olefinic methyl peaks at 2.26 ppm in **1** and 2.66 ppm in **10** clearly differentiated the two isomers.

The ir spectra of natural Y base (KBr, 1725, 1700, 1690, 1570 cm^{-1}) and synthetic Y base (KBr, 1726, 1698, 1583, 1568 cm^{-1}) were very similar except for minor differences. Synthetic and natural Y base both emitted at 445 nm (in H_2O) when excited at 320 nm. The uv and pK_a' of natural Y base were previously measured in 10% methanol for solubility reasons. However, as it was found that methanol was not a suitable solvent,[14] the data were remeasured in water. The uv data of synthetic (Table I) and natural Y base were in complete accord excepting for the uniformly smaller ϵ values (*ca.* 90%) of the latter due to purification difficulties arising from the minute amount available. The dissociation constants were 3.70 and 8.60 ($\pm$0.05) with both specimens. The nmr and mass spectral data of *dl*-Y and natural Y[1] were also in complete agreement, including the appearance of a set of mass spectral peaks 14 mass units higher when the sample was injected into the spectrometer as a methanol solution. This is a unique feature of the Y base structure and, as interpreted previously,[1] is due to reaction of methanol with the Y nucleus[14] (*i.e.*, CO or C–OH → C–OMe).

Table I. Uv Data of Synthetic Y Base

Solvent	nm (ϵ) Peak A	Peak B	Peak C
Water[a]	235 (32,000)	263 (5800)	313 (5000)
Water (pH 2.0)	233 (35,600)	286 (7600)	
Water (pH 10.0)	236 (32,800)	265 (6800)	304 (7200)
100% MeOH	235 (48,100)	263 (8200)	310–315 (7400)

[a] The data were obtained after stirring for 24 hr because of the insolubility of Y base in water.

(*S*)-(+)-Glutamic acid was converted into (*S*)-dimethyl 2-methylcarbamoylglutarate (**11**), oil,[9] CD (MeOH) $\Delta\epsilon$ −0.14 (232 nm) and −0.76 (206), by carbamoylation (with methyl chloroformate–magnesium oxide, under conditions employed for N-benzoylation[15]) and dimethylation with diazomethane. Exhaustive microozonolysis[16] of natural Y base in ethyl acetate, removal of solvent, decomposition of the ozonide with hydrogen peroxide–aqueous sodium bicarbonate, extraction of acidic product with ethyl acetate, methylation with diazomethane, and tlc purification of product afforded **11** with negative and positive CD Cotton effects, respectively, at 232 and 207 nm. The structure of baker's yeast tRNA$^{\text{phe}}$ Y base, the most modified of the numerous minor bases playing important roles in codon–anticodon recognitions,[17] can thus be fully represented by **1** with an *S* configuration.[18]

Acknowledgments. We acknowledge Professors Zachau,[4] Keller,[6] and Takemura[7] for sending us preprints prior to publication. The work was supported by Public Health Service Grant No. CA 11572 and the Hoffmann-La Roche Company.

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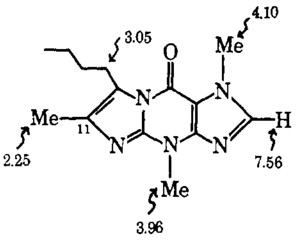
(14) It has been found that shapes of uv curves change considerably with methanol content and time, presumably due to tautomeric equilibria and/or addition of methanol (see below); the Y base kept in methanol, however, could be readily recovered by tlc. Comparison of the uv spectra of natural Y base and synthetic models employed in structural studies[1] were all carried out in 10% MeOH. Both natural and synthetic Y base described in the present communication displayed identical behavior in all respects under these conditions.

(15) M. Bergmann and L. Zervas, *Chem. Ber.*, **65**, 1192 (1932).

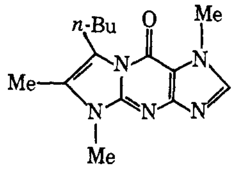
(16) The microozonizer was purchased from Supelco, Inc., Bellefonte, Pa.

(17) J. Eisinger, B. Feuer, and T. Yamane, *Nature (London), New Biol.*, **231**, 126 (1971).

(18) Errata for ref 1: (i) Structure **1**, place N in position 9 of nucleus; (ii) structure **11**, the 3.96-ppm Me should be attached to N^3; also C-2 should be tetravalent; (iii) structure **12**, C-2 should be tetravalent; (IV) in discussion on biogenesis (end of paper) glutaric acid should be glutamic acid.



11



12

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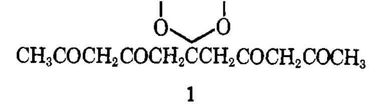
Received August 18, 1971

Synthesis of 1,3,5,7,9-Pentacarbonyl Compounds

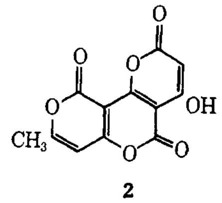
Sir:

Oligo-β-carbonyl compounds have long attracted attention because of their apparent involvement in the biosynthesis of phenolic natural products,[1] but investigations have been hindered by inaccessibility of the carbonyl compounds, Recently a versatile synthesis of 1,3,5,7-tetracarbonyl compounds was developed in this laboratory.[2] The synthesis involves treatment of 2,4,6-triketones with lithium diisopropylamide or other strong bases to give 1,3,5-trianions which undergo acylation or carboxylation at the 1 position. 1,3,5,7,9-Pentacarbonyl compounds have remained inaccessible. Birch and coworkers prepared ketal-protected pentaketone **1** but were unable to remove the protective group selectively.[3] Trislactone **2**, which is a derivative of 3,5,7,9-tetraoxodecanoic acid, was studied by Scott and coworkers.[4] Under basic conditions **2** underwent cleavage and recyclization to give phenolic products; however, the acyclic intermediates were not detected.



$$CH_3COCH_2COCH_2\overset{\overset{CH_2-CH_2}{O\quad O}}{C}CH_2COCH_2COCH_3$$

1



2

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(1) See J. H. Richards and J. B. Hendrickson, "Biosynthesis of Terpenes, Steroids, and Acetogenins," W. A. Benjamin, New York, N. Y., 1964.

(2) T. T. Howarth, G. P. Murphy, and T. M. Harris, *J. Amer. Chem. Soc.*, **91**, 517 (1969); T. M. Harris and R. L. Carney, *ibid.*, **89**, 6734 (1967).

(3) A. J. Birch, F. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963).

(4) T. Money, F. W. Comer, G. R. B. Webster, I. G.Wright, and A. I. Scott, *Tetrahedron*, **23**, 3435 (1967); F. W. Comer, T. Money, and A. I. Scott, *Chem. Commun.*, 231 (1967).

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]

$$\underset{\mathbf{4}}{\mathrm{CH_3COCH_2COCH_2COCH_3}} \xrightarrow[\mathrm{C_6H_5CO_2CH_3}]{\mathrm{LiN}(i\text{-Pr})_2}$$

$$\underset{\mathbf{5}}{\mathrm{C_6H_5COCH_2COCH_2COCH_2COCH_3}}$$

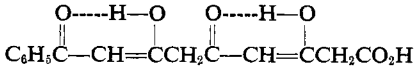
$$\Big\downarrow \begin{smallmatrix}\mathrm{LiN}(i\text{-Pr})_2\\ \mathrm{C_6H_5CO_2CH_3}\end{smallmatrix}$$

$$\underset{\mathbf{3}}{\mathrm{C_6H_5COCH_2COCH_2COCH_2COCH_2COC_6H_5}}$$

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.

$$\mathbf{5} \xrightarrow{\mathrm{LiN}(i\text{-Pr})_2} \underset{\mathbf{7}}{\mathrm{C_6H_5CO\bar{C}HCO\bar{C}HCO\bar{C}HCO\bar{C}H_2}} \xrightarrow[\mathrm{1.\ H^+}]{\mathrm{1.\ CO_2}}$$

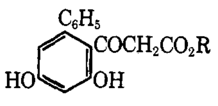
$$\underset{\mathbf{6}}{\mathrm{C_6H_5COCH_2COCH_2COCH_2COCH_2CO_2H}}$$



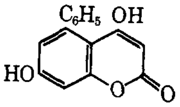
$$\mathrm{C_6H_5\overset{\overset{\text{O-----H—O}}{\|}}{C}—CH{=}\overset{|}{C}CH_2\overset{\overset{\text{O-----H—O}}{\|}}{C}—CH{=}\overset{|}{C}CH_2CO_2H}$$

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 = CH3



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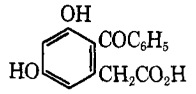

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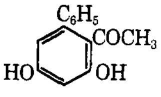

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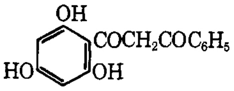

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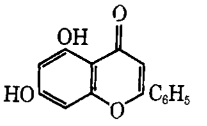
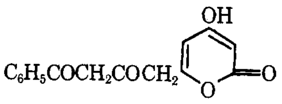


14



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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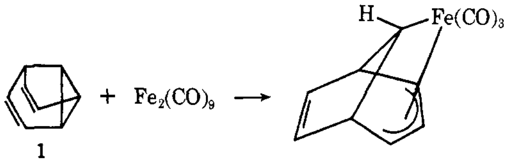
Received September 13, 1971

A New $C_8H_8Fe(CO)_3$ Complex. The Reaction between Semibullvalene and Diiron Nonacarbonyl

Sir:

A number of interesting monocyclic C_8H_8 iron carbonyl complexes are known.[1,2] We report now the first example of such a complex in which the C_8H_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 $C_8H_8Fe(CO)_3$ 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_8H_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).