

Valence tautomers of dimethyl cycloocta-2,5,7-triene-1,4-dicarboxylate and an iron tricarbonyl complex therefrom

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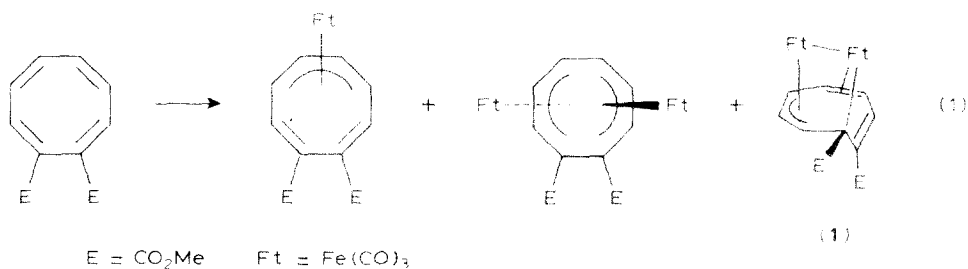
Abstract

Carboxylation of cyclooctatrienyldilithium, $\text{Li}_2\text{C}_8\text{H}_8$, gives predominantly tri-cyclo[5.1.0.0^{2,4}]oct-5-ene-3,8-dicarboxylic acid and *trans,cis,cis,trans*-deca-2,4,6,8-tetraene-1,10-dioic acid; in addition, a small quantity of cycloocta-2,5,7-triene-*trans*-1,4-dicarboxylic acid has been identified as its dimethyl ester. The tricyclooctene diester is in equilibrium with a small amount of the isomeric *cis*-disubstituted cycloocta-2,5,7-triene in solution, and heating such a solution results in formation of a dimer. Reaction of the tricyclooctene diester with iron pentacarbonyl produces *exo*(2–5) η -[3,8x-dicarbomethoxybicyclo[4.2.0]octa-2,4-diene]tricarbonyliron.

Introduction

Cycloocta-triene and -tetraene and their valence tautomers exhibit a rich organometallic chemistry, which has been of great value in clarifying important principles of structure and bonding. Incorporation of substituents onto the rings can affect the distribution of competitively-formed products in ways which are as yet unpredictable. Study of substituted derivatives of fluxional organometallic compounds, in which selective formation of specific positional isomers can reliably be attributed to thermodynamic factors rather than kinetic ones, can provide valuable information on interactions of substituents with organometallic groups and on mechanisms of fluxionality.

For example, in a recent study of iron carbonyl derivatives of dimethyl cyclooctatetraene-1,8-dicarboxylate, we found (eq. 1) that the most stable product was the $1,5,6-\eta^3:2-4 \eta^3\text{-Fe}_2(\text{CO})_6$ complex (**1**) and that only one regioisomer of each product type was found [1]. In contrast to its unsubstituted cycloocta-tetraene and -triene analogs, **1** showed no haptotropy. It appeared to us that the isomeric



dimethyl cyclooctatetraene-1,4-dicarboxylate (**2**) might provide a highly fluxional $\text{Fe}_2(\text{CO})_6$ complex, study of which would help to elucidate the mechanism of haptotropy.

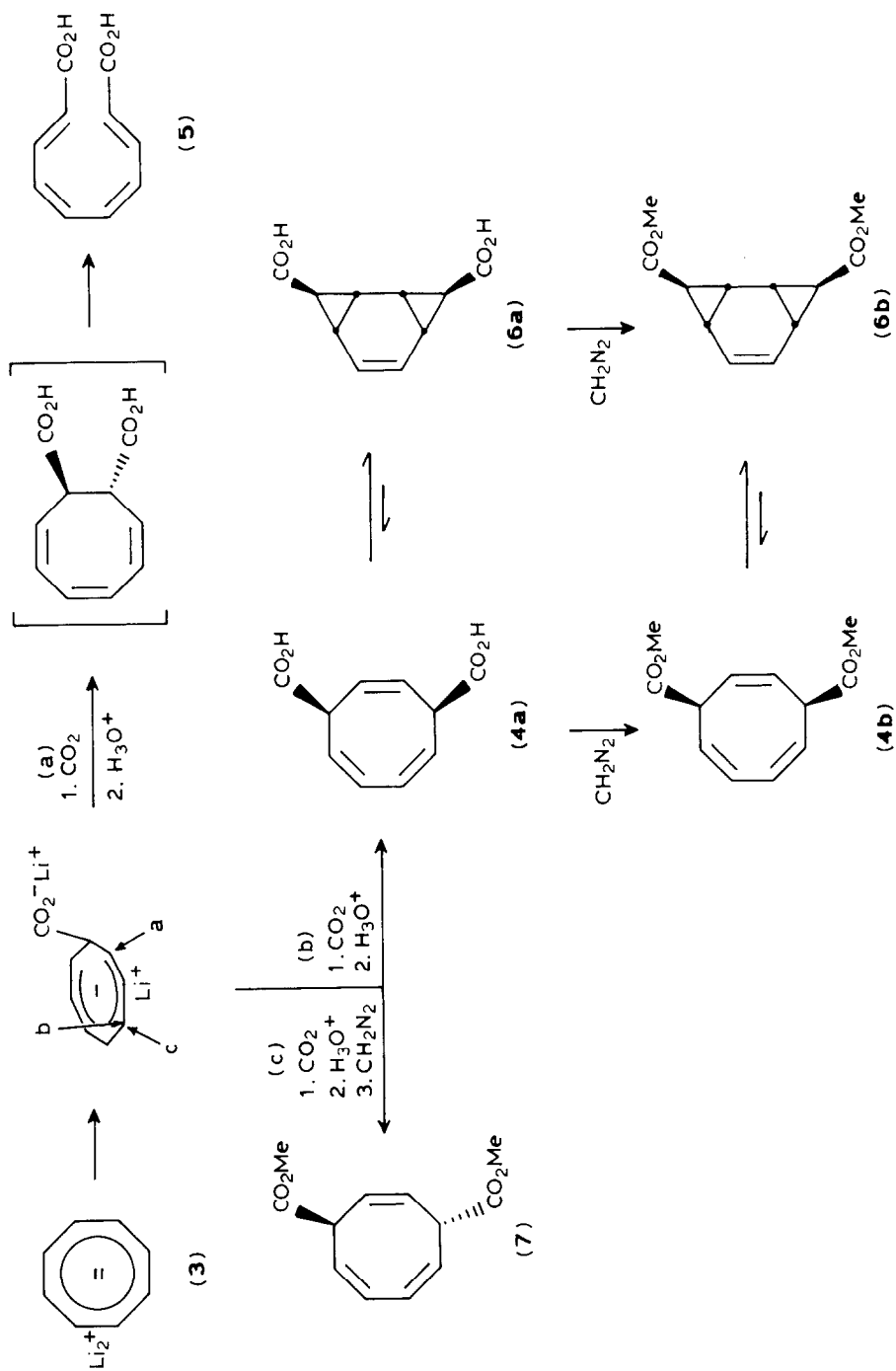
Although **2** has been synthesized by a 5-step sequence [2], we thought it worth investigating an alternative route involving carboxylation of the readily-prepared cyclooctatrienyldilithium, **3**. Although an early study by Reppe had indicated predominant formation of 2,5,7-cyclooctatriene-1,4-dicarboxylic acid (**4**) upon reaction of **3** with carbon dioxide, Cantrell reported that **4** was formed in only small amounts, with the acyclic 2,4,6,8-decatetraene-1,4-dioic acid (**5**), the principal product [3]. Kaupp and Rösch, however, obtained principally dimethyl *syn*-tricyclo[5.1.0.0^{2,4}]oct-5-ene-3,8-dicarboxylate (**6b**), after diazomethane esterification, along with the diester of **5** [4]. Since **6b** was said to equilibrate in solution with about 20% of **4b**, it appeared to us to hold promise as a precursor to **2**.

Results and discussion

Reaction of $\text{Li}_2\text{C}_8\text{H}_8$ (**3**) with Dry Ice gave, in our hands, a 20% yield of highly insoluble **5** and about 50% of crude **6a**, along with an 11% recovery of cyclooctatetraene. Esterification of the crude **6a** with diazomethane, followed by crystallization and column chromatography of the ester product, yielded 21% of pure **6b**, along with about 4% of an isomer (**7**), which was shown by its mass (m/z 222), IR ($\nu(\text{CO})$ 1755 cm^{-1}) and NMR spectra (δ 6.33 (2H, br. d, J 9.7 Hz), 5.95 (2H, br. s), 5.55 (2H, dd, J 9.7, 6 Hz), 3.8 (m) superimposed upon 3.7 (s, 8H overall)) to be a dimethyl 2,5,7-cyclooctatriene-1,4-dicarboxylate. Since it was clearly distinct from the *cis* isomer seen by NMR in equilibrium with **6b** (vide infra), **7** was deduced to be the *trans* isomer. This material underwent slow degradation over a period of a few days at room temperature.

These results, summarized in Scheme 1, are in generally good agreement with those previously reported by Kaupp and Rösch [4], only **7** having escaped their notice. The three products identified result from three of the four possible modes of electrophilic quenching of the initially-formed substituted cyclooctatrienyl anion, with *cis*-1,2 attack alone not being observable, presumably as a consequence of steric and electrostatic factors [5].

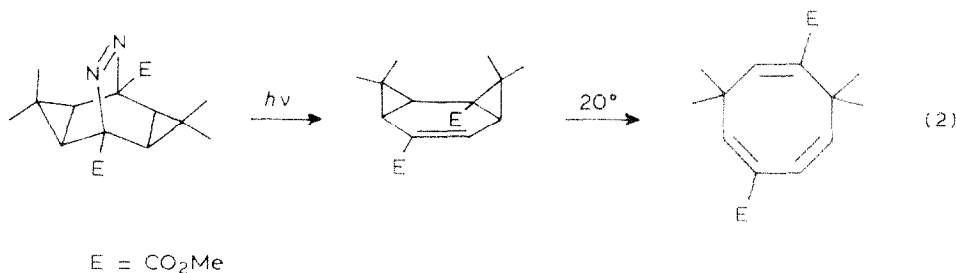
6b exists in the crystal solely in the tricyclic form. Upon dissolution at room temperature, equilibrium (by retro Diels–Alder reaction) with the monocyclic form, **4b**, is slowly established [4]; from the NMR, we find less than 10% of the material in the monocyclic form. The diacid **6a** also exists very predominantly in the tricyclic form, as shown by its NMR spectrum. The *trans*-diester, **7**, in contrast to the *cis*



Scheme 1

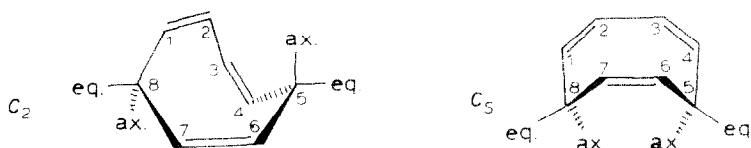
compounds, exists entirely in the monocyclic form, since the intramolecular diels–Alder reaction would form a tricycle with one ester group *endo* and in steric conflict with the *endo* hydrogen of the other cyclopropane ring.

1,3,6-Cyclooctatriene does not form any detectable *syn*-tricyclo[5.1.0.0^{2,4}]oct-5-ene by intramolecular Diels–Alder reaction, although the *anti*-isomer is among the products of photolysis [6]. Thus, the two electron-withdrawing groups play the determining role in stabilizing the bishomobenzene tricyclic forms, **6a** and **6b**, a result which is reminiscent of the stabilization of norcaradienes (relative to cycloheptatrienes) by electron-withdrawing groups [7]. We are aware of only one other isolated derivative of the *syn*-tricyclo[5.1.0.0^{2,4}]oct-5-ene system (eq. 2), a photo-product which was found to revert quantitatively to the cyclooctatriene upon standing [8]. Similarly, 3x,8x-dibromo-*syn*-tricyclo[5.1.0.0^{2,4}]octa-5-ene was reported to open quantitatively to *cis*-5,8-dibromocycloocta-1,3,6-triene upon formation at 20°C [9].



1,3,6-Cyclooctatriene derivatives bearing electron-withdrawing groups X on the 5- and 8-positions have been reported: X = NO₂ [10] and NF₂ [11]. Their failure to form tricyclo[5.1.0.0^{2,4}]octenes by intramolecular Diels–Alder addition argues that these substances, like **7**, possess *trans* stereochemical relationships of the groups X. Indeed, their proton NMR spectra, which are similar to those of **7**, have been interpreted in support of this assignment.

The key spectral characteristic of these *trans*-5,8-disubstituted-1,3,6-cyclooctatrienes is the absence of observable coupling between protons H(5) and H(6) (or H(7) and H(8)), which results in a singlet NMR signal for H(6) and H(7). [10–13]. This is a consequence of the *trans* substituents occupying equatorial positions in the preferred C₂ conformation [14] of 1,3,6-cyclooctatrienes, with the axial C–H bonds being nearly perpendicular to the vinyl C–H bonds of C(6) or C(7). MM2 calculations on the ground state of *trans*-5,8-dimethylcycloocta-1,3,6-triene (a diequatorially substituted C₂ conformer) show a H(5)–C(5)–C(6)–H(6) torsional angle of 103°.



In the spectrum of *cis*-substituted **4b**, in contrast, H(5) (and H(8)) appears as a broad triplet, resulting from significant coupling (about 5 Hz) of H(5) to both H(4) and H(6). The published spectrum of the 5,8-bis(trimethylsilyl)cycloocta-1,3,6-triene

isomer (**9**) obtained by quenching **3** with chlorotrimethylsilane, also shows strong coupling of H(5) with H(4) and H(6) [15], and we deduce that this product, like **4b**, has the *cis* geometry. The limiting conformations of such a *cis* isomer would be the equatorially-axially disubstituted C_2 conformation or the diequatorially-substituted C_s .

The C_s conformation of 1,3,6-cyclooctatriene, according to MM2, is only 2.5 kcal less stable than the C_2 (cf. Anet's calculated value of 1.8 kcal [14]). In contrast to the highly twisted C_2 conformation, the C_s enjoys a perfectly planar C(1)–C(4) diene unit, and hence some butadiene-type delocalization energy neglected by MM2. So the energy difference between the two conformations should be rather less than the calculated value. The presence of sufficiently bulky *cis* substituents may favor the C_s conformation. Indeed, MM2 calculations indicate that the $C_2 \rightarrow C_s$ energy difference is reduced from 2.5 kcal in C_8H_{10} to 1.3 kcal in the *cis*-dimethyl compound.

It should be mentioned that the true MM2 ground state of what we have described as the C_s conformation lacks the plane of symmetry implied by the C_s designation. The minimum energy structures are twisted in such a way as to relieve the interaction between the two axial hydrogens of the idealized C_s form. The amount of twist increases as the equatorial substituents change from H to methyl to t-butyl to trimethylsilyl. For ease of discussion, we shall continue to use the C_s designation.

The calculated coupling constants for the diequatorial C_s conformation of **9** are 9.5 and 3.2 Hz. These compare favorably with the values of 9 and 5 Hz visually estimated from the published spectrum of **9** [15], suggesting that **9** may exist predominantly in the C_s conformation. In **4b**, however, the coupling constants J_{45} and J_{56} each appear to be about 5 Hz, suggesting rapid equilibration between comparable populations of the diequatorial C_s and the equatorial-axial C_2 conformations. It is from the former that closure to form **6b** must occur.

The factors which favor formation of these *cis*-5,8-disubstituted products (mode b in Scheme 1) in reaction of **3** with chlorotrimethylsilane and carbon dioxide, but *trans* products (mode c) in its reaction with (for example) methyl iodide [13] and carbonyl compounds [16] remain obscure.

In an effort to obtain **2** by selective allylic bromination of the minor isomer **4b** in equilibrium with **6b**, reaction with *N*-bromosuccinimide in refluxing carbon tetrachloride, followed by dehydrobromination using triethylamine, was attempted. The result was a mixture of at least six products, one of which appeared to be **2**, based upon GC/MS results. However, the principal product (47% isolated yield) was a dimer of **4b** or a valence tautomer. The presence of four carbomethoxy groups in the NMR spectrum pointed to an unsymmetrical structure for the dimer, **8**, but the complexity of the NMR spectrum in the region δ 2.2–3.2 ppm prevented a structural assignment. Thermal dimerizations of cyclooctatriene and of dimethylcyclooctatrienes, which are believed to involve Diels–Alder additions of bicyclo[4.2.0]octadiene valence isomers to each other, have been reported [13,17].

Reaction of **6b** with iron pentacarbonyl in refluxing dioxane gave, in addition to the dimer **8**, a single organoiron product, **10**. Analysis and mass spectrum showed this to be a $[C_8H_8(CO_2Me)_2]Fe(CO)_3$ isomer. ^{13}C and 1H NMR spectra, the latter with extensive spin decoupling, indicated the structure **10**, *exo*(2–5) η -[3,8x-dicarbomethoxybicyclo[4.2.0]octa-2,4-diene]tricarbonyliron. NMR data for **10** and appropriate model compounds are presented in Tables 1 and 2.

(Continued on p. 364)

Table 1

¹H NMR data on 10 and model compounds ^a (Data in parentheses are not comparable due to effects of substituents.)

Compound	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_{7n}	δ_{7x}	J_{45}	J_{24}	J_{25}	J_{16}^{cis}	J_{12}, J_{56}	J_{67x}^{cis}	$J_{67n,18n}^{trans}$
10	2.88 (3.47)	3.98 (3.11)	CO ₂ Me (5.65)	6.29 (5.47)	3.65 (3.47)	2.68 (2.11)	1.41 (2.11)	2.12 (2.66)	7.0 (6.5)	1.5 (1.6)	sm	9.8	5.1, 4.7	9.2	4.4, 5.0
A^b	2.55 (4.40)	3.37 (3.37)	(5.36)	(5.36)	3.37	2.55	1.17	1.84	6.8	1.6	0.2	-	-	8.25	2.5, -
B^c	3.54 (ca. 1.7)	3.54 (ca. 1.7)	CO ₂ Me	6.35 (ca. 1.7)	3.8 (ca. 1.7)	2.37 (ca. 1.7)	-	-	7	1.5	-	10	4	-	-
D^e	3.70 (ca. 2.4)	3.70 (ca. 2.4)	CO ₂ Me	6.07 (5.22)	3.36 (5.22)	ca. 2.4	ca. 1.2	(ca. 1.2)	-	2	-	-	-	-	-
11^f	-	-	SiMe ₃	(5.22)	3.65	ca. 2.4	ca. 1.2	(ca. 1.2)	-	-	-	-	-	-	-

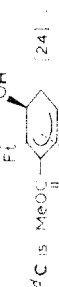
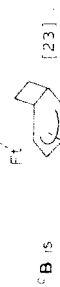
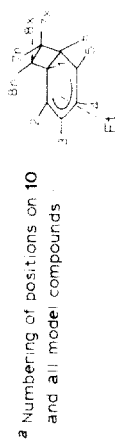
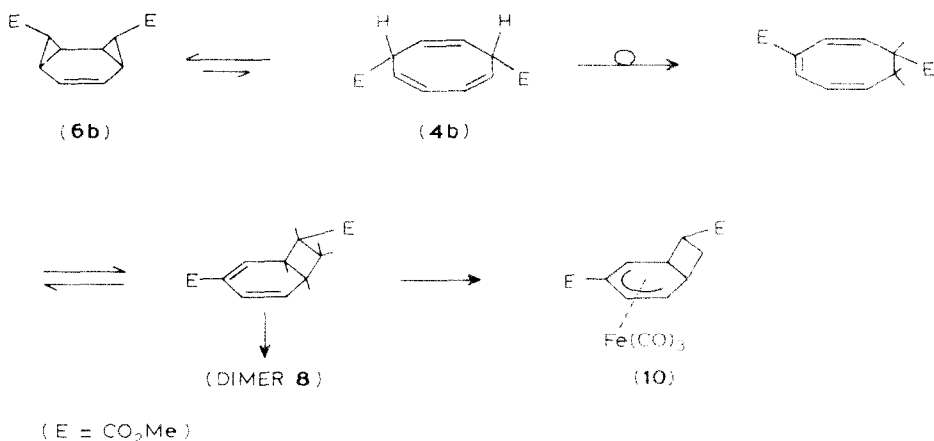
^f Data from ref. 21.

Table 2
¹³C NMR data on **10** and model compounds ^a

Compound	δ(C(1))	δ(C(2))	δ(C(3))	δ(C(4))	δ(C(5))	δ(C(6))	δ(C(7))	δ(C(8))	δ(CO ₂ R)	δ(Me)	δ(Ft)
10	40.3	65.7	86.8	89.5	70.8	34.1	27.2	41.3	169.5 175.0	51.7 52.3	209.2
A ^b	(30.1)	64.8	85.0	86.8	68.0	(58.0)	(48.0)	—	—	—	210.9
B ^c	37.4	70.1	85.9	85.9	70.1	37.4	24.4	(24.4)	—	—	212.1
D ^d	—	61.8	86.5	88.7	64.7	—	—	—	—	—	—

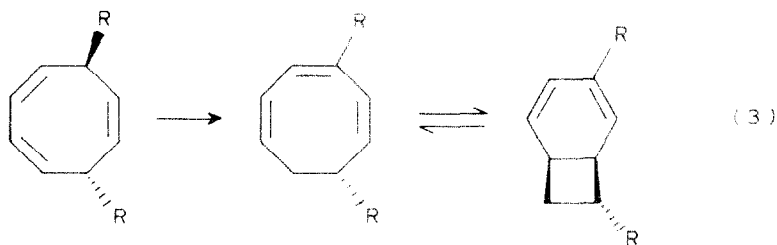
^a Numbering reference structures and references as in Table 1. Assignments between C(2) and C(5) (and C(3) and C(4) in A) are ambiguous. ^b As in Table 1. ^c Data from ref. 22. ^d Data from ref. 24.



Scheme 2

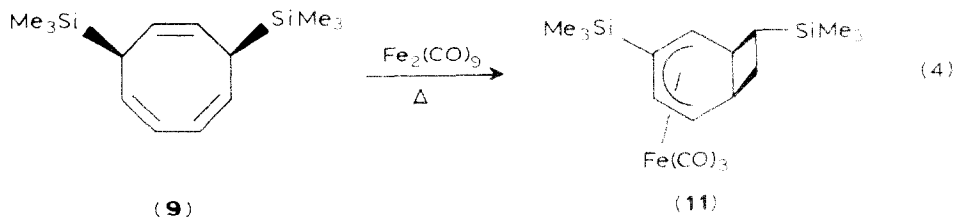
Of particular importance in assigning the stereochemistry of the carbomethoxy group on the cyclobutane ring was the assumption that the four-membered ring was planar, and hence that *cis* coupling constants were larger than *trans* [18]. (In fact, all of the *cis* coupling constants assigned in **10** are in the range 9–10 Hz, and the *trans* 4–7 Hz). The planarity of cyclobutane rings in several bicyclo[4.2.0]octadienetricarbonyliron complexes has been established by X-ray crystallography [19], and we believe that the stereochemical assignment is therefore quite secure.

Formation of **10** from **6b** obviously involves substantial rearrangement, and we propose the route shown in Scheme 2. All of the rearrangement steps shown represent thermally allowed pericyclic reactions and have ample precedent. Conversion of the 1,3,6-cyclooctatriene **4b** to the isomeric 1,3,5-triene involves a suprafacial 1,5-sigmatropic shift, a reaction which has been well-characterized in the case of unsubstituted cyclooctatriene [20], as well as in 5,8-disubstituted cycloocta-1,3,6-trienes (eq. 3). The latter were also reported to form bicyclo[4.2.0]octa-2,4-dienes with



($R = \text{Me}$ [13], CMe_2CN [12])

the substituents in the 3 and 8 positions, analogous to **10**. An overall conversion analogous to that in Scheme 2 occurred upon reaction of **9** with nonacarbonyldiiron to form **11** [21] (eq. 4).



Experimental

Solvents used were reagent grade or redistilled bulk grade. Reactions involving organometallic reagents or intermediates were conducted under nitrogen using degassed solvents. Evaporations were done on a rotary evaporator at aspirator pressure and temperatures below 40 °C. Proton NMR spectra (δ , ppm) were recorded on Varian EM-360, CFT-20, or Nicolet NT-300 spectrometers, in CDCl_3 solutions containing TMS internal standard unless otherwise specified. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. IR data were obtained on Pye Unicam SP-1000 or Perkin-Elmer 567 spectrometers. Mass spectra were obtained on a Hewlett Packard 5980 instrument. MM2 Calculations were done within the framework of Still's MODEL program, Version 1.31, run on a Vax 11/780.

Carboxylation of 3 [3,4]

Freshly distilled cyclooctatetraene (7.80 g, 0.075 mol) was slowly added to a refluxing mixture of 225 ml ether, 25 ml tetrahydrofuran (THF), and 1.06 g (0.15 mol) of lithium cut into small pieces. The heat of reaction kept the mixture at reflux for 90 minutes, after which stirring was continued overnight. The mixture was then cannulated onto a large excess of Dry Ice. Vigorous reaction resulted in formation of a yellow precipitate, which dissolved upon addition of 100 ml water. The layers were separated, the water layer washed with 30 ml ether, and the combined organic solution was dried over MgSO_4 and evaporated, leaving 1.56 g of recovered cyclooctatetraene (NMR).

Acidification of the water layer with 30 ml concentrated HCl gave a yellow precipitate, which was collected by filtration and allowed to dry, then extracted with several portions of ether. This left 2.85 g (20%) of highly insoluble **5**, m.p. 232–215 °C, dec. IR: 1690, 1620 cm^{-1} ; NMR ($\text{DMSO}-d_6$): 5.9 (d, J 15 Hz), 6.3 (m), 6.9 (m), and 7.6 (dd, J 15, 10 Hz). The aqueous filtrate was further acidified with 20 ml concentrated HCl and extracted with four 100-ml portions of ether. The residue from drying and evaporating these washings was combined with that from the ether extracts from the crude **5** to give 7.76 g of yellow solid (crude **6a**, 50%). This material was esterified by addition to a solution of diazomethane in ether at 0 °C. Evaporation of the ether left a yellow oil, which partly crystallized. Collection of the crystals yielded 2.81 g (17% overall) of **6b**, m.p. 87–89 °C. Lit. [4] m.p.: 87–89 °C. NMR: δ 6.05 (dd, H(5), J 2.2, 1.3 Hz), 2.12 (m, H(1)), 1.87 (m, H(4)), 0.82 (td, J 3.9, 1.3 Hz, H(3)), 3.69 (s, methyls). Chromatography of the remaining yellow oil using toluene eluant and a silica column gave, first, 0.69 g (4%) of **7** as a light yellow oil, then an additional 0.67 g (4%) of **6b**. NMR and IR data for **7**: see text; MS (direct inlet): m/z 222 (1.9%, P), 190 (14.2%, $P - \text{MeOH}$), 163 (58%, $P - \text{CO}_2\text{Me}$), 162 (65%), 131 (85%), 121 (55%), 105 (78%), 103 (100%), 91 (55%), 77 (67%), and 59 (40%).

Attempted conversion of 4b to 2

An NMR sample of **6b**, m.p. 88–89 °C, upon standing for 20 h under nitrogen, developed small peaks at δ 3.75 (methyls), 4.2–4.4 (br. t, J ca. 5 Hz, H_5), and 5.8–6.0 (m, H(1,2,6)), indicative of **4b** [4]. The amount did not exceed 10% of the total even after 4 days, based upon the heights of the methyl ester peaks.

A solution of 0.89 g (4.0 mmol) of **6b**, 0.74 g (4.2 mmol) of *N*-bromosuccinimide, and a few mg of dibenzoyl peroxide in 50 ml carbon tetrachloride was refluxed for 16 h. Succinimide was removed by filtration, and the filtrate was evaporated. The residue was taken up in 50 ml methanol and treated with 1.01 g (10 mmol) of triethylamine. After 15 h at room temperature, the solvent was evaporated and the resultant brown oil dissolved in 50 ml ether and 30 ml 0.1 *M* HCl. The layers were separated, and the aqueous layer was washed with three 30 ml portions of ether. The combined ether solution was washed with 0.1 *M* aq. HCl, twice with water, dried, and evaporated. Silica chromatography of the oily yellow product, eluting with methylene chloride, gave several impure fractions (NMR). GC-MS analysis of one of these showed at least ten peaks, whose mass spectra suggested the compositions $C_8H_6E_2$ (**2?**), $C_8H_8E_2$ (probably **6**), $C_8H_9BrE_2$, $C_8H_8Br_2E_2$, and others ($E = CO_2Me$). Eluting the column with methanol gave 0.415 g of a white solid, **8**, dec. pt. $> 200^\circ C$ after recrystallization from methanol. MS: m/z 444 (2.3%, *P*), 413 (3%, *P* - OMe), 385 (1%, *P* - CO_2Me), 353 (2%, *P* - MeOH - CO_2Me), 222 (12%, *P*/2), 190 (12%), 163 (8%), 162 (7%), 136 (100%), 105 (65%), 77 (9%), 59 (6%). NMR: 5.70 (s, 2H), ca. 3.7 (m, 2H), 3.77, 3.73, 3.57, 3.65 (each a s., 3H), and 3.3–2.1 (several overlapping m, 12H).

Reaction of 6 with iron pentacarbonyl

A solution of 0.67 g (3.0 mmol) of **6** and 1.76 g (9.0 mmol) of iron pentacarbonyl in 50 ml dioxane was refluxed under nitrogen for 69 h. After filtration and evaporation of the solvent, a brown oil (1.89 g) remained. Chromatography on silica gave yellow crystals (0.141 g, 13%) of **10**, which eluted with 90% toluene/hexane; recrystallization from hexane gave yellow crystals, m.p. 101–102°C. Anal: Found: C, 49.39; H, 3.96. $C_{15}H_{14}FeO_7$ calcd.: C, 49.72; H, 3.87%. MS: m/z 362 (1.0%, *P*), 334 (7%, *P* - CO), 331 (10%, *P* - OMe), 306 (45%, *P* - 2CO), 278 (97%, *P* - 3CO), 263 (88%), 222 (30%, *P* - $Fe(CO)_3$), 220 (37%), 134 (78%), 105 (100%), 84 (18%), 77 (45%), 56 (58%). IR: 2050, 1970, 1730 cm^{-1} . NMR: Tables 1 and 2. Elution of the column with methylene chloride gave 0.41 g (62%) of the dimer **8**, identical to that described above.

Acknowledgment

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