Annelation of Tricarbonyliron Complexes of Ortho-Disubstituted [4]Annulenes. Synthesis of a Dibenzobicyclo[6.2.0]decapentaene via Ortho,Ortho′ Cyclobisacylation of a Biphenyl

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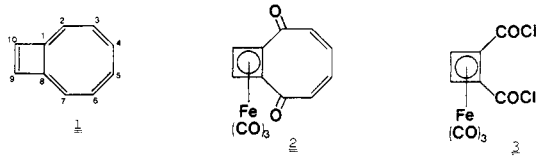
Abstract: Cyclobisacylation of para,para′-disubstituted biphenyls with diacid chloride **3** has been developed as a route to a dibenzo derivative of bicyclo[6.2.0]decapentaene. Application of this approach to *p,p′*-dimethylbiphenyl and 2,7-di-*tert*-butylfluorene afforded diketones **6** and **11,** respectively. ^{1}H NMR spectroscopy revealed that **6** is a twisted, highly rigid, enantiomerically stable, bridged biphenyl in contrast to **11,** in which the biphenyl unit is essentially planar due to the structural constraints of the fluorene moiety. Hydride reduction of **6** and **11** led to cis,syn-diols **7** and **12,** respectively. Attempts to decomplex **7** to hydrocarbon **8** with hydrochloric acid in tetrahydrofuran failed. Similar decomplexation of **12,** however, afforded hydrocarbon **13** as an unstable solid. The contrast in decomplexation results could reflect an increased stability in **13** through flattening of the biphenyl unit. Comparison with the known tribenzo derivative **17,** however, reveals that any stabilization gained through such a flattening process is much less effective than fusion of an additional benzene ring to the system. **13** exhibits dienophilic reactivity with 1,3-diphenylisobenzofuran at the cyclobutene olefinic bond to give adduct **14.** Significant shielding of methyl, methylene, olefinic, and fluorenyl protons in the latter could be due to shielding by distant aromatic moieties or to a paramagnetic ring current associated with a flattened [8]annulene system. **14** was dehydrated to the highly extended hydrocarbon **15.**

Introduction

In the course of developing the [4]annulene tricarbonyliron route to bicyclo[6.2.0]decapentaene (**1**),[1] we considered the possibility of applying to complexes of type **2** our previously reported method for conversion of *o*-diacyl[4]annulene tricarbonyliron complexes to dimethylenecyclobutenes.[2] Since **2** itself did not seem accessible by any straightforward existent

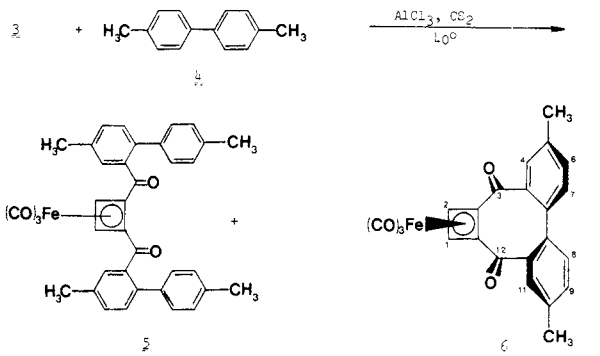


synthetic methodology, we directed our efforts instead toward exploration of ortho,ortho′-cyclobisacylation of biphenyls with bis(acid chloride) **3**[3] as a route to [3,4:5,6]dibenzo derivatives of **2.** Apparently the only precedent for this type of reaction is that of Liebermann who in 1911 reported the Friedel-Crafts acylation of 4,4′-dimethylbiphenyl with oxalyl chloride to give 2,7-dimethylphenanthra-9,10-quinone (45–50%) and who also pointed out the necessity of using a para,para′-disubstituted biphenyl to block preferred para attack.[4] We have now found that [8]annelation of this type can, in fact, be effected with **3** and describe here the preparation and decomplexation of two structural variants of **2.** The results are particularly interesting in demonstrating the dependence of the course of decomplexation on substrate stereochemistry and in leading to an isolable dibenzo derivative of **1** in which structural constraints force the eight-membered ring to be approximately planar.

Results and Discussion

When bis(acid chloride) **3** was arylated with 4,4′-dimethylbiphenyl (**4**) and aluminum chloride in refluxing carbon disulfide, there were obtained after separation by column chromatography two diones, **5** and **6,** corresponding to linear and intramolecular diarylation, respectively.

Dione **5** was obtained in 6% yield as a pale-yellow crystalline solid. While the ^{1}H NMR spectrum [δ (CCl_4) 2.40 (s, 12 H, $-CH_3$), 4.07 (s, 2 H, [4]annulene protons), and 6.98–7.14 (m, 14 H, aromatic protons)] was consistent with C_s molecular symmetry, there was no direct information on the directionality of acylation. Structure **5** has consequently been assigned on the basis of expected preferred ortho attack on **4.** However, the lack in **5** of chemical shift effects normally associated with aroyl and tricarbonyl[4]annulenoyliron groups[3] is itself noteworthy and suggests that the biphenyl and [4]annulene moieties twist with respect to the ketone carbonyl groups in order to avoid the steric congestion which is evident in models of various coplanar arrangements.



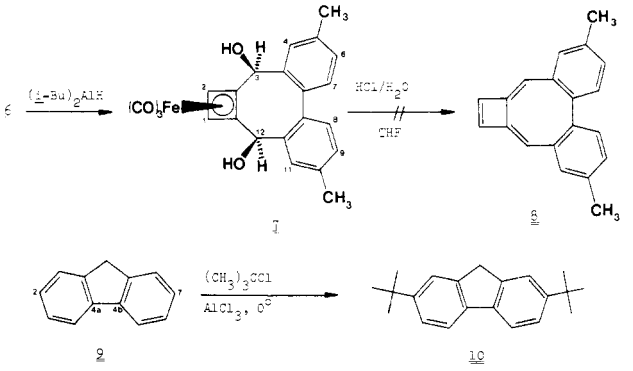
Dione **6** was obtained in 24% yield as bright-yellow crystals. While all spectral and analytical data supported the assigned structure, it was soon evident from a detailed ^{1}H NMR spectral examination that a bridged biphenyl of unusually high conformational rigidity had been generated. The ambient temperature ^{1}H NMR spectrum in $CDCl_3$ exhibited a singlet at δ 2.40 for six methyl protons, singlets at δ 4.91 and 4.94 for H(1) and H(2), a two-proton multiplet at δ 6.81–6.93, and a four-proton multiplet at δ 7.14–7.32. Upon addition of Eu(fod)$_3$[5] up to a twofold excess, differential shifts of all absorptions to lower field led to almost complete resolution of the spectrum as summarized in Table I. In this process, the separation and shift of two of the low field aromatic protons as slightly broadened singlets by $\Delta\delta$ 2.56 and 5.98 identified them collectively as H(4) and H(11). Since the shift reagent un-

doubtedly binds preferentially to the ketone carbonyl groups,[6] the large difference in induced shifts of H(4) and H(11) is most readily explained on the basis of a stereochemically controlled selectivity in complexation at these two nonequivalent sites. A molecular model of **6** supports this view since the oxygen at C-3 (only one enantiomer is shown) projects below the four-membered ring and is thus more exposed while that at C(12) projects up toward the tricarbonyliron group and should be relatively less accessible. On the assumption that induced shifts primarily reflect proximity to sites of complexation, this argument then leads to the conclusion that H(2) and H(4) correspond to the protons dramatically shifted by $\Delta\delta$ 4.28 and 5.98, respectively.

The remaining aromatic absorption, corresponding to H(6), H(7), H(8), and H(9), finally appeared as two overlapping AB quartets. By analogy to the relative chemical shifts in biphenyl itself,[7] H(7) and H(8) have been identified with the remaining two low field aromatic protons. The enantiomeric makeup of **6** was also confirmed via interaction with a chiral shift reagent. When 50 mol % of tris[3-(trifluoromethylhydroxymethylene-*d*-camphorato]europium[8] was added to **6** in $CDCl_3$, distinct resonances appeared for each enantiomer and, in particular, H(1) and H(2) appeared as four closely spaced but sharp singlets in the range δ 5.05–5.18.

An attempt was also made to observe enantiomeric interconversion by heating **6** in Me_2SO-d_6, using coalescence of the H(1) and H(2) singlets as a probe for racemization. However, at temperatures up to 180 °C, the two singlets never coalesced, the only observable change being a decrease in $\Delta\delta$ from 0.19 to 0.12. **6** thus represents another example of the formidable barriers to atropisomerism encountered in biphenyl bridged with four trigonal atoms[9] and, in principle, should be resolvable into stable enantiomers.[10]

Dione **6** was then subjected to our previously reported procedure for conversion of such diacyl complexes to the corresponding dimethylenecyclobutenes.[2] Reduction of **6** with diisobutylaluminum hydride produced a single crystalline diol in 82% yield to which we have assigned the cis,syn structure **7** on the assumption that hydride is delivered on the face of



each carbonyl group opposite to the bulky tricarbonyliron function. The ^1H NMR spectrum in Me_2SO-d_6 exhibited singlets at δ 2.35 and 2.38 for six methyl protons, singlets at δ 4.07 and 4.55 for H(1) and H(2), two AB quartets for vicinal methine and hydroxyl protons (δ_A 4.91, δ_B 5.47, J_{AB} = 4.1 Hz; δ_A 4.76, δ_B 5.64, J_{AB} = 5.3 Hz), a multiplet at δ 6.75–7.18 for H(6), H(7), H(8), and H(9), and two broadened, overlapping singlets between δ 7.38–7.43 for H(4) and H(11). The assignments of methine and hydroxyl protons were verified by D_2O exchange.

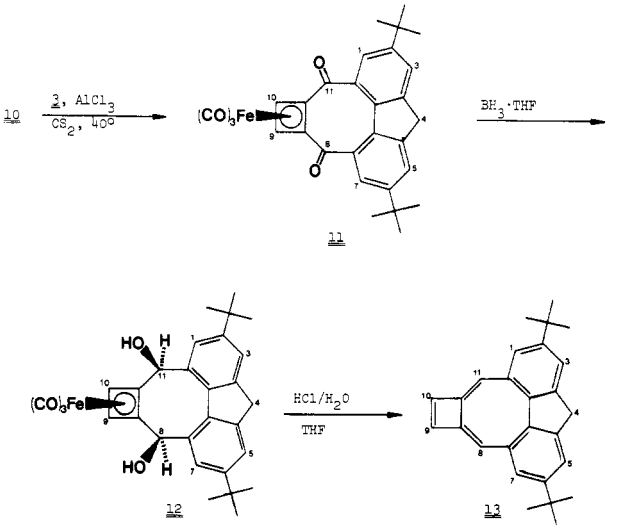
Attempts to generate the desired hydrocarbon **8** from **7** with hydrochloric acid in THF at room temperature failed completely. Careful monitoring by TLC indicated slow reaction of the diol without concurrent formation of nonpolar products.

Table I. Induced Chemical Shifts Resulting from Addition of 2 mol equiv of $Eu(fod)_3$ to ~0.25 M **6** in $CDCl_3$

Protons	$\delta_{initial}$	δ_{final}	$\Delta\delta$
CH_3	2.40	2.43, 2.68	0.03, 0.28
H(1)	4.91	7.40	2.49
H(2)	4.94	9.22	4.28
H(6), H(9)	6.84, 6.88	8.46, 8.12	1.62, 1.29
H(7), H(8)	7.20, 7.22	8.16, 7.60	0.96, 0.38
H(4)	7.28	13.26	5.98
H(11)	7.20	9.76	2.56

Since it appeared likely that the sluggish reactivity of **7** and the failure to isolate **8** reflected the stringent conformational requirements of the bridged biphenyl system, either through diversion of the decomplexation process or through destabilization of **8**, we next considered suitable approaches to overcome these problems. While variation of decomplexation conditions is a line of attack which may yet prove fruitful, we were at this stage instead attracted to the strategy of stabilizing **8** by incorporation of the biphenyl framework as a fluorene moiety. Employment of such a doubly bridged derivative was thus envisaged to flatten the system to such an extent that biphenyl twist would be eliminated as a destabilizing factor, although not without the concomitant expense of increased bond angle strain in the eight-membered ring. However, offsetting this latter effect was the expectation that deformation of the fluorene system with the attendant spreading of exterior angles at C(4a) and C(4b) (see **9**) to about 130°[11] would facilitate fusion of a planar [8]annulene moiety by virtue of closer compatability with natural interior angles of ~135° in the latter unit. Equally attractive was the general prospect of developing synthetic access to [8]annulene derivatives which might contribute to current understanding of the electronic consequences of enforced flattening of this much studied system.[12]

Since fluorene itself undergoes electrophilic substitution in a manner analogous to biphenyl, i.e., preferentially at C(2) and C(7),[13] the use of a blocked derivative was also necessary in this approach. While 2,7-dimethylfluorene would have been the conventional substrate for this purpose, the reported synthesis of the compound is tedious and time consuming.[14] We consequently sought a more accessible derivative and, after some exploratory work, discovered that alkylation of fluorene at 0 °C in *tert*-butyl chloride with a catalytic amount of aluminum chloride afforded a crystalline di-*tert*-butyl derivative in 68% yield which on the basis of full ^1H NMR analysis[15] was identified as the desired 2,7-isomer **10**.[16] Acylation of the latter

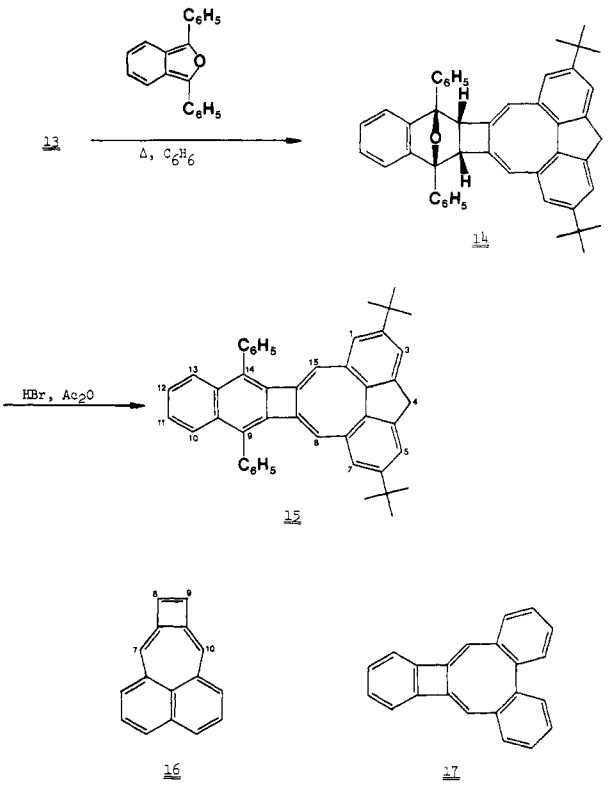


with **3** then proceeded to give a single diketone, **11,** in 27% yield as a bright-yellow solid. The ^{1}H NMR spectrum of **11** [δ ($CDCl_3$) 1.39 (s, 18 H, $-CH_3$), 3.95 (broad s, $-CH_2-$), 5.13 (s, 2 H, H(9) and H(10)), and 7.96 and 8.15 (AB quartet, 4 H; H(3), H(5) and H(1), H(7), respectively; J_{AB} = 2.4 Hz)] clearly reflected the anticipated flattening effect of the fluorene moiety. Reduction of **11** with borane in THF then afforded a single diol in 80% yield (diisobutylaluminum hydride gave the diol in only 52% yield) which, by the same steric argument given with regard to **7,** we designate as the cis,syn stereoisomer **12.** The ^{1}H NMR spectrum of **12** [δ (Me_2SO-d_6) 1.33 (s, 18 H, $-CH_3$), 3.95 (broad s, 2 H, $-CH_2-$), 4.31 (s, 2 H, H(9) and H(10)), 4.91 (d, 2 H, J = 7.0 Hz, methine protons), 7.02 (d, 2 H, J = 7.0 Hz, OH, confirmed by D_2O exchange), and 7.32 and 7.56 (two d's, 4 H; H(1), H(3), H(5), and H(7); J = 1.8 Hz)] was in accord with a symmetrical (C_s) isomer. In contrast to **7,** decomplexation of **12** with hydrochloric acid in THF at room temperature proceeded rapidly, with observable gas evolution, to give an unstable but isolable pale-yellow crystalline solid in 35% yield. Although the inherent instability of the compound precluded a satisfactory compositional analysis, spectral data were fully consistent with the assigned structure **13.** The ^{1}H NMR spectrum of **13** in $CDCl_3$ exhibited a singlet at δ 1.37 for 18 methyl protons, a broad singlet at δ 3.90 for two methylene protons, a singlet at δ 6.29 for H(8) and H(11), and a multiplet at δ 7.21–7.43 for four aromatic protons plus H(9) and H(10). In the mass spectrum, the molecular ion appeared as base peak at *m/e* 352, and the electronic spectrum in cyclohexane exhibited several strong maxima and shoulders between ~225–400 nm (see Experimental Section).

With regard to chemical properties, **13** has thus far been shown to exhibit dienophilic reactivity at C(9)–C(10). When the hydrocarbon was heated in benzene with 1,3-diphenylisobenzofuran, there was obtained a single stable, bright-red crystalline adduct in 15% yield (based on diol **12**). The ^{1}H NMR spectrum of this material [δ ($CDCl_3$) 1.14 (s, 18 H, $-CH_3$), 3.19 (s, 2 H, methine protons), 3.29 (broad s, 2 H, $-CH_2-$), 4.53 (s, 2 H, olefinic protons), 5.98 and 6.83 (AB quartet, 4 H, J_{AB} = 2.0 Hz, fluorenyl protons), and 7.41–7.78 (m, 14 H, aromatic protons)] is notable for the pronounced shift of methyl, methylene, olefinic, and fluorenyl protons relative to **13.** Since models indicate that shielding of these protons by the three aromatic rings introduced with the enophile should be significantly greater in the endo adduct, the latter stereochemistry has been assigned on this basis. Clouding this interpretation, however, is the possibility that part of the shifts are due to a paramagnetic ring current[17] associated with an [8]annulene system which, as mentioned above, was anticipated to be considerably flattened.[12] Although the potential operation of the latter effect prevents individual assessment of both shielding mechanisms, the indicated reactivity of **13** at the cyclobutene olefinic bond suggests routes to simpler derivatives which should help clarify this intriguing question.

Compound **14** was also characterized by dehydration with hydrogen bromide in acetic anhydride to the highly extended, brick red hydrocarbon **15** in 72% yield.

The question as to what extent benzo annelation in **13** attenuates properties which might otherwise be attributable to a flattened bicyclo[6.2.0]decapentaene unit is difficult to answer on the basis of presently available data. The electronic spectrum of **13** reveals interaction between the dimethylenecyclobutene and fluorene moieties,[18] but an evaluation of ring current effects in the ^{1}H NMR spectrum suffers from the difficulty of defining suitable reference data.[20,21] However, the close similarity of the olefinic proton chemical shifts of **13** to those of cyclobutadienopleiadiene (**16**) [δ ($CDCl_3$) 6.27 (H(7), H(10)), 7.08 (H(8), H(9))][2] suggests the absence of any special delocalization effects. On the other hand, if the success



and failure in isolating **13** and **8,** respectively, reflect the relative stabilities of the two systems, then comparison of these two with the known tribenzo derivative **17,** which is very stable and probably nonplanar,[22] is instructive. If **8** is also nonplanar, a not unreasonable conclusion in view of the close structural relationship to **17,** then the pronounced electronic stabilizing effect of additional benzo annelation in the latter is evident. The greater stability of **13** compared with **8,** however, would appear to reflect some extra electronic stability attendant upon flattening of the ring system and large enough to overcome the increased bond angle strain incurred in the same process. Studies currently in progress on the chemistry of **13** will hopefully clarify this interrelationship of electronic and conformational factors.

Experimental Section

General. The general procedures followed are described in ref 1. Instantaneous melting points (inst mp) were obtained for compounds which decomposed prior to melting and are uncorrected. All NMR spectra were measured at 100 MHz.

Tricarbonyl[1,2,2a,12a-η-5,10-dimethyldibenzo[*a,c*]cyclobuta[*f*]cyclooctene-3,12-dione]iron (6) and Tricarbonyl[1,2,3,4-η-1,2-bis(4,4′-dimethylbiphenyl-2-carbonyl)cyclobutadiene]iron (5). A vigorously stirred suspension of diacid chloride **3** (2.00 g, 6.40 mmol), 4,4′-dimethylbiphenyl (0.39 g, 2.13 mmol), and anhydrous aluminum chloride (2.56 g, 19.2 mmol) in 150 ml of carbon disulfide was heated at reflux in a 500-ml round-bottomed flask fitted with a mechanical stirrer and a condenser protected with a drying tube ($CaSO_4$). Additional 0.39-g increments of 4,4′-dimethylbiphenyl were added after 48 and 96 h, respectively. The mixture was stirred at reflux 72 h longer, cooled to room temperature, and evaporated under reduced pressure. The residue was stirred for 1 h with 200 ml of 1% hydrochloric acid and then extracted with 3 × 200 ml of methylene chloride. The combined extracts were washed subsequentially with 300 ml of saturated aqueous $NaHCO_3$ and 300 ml of water, dried ($MgSO_4$), filtered, and evaporated in vacuo to give a viscous, yellow-orange oil. Chromatography of the latter on a 5 × 45 cm column of alumina effected separation of the respective acylation products. The less polar diketone was resolved with carbon tetrachloride and eluted with benzene. Evaporation of the eluate and recrystallization of the residual solid from cyclohexane afforded 650 mg (24%) of **6** as bright-yellow rods: mp 228.5–232 °C dec; IR ($CHCl_3$) 2065 (vs), 2005 (vs), 1640 (s), and 1602 cm^{-1} (m); NMR, see text; electronic

spectrum (EtOH), max (ϵ), 258 nm (18 200), sh (ϵ), 322 nm (5750); *m/e* 426 (2.5%), 342 (100%).

Anal. Calcd for $C_{23}H_{14}FeO_5$: C, 64.81; H, 3.31; Fe, 13.10. Found: C, 64.85; H, 3.37; Fe, 12.99.

The more polar diketone was resolved with benzene and eluted with chloroform. Evaporation of the eluate afforded a viscous yellow oil which crystallized slowly at −20 °C. Repeated recrystallization from hexane gave 212 mg (6%) of **5** as pale-yellow microcrystalline rods: mp 167–171 °C; IR ($CHCl_3$) 2058 (vs), 2002 (vs), 1993 (vs), 1652 cm^{-1} (s); NMR, see text; *m/e* 608 (0.25%), 524 (100%).

Anal. Calcd for $C_{37}H_{28}FeO_5$: C, 73.03; H, 4.64; Fe, 9.18. Found: C, 73.35; H, 4.88; Fe, 8.84.

***cis,syn*-Tricarbonyl[1,2,2a,12a-η-3,12-dihydro-5,10-dimethyldibenzo[*a,c*]cyclobuta[*f*]cyclooctene-3,12-diol]iron (7).** In a 25-ml round-bottomed flask equipped with a rubber septum and a source of dry nitrogen was prepared a solution of diketone **6** (213 mg, 0.500 mmol) in 5 ml of anhydrous benzene. To the solution, at 0 °C under nitrogen, was then added, with magnetic stirring, 3.33 ml of a 1.5 M solution of diisobutylaluminum hydride (5.00 mmol) in benzene. The mixture was stirred 0.25 h at 0 °C and 1.5 h at ambient temperature, at which point excess hydride was destroyed by slow addition of 0.24 ml of methanol in 2.5 ml of benzene, and 0.25 h thereafter, 0.27 ml of water in 3 ml of methanol. The resulting suspension was stirred 1 h longer, and then filtered with suction. The gelatinous solid thus collected was thoroughly washed with benzene, ether, and methanol, respectively. Evaporation of the combined filtrate and washings then afforded an off-white solid which was recrystallized from hexane to give 176 mg (82%) of **7** as very pale-yellow rectangular plates, inst mp 202–204 °C dec; IR ($CHCl_3$) 3605 (m), 2045 (vs), and 1970 cm^{-1} (vs); NMR, see text; electronic spectrum (EtOH), sh (ϵ), 285 nm (2040); *m/e* 430 (15%), 346 (100%).

Anal. Calcd for $C_{23}H_{18}O_5Fe$: C, 64.71; H, 4.22; Fe, 12.98. Found: C, 64.46; H, 4.02; Fe, 12.70.

Attempted Preparation of 5,10-Dimethyldibenzo[*a,c*]cyclobuta[*f*]-cyclooctene (8). A solution of diol **7** (43 mg, 0.10 mmol) in 0.5 ml of methylene chloride was stirred vigorously at room temperature for 24 h with 0.5 ml of concentrated hydrochloric acid. The reaction was monitored periodically by analytical TLC (silica gel/hexane). Diol **7** was gradually consumed, but at no point could the formation of a nonpolar reaction product be detected. The mixture was diluted with 10 ml of methylene chloride and poured into an equal volume of water. The organic layer was separated, washed with 2 × 10 ml of saturated aqueous $NaHCO_3$, dried (Na_2SO_4), filtered, and evaporated. Examination of the residue by TLC (silica gel/benzene) indicated the product to be a complex mixture of at least five moderately polar components which were not characterized further.

2,7-Di-*tert*-butylfluorene (10). In a 50-ml flask fitted with a drying tube ($CaSO_4$) was prepared a solution of fluorene (0.83 g, 5.0 mmol) in 10 ml of 2-chloro-2-methylpropane (5.50 g, 100 mmol). The solution was cooled quickly with magnetic stirring to 0 °C to produce a fine suspension of the substrate. Anhydrous aluminum chloride (50 mg, 0.38 mmol) was added, and the mixture was stirred 1 h longer at 0 °C. Unreacted 2-chloro-2-methylpropane was then evaporated at ambient temperature under reduced pressure. The residue was mixed with 25 ml of water and extracted with 2 × 50 ml of methylene chloride. The combined extracts were washed with 50 ml of saturated aqueous $NaHCO_3$ and 50 ml of water, dried ($MgSO_4$), filtered, and evaporated in vacuo to give crude **10** as an off-white crystalline solid. Recrystallization from 95% ethanol followed by sublimation [bath temperature 110–115 °C (0.05–0.10 mm Hg)] afforded 945 mg (68%) of **10** as colorless, rhombohedral plates, mp 122–127 °C. An analytical sample was prepared by repeated recrystallization from methanol to give colorless needles: mp 128.5–130 °C; IR (CCl_4) 1478 (s), 1460 (m), 1415 (m), 1390 (m), 1360 (s), 864 (m), 820 cm^{-1} (m); NMR (CCl_4) δ 1.35 (s, 18 H, $-CH_3$), 3.74 (s, broad, 2 H, $-CH_2-$), and 7.18–7.54 (m, 6 H, aromatic); electronic spectrum (EtOH), max (ϵ), 260 (15 800), 267 (17 800), 271 (18 600), 278 (14 100), 295 (6310), 300 (5500), and 306 nm (8320), sh (ϵ), 221 (12 600), and 283 nm (10 700); *m/e* 278 (100%).

Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.47; H, 9.53.

Full analysis of the aromatic proton absorption, with spin decoupling of the methylene protons, and correlation of chemical shifts with those of other fluorene derivatives[14] yielded the following parameters: δ 7.24 (H(3), H(6)), 7.42 (H(1), H(8)), 7.50 (H(4), H(5)); $J_{1,3} = J_{6,8} = 1.7$, $J_{3,4} = J_{5,6} = 8.0$, $J_{1,4} = J_{5,8} = 0.2$ Hz.

Tricarbonyl[8a,9,10,10a-η-2,6-di-*tert*-butyl-4*H*-cyclobuta-[6,7]cycloocta[1,2,3,4-*def*]fluoren-8,11-dione]iron (11). A vigorously stirred suspension of diacid chloride **3** (3.00 g, 9.60 mmol), 2,7-di-*tert*-butylfluorene (0.88 g, 3.20 mmol), and anhydrous aluminum chloride (3.84 g, 28.8 mmol) in 225 ml of carbon disulfide was heated at reflux in a 1-l. round-bottomed flask fitted with a mechanical stirrer and a condenser protected with a drying tube ($CaSO_4$). After periods of 48 and 96 h, respectively, additional 0.88-g increments of 2,7-di-*tert*-butylfluorene were added to the flask. The mixture was stirred at reflux 72 h longer, cooled to room temperature, and evaporated under reduced pressure. The residue was stirred for 1 h with 200 ml of 1% aqueous hydrochloric acid and then extracted with 4 × 250 ml of methylene chloride. The combined extracts were washed successively with 500 ml of saturated aqueous $NaHCO_3$ and 500 ml of water, dried ($MgSO_4$), filtered, and evaporated in vacuo to give a viscous, yellow-orange oil which was chromatographed with carbon tetrachloride on a 5 × 45 cm column of alumina. After elution of unreacted 2,7-di-*tert*-butylfluorene with carbon tetrachloride, elution with benzene afforded, upon evaporation of solvent and recrystallization from hexane, 1.36 g (27%) of diketone **11** as bright-yellow rectangular plates: mp 194–197 °C; IR ($CHCl_3$) 2058 (vs), 1998 (vs), 1627 (s), and 1598 cm^{-1} (s); NMR, see text; electronic spectrum (EtOH), max (ϵ), 266 (26 300) and 354 nm (10 500), sh (ϵ), 299 nm (1450); *m/e* 522 (1%), 438 (100%).

Anal. Calcd for $C_{30}H_{26}O_5Fe$: C, 68.98; H, 5.02; Fe, 10.69. Found: C, 69.07; H, 5.18; Fe, 10.50.

***cis,syn*-Tricarbonyl[8a,9,10,10a-η-2,6-di-*tert*-butyl-8,11-dihydro-4*H*-cyclobuta[6,7]cycloocta[1,2,3,4-*def*]fluorene-8,11-diol]iron (12).** Into a 50-ml flask equipped with a condenser protected with a drying tube ($CaSO_4$) were placed diketone **11** (832 mg, 1.60 mmol) and 24 ml of a 1 M solution of borane in THF. The mixture was stirred 2 h at room temperature and 2 h at reflux, cooled to 0 °C, and poured onto 100 g of crushed ice. After standing 1 h, the hydrolysate was extracted with 3 × 150 ml of methylene chloride. The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give crude **12** as an off-white crystalline solid. Recrystallization was effected by dissolving the crude solid in a minimum volume of boiling cyclohexane, adding an equal volume of hexane, and cooling the mixture to 0 °C to afford 674 mg (80%) of **12** as rectangular prisms. An analytical sample was prepared by further recrystallization from hexane: inst mp 236–238 °C; IR (CCl_4) 3565 (w), 3495 (w), 3475 (w), 3385 (w), 2039 (vs), 1980 (vs), and 1968 cm^{-1} (vs); NMR, see text; electronic spectrum (EtOH), max (ϵ), 269 (13 800), 298 (10 500), and 310 nm (11 200), sh (ϵ), 241 nm (18 600); *m/e* 526 (0.25%), 352 (100%).

Anal. Calcd for $C_{30}H_{30}O_5Fe$: C, 68.45; H, 5.74; Fe, 10.61. Found: C, 68.61; H, 5.83; Fe, 10.40.

2,6-Di-*tert*-butyl-4*H*-cyclobuta[6,7]cycloocta[1,2,3,4-*def*]fluorene (13). A solution of diol **12** (106 mg, 0.200 mmol) in 10 ml of methylene chloride was shaken vigorously in a separatory funnel with 3 ml of concentrated hydrochloric acid for 5 min. Gas evolution was observed immediately upon mixing. the organic layer was separated, washed successively with 10 ml of water and 10 ml of saturated aqueous $NaHCO_3$, dried (Na_2SO_4), filtered, and evaporated at room temperature under reduced pressure. The residue was chromatographed in the dark with carbon tetrachloride on four preparative silica gel TLC plates. Extraction of the least polar band with methylene chloride and evaporation of the extract in vacuo afforded 24 mg (35%) of crude **13** as an air- and light-sensitive pale-yellow crystalline solid. The latter was taken up in a minimum volume of cold ether, and the resulting solution was filtered, diluted with methanol, and evaporated under a stream of nitrogen until a thick slurry of crystals formed. Crystallization was then completed at −20 °C. The solid was collected by filtration, washed with cold methanol, and dried in vacuo to give 16 mg (24%) of relatively pure **13** as pale-yellow rectangular prisms which decomposed without melting; IR ($CHCl_3$) 3005 (m), 2960 (s), 2862 (m), 1632 (w), 1600 (m), 1470 (m), 1395 (m), 1364 (m), 850 (m), and 712 cm^{-1} (s); NMR, see text; electronic spectrum (cyclohexane), max (ϵ), 278 (50 100), 325 (5650), 335 (4270), and 342 nm (3980), sh (ϵ), 226 (16 200), 251 (21 400), 254 (25 700), 262 (32 400), 272 (43 700), 287 (33 100), 297 (18 600), 310 (8320), 350 (2570), 367 (1860), 380 (1450), 393 (1000), and 413 nm (330); *m/e* 352 (100%).

Because of the inherent instability of the compound, a satisfactory elemental analysis could not be obtained.

Adduct of 1,3-Diphenylisobenzofuran and Hydrocarbon (13). Hydrocarbon **13** was prepared as described in the preceding experiment

from diol **12** (212 mg, 0.400 mmol) and chromatographed with carbon tetrachloride in the dark on a preparative silica gel TLC plate. To the product was added 108 mg (0.400 mmol) of 1,3-diphenylisobenzofuran and 3 ml of benzene. The resulting mixture was refluxed for 3 h, cooled to room temperature, and evaporated under reduced pressure. The residue was chromatographed in the dark with carbon tetrachloride on two preparative silica gel TLC plates. Unreacted 1,3-diphenylisobenzofuran separated first followed by **14** as a bright red-orange band. Extraction of the latter with methylene chloride and evaporation of the extract in vacuo afforded a red-orange oil which, upon crystallization from hexane, gave 36 mg (15% yield based on **12**) of adduct **14** as red monoclinic prisms, mp 238–243 °C dec. An analytical sample was prepared by repeated recrystallization from hexane: mp 245–249 °C; IR ($CHCl_3$) 1665 (w), 1600 (m), 1555 (w), 1535 (w), 1492 (m), 1395 (sh), 1355 (m), 853 (m), and 695 cm^{-1} (s); NMR, see text; electronic spectrum (cyclohexane), max (ϵ), 262 (28 200), 272 (29 500) 281 (29 500), 293 (31 600), 306 (33 900), 326 (5620), 340 (6030), 363 (4470), and 383 nm (4070), sh (ϵ), 224 (20 900); *m/e* 622 (3%), 270 (100%).

Anal. Calcd for $C_{47}H_{42}O$: C, 90.63; H, 6.80. Found: C, 90.56; H, 6.92.

2,6-Di-*tert*-butyl-4*H*-naphtho[2″,3″:3′,4′]cyclobuta[1′,2′:6,7]cycloocta[1,2,3,4-*def*]fluorene (15). A suspension of adduct **14** (36 mg, 0.060 mmol) in 0.60 ml of acetic anhydride was prepared in a 5-ml flask equipped with a condenser protected with a drying tube ($CaSO_4$). After the suspension was cooled to 0 °C, 0.10 ml of 48% aqueous hydrobromic acid was slowly added with magnetic stirring. The mixture was heated for 1 h at reflux, cooled to room temperature, and poured into 50 ml of water. The resulting suspension was extracted with 2 × 50 ml of methylene chloride, and the combined extracts were washed successively with 3 × 50 ml of saturated aqueous $NaHCO_3$ and 50 ml of water, dried (Na_2SO_4), filtered, and evaporated. The residue was chromatographed with carbon tetrachloride on a preparative silica gel TLC plate with repeated solvent development. Extraction of the resulting bright-red band with methylene chloride, evaporation of the extract in vacuo, and recrystallization of the resulting solid from hexane–carbon tetrachloride at −20 °C afforded 25 mg (72%) of **15** as a brick-red, microcrystalline powder. An analytical sample was prepared by further recrystallization from carbon tetrachloride: mp 288–290 °C; IR (KBr) 1598 (m), 1584 (m), 1532 (w), 1508 (m), 1385 (m), 1352 (m), 852 (m), 772 (s), 755 (s), 748 (s), and 698 cm^{-1} (s); NMR δ (CCl_4) 1.26 (s, 18 H, $-CH_3$), 3.58 (broad s, 2 H, $-CH_2-$), 5.94 (s, 2 H, olefinic protons), 6.50 and 7.07 (AB quartet, 4 H, fluorene protons; J_{AB} = 2.0 Hz), 7.30 and 7.83 (AA′BB′ multiplet, 4 H, aromatic protons), and 7.42–7.70 (m, 10 H, aromatic protons); electronic spectrum (cyclohexane), max (ϵ), 257 (32 400) 310 (69 200), 326 (67 600), 360 (8510), 381 (8130), 401 (13 200), 425 (15 800), 470 (1620), and 505 nm (813), sh (ϵ), 218 (20 900), 247 (24 500), 287 (31 600), 297 (45 700), and 314 nm (64 600); *m/e* 604 (100%).

Anal. Calcd for $C_{47}H_{40}$: C, 93.33; H, 6.67. Found: C, 93.14; H, 6.84.

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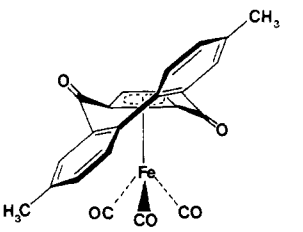
References and Notes

(1) F. A. Kaplan and B. W. Roberts, preceding paper in this issue.
(2) B. W. Roberts and A. Wissner, *J. Am. Chem. Soc.*, **94,** 7168 (1972).
(3) G. Berens, F. Kaplan, R. Rimerman, B. W. Roberts, and A. Wissner, *J. Am. Chem. Soc.*, **97,** 7076 (1975).
(4) (a) C. Liebermann, *Chem. Ber.*, **44,** 1453 (1911). (b) For a review of ketone synthesis via Friedel-Crafts acylation, see P. H. Gore in "Friedel-Crafts and Related Reactions", Vol 3, G. A. Olah, Ed., Interscience, New York, N.Y., 1964, Chapter 31.
(5) Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III): R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, **93,** 1522 (1971).
(6) (a) M. I. Foreman and D. G. Leppard, *J. Organomet. Chem.*, **31,** C31 (1971); (b) T. J. Marks, J. S. Kristoff, A. Alich, and D. F. Shriver, *ibid.*, **33,** C35 (1971); (c) J. Paul, K. Schlögl, and W. Silhan, *Monatsch. Chem.*, **103,** 243 (1972).
(7) F. A. Bovey, F. P. Hood, III, E. Pier, and H. E. Weaver, *J. Am. Chem. Soc.*, **87,** 2060 (1965); (b) R. E. Mayo and J. H. Goldstein, *Mol. Phys.*, **10,** 301 (1966).
(8) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Am. Chem. Soc.*, **93,** 5913 (1971).
(9) (a) N. L. Allinger, W. Szkrybalo, and M. A. DaRooge, *J. Org. Chem.*, **28,** 3007 (1963); (b) D. M. Hall and J. M. Insole, *J. Chem. Soc.*, 2326 (1964). (c) **6** differs importantly from previous examples exhibiting this phenomenon in that the ortho,ortho′ bridge is of the enedione type rather than a diazabutadiene unit.
(10) A full x-ray crystallographic analysis of **6** by Dr. William Stallings and Professor Jerry Donohue has confirmed the assigned structure and has revealed a number of interesting stereochemical details. A perspective drawing of one enantiomer of **6** viewed along a line passing through the center of the interannular biphenyl bond [C(7a)–C(7b)] and the center of the facing edge of the [4]annulene ring [C(2a)–C(12a)] is shown in i. Important structural features are (a) tilting of the ketone carbonyl groups above and below the plane of the four-membered ring with concomitant tilting of each proximate aromatic ring in the opposite sense, (b) bending of the carbonyl carbon atoms above and below the four-membered ring with an average C(3)–C(2a)–C(12a)–C(12) torsion angle of 26°, (c) twisting of the biphenyl system an average of 74°, and (d) tilting of the aromatic ring proximate to the tricarbonyliron group 22° more from the [4]annulene centroid-iron axis than the other aromatic ring, evidently in response to steric interaction with the metal carbonyl unit. From these results, adjustment of the cyclooctatrienedione-related ring to a rigid, strained environment is apparent.



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(11) D. M. Burns and J. Iball, *Proc. R. Soc. London, Ser. A,* **227,** 200 (1955).
(12) For the synthesis of flattened [8]annulene derivatives and studies on possible associated paramagnetic ring currents, see: (a) C. F. Wilcox, Jr., J. P. Uetrecht, and K. K. Grohman, *J. Am. Chem. Soc.*, **94,** 2532 (1972); (b) H. N. C. Wong, P. J. Garrett, and F. Sondheimer, *ibid.*, **96,** 5604 (1974); (c) R. Destro, T. Pilati, and M. Simonetta, *ibid.*, **97,** 658 (1975); (d) C. F. Wilcox, Jr., J. P. Uetrecht, G. D. Grantham, and K. G. Grohmann, *ibid.*, **97,** 1914 (1975); (e) H. N. C. Wong and F. Sondheimer, *Angew. Chem., Int. Ed. Engl.*, **15,** 117 (1976); (f) I. Willner and M. Rabinowitz, *Tetrahedron Lett.*, 1223 (1976); (g) H. N. C. Wong, F. Sondheimer, R. Goodwin, and R. Breslow, *ibid.*, 2715 (1976).
(13) For an early review of fluorene chemistry, see: G. Rieveschl, Jr., and F. E. Ray, *Chem. Rev.*, **23,** 287 (1938).
(14) L. Mascarelli and B. Longo, *Gazz. Chim. Ital.*, **71,** 289 (1941).
(15) Cf. A. Mathieu, *Bull. Soc. Chim. Fr.*, 1533 (1971).
(16) M. Bruch, M. Grosse, and D. Rewicki, *Justus Liebigs Ann. Chem.*, 74 (1976).
(17) J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88,** 4811 (1966).
(18) Dimethylenecyclobutene: $\lambda_{max}^{isooctane}$ 211.5 (100 000) and 248 nm (20 000).[19] For 2,7-di-*tert*-butylfluorene, see Experimental Section.
(19) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc. London,* 332 (1961). See also, M. L. Heffernan and A. J. Jones, *Chem. Commun.*, 120 (1966).
(20) Contributing to this problem is the sensitivity of proton chemical shifts in dimethylenecyclobutenes to substituent effects: (a) W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **89,** 392 (1967); (b) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *ibid.*, **89,** 4804 (1967); (c) H. Huther and H. A. Brune, *Org. Magn. Reson.*, **3,** 737 (1971); (d) ref 2.
(21) It has been noted that the downfield shift of the methyl and cyclobutenyl protons in 9-methylbicyclo[6.2.0]decapentaene by ~0.6 and 1 ppm in comparison with model compounds could reflect some delocalization: G. Schröder, S. R. Ramadas, and P. Nikoloff, *Chem. Ber.*, **105,** 1072 (1972).
(22) P. J. Garrett, K. P. C. Vollhardt, and R. H. Mitchell, *J. Chem. Soc. C,* 2137 (1970).