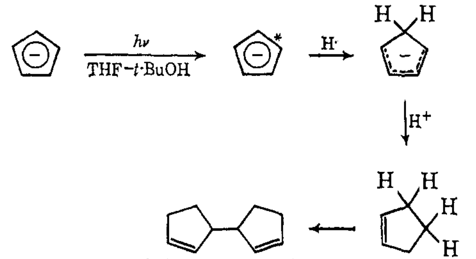
[vinyl, τ 4.36 (4); methine allylic, 7.3 (2); allylic, 7.7 (4); methylene, 8.0–8.8 (4)], are consistent with the postulated structures. Identities were confirmed by comparison with authentic *meso*- and *dl*-3-(3′-cyclopentenyl)cyclopentenes, prepared by Grignard coupling of 3-chlorocyclopentene.

That of all possible dimeric photoproducts only these dicyclopentenyls are observed, and in equal amounts, suggests that the final step in product formation is coupling of cyclopentenyl radicals,[9] perhaps produced *via* hydrogen abstraction by photoexcited cyclopentadienide to give an anion radical which is then protonated (eq 1).



I (*meso* and *dl*)

(1)

Since the photochemical event occurring with cyclopentadiene in neutral or less basic solution differs entirely from that observed under the present, more strongly basic, conditions, cyclopentadienide *per se* must be involved in conversion to the dicyclopentenyls. Also, since yields of Ia,b are not enhanced when a 50:50 mixture of cyclopentadiene and cyclopentadienide is photolyzed, neither ground- nor excited-state cyclopentadiene is implicated in the reaction. Furthermore, the photoproducts are not produced when *t*-butyl alcohol is absent from the THF–sodium cyclopentadienide photolysis solution.

In an experiment designed to locate the source of the abstracted hydrogen atom, all exchangeable protons in the reaction system were replaced by deuterium. Perdeuteriocyclopentadienide was prepared from perdeuteriocyclopentadiene and photolyzed in the presence of 20% *t*-butyl alcohol-O-*d*. The 3,3′-dicyclopentenyls obtained in this experiment were shown by mass spectral analysis to be perdeuterated. Consequently, photoexcited cyclopentadienide is not hydrogen abstracting from solvent in the customary fashion (*i.e.*, from the methyl groups of *t*-butyl alcohol or the α-methylenes of tetrahydrofuran). Abstraction of the hydrogen atom bonded to oxygen would not be expected on the basis of bond strengths; however, there is available from photoexcitation sufficient energy for this reaction, and this hydroxylic hydrogen may well be in an optimal position for abstraction. Close association in the ground state between exchangeable protons and cyclopentadienide may be favored because of hydrogen bonding or solvation of sodium ions, which in turn are associated with cyclopentadienide. The resulting chemistry is, then, expected to be a unique consequence of carbanion photoexcitation in protic solvent.

Acknowledgment. The authors are grateful to Dr. Lois Durham and Dr. Alan Duffield for valuable consultation and to ARO(D) for financial assistance.

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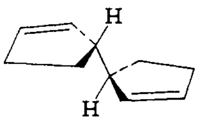
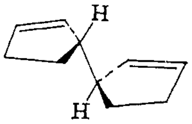
influence on each other than do those of the *meso* isomer. Thus Ib, exhibiting greater olefinic fine splitting, is assigned the *dl* configuration.



Ia



Ib

[9] Equal amounts of the hydrocarbons Ia,b have been obtained by the benzophenone-sensitized photolysis of neat cyclopentene, presumed to generate cyclopentenyl radicals (K. S. Sidhu, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, 44, 531 (1966). The configurational assignments suggested by these authors are opposite to those proposed herein.[8]

[10] National Science Foundation Fellow, 1964–1966, and Weiss Fellow, 1966–1967.

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New Synthesis of Cyclobutadieneiron Tricarbonyl

Sir:

Metal complexes of substituted cyclobutadienes have been prepared either through cycloaddition of acetylenes catalyzed by metal carbonyls or metal complexes,[1] by demetalation of heterocyclopentadienes,[2] by ligand transfer reaction,[3] or by the reduction of 3,4-dihalocyclobutenes with suitably chosen metal carbonyls.[4] Of these, only the latter method has been successfully applied to the synthesis of a complex of the parent hydrocarbon itself, namely cyclobutadieneiron tricarbonyl.[4b] We now report the preparation of this substance in essentially one step from α-pyrone.

Photolysis of α-pyrone (**1**) in ether solution has been reported to give the photoproduct **2** in quantitative yield.[5] When iron pentacarbonyl is added to these solutions and irradiation is continued for a brief period, both cyclobutadieneiron tricarbonyl (**3**) [infrared (C≡O) 4.87, 5.05 μ; nmr τ 6.00 (CCl_4); ultraviolet $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 215, 360 mμ (ϵ 19,000, 84); mass spectroscopy m/e 192, 164, 136, 108] and α-pyroneiron tricarbonyl (**4**) are formed in 10–15% combined yield.[6] The relative yields of these two substances appear to vary somewhat with temperature. At −15° **3** is the principal component in the reaction mixture but at room temperature both products are formed in approximately equal amounts.[7]

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[1] W. Hübel, E. H. Braye, A. Clauss, E. Weiss, D. A. Brown, G. S. D. King, and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); W. Hübel and R. Merenyi, *J. Organometal. Chem.* (Amsterdam), **2**, 213 (1964); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961); P. M. Maitlis, D. F. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965). These and the citations in ref 2–4 are illustrative only. A more complete listing of references is to be found in the review of P. M. Maitlis, *Advan. Organometal. Chem.*, **1**, 95 (1966).

[2] H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

[3] P. M. Maitlis and A. Efraty, *J. Organometal. Chem.* (Amsterdam), **4**, 172, 175 (1965); P. M. Maitlis and M. L. Games, *J. Am. Chem. Soc.*, **85**, 1887 (1963).

[4] (a) R. Criegee and G. Schroeder, *Ann.*, **623**, 1 (1959); (b) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

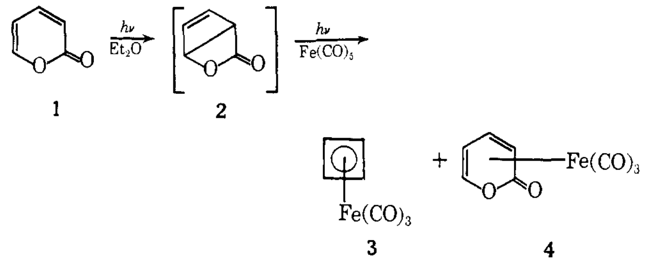
[5] E. J. Corey and J. Streith, *ibid.*, **86**, 950 (1964). No more than 1% α-pyrone remains at the end of the reaction.

[6] The low yield of **3** and **4** has been shown to be due principally to photolytic decomposition of both of these substances under the conditions of their formation. The decomposition of **3** by ultraviolet light has been reported recently by W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strauszand, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

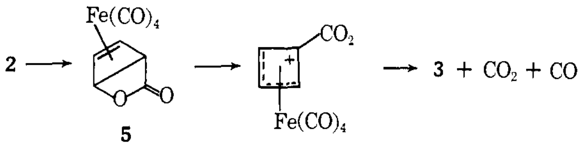
[7] The ratio of products was estimated by determination of the nmr spectrum of the mixture after the crude reaction product had been chromatographed on alumina. Alternatively the α-pyrone complex **4** may be separated from **3** either by crystallization of **4** from pentane solution or by fractional sublimation of **3** at room temperature and 0.1 mm.

The photopyrone **2** in ether or heptane solution is also transformed rapidly but in low yield (5%) to mixtures of **3** and **4** in the absence of light by treatment with iron enneacarbonyl.

α-Pyroneiron tricarbonyl (**4**) is a yellow crystalline substance, mp 140–141°, which may be prepared directly from α-pyrone and iron enneacarbonyl by warming the components in heptane and crystallizing the crude product from pentane. *Anal.* Calcd for $C_5H_4O_2\cdot Fe(CO)_3$: C, 40.68; H, 1.69; Fe, 23.73. Found: C, 40.74; H, 1.90; Fe, 23.78. Spectral properties include: infrared (C≡O) 4.80, 4.93, 4.96, (C=O) 5.62; ultraviolet $\lambda_{max}^{95\%\ EtOH}$ 214, 360 mμ (ϵ 21,000, 220); mass spectroscopy *m/e* 236, 208, 180, 152, 124, 96. Its nmr spectrum exhibits three complex resonances centered at τ 6.99, 4.39, and 3.69 with relative integrated areas of 1:2:1.



It seems probable that the iron tetracarbonyl complex, **5**,[8] of the photopyrone is an intermediate in the formation of **3** in both the thermal and photochemical processes. The loss of CO_2 from this intermediate may proceed either in a concerted fashion or stepwise as shown below.



Further studies are in progress to determine whether the reaction sequence may be applied to substituted α-pyrones and to examine the reactions of other metal carbonyls and metal carbonyl complexes with the photopyrone.

Acknowledgment. This research was supported by National Institutes of Health Grant GM 05978.

[8] Similar monoeneiron tetracarbonyl complexes have been reported: H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1156 (1962); E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdock, *ibid.*, **46**, 288 (1963); H. D. Murdock and E. Weiss, *ibid.*, **46**, 1588 (1963).

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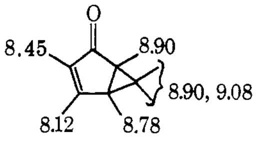
Equilibrating Cyclopropylcarbinyl Cations

Sir:

The possibility exists that an appropriately substituted ion with the skeletal structure shown in **1** would show fivefold degeneracy, wherein the small ring can be considered to revolve about the perimeter of the larger ring. We wish to report experiments most simply interpreted in terms of carbonium ions in which four of five such structures rapidly equilibrate.

1

When a solution of hexamethylbicyclo[3.1.0]hex-3-en-2-one (**2**)[1] in 97% sulfuric acid was allowed to stand at 22.6° for 30 min, then hydrolyzed, a nearly quantitative yield of hexamethyl-2,4-cyclohexadienone (**3**) was obtained.[2] The allylic methyl groups at C-2, C-4, and C-5 of **3** appear, in the unlabeled compound, as a broad singlet centered at τ 8.14. In labeling experiments described below it was necessary to distinguish these methyls from one another. This was accomplished by converting **3** to its crystalline adduct **4** (mp 65°) with dimethyl acetylenedicarboxylate.[2,3]



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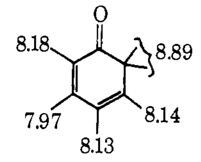

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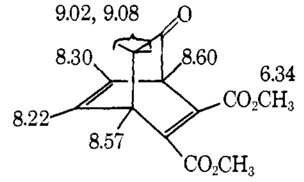
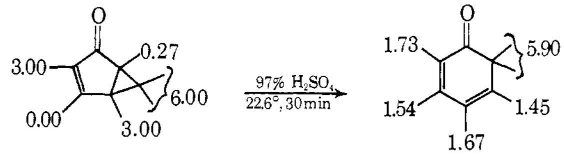


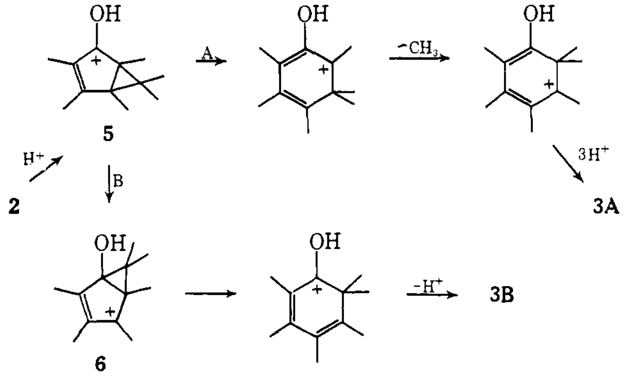
4

Labeled **2**-d_6,[1] with the hydrogen distribution shown,[4] when treated with acid as described above, afforded dienone **3**-d_6 with the hydrogen distribution shown (as determined from the nmr spectra of **3** and **4**[5]). This result eliminates the two obvious mechanisms A and B,



2-d_6 **3**-d_6

since these would be predicted to give **3** with the label distribution shown in **3A** and **3B**, respectively.



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[1] H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

[2] The chemical shifts (τ) shown in the formulas were deduced from the spectra of appropriately labeled (CD_3) compounds.

[3] T. Kakihana, M.S. Thesis, Michigan State University, 1966.

[4] Exchange was complete at the C-4 methyl, but only 91% complete at the C-1 methyl, as determined by integration[5] of the nmr spectrum.

[5] The maximum error in integration was 8%.