Reactions of 5,6-Dilithioacenaphthene-*N,N,N',N'*-Tetramethyl-1,2-ethanediamine Complex with α-Diketones. I. *cis*-Directing 1 : 1 Cyclic Additions with Acyclic and Cyclic α-Diketones and Related Compounds[1]

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The title complex (**3**) is readily generated from 5,6-dibromoacenaphthene with butyllithium and the diamine in ether at −10—0 °C. The reaction of **3** with biacetyl gave *cis*-1,2,5,6-tetrahydro-1,2-dimethylcyclopent[*fg*]-acenaphthylene-1,2-diol but no *trans*-isomer, whereas the reaction of pyracenequinone (PYQ) with methylmagnesium bromide gave both the *cis*- and *trans*-diols. The reactions of **3** with acenaphthenequinone and PYQ also gave *cis*-diols. On treatment with phenylboronic acid, these *cis*-diols quantitatively yielded the corresponding cyclic esters. The diols and their derivatives tend to form crystalline molecular compounds with solvent molecules. The stereoselectivity of the cyclic addition between **3** and the acyclic α-diketone can be best explained in terms of five-membered chelate-ring formation in a transition state.

5,6-Dilithioacenaphthene (**1**)[2,3] can be regarded as a nucleophile like 1,8-dilithionaphthalene (**2**)[4,5] which possesses two reaction sites at the peri positions of a naphthalene nucleus; thus, its synthetic conditions and reaction modes are of interest in connection with the peri interaction in naphthalene derivatives.[6] This paper describes an improved method for the generation of **1** as a *N,N,N',N'*-tetramethyl-1,2-ethanediamine (TMEDA) complex, and reports its *cis*-directing 1 : 1 cyclic additions with some α-diketones.

Results and Discussion

Generation of 5,6-Dilithioacenaphthene–TMEDA Complex (3).[7] The dihaloprecursor, 5,6-dibromoacenaphthene (**4**), can readily be prepared in a 15—20% yield from the reaction of acenaphthene (**5**) with *N*-bromosuccinimide by use of the procedure developed in our laboratory.[2]

An ethereal suspension of **4** was quantitatively converted into the solution of **3** by a 1 : 1 mixture of butyllithium (*n*-BuLi)[8] and TMEDA[9] at −10—0 °C within 15—30 min. Such mild conditions are preferable to those without TMEDA, in which case at least 1 h of refluxing is essential.[2] The substantially quantitative formations of 5,6-acenaphthenedicarboxylic anhydride (**6**) and 5,6-diiodoacenaphthene (**7**) confirm that the structure of **3** possesses two reaction sites at the peri positions (Eq. 1).[10]

cis-Directing 1 : 1 Cyclic Additions between 3 and α-Diketones. The reactions of **3** were investigated with three α-diketones: acenaphthenequinone (ACQ), pyracenequinone (5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione; PYQ), and biacetyl (Ac_2). Reaction conditions and results are summarized in Table 1.

The 1 : 1 cyclic additions of both ACQ and PYQ with **1** have been reported by Mitchell *et al.*[3] The reactions of the TMEDA complex (**3**) also gave the identical products (**8** and **9**) in almost the same yields

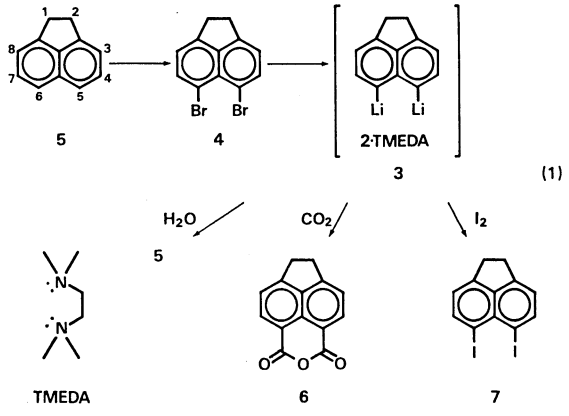
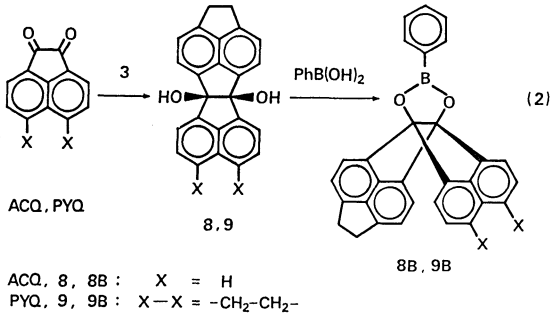


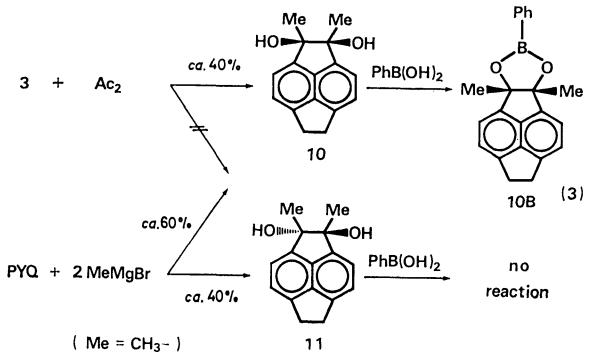
Table 1. Reactions of 5,6-dilithioacenaphthene–TMEDA complex (**3**) with α-diketones (in Et_2O)

α-Diketone	Mole ratio (diketone/**3**)	Reaction time/h[a] i	ii	iii	iv	Consumption of **3**/%[b]	Recovery of diketone/%	Product	Yield/%[c] A	B	Mp/°C[d]
ACQ	1.0	0.5	2	1	0	70	10	**8**[e]		22	320.0—322.0 (dec/Ar)
PYQ	0.5	0.5	4	1	0	60	16	**9**[f]		18	347.0—348.0 (dec/Ar)
	1.0	0.5	2	1	0	60	28	**9**		18	
	1.5	0.5	2	1	0	93	31	**9**	27		
	2.0	0.5	2	1	0	96	37	**9**	27		
Ac_2	1.1	0.5	1	1	1	85	—	**10**	40		134.0—135.0
	1.6	0.5	1	1	0	86	—	**10**	41		

a) Step i: Adding of diketone to **3** at −10—0 °C; Step ii: Stirring at −10—0 °C; Step iii: Warming to room temperature; Step iv: Refluxing. b) Based on GLC-peak-area of acenaphthene in hydrolyzed sample. c) A: Based on 5,6-dibromoacenaphthene; B: Based on α-diketone used. d) See Experimental. e) Lit,[3] mp 304—308 °C (dec), 10—20% yield. f) Lit,[3] mp 316—320 °C (dec), 13—26% yield.

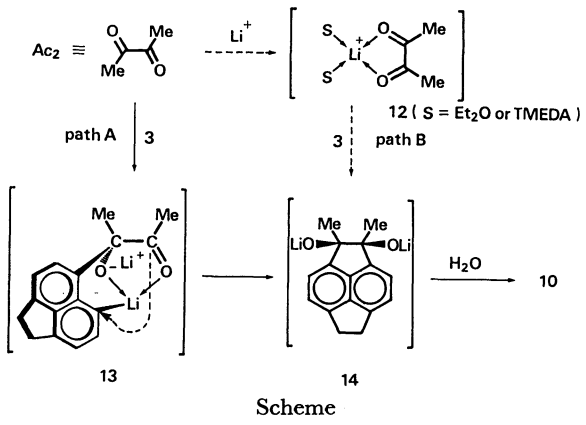
as those reported. The use of TMEDA considerably shortened each reaction-time (see Table 1) in comparison with that in the literature[3] (14 h at room temperature or 6 h on refluxing in ether). The reactions of **8** and **9** with phenylboronic acid (dihydroxyphenylborane; PhB-$(OH)_2$)[5] quantitatively yielded cyclic esters **8B** and **9B**, respectively (Eq. 2). These facts prove the *cis*-conformation of the 1,2-diols.



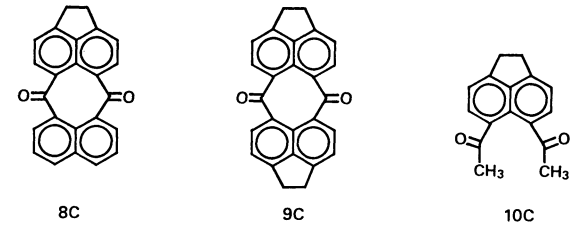


A 1 : 1 cyclic addition also took place between **3** and biacetyl and gave *cis*-diol **10** (mp 134—135 °C), which was quantitatively converted into cyclic ester **10B** with $PhB(OH)_2$. The *trans*-isomer (**11**; mp 171—172 °C) was separately synthesized from the reaction of PYQ with methylmagnesium bromide, and did not react with $PhB(OH)_2$. In this Grignard reaction, *cis*-diol **10** was also yielded in the *cis* : *trans* ratio of about 3 : 2 (Eq. 3). On the other hand, no **11** was detected in the reaction mixture of **3** with biacetyl. Hence, it is concluded that the cyclic addition of each of the three α-diketones to **3** proceeds in a completely *cis*-directing mode.

As Letsinger and Gilpin[5] have discussed in the case of **2** with ACQ, the five-membered *o*-quinone parts of ACQ and PYQ sterically require the *cis*-orientation of the addition product with **1** or **2**. But biacetyl itself, whose quasi-*trans*-conformation has been confirmed in the literature,[11] does not require the *cis*-directing cyclization. The possibility that biacetyl forms a chelate (**12**) and adopts a *cis*-conformation before the addition (Scheme, path B) has been disproved spectroscopically: The electron spectrum of biacetyl was uninfluenced by the presence of lithium cation.[12] The cyclic addition is, therefore, considered to be a two-step process that involves an α-oxide ketone intermediate (**13**) in which a five-membered chelate-ring permits only the *cis*-directing intramolecular cyclization (Scheme, path A). An analogous transition state has been proposed by Cram



Scheme



et al.[13] in order to explain the stereoselectivities in the reactions of α-hydroxy ketones and α-methoxy ketones with monofunctional organolithium compounds. In comparison with their results, the stereoselectivity of the present system is very high. This must be ascribed to the specific structure of **3** described before.

The reactions of *cis*-diols **8**, **9**, and **10** with lead(IV) acetate gave diketones **8C**, **9C**, and **10C** in 81, 84, and 92% yields, respectively, under the appropriate conditions described later. Because it has been confirmed that the reaction of **5** with acetyl chloride in the presence of aluminium chloride yields only 3,6-diacetylacenaphthene (mp 149 °C),[14] the cleavage of **10** is a new method for the synthesis of authentic 5,6-diacetylacenaphthene (**10C**; mp 156—157 °C).

It is worth noting that diols **8**, **9**, **10**, and **11**, cyclic esters **8B** and **9B**, and diketones **8C** and **9C** tend to form crystalline molecular compounds with some solvent molecules. Some of them are listed in Table 2. Notice that *cis*-diol **10** (mp 134—135 °C) formed a white molecular compound (mp 143—144 °C) with **5** (mp 94—95 °C). The solvent molecules in these crystals did not dissociate under an aspirator pressure at room temperature, whereas recrystallizations from suitable solvents separated their components, except in the case

Table 2. Crystalline molecular compounds

Component A	Component B	Composition (A : B)[a]	Mp/°C
10	Acenaphthene	2 : 1	143.0—144.0
10	Benzene	3 : 1	127.0—129.0
11	Cyclohexane	3 : 1	170.0—171.0
9B	Benzene	1 : 1	302.0—304.0[b]
9B	Cyclohexane	1 : 1	190[b]

a) Determined by elemental analysis and ^1H NMR spectrum. b) Dissociation in an argon-filled, sealed capillary.

of cyclohexane- or benzene-**9B** (see Experimental). "Solvated" crystals were also observed in the following systems: **8**/ethanol, **8**/acetone, **9**/benzene, **10**/cyclohexane, **11**/carbon tetrachloride, **8B**/cyclohexane, **8C**/acetic acid, and **9C**/acetic acid. By reference to analogous compounds known as "clathrate compounds,"[15] the three-dimensional bulkinesses of the diols and their derivatives seem to be related to the solvent inclusions.

The reactions of benzil and 9,10-phenanthrenequinone with **3** gave no 1 : 1 cyclic addition product, but rather gave unexpected, novel products. Their details will be reported separately.[16]

Experimental

General Procedures. All melting points except that over 360 °C are corrected; some of them were measured in argon-filled, sealed capillaries after degassing. Electron spectra were determined on a Shimadzu UV-200 double beam spectrophotometer. Fluorescence excitation- and emission-spectra were measured on a Shimadzu RF-501 recording spectrofluorophotometer. IR spectra were taken on a JASCO IRA-1 spectrophotometer, using KBr pressed discs. ^{1}H NMR spectra were recorded on a JEOL JNR-PS-100 (100 MHz) or a Hitachi R-40 (90 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane as an internal standard. In assignments, abbreviations PhH, NpH, ActH, and ArH mean benzene-, naphthalene-, and acenaphthene-ring protons and aromatic protons, respectively. Mass spectra were taken on a JEOL JMS-D-100 or a Hitachi RMU-7M mass spectrometer at an ion-source temperature of 200 °C and an ionizing voltage of 70 eV unless otherwise indicated. Analytical determinations by GLC were performed on a Shimadzu GC-3BT gas chromatograph operated at 220 °C with a 3 m×3 mm column of 10% SE-30 on Celite 545SK and with helium as carrier gas.

Pyracenequinone was prepared according to the reported method;[17] mp 304.0—306.0 °C (dec), (lit,[17a] mp 305—306 °C). All other chemicals were obtained commercially.[18] Acenaphthenequinone[18a] was recrystallized from toluene. Each of the quinones was ground down and degassed *in vacuo* before use. The biacetyl used was freshly distilled. Lithium perchlorate[18c] was dried at 200 °C/0.1 mmHg† for 2 h. Acetonitrile (Dotite Spectrosol)[18b] was dried with Molecular Sieves 5A. Under an argon atmosphere, "dry" solvents (diethyl ether and benzene) were distilled from sodium wire and then stored with Molecular Sieves 4A or 5A. TMEDA[18a] was refluxed with calcium hydride for 2—3 h and distilled.

All the reactions of **3** and of lead(IV) acetate were carried out under an argon atmosphere. All organic extracts were washed with aqueous concd sodium chloride and dried with anhydrous magnesium sulfate unless otherwise indicated. All evaporations were carried out under a reduced pressure on a rotary evaporator below *ca.* 50 °C.

5,6-Dibromoacenaphthene (4). This was prepared by the method of Yoshiwara[2] with modifications. To a *N,N*-dimethylformamide (DMF) suspension of acenaphthene (77.1 g, 0.50 mol in 250 cm^3), a DMF solution of *N*-bromosuccinimide (NBS)[18c] (89.0 g, 0.50 mol in 250 cm^3) was added dropwise over a period of 90 min at 30—40 °C. After the mixture had been stirred for 1 h at about 30 °C, additional NBS (133.5 g, 0.75 mol) was added in portions over a period of 90 min, the temperature being maintained at 30—40 °C. The dark mixture which formed was stirred for 2 h at about 30 °C and then allowed to stand overnight in a refrigerator. The pale yellow crystalline **4** which precipitated was filtered off, washed with a small amount of DMF and 100 cm^3 of methanol, and dried *in vacuo*. This crude product (mp 166.5—171.5 °C) was recrystallized from carbon tetrachloride,[19] giving 24—31 g (15—20%) of pure **4** as almost colorless needles: mp 174.0—176.0 °C, (lit,[3] mp 173—175 °C).

Generation of 3. All solutions of **3** were prepared just before use as follows. All glassware pieces were heated in a drying oven (*ca.* 100 °C) and then quickly assembled; **4** (1.560 g, 5.00 mmol) was introduced into a four-necked 500 cm^3-flask which was then equipped with a thermometer, a stopcock for sampling, a pressure-equalizing addition funnel joined with a stopcock, and a reflux condenser joined with a three-way stopcock for attachment to a vacuum-line and an argon-line. During a few repetitions of the pumping—argon-introducing cycle, the crystals of **4** were milled with a magnetic stirrer. Dry ether (300 cm^3 or 150 cm^3) was introduced into the flask with syringe-technique and then cooled on an ice–ethanol bath. During the period of cooling, *n*-BuLi (12.0 mmol in 5.5 cm^3 of hexane) was injected into the addition funnel and then mixed with TMEDA (2 cm^3, 13.3 mmol). After the yellow suspension which resulted had been allowed to stand for 15 min, it was added dropwise to the ethereal suspension over a period of 15 min with gentle stirring, and the pale red solution which formed was then stirred for 15 min. During these operations, the temperature was maintained at −10—0°C. A 0.5—1.0 cm^3 of sample of the solution was added to aqueous ammonium chloride and then analyzed gas-chromatographically. The relative peak-area of acenaphthene is usually≥99% within 5—12 min after the adding of *n*-BuLi–TMEDA. In case that a theoretical amount of *n*-BuLi was used, 5—10% of 5-bromoacenaphthene[20] was observed.

5,6-Acenaphthenedicarboxylic Anhydride (6). A solution of **3** (5.00 mmol in 150 cm^3 of ether) was cooled below −70 °C and poured onto crushed dry ice under an argon atmosphere. After the mixture had been allowed to come to room temperature, the white salt which formed was filtered off, washed with ether, and dried *in vacuo*. The quantitative yield of lithium salt (mp>340 °C) was extracted with 30 cm^3 of aqueous 5% sodium carbonate, and the extract was acidified with concd hydrochloric acid, giving 1.11 g (91.4%) of crude 5,6-acenaphthenedicarboxylic acid: mp 282.0—289.0 °C (dec/Ar); IR 3600—2400 (broad band) and 1670 cm^{-1} (C=O). Recrystallization from acetic acid gave anhydride **6**: mp 298.5—299.5 °C (under Ar), (lit,[21] mp 293—294 °C); $UV_{max}(C_2H_5OH)$ 213.5 (log ε 4.20), 237 (4.41), 247 (4.34), 332 (3.89), and 352 nm (3.88); IR 1790, 1765, and 1740 cm^{-1} (C=O).

(Found: C, 75.41; H, 3.26%).

5,6-Diiodoacenaphthene (7). To a solution of **3** (5.00 mmol in 300 cm^3 of ether), a solution of iodine (2.82 g, 11.1 mmol in 25 cm^3 of ether) was added dropwise over a period of 30 min at −10—0 °C. The dark mixture was stirred for 30 min with cooling and for 1 h without cooling. To the mixture 100 cm^3 of aqueous 5% sodium thiosulfate was added with vigorous stirring. The organic layer which separated was washed with aqueous sodium thiosulfate and then water, dried, and evaporated. The pale brown residue, 1.94 g (95.4%) of crude **7** (mp 144.0—148.5 °C), was recrystallized from hexane and then ethanol,[19] giving 1.26 g (62%) of pure **7**: mp 159.0—160.5 °C (dec), (lit,[22] mp 159—160 °C).

(Found: C, 35.44; H, 1.90; I, 62.24%).

cis-1,2-Dihydrocyclopenta[1,2-a: 3,4,5-f'g']diacenaphthylene-4b,10b-diol (8). Acenaphthenequinone (0.900 g, 4.94 mmol)

† 1 mmHg≃133.3 Pa.

was added to a solution of **3** (5.13 mmol in 300 cm³ of ether) with vigorous stirring over a period of 30 min at −10—0 °C. The deep violet suspension which resulted was stirred for 2 h with cooling and for 1 h without cooling. Aqueous ammonium chloride (30 g/100 cm³) was added to the suspension with vigorous stirring. The dark yellow solid which precipitated was filtered off, washed with water and ether, and dried *in vacuo*; 87 mg (9.7%) of the quinone being recovered. The combined organic layer was washed, dried, and evaporated. The residue was washed with hot carbon tetrachloride and water and dried *in vacuo*, giving 326 mg (21.8%) of crude **8** (mp 280—283 °C (dec)). Recrystallization from benzene[19] gave 269 mg (16.2%) of pure **8** as white needles: mp 320.0—322.0 °C (dec/Ar), (lit,[3] mp 304—308 °C (dec)); UV_{max} (C_2H_5OH) 219 (log ε 4.89), 265 (3.54), 275 (3.75), 287 (3.88), 316 (4.13), and 330 nm (4.15); $Fluorescence_{max}$ (C_2H_5OH) 398 nm (excitation at 325 nm); IR 3500 and 3350 cm^{-1} (OH); MS (215 °C, 30 eV), *m/e* (rel intensity), 336 (100), 318 (34), 317 (21), and 290 (25).

(Found: C, 85.89; H, 4.58%).

cis-*1,2,7,8-Tetrahydropentaleno*[*1,2,3*-fg: *4,5,6*-f′g′]*diacenaphthylene-4b,10b-diol* (**9**). A solution of **3** (5.00 mmol in 300 cm³ of ether) was treated with pyracenequinone (1.60 g, 7.67 mmol) as described above for **8**. After hydrolysis, the unreacted pyracenequinone was extracted with aqueous 10% sodium hydrogensulfite,[17] 499 mg (31.2%) of the quinone being recovered. Crude **9** (27.4%, mp 292—295 °C (dec)) was recrystallized from benzene[19] and then acetone, giving 386 mg (21.3%) of pure **9** as a white powder: mp 347.0—348.0 °C (dec/Ar), (lit,[3] mp 316—320 °C (dec)); UV_{max} (C_2H_5OH) 216 (log ε 4.80), 230 (4.87), 259 (3.28), 269 (3.51), 280 (3.78), 291 (3.96), 319 (4.19), and 333 nm (4.24); $Fluorescence_{max}$ (C_2H_5OH) 394 nm (excitation at 328 nm); IR 3435 and 3315 cm^{-1} (OH); MS, *m/e* (rel intensity), 362 (100), 361 (27), 360 (44), 359 (23), 345 (29), 344 (69), 343 (36), 334 (19), 333 (36), and 332 (16).

(Found: C, 86.22; H, 4.79%).

cis-*1,2,5,6-Tetrahydro-1,2-dimethylcyclopent*[fg]*acenaphthylene-1,2-diol* (**10**). To a solution of **3** (10.0 mmol in 300 cm³ of ether), a solution of biacetyl (1.35 g, 15.6 mmol in 50 cm³ of ether) was added over a period of 30 min at −10—0 °C. The pink suspension which resulted was stirred for 1 h with cooling and for 1 h without cooling, and then hydrolyzed with aqueous ammonium chloride (30 g/100 cm³). The organic layer which separated was washed, dried, and evaporated. The dark residue was dissolved in 10 cm³ of hot benzene and allowed to stand at room temperature for one day, giving 950 mg of a colorless crystal (mp 127.0—129.0 °C). This was spectrally identical with the molecular compound, benzene-**10**, prepared separately; the yield as $C_6H_6 \cdot 3C_{16}H_{16}O_2$ was 35.7%. The combined filtrate was evaporated and allowed to stand for four days, giving 162 mg of a pale brown crystal (mp 133.0—143.0 °C). This was spectrally identical with the molecular compound, acenaphthene-**10**, the yield as $C_{12}H_{10} \cdot 2C_{16}H_{16}O_2$ being 5.1%. Each of the molecular compounds was recrystallized from hexane,[19] giving a total of 914 mg (38.0%) of pure **10** as white needles: mp 134.0—135.0 °C; UV_{max} (*c*-C_6H_{12}) 226sh (log ε 4.71), 232 (4.87), 250 (2.83), 260sh (3.09), 273sh (3.58), 284 (3.84), 292sh (3.90), 296 (3.93), 305 (3.78), 311 (3.69), 319sh (3.12), and 325 nm (3.27); $Fluorescence_{max}$ (*c*-C_6H_{12}) 386 nm (excitation at 303 nm); IR 3350 (OH), 3035, 2975, 2930 sh, 2915, 2835, 1165, and 1090 cm^{-1}; NMR ($CDCl_3$) δ=7.33 (2H, d, J=7.0 Hz, *m*-CH_2–ActH), 7.26 (2H, broad d, J=7.0 Hz, *o*-CH_2–ActH), 3.42 (4H, s, $2CH_2$), 3.14 (2H, s, exch., 2OH), and 1.59 (6H, s, $2CH_3$); MS, *m/e* (rel intensity), 240 (14), 222 (12), 221 (16), 207 (48), 198 (17), 197 (100), and 179 (19).

Found: C, 79.95; H, 6.72%; M^+ 240.1121. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%; M, 240.1150.

Molecular Compounds of **10**. *With Benzene*: A recrystallization of **10** from benzene gave benzene-**10** (1/3) as white needles; mp 127.0—129.0 °C. The IR spectrum and NMR spectrum were identical with those of pure **10**, except for the bands at 1485 and 680 cm^{-1} and δ 7.29 ppm, which are characteristic of benzene. The ratio of NMR peaks was ArH : CH_2 : OH : CH_3=6 : 4 : 2 : 6. The benzene molecule in the crystal did not dissociate at 20 °C/20 mmHg, but the crystal sublimed at 100 °C/0.1 mmHg, giving pure **10**.

Found: C, 81.18; H, 6.79%. Calcd for $C_6H_6 \cdot 3C_{16}H_{16}O_2$: C, 81.17; H, 6.81%.

With Acenaphthene: Acenaphthene (64 mg) and **10** (99 mg) were dissolved in 6 cm³ of ether and allowed to stand for one day at −20 °C. A white precipitate formed (76 mg, mp 142—144 °C); this was filtered off and recrystallized once from ether, giving acenaphthene-**10** (1/2); mp 143.0—144.0 °C; UV_{max} (*c*-C_6H_{12}) 228 (log ε based on the assumption that the molecular weight is 317.40: 4.99), 250 sh (2.88), 286 (3.97), 292 (4.02), 296 (4.01), 305 (3.85), 310 (3.71), 320 (3.31), and 325 nm (3.26); IR 3350 and 3310 sh (OH), 3070, 3035, 2995, 2970, 2920, 2840, 1165, and 1090 cm^{-1}; NMR ($CDCl_3$) δ= 7.57—7.18 (7H, m, ArH), 3.42 (4H, s, CH_2 of **10**), 3.37 (2H, s, CH_2 of **5**), 3.00 (2H, s, exch., 2 OH), and 1.60 (6H, s, $2CH_3$).

Found: C, 82.87; H, 6.59%. Calcd for $C_{12}H_{10} \cdot 2C_{16}H_{16}O_2$: C, 83.25; H, 6.67%.

Reaction of Pyracenequinone with Methylmagnesium Bromide. Under an argon atmosphere, methylmagnesium bromide[18a] (16.8 mmol in 5.6 cm³ of dibutyl ether) and 150 cm³ of dry ether were introduced into a three-necked 300 cm³-flask, and pyracenequinone (848 mg, 4.07 mmol) was added to the solution over a period of 30 min. After 2 h of refluxing, the mixture was cooled on an ice bath and hydrolyzed with aqueous ammonium chloride (15 g/50 cm³). The organic layer which separated was washed, dried, and evaporated. The resulting dibutyl ether suspension was allowed to stand at −20 °C for 16 h. The pale yellow precipitate was then filtered off, washed with carbon tetrachloride, and dried *in vacuo*, giving 287 mg (29.3%) of crude *trans*-diol **11** (mp 168.5—170.0 °C). The combined filtrate was treated three times in a similar manner, giving 200 mg (20.4%) of crude *cis*-diol **10** (mp 130.0—132.5 °C) and 452 mg in total of a mixture of **10** and **11** (NMR spectral isomeric ratio *cis* : *trans*= 8 : 1—4 : 1). Averaged over repeated runs, the total yield of **10** and **11** was >95% and the total *cis* : *trans* ratio was approximately 3 : 2. The crude **10** and **11** on this run were individually recrystallized from hexane,[19] giving 123 mg (12.6%) of pure **10** and 237 mg (24.2%) of pure **11**: mp 171.0—172.0 °C; UV_{max} (*c*-C_6H_{12}) 224sh (log ε 4.63), 232 (4.89), 273sh (3.58), 284 (3.83), 295 (3.92), 305 (3.76), 310sh (3.65), 320sh (3.12), and 325 nm (3.18); $Fluorescence_{max}$ (*c*-C_6H_{12}) 387 nm (excitation at 304 nm); IR 3330 (OH), 3085, 3045, 2975, 2925, 2840, 1180, 1055, and 1025 cm^{-1}; NMR ($CDCl_3$) δ=7.34 (2H, d, J=7.5 Hz, *m*-CH_2–ActH), 7.28 (2H, broad d, J=7.5 Hz, *o*-CH_2–ActH), 3.44 (4H, s, $2CH_2$), 1.85 (2H, s, exch., 2OH), and 1.70 (6H, s, $2CH_3$); MS (150 °C, 75 eV), *m/e* (rel intensity), 240 (30), 222 (12), 221 (15), 207 (36), 198 (18), 197 (100), and 179 (11).

Found: C, 80.04; H, 6.70%; M^+ 240. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%; M, 240.

Molecular Compound of **11** *with Cyclohexane*: A recrystallization of **11** from cyclohexane gave cyclohexane-**11** (1/3) as white hair-like crystals; mp 170.0—171.0 °C; IR 3340 (OH), 3085, 3040, 2980, 2925, 2840, 1180, 1055, and 1025 cm^{-1}.

The NMR spectrum was identical with a 1 : 3 mixture of cyclohexane and **11**. The cyclohexane molecule in the crystal did not dissociate at 20 °C/20 mmHg for 48 h, but did at 20 °C/0.1 mmHg, the weight-loss-ratio being 9.95% after 8 h (Calcd for: 10.45%).

Found: C, 80.07; H, 7.28%. Calcd for $C_6H_{12}\cdot 3C_{16}H_{16}O_2$: C, 80.56; H, 7.51%.

1,2-Dihydro-14-phenyl-4b,10b-(epoxyboroxy)cyclopenta[1,2-a : *3,4,5*-f'g']*diacenaphthylene (8B).* A mixture of *cis*-diol **8** (168.25 mg, 0.5002 mmol) and phenylborenic acid[18a] (62.39 mg, 0.5116 mmol) in 50 cm³ of benzene was refluxed for 2 h. After a trace amount of suspended matter had been filtered off, the solution was evaporated to dryness, giving a quantitative yield of crude **8B** (mp 303—305 °C (under Ar)). Recrystallization from benzene gave 187.3 mg (88.7%) of pure **8B** as white needles: mp 307.0—308.0 °C (under Ar); UV_{max} (c-C_6H_{12}) 220sh (logε 4.79), 227 (4.81), 254 (3.50),264 (3.69), 274 (3.91), 280sh (3.75), 285 (4.01), 300sh (3.96), 313 (4.18), and 328 nm (4.22); $Fluorescence_{max}$ (c-C_6H_{12}) 390 nm (excitation at 322 nm); IR 3045, 2915, 2835, 1605, 1385, 1345 (-B-O-), and 1085 cm^{-1}; NMR ($CDCl_3$) δ=8.04—7.96 (2H, m, α-NpH), 7.89 (2H, d, J=7.1 Hz, m-CH_2-ActH), 7.89—7.78 (2H, m, o-B-PhH), 7.78—7,51 (4H, m, β-NpH), 7.43—7.17 (3H, m, m- and p-B-PhH), 7.27 (2H, d, J=7.1 Hz, o-CH_2-ActH), and 3.41 (4H, s, $2CH_2$); MS (220 °C, 75 eV), m/e (rel intensity), 422 (100), 421 (23), 318 (21), 300 (23), 288 (22), 262 (73), 186 (84), 149 (66), 104 (42), and 77 (30).

Found: C, 85.38; H, 4.44%; M$^+$ 422 and 421. Calcd for $C_{30}H_{19}BO_2$: C, 85.33; H, 4.53%; M-^{11}B, 422 and M-^{10}B, 421.

1,2,7,8-Tetrahydro-14-phenyl-4b,10b-(epoxyboroxy)pentaleno[1,2,-3-fg : *4,5,6*-f'g']*diacenaphthylene (9B) and Its Molecular Compounds.* *cis*-Diol **9** (181.44 mg, 0.5006 mmol) was treated with phenylboronic acid (62.41 mg, 0.5119 mmol) in 50 cm³ of benzene as described above for **8B**. The white crystalline residue was dried overnight under an aspirator pressure, giving 262.4 mg (99.6%) of crude benzene-**9B** (mp 299—302 °C (under Ar)). Recrystallization from benzene gave pure benzene-**9B** (1/1) as white needles: mp 302.0—304.0 °C (under Ar); MS (150 °C, 75 eV), m/e (rel intensity), 448 (100) and 78 (48). The λ_{max}'s of the UV spectrum in cyclohexane were identical with those of pure **9B** and the logε's, based on the assumption that the molecular weight is 526.44, were consistent with those of **9B** within $\pm$0.03. The IR spectrum and NMR spectrum were identical with those of pure **9B**, except for the bands at 3090, 3075, 1485, and 680 cm^{-1} and δ 7.33 (6H, s).

Found: C, 87.06; H, 5.00%. Calcd for $C_6H_6\cdot C_{32}H_{21}BO_2$: C, 86.70; H, 5.17%.

On recrystallization from cyclohexane, benzene-**9B** was converted into cyclohexane-**9B** (1/1). Under an argon atmosphere, these white needles melt at 190 °C with foaming and immediately solidify, and then re-melt at 300.0—301.0 °C. The UV spectrum, IR spectrum, NMR spectrum, and MS confirmed the composition to be the same as in the case of benzene-**9B**.

Found: C, 85.51; H, 5.87%. Calcd for $C_6H_{12}\cdot C_{32}H_{21}BO_2$: C, 85.71; H, 6.25%.

On heating at 100 °C/0.1 mmHg for 16 h and at 160 °C/0.1 mmHg for 8 h, 47.749 mg of cyclohexane-**9B** (1/1) gave 40.311 mg of pure **9B**: mp 306.0—307.0 °C; Weight loss, found: 15.58%, calcd: 15.81%; UV_{max} (c-C_6H_{12}) 224sh (logε 4.96), 230 (5.01), 258sh (3.01), 268 (3.56), 275sh (3.68), 278 (3.85), 286sh (3.81), 290 (4.04), 304sh (4.00), 315 (4.23), and 330 nm (4.30); $Fluorescence_{max}$ (c-C_6H_{12}) 390 nm (excitation at 326 nm); IR 3030, 2915, 2835, 1605, 1380, 1345 (-B-O-), 1115, and 1080 cm^{-1}; NMR ($CDCl_3$) δ=7.87 (4H, d, J=7.1 Hz, m-CH_2-ActH), 7.88—7.78 (2H, m, o-B-PhH), 7.36—7.22 (3H, m, m- and p-B-PhH), 7.27 (4H, d, J=7.1 Hz, o-CH_2-ActH), and 3.40 (8H, s, $4CH_2$); MS (150 °C, 75 eV), m/e (rel intensity), 448 (100), 447 (27), 420 (8), 344 (12), 343 (16), 326 (8), 316 (10), 315 (10), 313 (11), 262 (17), 186 (13), 149 (34), 104 (5), and 77 (25).

Found: C, 85.69; H, 4.65%; M$^+$ 448 and 447. Calcd for $C_{32}H_{21}BO_2$: C, 85.73; H, 4.72%; M-^{11}B, 448 and M-^{10}B, 447.

1,2,4b,7a-Tetrahydro-4b,7a-dimethyl-6-phenylcyclopent[5,6]acenaphtho[1,2-d][*1,3,2*]*dioxaborole (10B).* *cis*-Diol **10** (240.76 mg, 1.002 mmol) was treated with phenylboronic acid (126.10 mg, 1.034 mmol) as described above for **8B**. A quantitative yield of crude **10B** (mp 164—168 °C) was recrystallized from hexane, giving 262.8 mg (80.4%) of pure **10B**: mp 169.5—171.0 °C; UV_{max} (c-C_6H_{12}) 227 (logε 4.83), 231 (4.93), 254 (3.21), 261sh (3.41), 269sh (3.62), 274 (3.72), 279sh (3.81), 283 (3.90), 291 (3.95), 295 (3.99), 304 (3.83), 310 (3.71), 319 (3.09), and 324 nm (3.13); $Fluorescence_{max}$ (c-C_6H_{12}) 387 nm (excitation at 303 nm); IR 3060, 2985, 2945, 2915, 1600, 1390, 1385, 1350 (-B-O-), and 1090 cm^{-1}; NMR ($CDCl_3$) δ=7.81—7.71 (2H, m, o-B-PhH), 7.49 (2H, d, J=7.1 Hz, m-CH_2-ActH), 7.43—7.14 (3H, m, m- and p-B-PhH), 7.29 (2H, broad d, J=7.1 Hz, o-CH_2-ActH), 3.43 (4H, s, $2CH_2$), and 1.86 (6H, s, $2CH_3$); MS (160 °C, 75 eV), m/e (rel intensity), 326 (100), 325 (24), 311 (4), 283 (66), 282 (17), 222 (22), 221 (19), 207 (15), 205 (12), 189 (10), 179 (18), 178 (13), 152 (12), 149 (8), 104 (16), and 77 (12).

Found: C, 81.24; H, 5.81%; M$^+$ 326 and 325. Calcd for $C_{22}H_{19}BO_2$: C, 81.01; H, 5.87%; M-^{11}B, 326 and M-^{10}B, 325.

1,2-Dihydronaphtho[1',8': 5,6,7]cyclooct[1,2,3-fg]*acenaphthylene-5,12-dione (8C).* A mixture of diol **8** (132.5 mg, 0.3939 mmol) and lead(IV) acetate[18a] (291 mg, 1.50 molar ratio) in 30 cm³ of dry benzene was stirred at room temperature for 2 h, refluxed for 30 min, and allowed to come to room temperature. To the mixture 20 cm³ of dil hydrochloric acid was added dropwise. The pale yellow precipitate which formed was filtered off, washed with benzene, dil hydrochloric acid, and then water, and dried *in vacuo*, giving 106 mg (80.5%) of crude **8C**. Recrystallization from benzene gave pure **8C**: mp 343.0—345.0 °C (dec/Ar), (lit,[3] mp 330—334 °C (dec)); UV_{max} (C_6H_6) 320sh (logε 4.08) and 334 nm (4.13); $Fluorescence_{max}$ (C_6H_6) 401 nm (excitation at 333 nm); IR 1680 cm^{-1} (C=O); MS, m/e (rel intensity), 334 (100), 333 (45), 306 (17), 278 (41), 277 (52), 276 (61), and 275 (12).

(Found: C, 85.84; H, 3.78%).

1,2,8,9-Tetrahydrocycloocta[1,2,3-fg : *5,6,7*-f'g']*diacenaphthylene-5,12-dione (9C).* A mixture of diol **9** (135.0 mg, 0.3725 mmol) and lead(IV) acetate (300 mg, 1.63 molar ratio) in 20 cm³ of dry benzene was treated as described above for **8C**, giving 112.8 mg (84.0%) of almost pure **9C**. Recrystallization from benzene gave pure **9C** as pale yellow needles: mp 390—400 °C (uncorrected, dec/Ar), (lit,[3] mp >330 °C (dec)); UV_{max} (C_6H_6) 326sh (logε 4.04) and 341 nm (4.12); $Fluorescence_{max}$ (C_6H_6) 400 nm (excitation at 339 nm); IR 1680 cm^{-1} (C=O); MS (240 °C, 35 eV), m/e (rel intensity), 360 (100), 359 (24), 332 (9), 331 (20), 304 (9), and 303 (13).

(Found: C, 86.63; H, 4.21%).

5,6-Diacetylacenaphthene (10C). A mixture of diol **10** (240.6 mg, 1.001 mmol) and lead(IV) acetate (600 mg, 1.22 molar ratio) in 25 cm³ of dry benzene was treated as described above for **8C**, except that the lead(II) acetate which precipitated was filtered off and the filtrate was chromatographed on a column of Wakogel C-200[18b] (40 g). After tarry matters (mainly silicone grease) had been extracted with benzene, the effluent with chloroform was collected and evaporated to dryness, giving 219 mg (91.8%) of crude **10C** (mp 153—155

°C). Recrystallization from cyclohexane gave 156 mg (65.4%) of pure **10C** as pale yellow plates: mp 156.0—157.0 °C; UV_{max} (*c*-C_6H_{12}) 230 (logε 4.60), 277sh (3.63), 310 (3.93), and 324sh nm (3.84); (Fluorescence was not detected.); IR 3045, 3015, 2940, 2910, 1670 (C=O), 1605, 1275, 1210, and 1115 cm^{-1}; NMR ($CDCl_3$) δ=7.80 (2H, d, J=7.1 Hz, *o*-CH_3CO-ActH), 7.35 (2H, broad d, J=7.1 Hz, *o*-CH_2-ActH), 3.44 (4H, s, $2CH_2$), and 2.70 (6H, s, $2CH_3CO$); MS (70 °C, 75 eV), *m/e* (rel intensity), 238 (29), 224 (19), 223 (100), 195 (14), 165 (22), 152 (21), 151 (10), 150 (5), and 149 (5).

Found: C, 80.53; H, 5.84%; M^+ 238. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%; M, 238.

References

1) Presented partly at 37th National Meeting of the Chemical Society of Japan, Yokohama, April 1978, Abstr. No. 2D04.

2) T. Kasai and J. Yoshiwara, 34th National Meeting of the Chemical Society of Japan, Hiratsuka, April 1976, Abstr. No. 2G22.

3) R. H. Mitchell, T. Fyles, and L. M. Ralph, *Can. J. Chem.*, **55**, 1480 (1977).

4) R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, **27**, 672 (1962); J. Meinwald, D. Dauplaise. F. Wudl, and J. J. Hauser, *J. Am. Chem. Soc.*, **99**, 255 (1977); J. F. Blount, F. Cozzi, J. R. Damewood, Jr., L. D. Iroff, U. Sjöstrand, and K. Mislow, *ibid.*, **102**, 99 (1980) and the references cited therein.

5) R. L. Letsinger and J. A. Gilpin, *J. Org. Chem.*, **29**, 243 (1964).

6) For an extensive review, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

7) See a) B. J. Wakefield, "The Chemistry of Organolithium Compounds," Pergamon Press, New York (1974); b) J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969).

8) Probably because of technical losses, a 10—20% excess of *n*-BuLi was required for the quantitative conversion of **4** into **3** (see Experimental).

9) Refs. 7a p. 8 and 7b p. 695.

10) Apparently the metal–bromine exchange exceeded the abstraction of the benzylic hydrogens[10a,b] in reaction rate: a) L. D. Kershner, J. M. Gaidis, and H. H. Freedman, *J. Am. Chem. Soc.*, **94**, 985 (1972); b) W. E. Rhine, J. H. Davis, and G. Stucky, *J. Organomet. Chem.*, **134**, 139 (1977).

11) P. H. Cureton, C. G. Le Fèvre, and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1961**, 4447 and the references cited therein.

12) λ_{max}/nm (acetonitrile, [biacetyl]=0.02293 mol dm^{-3}) 270 (ε 16.8), 280sh (15.4), 416 (19.95), and 436sh (16.9); λ_{max}/nm (acetonitrile, [biacetyl]=0.02293 mol dm^{-3}, [$LiClO_4$] =0.024 mol dm^{-3}) 270 (ε 16.9), 280sh (15.7), 416 (19.9), and 436sh (16.8). Metal cation effects in UV spectra of some other diketones have been reported by K. Sasaki and A. Kitani, *J. Electroanal. Chem. Interfacial Electrochem.*, **94**, 201 (1978).

13) D. J. Cram and D. R. Wilson, *J. Am. Chem. Soc.*, **85**, 1245 (1963); *cf.* Ref. 7a p. 131.

14) H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 214 (1959); L. A. Carpino and S. Göwecke, *ibid.*, **29**, 2824 (1964).

15) N. Kaneniwa, *Kagaku No Ryoiki*, **15**, 252, 345, 427 (1961); K. Takemoto, "Hosetsu-kagoubutsu No Kagaku," Tokyo Kagaku Dojin, Tokyo (1969).

16) N. Tanaka and T. Kasai, *Bull. Chem. Soc. Jpn.*, **54**, 3026 (1981).

17) a) B. M. Trost, *J. Am. Chem. Soc.*, **91**, 918 (1969); b) J. K. Stille, G. K. Noren, and L. Green, *J. Polym. Sci., Part A-1, Polym. Chem.*, **8**, 2245 (1970).

18) a) Tokyo Kasei Kogyo Co., Ltd.; b) Wako Pure Chemical Industries, Ltd.; c) Nakarai Chemicals, Ltd.

19) The hot solution was treated with decolorizing charcoal.

20) Authentic 5-bromoacenaphthene (mp 54.0—55.0 °C, lit,[3] mp 53.5—55.0 °C) was prepared according to the reported method: S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **80**, 4327 (1958).

21) M. Freund and K. Fleischer, *Justus Liebigs Ann. Chem.*, **399**, 182 (1913).

22) R. L. Clough, P. Mison, and J. D. Roberts, *J. Org. Chem.*, **41**, 2252 (1976).