-117.49° (c 1.32, $CHCl_3$); yield 68%; IR ($CHCl_3$) cm^{-1} 3663, 3455, 3078, 3013, 2962, 2868, 1679, 1556, 1537, 1476, 1469, 1457, 1395, 1367, 1335, 1276, 1237, 1184, 1163, 1115, 1086, 1067, 1024, 982, 953, 931, 861, 846, 804, 699; ^1H NMR ($CDCl_3$) δ 0.70–0.83 (10, m), 1.14–1.40 (2, m), 1.53–1.83 (4, m), 2.04–2.20 (2, m); ^{13}C NMR ($CDCl_3$) δ 19.1 (CH_2), 19.4 (CH), 24.8 (CH_2), 25.0 (CH), 26.8 (CH_3), 32.4 (C), 38.2 (CH_2), 50.2 (CH), 211.7 (C); mass spectrum (70 eV) m/z (rel intensity) 166 (3), 149 (2), 137 (3), 129 (2), 125 (1), 123 (3), 111 (6), 110 (47), 109 (11), 107 (4), 105 (2), 99 (2), 98 (2), 97 (8), 95 (26), 81 (26), 69 (38), 67 (15), 61 (37), 57 (100), 55 (28); exact mass calcd for $C_{11}H_{18}O$ 166.1358, obsd 166.1365.

(1*R*,4*S*,6*S*)-4-(1,1-Dimethylethyl)bicyclo[4.1.0]heptan-2-one (9b). Column chromatography of the crude product from **8b** on silica gel 60 eluted with 7% EtOAc/hexanes gave the product **9b** as a colorless oil: R_f 0.13 (10% EtOAc/hexanes); $[\alpha]^{23}_D$ -52.18° (c 0.55 $CHCl_3$): yield 79%; IR ($CHCl_3$) cm^{-1} 3663, 3017, 3011, 2963, 2869, 1671, 1557, 1537, 1476, 1469, 1445, 1396, 1367, 1351, 1308, 1282, 1236, 1182, 1128, 1094, 1057, 1023, 1000, 972, 921, 847, 827, 666; ^1H NMR ($CDCl_3$) δ 0.75–0.85 (9, s), 0.93–1.08 (1, m), 1.16–1.24 (1, q, J = 5.0 Hz), 1.33–1.87 (5, m), 2.02–2.11 (1, m), 2.23–2.36 (1, m); ^{13}C NMR ($CDCl_3$) δ 9.5 (CH_2), 16.9 (CH), 22.1 (CH_2), 25.3 (CH), 27.0 (CH_3), 32.1 (C), 37.3 (CH), 39.0 (CH_2), 210.5 (C).

Preparation of (3*S*,5*R*)-*cis*-3-*tert*-Butyl-5-methylcyclohexanone (10b). To a well-stirred solution of Li metal (45 mg, 6.49 mmol) in liquid ammonia (10 mL) at -78 °C was added a solution of *t*-BuOH (0.003 mL) and ketone **9b** (21 mg, 0.126 mmol) in ether (3 mL). The cold bath was removed and the mixture allowed to reflux (-33 °C). Progress of the reaction was monitored by TLC. After 30 min, the reaction was quenched with solid NH_4Cl (1 g), diluted with ether (20 mL), and warmed to room temperature, and the ammonia was allowed to evaporate. The mixture was filtered and concentrated, leaving an oil.

To a well-stirred solution of the above oil in CH_2Cl_2 (5 mL) at room temperature was added pyridinium dichromate (71 mg, 0.189 mmol). After 1 h, the mixture was diluted with ether and filtered through a short plug of silica gel. After concentration, the crude product was purified via column chromatography on silica gel 60 (40 g) eluted with 10% EtOAc/hexanes: yield of **10b** 7.5 mg, 0.0446 mmol, 36%; ^1H NMR ($CDCl_3$) δ 0.84–0.92 (9, s), 1.03–1.07 (3, d, J = 6.0 Hz), 1.0–2.48 (8, m).

Authentic *trans*- and *cis*-3-*tert*-Butyl-5-methylcyclohexanones (10a and 10b).[8] These compounds were prepared as described for **7** by substituting 5-methyl-2-cyclohexen-1-one for 2-cyclohexen-1-one. Column chromatography of the crude mixture of cis and trans products on silica gel 60 (100 g) eluted with 10% EtOAc/hexanes gave analytical samples of the separated products.

The less polar product **10b** was the cis isomer: R_f 0.45 (20% EtOAc/hexanes); ^1H NMR ($CDCl_3$) δ 0.87–0.91 (9, s), 1.03–1.06 (3, d, J = 6.0 Hz), 1.0–2.38 (8, m); ^{13}C NMR ($CDCl_3$) δ 22.6 (CH_3), 27.2 (CH_3), 32.6 (C), 33.2 (CH), 35.1 (CH_2), 42.8 (CH_2), 48.0 (CH), 49.6 (CH_2), 212.8 (C).

The more polar and major product **10a** was the trans isomer: R_f 0.42 (20% EtOAc/hexanes); ^1H NMR ($CDCl_3$) δ 0.87–0.91 (9, s), 0.94–0.98 (3, d, J = 7.5 Hz), 1.58–1.81 (3, m), 1.99–2.18 (2, m), 2.33–2.51 (3, m) [lit.[8] ^1H NMR (CCl_4) δ 0.92 (9 H, s), 0.96 (3 H, d, J = 6 Hz)]; ^{13}C NMR ($CDCl_3$) δ 19.2 (CH_3), 27.0 (CH_3), 29.4 (CH), 31.7 (CH_2), 32.3 (C), 42.8 (CH), 43.1 (CH_2), 47.3 (CH_2), 213.2 (C).

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Registry No. **7**, 125413-68-5; **8a**, 125413-70-9; **8b**, 125473-20-3; **9a**, 125413-72-1; **9b**, 125413-73-2; (±)-**10a**, 125413-75-4; (±)-**10b**, 125413-74-3; **11**, 125413-69-6; **12**, 125514-91-2; **13a**, 125413-71-0; **13b**, 125473-21-4; **14b**, 125473-22-5; **16**, 97590-69-7; **17**, 7381-30-8; **18**, 125473-19-0; **19**, 108813-04-3; CH_2I_2, 75-11-6; (3*S*)-3-*tert*-butylcyclohexanone, 57287-85-1; ethylene glycol, 107-21-1; (2*R*,3*R*)-2,3-butanediol, 24347-58-8; (2*S*,3*S*)-2,3-butanediol, 19132-06-0; (±)-5-methyl-2-cyclohexen-1-one, 54352-35-1.

Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra of all new compounds (26 pages). Ordering information is given on any current masthead page.

Reactive Annulenones: A Comparative Study

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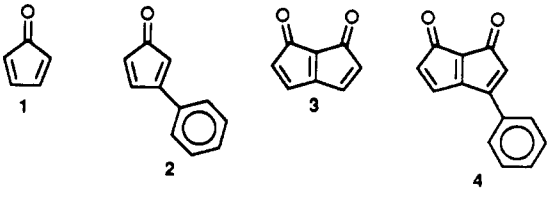
Two new and hitherto elusive annulenones, 3-phenylcyclopentadienone and bicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione, are reported. Their lifetimes and reactivities have been studied in comparison with those of the related annulenones cyclopentadienone and 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione. The influence of structure and substituents on the stabilities of these species has thereby been established.

As part of our ongoing studies of highly reactive mono- and bicyclic annulenones, we decided to carry out a comparative experimental study of both the stabilities and Diels–Alder reactivities of unstable ketones **1**–**4** (Chart I). The parent compound cyclopentadienone (**1**) has been extensively studied in our research group.[1,2] In the course of these studies, we demonstrated the existence of this ketone as a monomeric free species in solution as well as its ability to perform as a diene as well as a dienophile in Diels–Alder processes. The lifetime of this intermediate was determined as well by using the polyphasic dynamic reactor (PDR), devised by us for this purpose.[2]

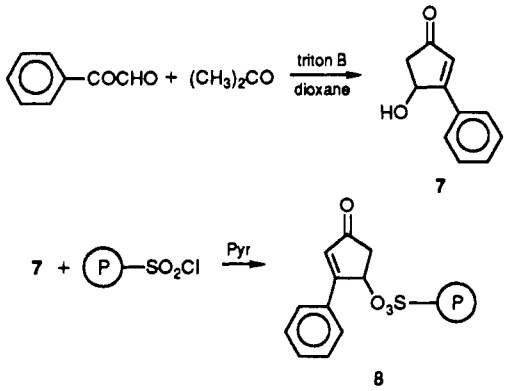
Chart I



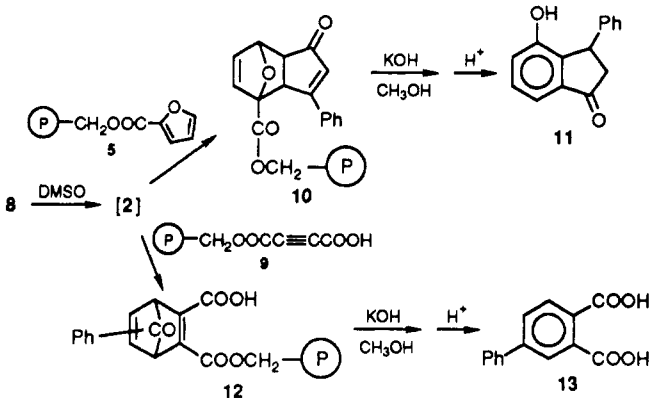
(1) Gaviña, F.; Costero, A. M.; Gil, P.; Palazón, B.; Luis, S. V. *J. Am. Chem. Soc.* **1981**, *103*, 1797–1798.
(2) Gaviña, F.; Costero, A. M.; Gil, P.; Luis, S. V. *J. Am. Chem. Soc.* **1984**, *106*, 2077–2080.

0022-3263/90/1955-2060$02.50/0

Scheme I



Scheme II



We have also synthesized a suitable precursor to 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (4), demonstrated its free existence, and studied its reactivity in cycloaddition processes.[3]

At this time, we report the generation of unstable ketones 2 and 3 and describe their behavior in Diels–Alder reactions.

Results and Discussion

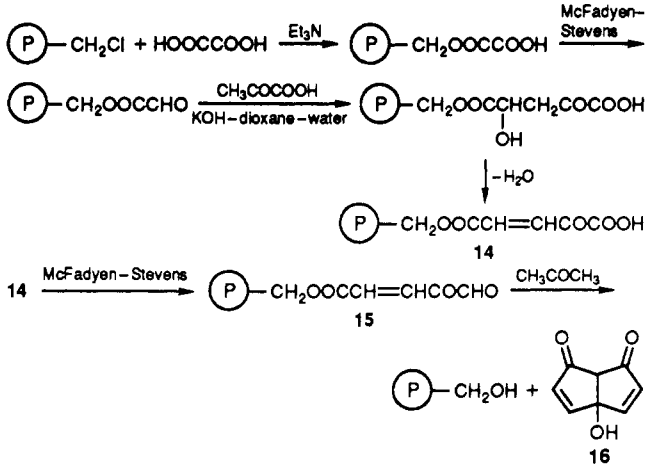
3-Phenylcyclopentadienone (2). The precursor used in the generation of 2 was the polymeric phenylcyclopentenone 8, synthesized as shown in Scheme I.

Phenylglyoxal and acetone were condensed in the presence of triton B,[4,5] giving 4-hydroxy-3-phenylcyclopent-2-en-1-one (7). Chlorosulfonated resin reacted with 7 in the usual way[1,3] to yield the polymeric precursor 8.

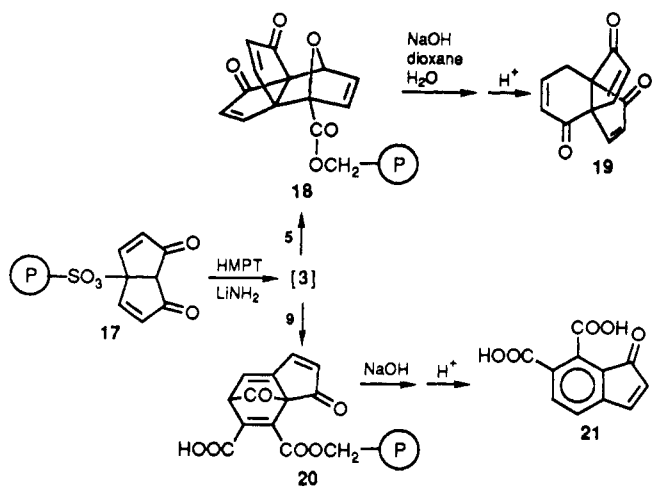
To determine the free existence of intermediate 2 in solution, a three-phase test[6] was used. A dienic reagent, the polymeric ester of 2-furoic acid (5), and a dienophilic reagent, the polymeric monoester of acetylenedicarboxylic acid (9), were used as trapping agents (Scheme II). The use of these polymers allowed us to simultaneously study both the existence and cycloaddition reactivities of these annulenones.[1]

Our studies allowed us to conclude that 3-phenylcyclopentadienone (2) can exist in solution as a free monomeric species and that it is capable of acting both as a diene and as a dienophile in Diels–Alder reactions. Products 11 and 13 from the three-phase tests were identified by comparison (IR, NMR, TLC, mp) with authentic samples, which were prepared as indicated below. Conversion of 10 into 11 involves an aromatization process with hydrogen rearrangement.[1]

Scheme III



Scheme IV



Bicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (3). The study of intermediate 3 was accomplished in a similar way. Precursor polymer 17 was obtained by reaction of 16 with polymeric sulfonyl chloride. Synthesis of 16 was performed in the solid phase, as indicated in Scheme III. The polymeric monoester of oxalic acid was reduced to an aldehyde by a McFadyen–Stevens reaction. Condensation of this aldehyde with pyruvic acid gave the α,β-unsaturated product 14. A second reduction of 14, followed by condensation with acetone, yielded 16.

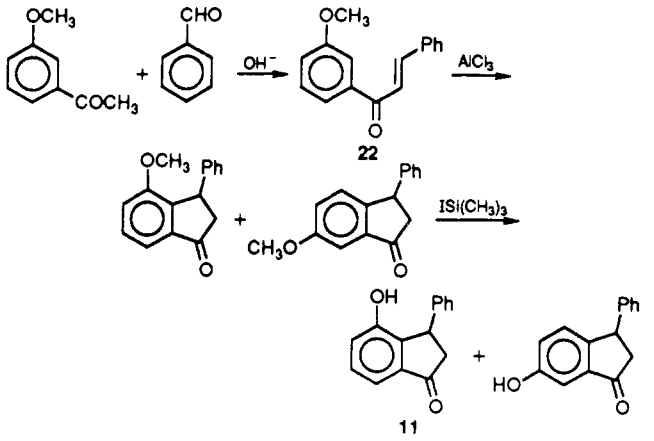
The trapping polymers used in studying 3 were the same as those used for reactive intermediate 2 (Scheme IV). The conditions for liberating 3 from the precursor polymer 17 were more drastic than those in the case of 2. Instead of DMSO, it was necessary to use $LiNH_2$–HMPT. Subsequently, we were able to generate and trap 3 as a diene and as a dienophile.

The structure of 21 was identified by comparison (NMR, IR, TLC) with a sample synthesized independently. Product 19 was studied by IR, NMR, and MS and analyzed for C and H. Attempts to synthesize 19 unambiguously are underway.

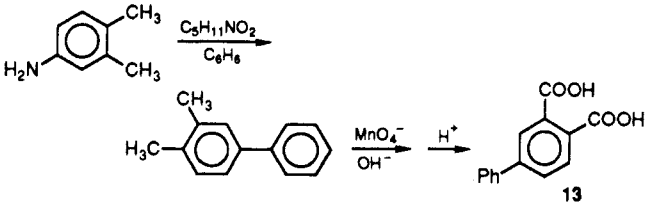
Reference Compounds. (a) 3-Phenyl-4-hydroxyindanone (11). The synthesis began with the condensation of 3-methoxyacetophenone (Scheme V) with benz-

(3) Gaviña, F.; Costero, A. M.; Luis, S. V. *J. Org. Chem.* **1984**, *49*, 4616–4618.
(4) Matsumano, T.; Shirahawa, H.; Ichigas, T.; Shin, H. *Tetrahedron Lett.* **1967**, 4097–4100.
(5) Clark, T. J. *J. Org. Chem.* **1973**, *38*, 1749–1751.
(6) Rebek, J., Jr.; Gaviña, F. *J. Am. Chem. Soc.* **1974**, *96*, 7112–7114.

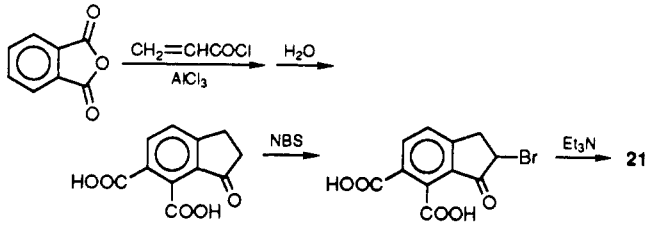
Scheme V



Scheme VI



Scheme VII



aldehyde, giving **22**. This was cyclized by using $AlCl_3$ in cyclohexane, giving better yields of the ortho product than other Lewis acids.[7] The methoxyindanones were demethylated with iodotrimethylsilane, yielding 4- and 6-hydroxyindanones. From this mixture **11** could be chromatographically isolated.

(b) 4-Phenylphthalic Acid (13). **13** was synthesized as indicated in Scheme VI. 4-Amino-*o*-xylene was condensed with benzene in the presence of isoamyl nitrite, through the diazonium salt, giving 3,4-dimethylbiphenyl.[8] Oxidation of the methyl groups with permanganate gave **13**.

(c) 6,7-Dicarboxy-2-inden-1-one (21). Synthesis of compound **21** was carried out as shown in Scheme VII. Phthalic anhydride reacted with acryloyl chloride to give the indanone with carboxylic groups in the appropriate positions.[3] Treatment with NBS, followed by triethylamine, gave the indenone **21**, which was identical with the sample obtained through the three-phase test.

Lifetime Determinations. The three-phase test has recently been adapted by us for lifetime determinations of free intermediates in solution, by using the so-called "polyphasic dynamic reactor" (PDR).[2,9] We applied this method previously to determine the lifetime of the parent cyclopentadienone, and now the lifetimes of the other three annulenones **2**–**4** have been measured and are shown in Table I.

Table I. Lifetimes of Annulenones in Solution

annulenones	lifetimes,[a] s
cyclopentadienone (**1**)	13.3 ± 0.5
3-phenylcyclopentadienone (**2**)	22.1 ± 0.5
bicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (**3**)	63.9 ± 0.5
4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (**4**)	74.1 ± 0.5

[a] Identical experimental conditions (see Experimental Section).

Conclusions

For the first time, the free existence in solution of the new cyclopentadienone-related species, 3-phenylcyclopentadienone (**2**) and bicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (**3**), have been demonstrated. Both are able to act as dienes as well as dienophiles in Diels–Alder reactions. Only 3-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (**4**), among all annulenones studied by us, exhibits no detectable behavior as a dienophile.[3] Thus, disappearance of this species in the lifetime experiments was probably due to a more complicated process than simple dimerization.

Data from the PDR experiments show relative dimerization rates for these species. We are therefore reporting in terms of relative kinetic stabilities. Bicycloannulenones appear to be the most stable, with lifetimes longer than 1 min. Phenyl substituents stabilize the systems modestly.

Experimental Section

General methods for working with polymeric reagents and multiphase systems, including PDR lifetime measurements, have been described.[2,6]

Synthesis of 3-Phenyl-4-hydroxycyclopent-2-en-1-one (7). A solution of 5 g of phenylglyoxal, 2.5 g of acetone, and 1 mL of triton B in 10 mL of dioxane was heated under reflux for 20 h. The solution was then distilled in vacuo (15 mm), and 3-phenyl-4-hydroxycyclopent-2-en-1-one (**7**) was collected as the fraction between 74 and 76 °C. The yield was 15%: IR 3400 (OH), 3060, 3020, 2950, 2910, 1710 (CO), 1590, 1450 cm^{-1}; ^1H NMR (CCl_4) δ 2.90 (2 H, d), 4.01 (1 H, br, s, OH), 4.55 (1 H, t, C*H*OH), 7.0–7.6 (6 H, m); MS, *m*/*z* 174 (10), 173 (20), 157 (15), 156 (8), 146 (50), 128 (10), 80 (25), 77 (100). Anal. Calcd: C, 75.85; H, 5.76. Found: C, 75.80; H, 5.75.

Reaction of 7 with Polymeric Sulfonyl Chloride. Polymeric sulfonyl chloride[10] (1 g) was stirred with **7** (1 g) and pyridine (6 mL) in 25 mL of dioxane for 72 h at room temperature. After the reaction mixture was filtered and washed with HCl–water, dioxane, acetone, and ether, resin **8** was obtained: IR (KBr) 1650 (CO), 1600, 1300 (SO_3), 1185, 900, 750, 690 cm^{-1}.

Three-Phase Reaction of 8 and Polymeric Ester of 2-Furoic Acid (5). **8** (0.4 g) and 0.6 g of **5**[1] were suspended in 100 mL of DMSO, and the mixture was stirred for 64 h at 100–110 °C. Then the resin was washed with dioxane, acetone, and ether and separated, giving **10**: IR 1735 (CO_2CH_2), 1715 (CO), 1460, 1300, 1130 cm^{-1}. Hydrolysis of **10** with 0.5 M KOH (dioxane–water, 1:1) at 60 °C for 10 h, followed by acidification and purification by preparative TLC (Cl_3CH), gave **11**. The identity of **11** and authentic 3-phenyl-4-hydroxyindanone was confirmed by IR, NMR, UV, and TLC.

Three-Phase Reaction of 8 and Polymeric Monoester of Acetylenedicarboxylic Acid (9). **8** (0.4 g) and 0.6 g of **9**[1] were suspended in 100 mL of DMSO, and the mixture was stirred for 87 h at 120 °C. Then **12** was separated, washed with dioxane, acetone, and ether, and dried: IR 3400–3100 (COOH), 1750 (CO), 1735 (CO_2CH_2), 1720 (CO_2H), 1690, 1450, 1260, 1180, 1100 cm^{-1}. Hydrolysis of **12** was carried out with 0.5 M KOH for 10 h at 80 °C. After acidification, ether extraction, and chromatography,

(7) Buckley, T. F.; Rapoport, H. *J. Am. Chem. Soc.* **1980**, *102*, 3056–3062.
(8) Olden, E. *J. Chem. Eng. Data* **1970**, *15*, 459–460.
(9) Gaviña, F.; Luis, S. V.; Costero, A. M.; Gil, P. *Tetrahedron* **1986**, *42*, 155–166.
(10) Roush, W.; Feitler, D.; Rebek, J. *Tetrahedron Lett.* **1974**, 1391–1392.

13 was found to be identical with authentic 4-phenylphthalic acid (TLC, IR, NMR).

Preparation of Polymeric Monoester of 2-Oxo-3-pentenedioic Acid (14). Oxalic acid (3.78 g) and triethylamine (10 mL) were dissolved in 125 mL of benzene, 4 g (14 mequiv) of Merrifield's resin was added, and the mixture was stirred under reflux for 20 h. The product resin was washed with dioxane, acetone, and ether: IR, 3300 (CO_2H), 1760 (CO_2CH_2), 1710 (CO_2H), 1450, 1165 cm^{-1}. This polymer was treated with 9 mL of $SOCl_2$ in 100 mL of benzene and stirred with 12 mL of 80% hydrazine in 100 mL of benzene at room temperature for 24 h. The filtered and washed resin was suspended in 100 mL of pyridine containing 10 g of *p*-toluenesulfonyl chloride and allowed to stand at room temperature for 40 h. After washing with dioxane, acetone, and ether, the resin was suspended in 150 mL of ethylene glycol and heated at 167 °C, and then 14 g of Na_2CO_3 was added. After heating at 167 °C for 70 h, the polymer was filtered and washed with HCl–dioxane–water, dioxane, acetone, and ether: IR 1720 (CO_2CH_2), 1700 (CHO), 1490, 1450, 1210 cm^{-1}. The oxo ester (3.7 g) so obtained was suspended in 120 mL of dioxane–water (1:1) with 1 g of KOH and 4 mL of pyruvic acid and heated under reflux for 24 h. After filtering and washing with HCl–dioxane–water, acetone, and ether, the polymer (**14**) yielded the following data: IR 3300 (CO_2H), 3020, 2920, 1750 (CO_2CH_2), 1710–1670 (CO, CO_2H), 1600, 1440, 1165, 1020 cm^{-1}.

Synthesis of 5-Hydroxybicyclo[3.3.0]octa-3,6-diene-2,8-dione (16). **14** (4.9 g) was reduced by the McFadyen–Stevens procedure,[11] as described for the polymeric monoester of oxalic acid, to give **15**: IR 3010, 1720 (CO_2CH_2, CHO), 1695 (CO), 1600, 1440, 1280, 1190 cm^{-1}. **15** (0.4 g) was suspended in a mixture of 125 mL of benzene, 50 mL of acetone, and 20 mL of triton B and was heated with stirring at 70 °C for 80 h. From the solution, 5-hydroxybicyclo[3.3.0]octa-3,6-diene-2,8-dione (**16**) was obtained after preparative TLC (benzene): IR 3400 (OH), 3020, 2960, 1705 (CO), 1640, 1460, 1214, 1020 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.0 (1 H, br s, OH), 3.6 (1 H, s, COCHCO), 5.5 (2 H, d), 6.9 (2 H, d); MS *m/z* 150 (5), 149 (7), 132 (20), 122 (8), 96 (20), 95 (30), 28 (100), 26 (30). Anal. Calcd: C, 64.02; H, 3.99. Found: C, 64.09; H, 4.04.

Preparation of Polymeric Precursor 17. Polymeric sulfonyl chloride[10] (0.9 g) was stirred at room temperature with **16** (0.5 g) and pyridine (3 mL) in 10 mL of dioxane for 72 h. After the reaction mixture was filtered and washed with HCl–water–dioxane, dioxane, acetone, and ether, resin **17** was obtained: IR 1710 (CO), 1620, 1380 (SO_3), 1190, 1080 cm^{-1}.

Three-Phase Reaction of 17 and 5. **17** (0.3 g) and 0.9 g of the polymeric ester of furoic acid (**5**) were suspended in 50 mL of HMPT. Then 1.5 g of lithium amide in 15 mL of HMPT was added dropwise. The solution was allowed to stand at room temperature for 24 h. The trapping polymer was separated and washed with dioxane, methanol, and ether, giving **18**. Hydrolysis of **18** with 0.5 M NaOH (dioxane–water, 1:1), followed by acidification, ether extraction, and preparative TLC, gave tricyclo[4.3.3.0]dodeca-3,8,10-triene-2,7,12-trione (**19**) as pale yellow crystals (yield, 30%): mp 116 °C dec; IR 2980, 2850, 1715–1700 (CO), 1560, 1460, 1310, 1280, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3 (2 H, d, C(5)H), 6.0 (2 H, d), 6.2 (1 H, d, C(3)H), 6.8 (1 H, m, C(4)H), 7.1 (2 H, d); MS, *m/z* 200 (5), 172 (10), 146 (100), 132 (70), 67 (80). Anal. Calcd: C, 72.01; H, 4.03. Found: C, 72.09; H, 4.10.

Preparation of Reference Compound 11 (Scheme V). NaOH (2.18 g) in 20 mL of water was poured at 0 °C into a solution of 6.45 g of 3-methoxyacetophenone in 20 mL of ethanol. Benzaldehyde (4.6 g) was then added, and the mixture was stirred at 14 °C for 10 h. A pale yellow precipitate formed, which was filtered and washed with 96% ethanol. Spectroscopic characteristics of **22** corresponded with 3′-methoxychalcone: IR 3018, 1670 (CO), 1330, 1100, 890, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.71 (3 H, s, OMe), 6.80 (1 H, d), 6.92–7.25 (5 H, m), 7.30 (5 H, s, Ph).

A solution of **22** (2.1 g) in 100 mL of cyclohexane was treated with 5.0 g of $AlCl_3$ under reflux for 20 h. Then the mixture was washed with a solution of $NaHCO_3$ and distilled, to give 4- and 6-methoxy-3-phenylindanone as yellow crystals (1.11 g, yield 53%). These crystals were treated with iodotrimethylsilane at 50 °C for 20 h, according to the Jung and Lyster procedure,[12] yielding 4- and 6-hydroxy-3-phenylindanone. This mixture was separated by TLC (benzene), giving 0.51 g of 3-phenyl-6-hydroxyindanone and 0.40 g of **11**, recrystallized from benzene: mp 95 °C; IR 3500 (OH), 2990, 1710 (CO), 1450, 1260, 1050, 790, 700 cm^{-1}; λ_{MeOH} 228–230 nm; λ_{MeONa} 260 nm; ^1H NMR ($CDCl_3$) δ 3.0 (1 H, t, C(3)H), 3.8 (2 H, d, C(2)H), 7.0–7.3 (3 H, m), 7.6 (5 H, s, Ph), 9.2 (1 H, s, OH); MS, *m/z* 224 (4), 223 (8), 207 (15), 196 (100), 182 (40), 157 (20), 104 (70). Anal. Calcd: C, 80.31; H, 5.35. Found, C, 80.23; H, 5.41.

Synthesis of Reference Compound 4-Phenylphthalic Acid (13) (Scheme VI). To 3,4-dimethylaniline (3 g) dissolved in 80 mL of benzene and heated under reflux was added 5 mL of isoamyl nitrite. The mixture was refluxed for an additional 48 h, chilled, and evaporated until 3,4-dimethylbiphenyl precipitated: IR 1520, 1420, 1350, 890, 810, 770, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2 (6 H, br s, Me), 6.8–7.5 (6 H, m), 7.8 (2 H, d).

3,4-Dimethylbiphenyl (4.8 g) was oxidized with $KMnO_4$ in the usual way, to give 4-phenylphthalic acid (**13**), which sublimed at 110 °C and 12 mmHg, yielding white crystals: IR 3100–2400 (COOH), 1690 (COOH), 890, 810, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–7.5 (3 H, m), 7.7–7.9 (3 H, m), 8.1 (1 H, d, C(6)H), 8.4 (1 H, s, C(3)H), 11.2 (2 H, br s, COH); MS, *m/z* 224 (80), 198 (100), 147 (20), 131 (30), 77 (80). Anal. Calcd: C, 69.39; H, 4.10. Found: C, 69.45; H, 4.05.

Reference Compound 6,7-Dicarboxy-2-indenone (21) (Scheme VII). A solution of phthalic anhydride (10.0 g) and $AlCl_3$ (3.5 g) in 50 mL of cyclohexane was heated at 114 °C, and 12 g of freshly prepared acryloyl chloride was added. The mixture was stirred under reflux for 20 h and then poured into ice water. The solid was filtered, washed with water and acetone, and chromatographed in silica gel with benzene, yielding phthalic acid and 5.2 g of 6,7-dicarboxyindanone: IR 3450–2900 (COOH), 1730 (CO), 1690 (COOH), 1590, 1420, 1300, 1155, 860 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.7 (2 H, t, C(3)H), 3.82 (2 H, t, C(2)H), 7.35 (1 H, d), 7.8 (1 H, d), 10.2 (2 H, br s, COOH).

6,7-Dicarboxyindanone (3.22 g) in 500 mL of CCl_4 was treated with 1.88 g of NBS and a catalytic amount of benzoyl peroxide. The solution was stirred at 100 °C for 1 h, and the mixture was then chilled, filtered, and extracted with cold 25% aqueous $Na_2S_2O_3$. The organic phase was evaporated to dryness at reduced pressure, giving 2-bromo-6,7-dicarboxyindanone as a deep yellow oil, which was directly dissolved in 200 mL of ether. To this solution was added 100 mL of triethylamine, and the mixture was stirred at room temperature for 8 h, filtered, acidified, and extracted with ether. The ether solution was dried and evaporated and the residue chromatographed (benzene, silica gel), to give 6,7-dicarboxy-2-indenone (**21**), which was recrystallized as yellow needles: mp 142–143 °C dec; IR 3300–3000 (COOH), 1700–1690 (CO), 1600, 1450, 1400, 1120, 845 cm^{-1}; ^1H NMR (CCl_4) δ 7.0 (1 H, d, C(3)H), 7.4–7.9 (3 H, m), 10.2 (2 H, br s, COOH); MS, *m/z* 217 (20), 200 (25), 189 (8), 184 (15), 173 (80), 172 (25), 128 (100), 100 (70). Anal. Calcd: C, 60.55; H, 2.75. Found: C, 60.50; H, 2.81.

PDR Lifetime Determinations. Lifetime measurements were made as described,[2,9] by using, as precursors, 6.5 mequiv of the following resins: **8**, **17**, polymeric sulfonate of 4-hydroxy-2-cyclopentenone[1] and polymeric sulfonate of 5-hydroxy-4-phenylbicyclo[3.3.0]octa-3,6-diene-2,8-dione.[3] Polymeric monoester of acetylenedicarboxylic acid (5.0 g, 4.5 mequiv) was used as a trapping agent in each experiment. Reactions were carried out with 1.5 g of lithium amide in 100 mL of HMPT. The lifetimes thus obtained are shown in Table I.

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(11) Sprecher, M.; Feldkimel, M.; Wildher, M. *J. Org. Chem.* **1961**, *26*, 3664–3669.

(12) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761–3764.