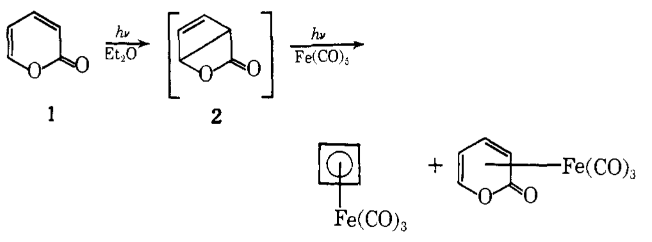
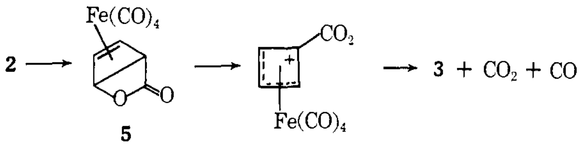
The photopyrone **2** in ether or heptane solution is also transformed rapidly but in low yield (5%) to mixtures of **3** and **4** in the absence of light by treatment with iron enneacarbonyl.

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 $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 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.



1 2 3 4

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.



5

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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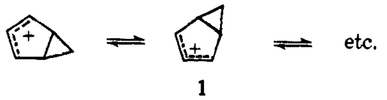
Equilibrating Cyclopropylcarbinyl Cations

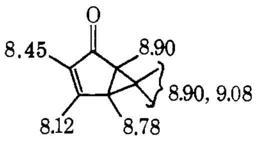
Sir:

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.

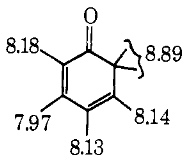


1

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]



2



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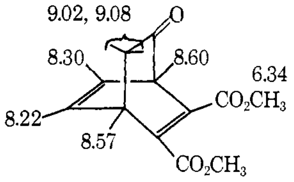
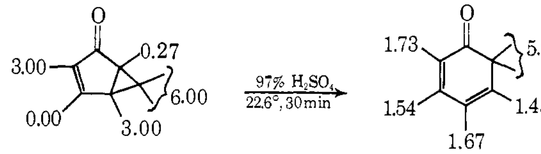
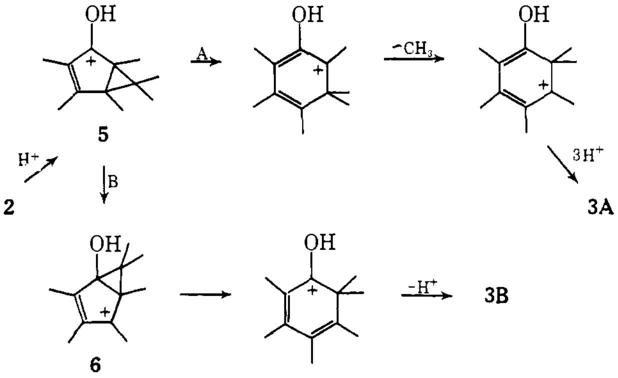


4

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



2-d_6 **3**-d_6



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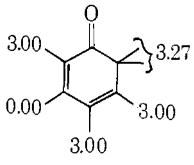
[1] H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

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

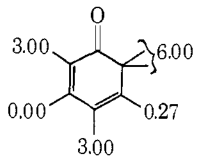
[3] T. Kakihana, M.S. Thesis, Michigan State University, 1966.

[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%.

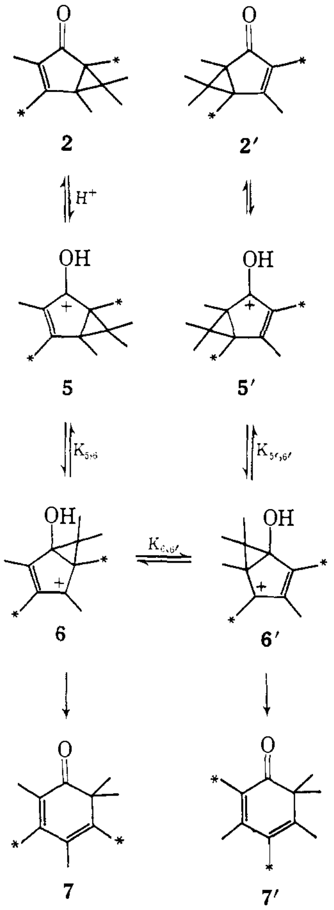


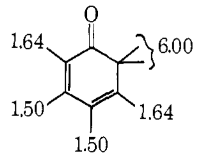
3A



3B

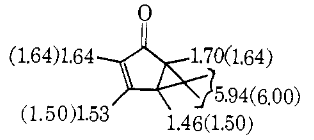
The result is, however, consistent with a mechanism in which **6** and its "enantiomer" **6′** are rapidly equilibrated, and each can collapse by proton loss (to **7** and **7′**). This is shown schematically, with CD_3 groups marked with an asterisk. Rapid equilibration of **6** and **6′** ($K_{6,6'}$) prior to collapse should lead to a 50:50 mixture of **7** and **7′**, with the label distribution shown. This is in rather good agreement with the observed product (**3**-d_6).[6]





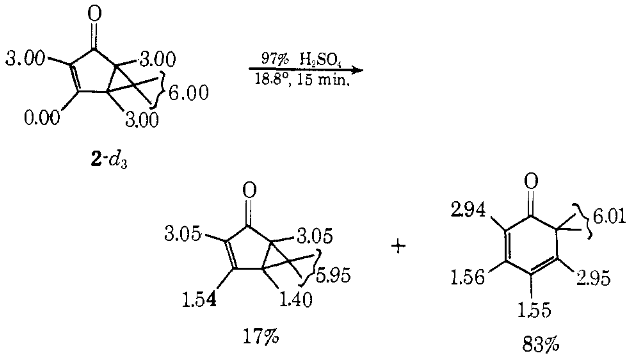
7-7′ (50 : 50)

To test the possibility that equilibria $K_{5,6}$ and $K_{5',6'}$ might also be rapidly established, and that **2** might be converted to **2′** under the reaction conditions, the following experiment was performed. Compound **2**-d_6 was treated with 97% sulfuric acid at 18.7° for 1 min; after quenching 63% of **2** and 37% of **3** were recovered. The hydrogen distribution in recovered **2** was



The figures in parentheses are the calculated values for complete equilibration of **2** and **2′**.

Consistent with the proposed scheme **2**-d_3 labeled as shown gave the indicated products. This experiment shows that it is specifically the methyls on C-4 and C-5[7] of **2** which equilibrate.



The exceedingly rapid migration of the cyclopropane ring around four of the five sides of the cyclopentane ring is thus clearly established.[8] The precise mechanism by which the carbon bearing the *gem*-dimethyl group migrates around the ring (**5** → **6** → **6′** → **5′**) is being investigated.[10,11]

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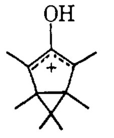
[6] An independent experiment showed that **7**, subjected to the rearrangement conditions, was recovered unchanged; thus *6* → *7* is not reversible.

[7] By implication, the methyls on C-1 and C-3 are the other exchanging pair.

[8] These experiments are inconclusive regarding the fifth side. One might expect ion **8** to collapse to **9**, which is not observed. In stronger sulfuric acid **3** is converted to **9**;[9] the mechanism of this rearrangement will be the subject of a separate communication.



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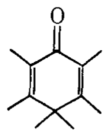

9

[9] H. Hart and D. W. Swatton, *J. Am. Chem. Soc.*, **89**, 1874 (1967); see also V. G. Shybin, V. P. Chzhu, A. I. Rezvukhin, and V. A. Koptyug, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2056 (1966).

[10] For example, *endo* and *exo* substituents on this carbon may retain their stereochemistry, invert, or become scrambled.

[11] We are indebted to the National Science Foundation for financial support of this work.

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Received June 21, 1967

Quintet Ground States of *m*-Dicarbene and *m*-Dinitrene Compounds

Sir:

We previously reported, as part of another study,[1] that photolysis of 1,3-bis(α-diazobenzyl)benzene (Ia) and 1,3-diazidobenzene (II) at 77°K yielded epr spectra which were much more complex than those observed with triplet states. The spectra were tentatively associated with quintet states of *m*-phenylenebis(phenyl-

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[1] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Am. Chem. Soc.*, **85**, 2526 (1963).