and cooled to room temperature. Water was added and the mixture extracted with ether. The ether layer was extensively washed with water, dried over sodium sulfate, and evaporated to dryness. The brown gummy mass was chromatographed over silica gel and eluted with dichloromethane (R_f 0.30 on silica gel; dichloromethane as the irrigant). The eluant was pooled and following concentration the residue was crystallized from hexane to furnish 400 mg (58%) of **21**: mp 118–121 °C (hexane); IR (KBr) 3340 (OH), 1220 cm^{-1} (C–S–C); UV (MeOH) λ_{max} 323 nm (ϵ 7.3 × 10^3), 308 (1.24 × 10^4), 304 (1.24 × 10^4), 294 (9.96 × 10^3), 277 (8.17 × 10^3); ^{1}H NMR (CDCl$_3$) δ 1.37 (t, 3 H, J = 7.3 Hz, CH$_2$CH$_3$), 3.0 (q, 2 H, J = 7.3 Hz, CH$_2$CH$_3$), 3.00 (s, 3 H, C7 or C12CH$_3$), 3.25 (s, 3 H, C7 or C12CH$_3$) 7.10 (dd, 1 H, J = 3.0, 7.5 Hz, C2H), 7.60 (d, 1 H, J = 10 Hz, C1H), 7.83 (d, 1 H, J = 3 Hz, C4H), 8.10 (s, 1 H, C6H), 8.20–8.50 (complex, 3 H, aromatic); MS, m/e (relative intensity) 332 (M$^+$, 100), 317 (M$^+$ – CH$_3$, 3.4), 304 (M$^+$ – C$_2$H$_4$, 5), 271 (M$^+$ – SC$_2$H$_5$, 1.0), 286 (33), 259 (57).

Anal. Calcd for $C_{22}H_{20}OS$: C, 79.50; H, 6.02; F, 0.00; O, 4.80; S, 9.60. Found: C, 79.45; H, 6.29; F, 0.07; O, 4.89; S, 9.38.

5-Fluoro-3-hydroxy-7,12-dimethylbenz[*a*]anthracene (22). To a solution of **20** (80 mg, 0.26 mmol) in dichloromethane (20 mL) was added BBr$_3$ (1.0 mL). The mixture turned violet. The progress of the reaction was followed by TLC over silica gel with dichloromethane as the irrigant. After 6 h, water (10 mL) was added and the mixture vigorously stirred for 10 min. The dichloromethane layer was separated, washed with water, dried over sodium sulfate, and evaporated under reduced pressure to furnish a gummy mass. This gum was chromatographed over silica gel with dichloromethane as the eluent. The fractions containing material with R_f 0.31 (silica gel; dichloromethane) were pooled and evaporated to furnish a pale yellow solid. Crystallization from hexane–dichloromethane provided 35 mg (46%) of **22**: mp 179–180 °C; IR (KBr), 3300 cm^{-1} (OH); UV (MeOH) λ_{max} 308.3 nm (sh, ϵ 4.67 × 10^4), 298 (9.0 × 10^4), 287.2 (9.46 × 10^4); ^{1}H NMR (CDCl$_3$) δ 3.00 (s, 3 H, C7 or C12 CH$_3$), 3.30 (s, 3 H, C7 or C12 CH$_3$), 5.25 (brs, 1 H, OH), 7.18 (dd, 1 H, J = 3, 8 Hz, C2 H), 7.50 (d, 1 H, J = 13 Hz, C4 H), 7.70 (d, 1 H, J = 13 Hz, C6 H), 8.35 (complex, 3 H, aromatic); MS, m/e 290 (M$^+$, 100), 275 (M$^+$ – CH$_3$, 38), 247 (M$^+$ – CO – CH$_3$, 6).

Anal. Calcd for $C_{20}H_{15}OF\cdot 0.5H_2O$: C, 80.30; H, 5.35; O, 8.02; F, 6.35. Found: C, 80.90; H, 5.00; O, 8.09; F, 6.10.

Forerun dichloromethane fractions from the silica gel column provided <1 mg of material which was homogeneous by HPLC and likely has structure **23**: ^{1}H NMR (CDCl$_3$) δ 3.00 (s, C7 or C12 CH$_3$), 3.30 (s, C7 or C12 CH$_3$), 7.00–8.00 (complex, aromatic); MS, m/e (relative intensity) 352, 350 (M$^+$, base peaks of equal intensity), 337, 335 (M$^+$ – CH$_3$, 16 each), 271 (M$^+$ – Br, 15), 270 (M$^+$ – HBr, 19), 256 (M$^+$ – Br – CH$_3$, 32), 255 (M$^+$ – HBr – CH$_3$, 23).

5-Fluoro-7,12-dimethylbenz[*a*]anthracene-3,4-dione (24). A solution of **22** (28 mg, 0.096 mmol) in THF (5 mL) was added to a suspension of diphenyldiselenic anhydride[23] (160 mg, 0.44 mmol) in THF (10 mL). The mixture was heated at 80 °C under N$_2$ for 30 min and evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (5 mL) and chromatographed over silica gel. The green band eluted with dichloromethane was evaporated to furnish a green solid which proved to be a mixture of three components by TLC. Preparative TLC on dichloromethane washed silica gel plates with dichloromethane as the irrigant furnished **24**: UV (MeOH) λ_{max} 328 nm, 274 (sh), 257, 242 (sh); IR (KBr) 1665 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.00 (s, 3 H, C7 or C12CH$_3$), 3.20 (s, 3 H, C7 or C12 CH$_3$), 6.44 (d, 1 H, J = 11 Hz, C1 H), 7.3–8.5 (complex, 6 H, aromatic); MS, m/e (relative intensity) 306 (M$^+$ + 2 H, 100), 304 (M$^+$), 302 (M$^+$ – 2 H). Two samples of **25** standard, one of which was prepared in these laboratories by employing Barton's reagent[23] according to Sukumaran and Harvey[10] and the other of which was prepared by Newman et al.[16] using Fremey's salt, also exhibited the following: MS, m/e (relative intensity) 288 (M$^+$ + 2 H, 100), 286 (M$^+$), 284 (M$^+$ – 2 H); ^{1}H NMR (CDCl$_3$) δ 6.32 (d, 1 H, J = 11 Hz, C1H).

Anal. Calcd for $C_{20}H_{13}O_2F\cdot O\cdot 5H_2O$: C, 76.6; H, 4.48. Calcd for $C_{20}H_{13}O_2F\cdot C_2H_5OH$: C_2H_5OH: C, 75.43; H, 5.43. Found: C, 76.17; H, 5.48.[24]

Acknowledgment. We thank Professor M. S. Newman for samples of 7,12-dimethylbenz[*a*]anthracene-3,4-dione and 3,4-dihydroxy-7,12-dimethylbenz[*a*]anthracene. Partial support of this work by U.S. Air Force Grant No. F49620-80-C-0086 and Cancer Center Core Grant No. P-30-CA-1605B is gratefully acknowledged.

Registry No. **3**, 13791-03-2; **4**, 118-46-7; **6**, 13916-98-8; **7**, 71493-51-1; **9**, 82995-06-0; **10**, 82995-07-1; **12**, 71493-39-5; **13**, 32664-13-4; **15**, 82995-08-2; **16**, 82995-09-3; **17**, 82995-10-6; **18**, 82995-11-7; **20**, 82995-12-8; **21**, 82995-13-9; **22**, 82995-14-0; **23**, 82995-15-1; **24**, 82995-16-2; ethanethiol, 75-08-1.

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(24) For combustion analysis purposes we only had approximately 1 mg of sample left following our chemical studies. Thus, a duplicate analysis could not be obtained. The H content found for **24** was high and may reflect either H$_2$O or EtOH of crystallization. The mass spectrum and UV data support the assigned structure. It should be noted that **24** was precipitated from EtOH/hexane. Concurrent with submission of this sample for analysis we also submitted a sample of 7,12-dimethylbenz[*a*]anthracene-3,4-dione standard prepared in our laboratory by using methodologies similar to those found in ref 10. That sample analyzed as follows. Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.9; H, 4.96; Found: C, 83.84; H, 5.17.

Notes

$_\pi 4_s + {}_\pi 2_s$ Photochemical Cycloaddition of Naphthalene to 1,3-Cyclohexadiene

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Recently Yang and his coworkers reported that there is an excellent correlation between the polarity of [arene*:1,3-diene] exciplexes or the role of eximers of arenes and the orientation of photocycloaddition of 1,3-dienes to arenes.[1,2] They have pointed out two possible pathways for stepwise $_\pi 4_s + {}_\pi 2_s$ photocycloaddition. One is tthat the addition may occur via highly polar exciplexes, and the other is the cycloaddition of excimers of arenes to 1,3-dienes. Photochemical cycloaddition of naphthalene to 1,3-cyclohexadiene (CHD) is known to produce the corresponding $_\pi 4_s + {}_\pi 4_s$ adducts (1 and 2,[3] Chart I), which may be derived from a relatively nonpolar exciplex,[1] and

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(1) Yang, N. C.; Srinivasachar, K.; Kim, B.; Libman, J. *J. Am. Chem. Soc.* **1975**, 97, 5006–5008.

(2) Yang, N. C.; Shou, H.; Wang, T.; Masunovi, J. *J. Am. Chem. Soc.* **1980**, *102*, 6652–6654.

(3) (a) Yang, N. C.; Libman, J.; Savitzky, M. F. *J. Am. Chem. Soc.* **1972**, *94*, 9226–9227. (b) Yang, N. C.; Libman, J. *Ibid.* **1972**, *94*, 9228–9229.

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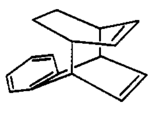
Chart I



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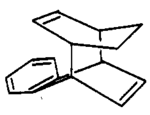

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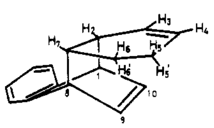

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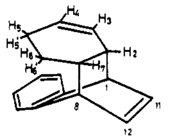

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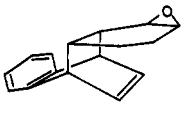

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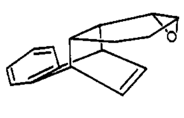
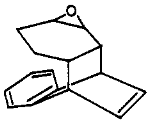
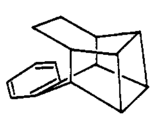


6



7



8

the corresponding ${}_{\pi}4_{s} + {}_{\pi}2_{s}$ adducts, which may be derived from a polar exciplex but have not been isolated from the photoreaction. We now report the first isolation of (1*RS*,2*RS*,7*SR*,8*SR*)-11,12-benzotricyclo[6.2.2.0^{2,7}]dodeca-3,9,11-triene (3) and (1*RS*,2*SR*,7*RS*,8*SR*)-9,10-benzotricyclo[6.2.2.0^{2,7}]dodeca-3,9,11-triene (4) as ${}_{\pi}4_{s} + {}_{\pi}2_{s}$ adducts.

When a solution of naphthalene and CHD in benzene was irradiated with a Toshiba 450-W high-pressure mercury lamp through a Pyrex filter for 24 h under a nitrogen atmosphere, naphthalene was completely consumed. After removal of the solvent, compound 1 (55.7%)[3b] was eliminated by treatment of an ethanol solution of the reaction mixture with aqueous silver nitrate. The residual mixture was chromatographed on activated charcoal treated with silver nitrate to give 2 (5.5%),[3b] 3 (11.8%), and 4 (4.6%). The nature of the ring fusions with the new six-membered rings derived from CHD for 3 and 4 are established as cis, because the coupling constants $J_{2,7}$ in the ^{1}H NMR spectra of 3 and 4 are 10 Hz and because the H-5′ protons of 3 (1.24 ppm) and 4 (0.52 ppm) located over the transannular double bond and the benzene ring, respectively, were shifted to higher field than the other methylene protons. If these ring fusions are trans, as the new six-membered rings are almost vertical to the planes of the double bond and the benzene ring, the H-5′ protons in 3 and 4 could not be deshielded by the double bond and the benzene ring. The treatment of 3 with DDQ in refluxing $CHCl_3$ gave 9,10-dihydro-9,10-ethenoanthracene[4] in 10% yield. Both 3 and 4 were decomposed at 200 °C to give naphthalene and CHD quantitatively. Compounds 3 and 4 reacted with 1 equiv of *m*-chloroperbenzoic acid in $CHCl_3$ to give epoxidated products 5 (68%) and 6 (27%) and product 7 (80%), respectively. These epoxides have ^{1}H NMR resonances for pseudo-A_2B_2-type vinyl protones around 6.4–6.5 ppm, and the double bonds in the six-membered ring were selectively attacked by *m*-chloroperbenzoic acid. The structural assignments of 3 and 4 were based on their spectral properties as well as NMR shift reagnet [Eu(fod)$_3$] experiments concerning the corresponding epoxides 5–7[5] and their chemical reactions mentioned above.

Table I

sensitizer[b]	ET, kcal/mol[8]	% product[a]	
		naphthalene	8
9,10-dibromoanthracene	40	~0	
2,3-benzphenanthrene	50	~0	
benzoquinone	50	~0	
benzil	55	~0	
2-naphthaldehyde	59	10.4	
α-naphthoquinone	60	~0	
xanthone[1]	74		~100
acetophenone	75		~100
acetone	80	50	40

[a] Isolated yields. [b] Concentrations of sensitizers are 5×10^{-3} M. Concentration of 1 is 4.5×10^{-2} M.

It is interesting question that how these ${}_{\pi}4_{s} + {}_{\pi}2_{s}$ adducts are formed in the photoreaction. Now we investigated another possibility for the formation of 3 and 4 other than those proposed by Yang et al. It is possible that the adducts in question are in fact secondary photoproducts resulting from either direct or sensitized photoisomerization of the ${}_{\pi}4_{s} + {}_{\pi}4_{s}$ adducts (1 and 2).[9] The possibility is ruled out by the following experiments. The direct irradiation of 1 with a Toshiba 450-W high-pressure mercury lamp through a Pyrex filter in benzene under a nitrogen atmosphere gave naphthalene quantitatively and polymerized materials. The irradiation of 1 with triplet sensitizers (>ET = 74 kcal/mol) in degassed benzene gave cage compound 8.[2] When the triplet energy of the sensitizer is less than 60 kcal/mol, only a trace of naphthalene was formed (Table I).

The quantum yields of the disappearance of naphthalene in the presence of CHD determined with degassed samples and a conventional merry-go-round apparatus by using 313-nm light at 15 ± 1 °C (Table II). The relative proportions of 1–4 are also summarized in Table II. As the concentration of naphthalene increases, there is a large increase in the quantum yield of naphthalene consumption and little change in the proportion of the adducts, and the yield of products also increased.[6] From these results, we assume that the role of the excimer of naphthalene may be negligible for the formation of the ${}_{\pi}4_{s} + {}_{\pi}2_{s}$ photocycloaddition. Now it should be noted that ${}_{\pi}4_{s} + {}_{\pi}2_{s}$ photocycloaddition may occur even from the relatively nonpolar exciplex. We would like to propose a possible pathway for ${}_{\pi}4_{s} + {}_{\pi}2_{s}$ addition, i.e., that a relatively nonpolar [naphthalene*:CHD] exciplex may decay to a vibrationally excited ground state to give 3 and 4 by thermally allowed cycloaddition.[7]

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(4) *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1966**, *263* (23), 1452–1455; *Chem. Abstr.* **1967**, *66*, 70389. The NMR spectrum of 9,10-dihydro-9,10-enthanoanthracene shows a sextet at 5.0 ppm attributed to H-9 and H-10 and aromatic protons and two vinyl protons between 6.5 and 7.2 ppm.

(5) In the plots of the induced shifts vs. the shift reagent [Eu(fod)$_3$]/substrate molar ratios (E/S) for 5–7, the shifts of each vinyl proton for 5 and 6 were greater than those of 7.

(6) See Table III.

(7) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1971.

(8) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(9) Wang, T.; Ni, J.; Masunovi, J.; Yang, N. C. *Tetrahedron Lett.* **1982**, *22*, 1231–1234.

Table II

		% adduct				
[naphthalene], M	[cyclohexa-1,3-diene], M	1	2	3	4	Φ (naphthalene)
0.26	1.75	74	11	4	11	0.27
0.026	1.75	65	13	6	16	0.10
0.010	1.00	66	13	6	15	0.038
0.0026	1.75	62	14	6	19	*a*
0.0052	1.75	*a*	*a*	*a*	*a*	0.015

[a] Not measured.

Table III

wt naphthalene,[a] g (mmol)	product yield, mg (% yield)			
	1	2	3	4
0.1 (0.82)	80 (52)	18 (11)	21 (14)	7 (5)
1.0 (8.2)	630 (41)	121 (8)	154 (10)	55 (4)

[a] Solvent benzene (300 mL); CHD, 50 mL (0.53 mmol). [b] Irradiation with a Toshiba 45-W HP lamp, Pyrex filter, under nitrogen gas bubbling. The irradiation time was 11 h in both cases.

Experimental Section[10]

(1*RS*,2*RS*,7*SR*,8*SR*)-11,12- and (1*RS*,2*SR*,7*RS*,8*SR*)-9,10-Benzotricyclo[6.2.2.$0^{2,7}$]dodeca-3,9,11-triene (3 and 4). A solution of naphthalene (2.2 g, 0.017 mol) and 1,3-cyclohexadiene (8.4 g, 0.11 mol) in benzene (300 mL) was irradiated with a Toshiba 450-W high-pressure mercury lamp through a Pyrex filter for 24 h under a nitrogen atmosphere. After removal of the solvent, 9,10-benzotricyclo[4.2.2.$2^{2,5}$]dodeca-3,7,9-triene [1; 1.75 g, 55.7%; mp 67–68 °C (lit.[3b] mp 62–64 °C)] was filtered out as a silver complex by treatment of an ethanol solution of the reaction mixture with silver nitrate (5 g, 0.028 mol). The residual mixture was chromatographed on activated charcoal treated with silver nitrate, eluting with *n*-hexane to give 7,8-benzotricyclo[4.2.2.$2^{2,5}$]dodeca-3,7,9-triene [2; 0.173 g, 5.5%; mp 80–82 °C (lit.[3b] mp 81.5–81.0 °C)], 3 (0.371 g, 11.8%; mp 55–56 °C), and 4 (0.146 g, 4.6%; mp 84–85 °C). For 3: ^{1}H NMR (200 MHz) δ 1.24 (1 H, m, H-5′), 1.60–1.92 (3 H, m, H-5, H-6, H-6′), 2.02 (1 H, m, H-7), 2.16 (1 H, d, $J_{1,6}$ = 10 Hz, H-7), 3.82 (2 H, pseudo A_2B_2, H-1, H-8), 5.72 (1 H, dt, $J_{3,4}$ = 13 Hz, H-3), 5.84 (1 H, m, H-4), 6.43 (2 H, pseudo A_2B_2, H-9, H-10), 7.09 (4 H, A_2B_2, ArH); IR (Nujol) 1595, 795, 762, 740, 722 cm^{-1}; UV (EtOH) λ_{max} 273 nm (ϵ 261), 264 (316), 258 (253), 206 (10 380); mass spectrum (70 eV), *m*/*e* 208 (M$^+$, $C_{16}H_{16}$). Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.68; H, 7.87. For 4: ^{1}H NMR (200 MHz) δ 0.52 (1 H, m, H-5′), 1.44–1.77 (3 H, m, H-5, H-6, H-6′), 2.14 (1 H, m, H-7), 2.30 (1 H, dt, $J_{1,6}$ = 10 Hz, H-7), 3.76 (2 H, pseudo A_2B_2, H-7, H-8), 5.56 (1 H, dt, $J_{3,4}$ = 10 Hz, H-3), 5.67 (1 H, m, H-4), 6.60 (2 H, pseudo A_2B_2, H-11, H-12), 7.11 (4 H, m, Ar H); IR (Nujol) 1598, 750, 698 cm^{-1}; UV (EtOH) λ_{max} 272 nm (ϵ 257), 264 (307), 258 (254), 206 (15 200); mass spectrum (70 eV) *m*/*e* 208 (M$^+$, $C_{16}H_{16}$). Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.32; H, 7.68. As the concentration of naphthalene increases, the yields of products incease as shown in Table III.

Dehydrogenation of 3. A solution of 3 (49.8 mg, 0.24 mmol) and DDQ (200 mg, 0.88 mmol) in $CHCl_3$ was refluxed for 24 h. After the solvent was removed, the residue was chromatographed on silica gel by eluting with *n*-hexane to give 9,10-dihydro-9,10-ethenoanthracene: 4.9 mg, (10%), mp 118–119 °C (lit.[4] mp 118–118.5 °C); ^{1}H NMR (60 MHz) δ 5.00 (2 H, sextet), 6.7–7.3 (10 H, m).[4]

Thermal Decomposition of 3 and 4. Compound 3 (15 mg, 0.07 mmol) sealed in an NMR tube purged with nitrogen gas was heated at 200 °C for a few minutes to give naphthalene and 1,3-cyclohexadiene(CHD) quantitatively. 4 was also decomposed into naphthalene and CHD quantitatively under the same conditions as for 3. The yields of naphthalene and CHD were determined by GLC (comparing responses with those of a standard solution).

(1*RS*,2*RS*,3*RS*,4*SR*,7*RS*,8*SR*)-11,12- and (1*RS*,2*RS*,3*SR*,4*RS*,7*RS*,8*SR*)-11,12-Benzo-3,4-epoxytricyclo[6.2.2.$0^{2,7}$]dodeca-9,11-diene (5 and 6). To a solution of 3 (123 mg, 0.59 mmol) in $CHCl_3$ (5 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (MCPBA; 102 mg, 0.59 mmol) in $CHCl_3$(5 mL). The reaction mixture was stirred for 12 h at room temperature. After the usual workup, the $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel by eluting with 10% ethyl acetate in *n*-hexane to give 5 (90 mg, 68%; mp 115–116.5 °C) and 6 (36 mg, 27%; mp 127–129 °C). For 5: ^{1}H NMR (60 MHZ) δ 1.26–2.07 (5 H, m), 2.33 (1 H, br d, J = 8 Hz), 2.86 (2 H, m), 3.55 (1 H, m), 3.87 (1 H, m), 6.43 (2 H, m), 6.95 (4 H, m); IR (Nujol) 1595, 1571, 810, 760, 709 cm^{-1}; UV (EtOH) λ_{max} 271 nm (ϵ 389), 264 (438), 258 (337), 204 (22 600). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.21; H, 7.48. For 6: ^{1}H NMR (60 MHz) δ 1.33–2.20 (6 H, m), 3.03 (2 H, m), 3.62 (1 H, br d, J = 5 Hz), 3.92 (1 H, br d, J = 5 Hz), 6.42 (2 H, m), 6.93 (4 H, m); IR (Nujol) 1595, 818, 795, 751, 708 cm^{-1}; UV (EtOH) λ_{max} 271 nm (ϵ 399), 264 (459), 258 (357), 207 (21 000). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.83; H, 7.44.

(1*RS*,2*SR*,3*SR*,4*RS*,7*SR*,8*SR*)-9,10-Benzo-3,4-epoxytricyclo[6.2.2.$0^{2,7}$]dodeca-9,10-diene (7). The reaction of 4 with MCPBA was carried out as described for 3. The crude product was purified by column chromatography (using 10% ethylacetate in benzene as an eluent) to give 7: 80%; mp 120–121 °C; ^{1}H NMR (60 MHz) δ 0.20–0.67 (1 H, m), 0.83–2.10 (4 H, m), 2.30 (2 H, m), 2.71 (1 H, d, J = 5 Hz), 3.53 (1 H, m), 3.80 (1 H, m), 6.48 (2 H, m), 6.98 (4 H, m); IR (Nujol) 1600, 824, 804, 752, 710 cm^{-1}; UV (EtOH) λ_{max} 272 nm (ϵ 273), 264 (348), 259 (282), 205 (24 400). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.57; H, 7.16.

Direct Irradiation of 1. A solution of 1 (102 mg, 0.49 mmol) in *n*-hexane (100 mL) in quartz cell was irradiated with a Ushio 100W HP lamp for 6 h under a nitrogen atmosphere at 20 °C to give naphthalene (38. 4 mg, 61%) and uncharacterized materials, and recover 1 (18 mg, 19%).

Sensitized Irradiation of 1 in Benzene. Solutions (4 mL) containing, the sensitizer used and 1 in spectrograde dry benzene were prepared as shown in Table I. These were degassed by using a vacuum line (8 × 10^{-1} Pa) by three freeze–thaw cycles. Irradiation at 3130 Å was performed by using a Toshiba 450-W high-pressure mercury lamp through a filter system [Pyrex, $NiSO_4$ (1 kg) H_2O (1 L), 0.5-cm path length, Toshiba UV-25] for 36 h at 25 °C. Analyses of naphthalene and cage compound 8 formed in each run were performed on their ^{1}H NMR (60 MHz) spectra. 8: mp 90–91 °C; ^{1}H NMR (60 MHz) δ 1.21 (4 H, m), 2.72–3.50 (6 H, m), 3.60–4.06 (2 H, m), 7.00 (4 H, s).[3b]

Quantum Yield Determination of the Consumption of Naphthalene in the Presence of CHD. Solutions were prepared as shown in Table II, and 4 mL of each was placed in Pyrex tubes. Each sample was degassed by using a vacuum line (8 × 10^{-1} Pa) and three freeze–thaw cycles with cooling in liquid nitrogen. In a given run all sample tubes were irradiated in parallel on a "merry-go-round" apparatus at 20 °C. Benzophenone–benzohydrol actinometry was used for the quantum yield determination at 3130 Å with the filter system mentioned in the previous experiment. The relative proportions of 1–4 were determined from

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(10) All melting points are uncorrected. Infrared spectra were obtained on a JASCO IRA-1 spectrometer. Ultraviolet spectra were measured with a Hitachi UV-200 spectrometer. ^{1}H NMR spectra were recorded on a JEOL-JNM-PX60 spectrometer (60 MHz) or a Varian XL-200 spectrometer (200 MHz) in CCl_4 with tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-D300 mass spectrometer. GLC analysis were performed on a Yanaco G-180 gas chromatograph (5% OV-17 Chamelite CK 80/60 column, 1.5 × 5 mm).

the integrated areas of their vinyl signals in the ^1H NMR spectra (60 MHz).

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Registry No. 1, 82730-02-7; 2, 82730-03-8; 3, 82679-53-6; 4, 82729-99-5; 5, 82679-54-7; 6, 82730-00-5; 7, 82730-01-6; 8, 40420-35-7; naphthalene, 91-20-3; 1,3-cyclohexadiene, 592-57-4; 9,10-dihydro-9,10-ethenoanthracene, 2734-13-6; 2-naphthaldehyde, 66-99-9; xanthone, 90-47-1; acetophenone, 98-86-2; acetone, 67-64-1.

Insertion of Carbon Monoxide into Carbon-Lithium Bonds. A Convenient One-Step Synthesis of 1,2-Diketone Diaryl Derivatives[1]

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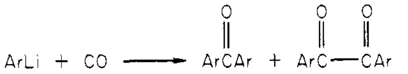
The insertion reaction of carbon monoxide into a two-center, two-electron metal-carbon bond is an extremely important transformation in organometallic chemistry.[2] Attention has recently focused on organometallic complexes of early transition metals[3,4] and actinides.[5,6] We recently reported the convenient insertion reaction of CO into the metal-carbon bond of phenyllithium to obtain α,α-diphenylacetophenone in a high yield (94%)[7] and the usefulness of the insertion reaction for the production of diphenylalkyl carbinols.[8] With the aim of exploring the scope of these interesting reactions, the behavior of 1-naphthyl- (**1a**) and (2,6-dimethylphenyl)lithium (**1b**) under several reaction conditions was examined. Only two products are formed (eq 1), and, in this sense, the reaction differs considerably from the previously studied reaction of phenyllithium with carbon monoxide in ethyl ether, for which several products were isolated.[9] The reaction of **1a** produces bis(1-naphthyl) ketone (**2a**) and 1,1-binaphthoyl (**3a**), and the reaction of (2,6-dimethylphenyl)lithium affords bis(2,6-dimethylphenyl) ketone (**2b**) and bis(2,6-dimethylphenyl)glyoxal (**3b**).



$$\underset{1}{ArLi} + CO \longrightarrow \underset{2}{ArC(=O)Ar} + \underset{3}{ArC(=O)-C(=O)Ar} \quad (1)$$

a, Ar = 1-naphthyl; b, Ar = 2,6-dimethylphenyl

Table I. Yields from Reaction of 1-Naphthyllithium with Carbon Monoxide[a]

temp, °C	THF		$(C_2H_5)_2O$		$CH_2(OCH_3)_2$		n-C_6H_{14}	
	2a	3a	2a	3a	2a	3a	2a	3a
−78	22.7	71.2[b]	32.7	58.2	32.9	61.1		
0	17.0	74.9	57.2	34.7	55.0	40.0	<1	<1
25	12.2	82.7	55.3	37.7	47.6	45.3	<1	<1

[a] The reported yields represent percent conversion.
[b] 96.1% in HMPT/THF (20:80, v/v).

Table II. Yields from Reaction of (2,6-Dimethylphenyl)lithium with Carbon Monoxide[a]

temp, °C	THF		$(C_2H_5)_2O$		$CH_2(OCH_3)_2$	
	2b	3b	2b	3b	2b	3b
−78	<1	96.4	18.3	75.7	17.1	74.4
0		96.1	31.0	62.8	28.3	64.7
25		97.5	33.2	61.6	30.5	63.8

[a] The reported yields represent percent conversion.

Table I gathers the results obtained from the reaction of **1a** at 1 atm of CO pressure. No CO absorption takes place in hexane solution at −78 °C, and the reaction is practically negligible even at higher temperatures. For the oxygenated solvents, no regular temperature effect is observed. The best result is obtained for the reaction in THF solution at 25 °C, for which a high yield of **3a** is found. The yield is improved to 96.1% when the reaction is run in HMPT/THF (20:80) at −78 °C. In the case of **1b** (Table II) the production of compound **3b** is always higher than of **3a**, and the conversion is almost complete in THF.

In the reaction of these aryllithiums the initial formation of a highly reactive acyllithium intermediate (5, eq 2) can

$$ArLi + CO \rightleftharpoons \underset{4}{[ArLi \leftarrow :CO]} \rightleftharpoons \underset{5}{[Ar\text{-}C(O)\text{-}Li \leftrightarrow Ar\text{-}C\text{-}OLi]} \quad (2)$$

be postulated as was recently proposed for the reaction of other aryllithiums (Ar = *o*-anisyl, *p*-tolil, and *o*-tolyl).[10] Evidence for the existence of benzoyllithium has been previously reported.[8,11] Alkoxy carbenes are nucleophilic in character,[12] and dimerization to form olefins is a well-characterized phenomenon.[13] Nevertheless, naphtoin is not isolated from the insertion reaction of **1a**, but its oxidation product, **3a**, is. Oxidation could occur in the reaction flask (carbon monoxide is known to be an effective oxidant toward a variety of aromatic radical ions and dianions)[14] or during the hydrolytic workup. Treatment of the reaction mixture of **1a** and carbon monoxide with acetic anhydride produces 1,2-diacetoxy-1,2-bis(1-naphthyl)ethene (**7a**, eq 3). This proves that the intermediate is the corresponding 1,2-dilithiumdiolate **6a** (formed by dimerization of **5a**) and that oxidation occurs

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