We wish to report the first preparation of unprotected 1,3,5,7,9-pentacarbonyl compounds. Pentaketone **3** has been prepared by two-stage benzoylation of 2,4,6-heptanetrione (**4**). Triketone **4** was treated with 5 equiv of lithium diisopropylamide followed by 3 equiv of methyl benzoate and then the sequence was repeated. The reaction gave pentaketone **3** as yellow plates, mp 67–68.5° (ethanol), in 20% yield.[5] The nmr spectrum indicated that **3** existed as a mixture of tautomers in which bis- and tris(enol) forms predominated. The reaction proceeded *via* tetraketone **5**, mp 59–60° (ethanol),[5] which was isolated in 19% yield from treatment of triketone **4** with 3 equiv of lithium diisopropylamide followed by 1 equiv of methyl benzoate.[5]

$$CH_3COCH_2COCH_2COCH_3 \xrightarrow[C_6H_5CO_2CH_3]{LiN(i\text{-}Pr)_2}$$

4

$$C_6H_5COCH_2COCH_2COCH_2COCH_3$$

5

$$\Big\downarrow {\scriptstyle LiN(i\text{-}Pr)_2 \atop C_6H_5CO_2CH_3}$$

$$C_6H_5COCH_2COCH_2COCH_2COCH_2COC_6H_5$$

3

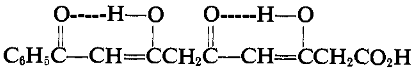
The availability of tetraketone **5**, which is the first one with an aliphatic terminus to be prepared, made the synthesis of tetraketo acid **6** practicable. Treatment of tetraketone **5** with excess lithium diisopropylamide gave a deep red solution (presumably tetranion **7**) into which carbon dioxide was introduced. Tetraketo acid **6**, mp 76–77° (chloroform–hexane), was obtained in 56% yield.[5] The nmr spectrum of **6** indicated that the compound existed as a mixture of tautomers in which **8** predominated.

$$5 \xrightarrow{LiN(i\text{-}Pr)_2} C_6H_5CO\overset{-}{C}HCO\overset{-}{C}HCO\overset{-}{C}HCO\overset{-}{C}H_2 \xrightarrow[1.\ H^+]{1.\ CO_2}$$

7

$$C_6H_5COCH_2COCH_2COCH_2COCH_2CO_2H$$

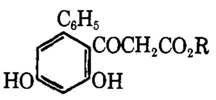
6



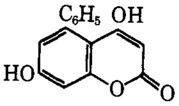
$$C_6H_5\overset{O}{\overset{\|}{C}}{-}CH{=}\overset{OH}{\overset{|}{C}}CH_2\overset{O}{\overset{\|}{C}}{-}CH{=}\overset{OH}{\overset{|}{C}}CH_2CO_2H$$

8

Acid **6** underwent an aldol-type cyclization in aqueous sodium bicarbonate to give 84% acid **9a**, mp 113–113.5° dec,[6] which cyclized rapidly in trifluoroacetic acid and slowly without exogenous catalysis to the coumarin **10**, mp 269–272° dec.[5] Treatment of **6** with 1 *M* aqueous potassium hydroxide gave 28% **9a** plus 67% of a second aldol product, **11**, mp 147–148°.[5] The methyl ester of **6**, mp 51–52° (ether–hexane)[5] (prepared from **6** and diazomethane), gave aldol-type products **9a,b**, **10**, **11**, and **12**; Claisen-type cyclization products **13** and **14** were not observed. An additional cyclization of **6** occurred in acetic anhydride; pyrone **15**, mp 150–154.5° dec (acetone–hexane),[5] was obtained in 71% yield.



9a, R = H
b, R = CH$_3$



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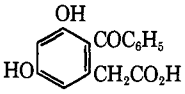

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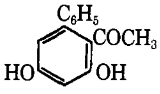

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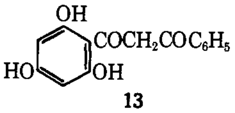

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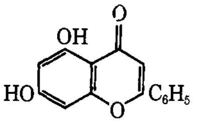

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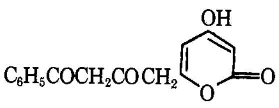

15

The aldol cyclization products **10** and **11** are structurally related to the polyketide natural products, kotanin[7] and curvulinic acid.[8] We are currently seeking additional cyclization products of **6** and studying the factors controlling these cyclizations.

Acknowledgment. We wish to thank the U. S. Public Health Service (Research Grant No. GM-12848) and the Alfred P. Sloan Foundation for support of this work.

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(5) Combustion analysis within 0.3% of theory. Ir, uv, nmr, and mass spectra in full agreement with the proposed structure.

(6) The compound was not sufficiently stable to permit elemental analysis and the parent ion was not observed in the mass spectrum. All other spectral data were consistent with the structural assignment.

(7) G. Buchi, D. H. Klaubert, R. C. Shank, S. M. Weinreb, and G. N. Wogan, *J. Org. Chem.*, **36**, 1143 (1971).

(8) A. Kamal, M. Ali Khan, and A. Ali Qureshi, *Tetrahedron*, **19**, 111 (1963).

(9) Research Career Development Awardee, K3-GM-27013, of the National Institutes of Health, U. S. Public Health Service.

(10) Shell Predoctoral Fellow, 1970–1971.

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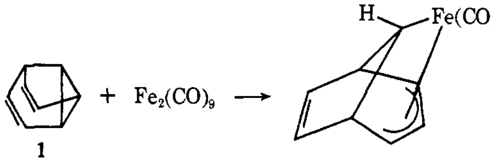
A New C$_8$H$_8$Fe(CO)$_3$ Complex. The Reaction between Semibullvalene and Diiron Nonacarbonyl

Sir:

A number of interesting monocyclic C$_8$H$_8$ iron carbonyl complexes are known.[1,2] We report now the first example of such a complex in which the C$_8$H$_8$ part exists in the bicyclo[3.2.1]octyl form.

Reaction of 1.0 mmol of semibullvalene (**1**)[3] with 2.6 mmol of Fe$_2$(CO)$_9$ at reflux in benzene for 1 hr under nitrogen gives a green liquid C$_8$H$_8$Fe(CO)$_3$ complex **2** in 70% yield which could be purified by repeated bulb-to-bulb distillation (60° (0.25 mm)).



1 **2**

The structure of **2** is based upon its composition: the mass spectrum showed a parent molecular ion, *m/e* 244 (2.5%), M − CO, *m/e* 216 (25%), M − 2CO, *m/e* 188 (35%), *m/e* 134 (100%), C$_8$H$_8$, *m/e* 104 (65%); the infrared spectrum showed C≡O absorption at 1975, 2035, and 2070 cm^{-1}; the uncomplexed C=C olefinic absorption appeared at 1570 cm^{-1}. (*Anal.* Calcd for

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(1) For a review, see: E. O. Fischer and H. Werner in "Metal π-Complexes," Vol. 1, Elsevier, New York, N. Y., 1966, pp 119–133.

(2) M. A. Bennett, *Advan. Organometal. Chem.*, **4**, 375 (1966).

(3) Semibullvalene was prepared starting with the Diels–Alder adduct of cyclooctatetraene and azo ester. For examples of the route, see: (a) L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5766 (1970); (b) R. Askani, *Tetrahedron Lett.*, **38**, 3349 (1970); (c) R. M. Moriarty, C.-L. Yeh, and N. Ishibe, *J. Amer. Chem. Soc.*, **93**, 3085 (1971).

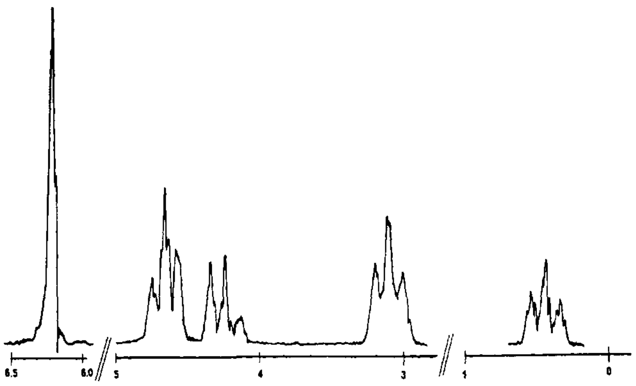
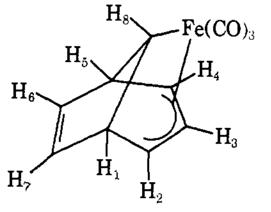


Figure 1. Nmr spectrum, 60 MHz, of $C_8H_8Fe(CO)_3$ (**2**) in solution in $CDCl_3$.

$C_8H_8Fe(CO)_3$: C, 54.09; H, 3.28. Found: C, 54.06; H, 3.37.) Catalytic hydrogenation caused smooth reduction of this bond to yield the dihydro derivative.

The nmr spectrum of **2** (Figure 1) provides convincing evidence for the proposed structure and excludes **3** or **4** as possibilities. The spectra at 60, 90, and 220 MHz were only interpretable on the basis of the presence of a plane of symmetry within the molecule. This was reflected in a pairwise equivalence of the vinylic, bridgehead, and outer protons of the π-allylic system. Table I presents the spectral parameters. The C_8 proton bonded to the carbon bearing the iron is expectedly highly shielded occurring at 0.6 ppm. All the other chemical shifts are normal.[4,5] The vicinal coupling constant J_{1-8} is rather large and probably indicates a bending of the iron toward the allylic system with a concomitant contraction of the CH_1–CH_8 dihedral angle. All the other vicinal coupling constants are as expected. The long-range coupling J_{2-8} and J_{4-8} of 1.4 Hz and the absence of coupling between H_6 and H_8 and H_7 and H_8 is important in confirming structure **2**.

Table I. Nmr Parameters for $C_8H_8Fe(CO)_3$ (**2**)[a]



Chemical shift, ppm[b]	Coupling constants,[c] Hz
$H_1 = H_5 = 3.10$	$J_{1-2} = J_{4-5} = 5.5$
$H_2 = H_4 = 4.70$	$J_{1-8} = J_{5-8} = 6.3$
$H_3 = 4.30$	$J_{1-7} = J_{5-6} = 1.5$
$H_6 = H_7 = 6.30$	$J_{2-8} = J_{8-4} = 1.4$
$H_8 = 0.60$	$J_{3-2} = J_{3-4} = 6.1$
	$J_{3-1} = J_{3-5} = 1.2$
	$J_{7-5} = J_{6-1} = 1.1$

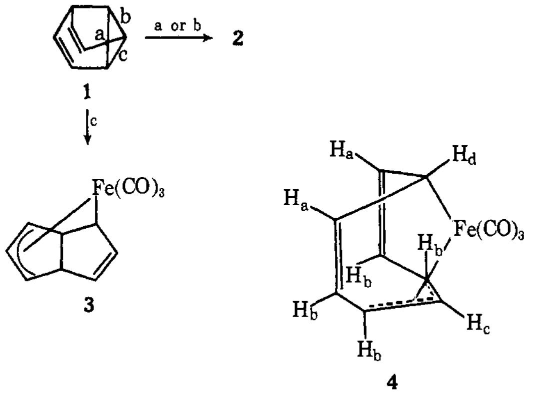
[a] No change in the spectrum was observed from −60 to 120°. [b] Determined at 60, 90, and 220 MHz and relative to TMS. [c] Coupling constants were determined by spin decoupling at 90 MHz.

Structure **4**, which is known in the case of C_8H_8–$Os(CO)_3$,[6,7] possesses the correct symmetry but must be excluded on the basis of chemical shifts and coupling constants. The lowest field proton in the spectrum of **2** (Figure 1) would have to correspond to the olefinic proton H_a in **4** and should appear as a doublet of doublets coupled to H_d to the extent of about 4.5 Hz and to H_b with a value larger than 6 Hz. This is clearly not the case. The olefinic protons in **2** are equivalent and are not mutually spin coupled. They are not coupled to the high-field proton and only couple with the bridgehead protons.

The bonding suggested for **2** involves a π-allyl component and a σ component to the $Fe(CO)_3$ unit. This type of bonding has been proposed to exist in the bullvalene–bis(tricarbonyliron) complex,[4] tetracyclo[4.4.0.-$0^{5,7}.0^{2,10}$]deca-3,8-diene–bis(tricarbonyliron) complex,[5] and isobullvalene–bis(tricarbonyliron) complex.[8,9]

Formation of complex **2** is reminiscent of the reaction of $Fe_2(CO)_9$ with bullvalene recently reported by Aumann.[4] An analogous reaction in the case of semibullvalene would yield **3**, but this compound was not isolated.

The mechanism for formation of **2** may involve a simple oxidative cleavage of one of the two equivalent σ bonds (a or b) of the cyclopropyl group in **1**. Cleavage of bond c yields **3**.



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(4) R. Aumann, *Angew. Chem.*, **83**, 175 (1971).

(5) R. Aumann, *ibid.*, **83**, 176 (1971).

(6) We wish to thank a referee for calling to our attention this work.[7]

(7) M. I. Bruce, M.Cooke, and M. Green, *Angew. Chem.*, **80**, 662 (1968); *Angew. Chem., Int. Ed., Engl.*, 7, 639 (1968); M. I. Bruce M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc. A*, 987 (1969).

(8) R. Aumann, *Angew. Chem.*, **83**, 177 (1971).

(9) The simplest example of this type of complex is the one formed between vinylcyclopropane and $Fe(CO)_5$.[10,11]

(10) S. Sarel, R. Ben-Shoshan, and B. Kirson, *J. Amer. Chem. Soc.*, **87**, 2517 (1965).

(11) R. Ben-Shoshan and S. Sarel, *Chem. Commun.*, 882 (1969).

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