time, we do not have an explanation for this abnormal behavior. The transition temperatures for the various liquid crystal phases are listed in Table I. In this table and Figure 1 we followed the usual convention for the nomenclature of smectic phases. The highest temperature smectic phase is always called smectic 1, the next lower one smectic 2, and so on. In Figure 1, transition temperatures have been plotted and connecting curves have been drawn on the basis of optical texture.

The optical studies indicate that smectic 1 is identical with smectic C, with the exception of the C_5 in which smectic 1 shows a mosaic texture. Smectic 2 cannot readily be identified with one of the smectic phases A, B, or C as defined by Sackmann and Demus.[3] It is comparable in texture with smectic C but shows fewer discontinuities in the schlieren texture. Smectic 3 could correspond to smectic B (mosaic texture); smectic 4 and 5 have the same basic texture as smectic 3 but with increased discontinuities and spontaneous flow at the boundaries of the blocks. The flow is the greatest in smectic 5. These phases are observable with the polarizing microscope if thin sections of the materials are prepared. With thick sections, the smectic phases tend to assume a fan texture in which it is difficult to observe the transitions.

Some substances have been reported with up to three thermotropic smectic phases, and they have been thoroughly studied for the classification of these phases (see, for instance, ref 3 and 4). These dianils with an unusually large number of smectic phases, up to five or maybe even six, show that there exists additional phases that have not yet been classified. Further work on the classification of these phases on the basis of the miscibility with other liquid crystalline phases is in progress.

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[3] H. Sackmann and D. Demus, *Mol. Crystals*, 2, 81 (1966).

[4] D. Demus, H. Sackmann, G. Kunicke, G. Pelzl, and R. Salffner, *Z. Naturforsch.*, 23a, 76 (1968).

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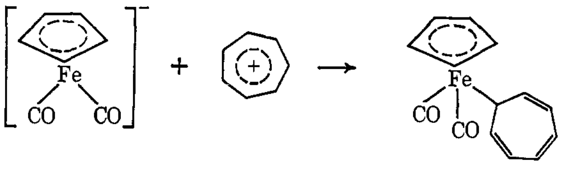
(7-*Monohapto*cycloheptatrienyl)-(*pentahapto*cyclopentadienyl)dicarbonyliron

Sir:

The class of fluxional organometallic complexes encompasses a number of *monohapto*[1] compounds all of which are h^1-cyclopentadienyl derivatives.[2] No complex having a transition metal similarly bonded to a cycloheptatriene ring is known. The purpose of the present communication is to report the preparation and properties of the first such complex, (7-*monohapto*cycloheptatrienyl)(*pentahapto*cyclopentadienyl)dicarbonyliron (**1**).

This substance is formed in 4% yield along with $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ and ditropyl when the anion $(h^5\text{-}C_5H_5)Fe(CO)_2^-$ is brought into reaction with tropylium tetrafluoroborate at −70° in tetrahydrofuran solution.



1

The complex, purified by column chromatography on alumina, is a red, crystalline material, mp 98–99°. Its general stability toward decomposition both in the solid state and in solution appears to be greater than the closely related *monohapto*cyclopentadienyl complex $(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)Fe(CO)_2$ (**2**).[3] Thus **1** is moderately stable in the air in the crystalline state and can be kept for prolonged periods in degassed solutions at 0°. It is, however, rapidly decomposed in hydroxylic media and when its otherwise stable organic solutions are exposed to air.

Its infrared spectrum, taken in $CHCl_3$, exhibits only a single broad carbonyl absorption at 1930 cm^{-1}, but in CCl_4 solution this is split into two sharp peaks at 2055 and 2010 cm^{-1} and a broad intense peak at 1920 cm^{-1}. In CS_2 solution the compound has peaks at 3020, 3007, 1925, 1890 (sh), 1416, 1010, 990, 887, 842, 831, 820, 705, 610, 577, and 525 cm^{-1}.

In conformity with structure **1**, the mass spectrum of the complex has intense peaks at *m/e* 268 (molecular ion) and at 240 and 212, corresponding to the loss of one and two carbonyl groups, respectively, from the parent ion. Other intense peaks occur at *m/e* 147 ($C_7H_7Fe^+$), 121 ($C_5H_5Fe^+$), 91 ($C_7H_7^+$), and 56 (Fe^+).

The temperature dependence of the nmr spectrum of **1** is typical of fluxional molecules. At 30°, the spectrum, taken in deuteriotoluene solution, consists of a sharp singlet at δ 4.1 and a broad absorption (width at half-height ~18 Hz) centered at δ 4.8, with relative areas of 5:7. These absorptions are assigned to cyclopentadienyl and cycloheptatrienyl protons, respectively. As the temperature is lowered, the cyclopentadienyl peak remains unchanged in aspect while the cycloheptatrienyl peak broadens further and is finally decomposed at about −15° into four broad absorptions. At −50° these appear as four well-defined complex absorptions of relative area 2:2:2:1, comprising a broad, unresolved multiplet centered at δ 6.05, a well-defined six-line multiplet centered at δ 5.20,[4] a

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[1] The nomenclature used is that recently suggested by F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).

[2] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *ibid.*, **88**, 4371 (1966); F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967); G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967); H. B. Fritz and G. G. Kreiter, *J. Organometal. Chem.*, **4**, 313 (1965); A. Davison and P. E. Rakita, *J. Am. Chem. Soc.*, **90**, 4479 (1968); E. Maslowsky and K. Nakamoto, *Chem. Commun.*, 257 (1968).

[3] G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 3, 104 (1956); B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

[4] Analysis of this multiplet as an AA′XX′ set ($H_{2,3,4,5}$) with $J_{2,5}$ = 0 Hz leads to the following values for the coupling constants: $J_{3,4}$ = 7.5, $J_{2,3}$ = 11.2, and $J_{2,4}$ = 1.1 Hz. These values compare closely with those reported recently for cycloheptatriene by J. B. Lambert, L. J. Durham, P. Lepoutre, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3986 (1965): $J_{3,4}$ = 10.67, $J_{2,3}$ = 5.26, $J_{2,4}$ = 0.80 Hz.

triplet at δ 4.32 (J = 7 Hz), and a triplet at δ 2.44 (J = 7 Hz). These are assigned to $H_{2,5}$, $H_{3,4}$, $H_{1,6}$, and H_7, respectively, from low-temperature double-resonance experiments. Thus, irradiation of the low-field multiplet centered at δ 6.05 leads to collapse of the signal at δ 5.20 to a singlet and of the signal at δ 4.32 to a doublet ($J \sim$ 7 Hz). This requires that the latter two absorptions be assigned to $H_{3,4}$ and $H_{1,6}$ respectively, or less likely that this assignment be reversed. The latter alternative is excluded by irradiation of the signal at δ 4.32, which results in the collapse of the H_7 triplet to a broad singlet and of the multiplet at δ 6.05 to a broad doublet. In further conformity with these assignments, irradiation of the signal at δ 5.20 results in the collapse of only the signal at δ 6.05 to a doublet ($J \sim$ 7 Hz).

The mechanism of proton averaging in **1** is being investigated.

Acknowledgment. We are indebted to Dr. G. Dudek of Harvard University for assistance in carrying out the double-resonance experiments and to Dr. E. Grunwald of this department for helpful discussions. This research was supported by a grant from the National Science Foundation (GP-8714) which is gratefully acknowledged.

(5) NDEA Title IV fellow.

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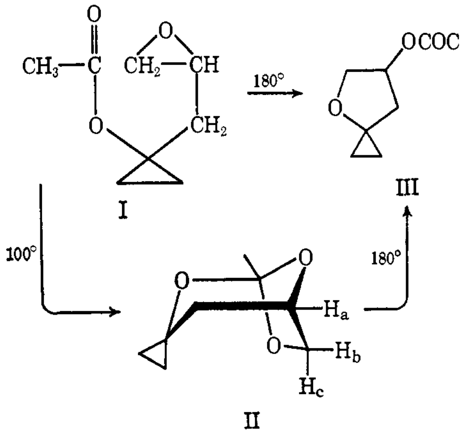
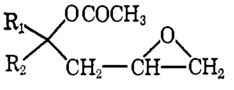
Carbonyl Epoxide Rearrangements. Synthesis of Brevicomin and Related [3.2.1] Bicyclic Systems

Sir:

During studies on the reactions of 1-alkenylcyclopropanols formed from cyclopropanone[1] we have observed that the epoxide of 1-allylcyclopropyl acetate (I) undergoes a novel thermal rearrangement (75% at 180°) to yield 2,2-dimethylene-4-acetoxytetrahydrofuran (III):[2] $\nu_{max}^{CCl_4}$ 3000, 1745 cm^{-1}; τ (CCl_4)[3] 4.85 (m, 1 H), 6.25 (m, 2 H), 7.96 (m, 2 H), 8.00 (s, 3 H), and 9.1-9.72 (m, 4 H). The intermediate in this transformation appears to be the orthoester II, since II may be formed from I at somewhat lower temperatures (80% at 100°). The trioxabicyclo[3.2.1]octane (II) shows no ir carbonyl absorption, a strong ether peak at 1125 cm^{-1}, and nmr absorption[4] at τ 5.4 (m, H_a), 5.88 (d, H_c), 6.2 (a doublet of doublets, H_b), 7.5 (d, 1 H), 8.53 (s, 3 H), 8.9-9.7 (m, 5 H). When heated to 180°, II is readily converted to III (85%).[5]



We have also found that pyrolysis of similarly constituted epoxy acetates such as IVa–c yields products analogous to II and III, along with unsaturated glycol monoacetates.[6] However, if the reaction is applied to the epoxides of δ,ϵ-unsaturated ketones, conversion to the [3.2.1] bicyclic system takes place exclusively and, as will be shown below, with a high degree of stereoselectivity.[7] Thus, 6,7-epoxy-2-heptanone (VIa)[8] may be transformed on heating at 210° to 1-methyl-7,8-dioxabicyclo[3.2.1]octane (VIIa) (75%).[9] The ketal VIIa shows no hydroxyl or carbonyl absorption in the ir and has the expected peaks in the nmr at τ (CCl_4) 5.63 (m,



IVa, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1, R_2 = (CH_2)_5$

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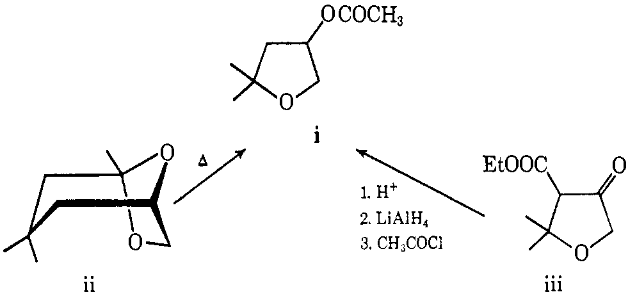
(1) H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).

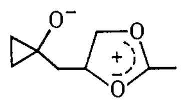
(2) The structures of all intermediates and products are consistent with their infrared and nmr spectra. Satisfactory elemental analyses were obtained for all new compounds.

(3) The nmr spectrum is in complete accord with the spectra of authentic tetrahydrofurans such as i. The latter, isolated from the pyrolysis of ii (28%), was prepared independently from iii by the method of M. A. Gianturco, P. Friedel, and A. S. Giammarino, *Tetrahedron*, **20**, 1763 (1964).



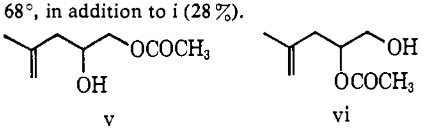
(4) This spectrum corresponds very well to the nmr spectrum of 2,7,8-trioxabicyclo[3.2.1]octane reported by G. Krank and F. W. Eastwood, *Australian J. Chem.*, **17**, 1385 (1964).

(5) Conversion of II to III appears to take place by heterolytic C–O cleavage with formation of the intermediate iv.



iv

(6) From IVa, and also from ii,[3] for example, v and vi (42%) are obtained at 168°, in addition to i (28%).



(7) Very recently, Y. Ganoni [*J. Chem. Soc., C*, 2925 (1968); 2934 (1968)] has reported the isolation of 2,7-dioxabicyclo[2.2.1]heptanes from the *m*-chloroperbenzoic acid oxidation of γ,δ-unsaturated ketones. Further peracid oxidation of the 2,7-dioxabicyclo[2.2.1]heptanes yielded 2,7,8-trioxabicyclo[3.2.1]octanes.

(8) The epoxy ketone VIa was prepared by condensation of 4-bromo-1-butene with acetoacetic ester followed by hydrolysis, decarboxylation, and epoxidation with *m*-chloroperbenzoic acid.

(9) At 210° in the absence of acid catalysis, 50% cyclization of VIa–c to VIIa–c took place in *ca.* 12 hr. For complete conversion, heating for a period of time up to 40 hr was necessary. Use of acid catalysts such as $SnCl_4$ or H_2SO_4 caused almost instant cyclization to VIIa–c but also resulted in substantial polymerization.