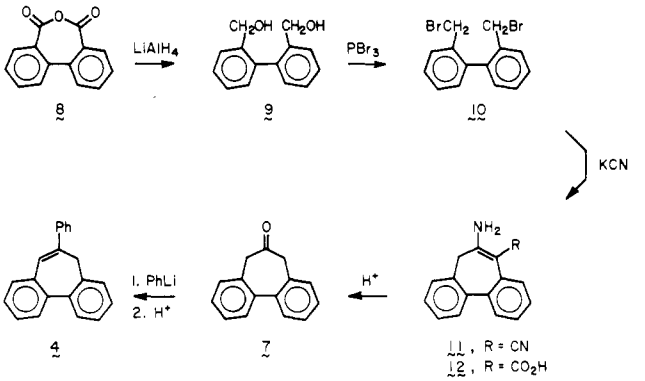
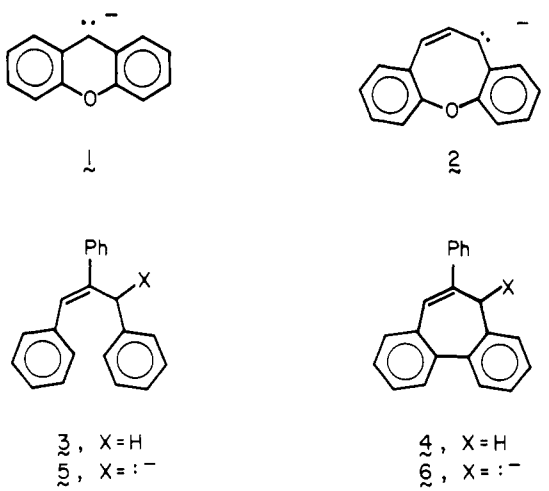
A major hindrance to the study of antiaromatic anions is the lack of stable examples that can be studied by conventional techniques. Staley has studied the 8-π-electron cycloheptatrienyl anion, for instance, and noted its instability and propensity for undergoing addition reactions.[1a] Its benzo analogue, moreover, has been studied by NMR techniques and exhibits decidedly paratropic behavior.[1b] Anastassiou has reported on the paratropic properties of the formally 8-π-electron xanthenyl anion (**1**),[2] which is in marked contrast to the potentially but apparently *not* aromatic dibenzo[*b*,*g*]oxocinide anion **2**.[3] Since the imponderables associated with electronegativity may obscure the effects of antiaromaticity for the former anion, we chose to investigate a carbocyclic analogue stabilized as in **1** and **2** by benzo groups. In the course of our photochemical studies of carbanions[4] we had occasion to synthesize 1,2,3-triphenylpropene (**3**) and its cyclic analogue, 1-phenyl-3,4:5,6-dibenzocycloheptatriene (**4**). This allowed us to investigate not only paratropic effects but also the potential destabilization induced by cyclization of an eight-electron system. In contrast to the conjugate base **5** of the former, the anion **6** derived from the latter showed definite paratropic behavior and other evidence of antiaromaticity in a system not encumbered by heteroatoms.

Scheme I. Synthesis of Dibenzocycloheptatriene 4.





1-Phenyl-3,4:5,6-dibenzocyclohepta-1,3,5-triene (**4**), mp 92–94 °C, was synthesized by phenyllithium addition to the known 3,4:5,6-dibenzocyclohepta-3,5-dien-1-one (**7**)[5] followed by dehydration in acetic acid/sulfuric acid. Ketone **7** itself was achieved in overall 43% yield through an improvement on the literature[4] procedure with use of more readily available starting materials (see Scheme I). Thus, lithium aluminum hydride reduction of diphenic anhydride (**8**) yielded [1,1′-biphenyl]-2,2′-dimethanol (**9**),

(1) (a) Staley, S. W.; Orvedal, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 1618. (b) *Ibid.* **1973**, *95*, 3382.

(2) Anastassiou, A. G.; Kasmai, H. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 43.

(3) (a) Anastassiou, A. G.; Kasmai, H. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 393. (b) Kasmai, H. S.; Whitlock, H. W., Jr. *J. Org. Chem.* **1972**, *37*, 2161.

(4) Tolbert, L. M.; Ali, M. Z. *J. Am. Chem. Soc.*, submitted for publication.

(5) Kenner, J.; Turner, E. G. *J. Chem. Soc.* **1911**, *99*, 2101.

0022-3263/82/1947-4793$01.25/0

Table I. Properties of Cyclic and Acyclic Anions and Neutrals

property[a]	hydrocarbon → anion			
	4 →	6	3 →	5
pK_a	30.7 ± 0.3		28.9 ± 0.3	
^{13}C NMR, ppm:				
(1)[a]	*b*, *c*	121.02[c]	*b*, *c*	111.96[c]
(3)	36.82	121.02	36.12	111.96
(2, 4-13)	125.64, 126.39, 126.76, 126.84, 127.38, 127.75, 128.50, 129.56, 129.83, 136.59, 138.40, 139.25, 141.57, 143.35	121.95, 124.00, 125.02, 127.03, 127.85, 130.00, 141.95, 163.95 (w)	125.92, 126.52, 126.94, 127.25, 128.35, 128.54, 130.29, 137.76, 139.16, 139.69, 142.50	122.48, 124.98, 126.79, 127.06, 127.75, 128.21, 128.87, 143.94, 144.81
^1H NMR, ppm:				
(1)[a]	6.86[e]	3.33[d]	*b*, *c*	5.14[d]
(3)	3.50	3.33	4.10	5.14
(2, 4-13)	7.25-7.80	5.35 (5,5'),[a] 5.64 (8,8'), 5.94 (7,7'),[f] 6.04 (6,6'),[f] 6.94-6.99, 7.12-7.28	7.04-7.41, 7.47-7.59	4.95 (9,9'),[g] 6.08 (7,7'), 6.88-6.86, 7.69 (5,5')

[a] Numbers listed in parentheses correspond to atoms labeled in Figure 1. [b] These absorptions cannot be distinguished from aromatic absorptions. [c] Me_2SO-d_6. [d] THF-d_8. [e] $CDCl_3$. [f] Identity determined through decoupling. [g] Details of these assignments will be published in a full paper.

which was converted to the dibromide **10** with phosphorus tribromide. Under conditions required for nucleophilic displacement with cyanide, simultaneous Thorpe cyclization to amino nitrile **11** occurred. A two-step hydrolysis with sulfuric acid followed by phosphoric acid yielded ketone **7** as a crystalline solid, mp 78–79 °C. The hydrocarbon underwent ready loss of a proton in dimethyl sulfoxide containing dimsyl potassium to yield a deep-purple solution. (*E*)-1,2,3-Triphenylpropene (**3**), mp 66–67 °C, was prepared according to the literature procedure[6] and underwent similar deprotonation.

A method similar to that of Bordwell[7] with biphenylyldiphenylmethane as indicator was used to determine the pK_a's of the hydrocarbons (see Table I). The ^1H and ^{13}C NMR spectra were also acquired of the hydrocarbons and their conjugate bases. At room temperature in Me_2SO, the ^{13}C chemical shift of the allylic carbon atoms underwent a marked downfield shift upon deprotonation. The interconversion of the *E,E* and *E,Z* forms of **5** obscured the room-temperature ^1H spectra, so low-temperature spectra in THF were obtained. At −50 °C, the *E,E* and *E,Z* forms of anion **5** were readily resolvable,[8] and thus a direct correlation between the cyclic anion **6** and the conformationally equivalent *E,E* propenyl anion was feasible. The significant chemical shifts of the atoms at C-1 of hydrocarbons and their conjugate bases are shown in Table I. The spectra of the cyclic hydrocarbon **4** and its conjugate base **6** are shown in Figure 1.

The decreased acidity of hydrocarbon **4** in comparison to **3** is consistent with less resonance stabilization in the cyclic anion than in the acyclic analogue. This is in marked contrast to the increase in acidity associated with a similar cyclization of triphenylmethane to 9-phenylfluorene, which has an aromatic conjugate base (see Chart I).[7,9] A complicating factor is the effect of cyclization on increased resonance stabilization through more efficient π overlap, independent of aromaticity effects. In the case of 9-phenyl-9,10-dihydro-10,10-dimethylanthracene (**13**) this enhancing effect was small. An opposing effect might be the strain induced in forming a seven-membered ring. The allylic protons of **4** are nonequivalent in the room-temperature proton NMR and coalesce at ca. 50 °C into a broad singlet at δ 3.5, indicating some barrier to attainment of planarity. However, for the seven-membered analogue phenyldibenzocycloheptadiene (**14**), the effect of ring formation was neutral.[9] In the particular case of the cyclic hydrocarbon **4**, then, ring formation alone might be expected to *increase* rather than decrease the acidity, in contrast to the observed results.

More intriguing are the NMR results. On the one hand, the downfield shift of the allylic *carbons* of cyclic anion **6** as compared to acyclic anion **5** is indicative of enhanced delocalization in the cyclic species, although slight hybridization differences may also play a role. This contrasts with the localizing effect of the oxygen atom in the xanthyl anion **1**.[2] On the other hand, the upfield shift of the allylic *protons* upon cyclization indicates the presence of a significant paramagnetic ring current. This ring current is in further evidence for the benzo protons, which show a shift from δ 7.0–8.0 to 5.0–6.0. Especially noteworthy is the shift of the peri protons from δ 8.0 to 5.5. Thus the presence of large upfield proton shifts in the presence of downfield carbon shifts for the cyclic as compared to acyclic anion is convincing evidence that the 1-phenyl-3,4:5,6-dibenzocycloheptatrienyl anion is a carbocyclic antiaromatic species.

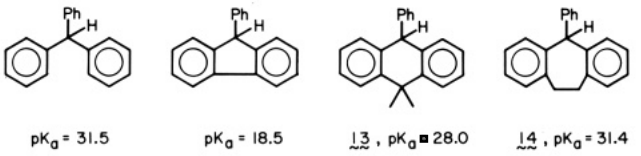
Experimental Section

Nuclear magnetic resonance spectra were obtained on a Varian XL-200 multinuclear spectrometer or on a Varian EM-390 spectrometer. Low-temperature spectra were run in tetrahydrofuran-d_8, while room-temperature spectra were acquired in both tetrahydrofuran-d_8 and dimethyl-d_6 sulfoxide. Analyses were performed by Galbraith Laboratories of Knoxville, TN.

Solutions of hydrocarbon anions were prepared in dimethyl sulfoxide by use of published methods.[7] The hydrocarbon acidities were determined by use of a modification of the method of Bordwell.[7] This method employed a Gilford Model 250 single-beam spectrophotometer interfaced to a DEC LSI-11 based minicomputer.[10] Dimethyl sulfoxide solutions of the unknown anion in the presence of excess hydrocarbon were subjected to successive dilutions with indicator hydrocarbon. The spectrum

(6) Mulvaney, J. E.; Savage, D. *J. Org. Chem.* **1971**, *36*, 2592.
(7) Matthews, W. S.; Bares, J. E; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, A.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.
(8) Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R. *Liebigs Ann. Chem.* **1980**, 1135.
(9) Streitwieser, A., Jr.; Nebenzahl, L. L. *J. Org. Chem.* **1978**, *43*, 598.
(10) Our apparatus and method will be described in a full paper.

Chart I. Effect of Cyclization on pK_a[9]



was acquired after each dilution, and the amount of each anion (indicator and unknown) was determined by a digital decomposition of the spectra, using least-squares techniques and the stored spectra of the pure anions. From the equilibrium constant between indicator and unknown determined by this measurement, the pK was calculated with the known pK_a of the indicator biphenylyldiphenylmethane.[7]

[1,1′-Biphenyl]-2,2′-dimethanol (9). This compound was prepared according to the procedure of Rieche and co-workers[11] and also by modification of their procedure. Two procedures were used. Procedure A gave better yields but used more expensive diphenic anhydride. Procedure B using diphenic acid was employed for large scale preparations.

Procedure A. To a stirred suspension of 3.5 g of $LiAlH_4$ (0.092 mol) in 80 mL of absolute Et_2O and 65 mL of dry benzene was added 10.0 g (0.044 mol) of solid diphenic anhydride. The mixture was refluxed for 12 h, quenched with H_2O, and fitlered. The residue was extracted with hot Et_2O, and the combined organic solutions were dried over $MgSO_4$ and evaporated in vacuo to yield 7.60 g (80%) of biphenyldimethanol: mp 110–112 °C (lit.[1] mp 112 °C); NMR ($CDCl_3$) δ 3.31 (s 2 H), 4.20 (s, 4 H), 6.76–7.42 (m, 8 H).

Procedure B. To a stirred suspension of 12.0 g of $LiAlH_4$ (0.300 mol) in 100 mL of dry THF was added dropwise 48.4 g (0.200 mol) of diphenic acid in 75 mL of dry THF (ca. 45 min). The mixture was refluxed for 48 h, quenched with H_2O, and filtered. The residue was dissolved in 150 mL of concentrated HCl and extracted with ether. The combined organic extract was washed with H_2O, dried over $MgSO_4$, and concentrated in vacuo to yield 26.5 g (62%) of biphenyldimethanol, mp 109–112 °C.

2,2′-Bis(bromomethyl)biphenyl (10). To a solution of 5.00 g of PBr_3 (18.5 mmol) in 50 mL of $CHCl_3$ was added 5.50 g (25.7 mmol) of [1,1′-biphenyl]-2,2′-dimethanol (**9**) in 50 mL of $CHCl_3$ over a period of 5 min and the solution refluxed for 48 h. Water quenching, successive washing with dilute HCl, $NaHCO_3$, and H_2O, drying over $MgSO_4$, and evaporation under reduced pressure produced the crude dibromide. Slow recrystallization from acetone gave 7.03 g (81%) of 2,2′-bis(bromomethyl)biphenyl as off-white plates: mp 87–88 °C (lit.[5] mp 87.5 °C); NMR ($CDCl_3$) δ 4.09 (AB q, J = 10.2 Hz, 4 H), 6.95–7.47 (m, 8 H).

1-Amino-2-cyano-3,4:5,6-dibenzocycloheptatriene (11). A saturated aqueous solution of potassium cyanide (72 g in 15 mL of H_2O) was mixed with 45 mL of EtOH. The mixture was heated to reflux, and 16.2 g (48 mmol) of finely powedered 2,2′-bis(bromomethyl)biphenyl (**10**) was added in small portions (ca. 45 min). The solution was refluxed for 16 h and upon cooling to room temperature, a solid formed. Water (ca. 100 mL) was added and the solid was recovered by suction filtration and washed twice with 25 mL of H_2O. Recrystallization in 95% ethanol yielded 10.6 g (80%) of colorless needles: mp 188–190 °C (lit.[5] mp 189 °C); NMR ($CDCl_3$) δ 3.23 (AB q, J = 12.0 Hz, 4 H, 7.13–7.77 (m, 8H).

1-Amino-3,4:5,6-dibenzocycloheptatriene-2-carboxylic Acid (12). To 30 mL of ice-cold concentrated H_2SO_4 was added 6.08 g (25.9 mmol) of 1-amino-3-cyano-3,4:5,6-dibenzocycloheptatriene (**11**) and the resulting mixture was allowed to stand over night at room temperature. The solution was poured onto 100 mL of crushed ice and the precipitate was collected by suction filtration. Recrystallization from 95% ethanol yielded 5.66 g (86%) of colorless needles: mp 178–180 °C (lit.[5] mp 180 °C); NMR ($CDCl_3$) δ 3.01 (s, 2 H), 5.32 (br s, 2 H), 6.63–7.27 (m, 9 H). This compound was also prepared according to the procedure of Kenner and Turner in 86% yield.[5]

(11) Rieche, A.; Hoeft, E.; Schultze, H. *Justus Liebigs Ann. Chem.* **1966**, *697*, 188.

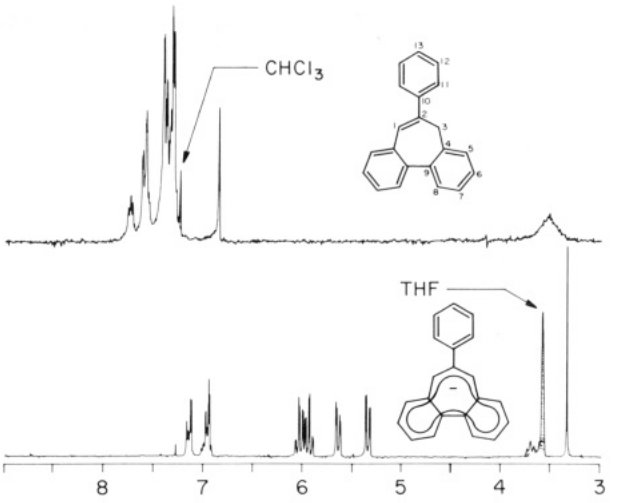


Figure 1. Proton NMR spectra of **4** and **6** (200 MHz).

3,4:5,6-Dibenzocycloheptatrien-1-one (7). This compound was prepared by adapting the procedure of Baldwin,[12] since attempted direct conversion of amino nitrile **11** to the ketone resulted in formation of a keto nitrile that resisted further hydrolysis.

Under an argon atmosphere, 2.90 g (11.7 mmol) of 1-amino-3,4:5,6-dibenzocycloheptatriene-2-carboxylic acid (**12**) was dissolved in a solution of 25 mL of glacial acetic acid and 1.5 mL of distilled water. The solution was gently refluxed for 10 min and then 30 mL of 85% phosphoric acid was added dropwise. The reflux was continued for another 16 h, and the solution was cooled and poured onto 100 g of crushed ice. Ether extraction, washing with H_2O and $NaHCO_3$, drying over $MgSO_4$, and vacuum evaporation gave a light-yellow liquid, which solidified upon standing. Recrystallization in absolute ethanol yielded 1.9 g (80%) of light-yellow hexagonal prisms: mp 78–79 °C (lit.[5] mp 78–79 °C); NMR ($CDCl_3$) δ 3.33 (s, 4 H), 6.73–7.30 (m, 8 H).

1-Phenyl-3,4:5,6-dibenzocycloheptatriene (6). A solution of 1.91 g (9.2 mmol) of 3,4:5,6-dibenzocycloheptatrien-1-one (**7**) in 30 mL of anhydrous ether was cooled by dry ice–acetone (–78 °C) and PhLi (prepared from 6.9 mL of 1.6 N *n*-BuLi and 1.2 mL of bromobenzene in 15 mL of anhydrous ether) was added dropwise via syringe. The solution was allowed to warm to room temperature, decomposed with water, extracted with ether, dried over magnesium sulfate, and concentrated *in vacuo*. The NMR indicated 66% starting ketone. The treatment with PhLi, extraction, drying, and solvent removal was repeated twice. The crude alcohol was dissolved in 20 mL of glacial acetic acid, 3–4 drops of sulfuric acid were added, and the solution was refluxed until all the alcohol had disappeared (ca. 2 h, monitored by TLC). The solution was allowed to cool to room temperature, and 30 mL of water was added. The resulting mixture was extracted with ether, washed with sodium bicarbonate, water, dried over magnesium sulfate, and concentrated. Chromatography on a 2 × 40 cm silica gel column packed in hexane and eluted with 500 mL of 20% chloroform–hexane yielded 0.89 g (36%) of 1-phenyl-3,4:5,6-dibenzocycloheptatriene (**6**) as colorless prisms: mp 92–94 °C; NMR ($CDCl_3$) δ 3.50 (br s, 2 H), 6.84 (s, 1 H), 7.26–7.80 (m, 13 H); MS, m/e 268, 267, 191, 165.

Anal. Calcd for $C_{21}H_{16}$: C, 93.97; H, 6.03. Found: C, 93.95; H, 6.15.

Acknowledgment. Support by the Division of Chemical Sciences, U.S. Department of Energy is gratefully acknowledged.

Registry No. 3, 3239-33-6; **4**, 83269-91-4; **5**, 75245-59-9; **5** K^+ salt, 66018-18-6; **6**, 83269-92-5; **6** K^+ salt, 83291-32-1; **7**, 1139-82-8; **9**, 3594-90-9; **10**, 38274-14-5; **11**, 6672-73-7; **12**, 83269-93-6; diphenic anhydride, 6050-13-1; diphenic acid, 482-05-3; 6-phenyl-6,7-dihydro-5*H*-dibenzo[*a*,*c*]cyclohepten-6-ol, 83269-94-7.

(12) Baldwin, S. *J. Org. Chem.* **1961**, *26*, 3280.