plots of the chemical shifts of the two singlet methyl absorptions (δ 1.16 and 1.58 in $CDCl_3$) in hertz downfield from TMS $vs.$ Eu(fod)$_3$ concentration were linear[11] and gave Δ_{Eu} values[12] of -4.09 and -3.62, respectively. These observations, in tandem with the finding that the protons of one phenyl ring were negligibly affected under these conditions, are consistent in detail with topside complexation of the Eu(fod)$_3$ to oxygen with attendant comparable influence on C_3–CH_3 ($R = 2.5$) and exo-C_4–CH_3 ($R = 3.0$).[13] In view of the structural rigidity of **11**, the data are entirely incompatible with endo positioning of the methyl substituent at C_4 ($R = 4.2$).[13] It follows then that **10** has the indicated stereochemistry, the result of methyl migration exclusively from the exo face of the bicyclic structure.

Although the observation of such a remarkably high level of stereoselectivity (and perhaps stereospecificity[14]) is frequently considered as suitable evidence against the intervention of a planar carbonium ion, this conclusion must be tempered in the present instance because of possible steric control resulting from the proximate fused cyclobutane ring. The influence of steric and substituent factors on these reactions, as well as the likelihood of the intervention of other organosilver and carbonium ion intermediates, forms the subject of continuing studies. Notwithstanding, Ag$^+$ is seen to play a definitive, and perhaps uniquely specific, role in these rearrangements which is not shared by Brønsted acids (p-toluenesulfonic acid and anhydrous HBr in $CDCl_3$ at 40° did not rearrange **9** after 30 hr), other transition metals ($e.g.$, **9** was inert to [Rh(CO)$_2$Cl]$_2$), or the fluoroborate anion (no change in the presence of NaBF$_4$ before and after acidification).

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(11) Least-squares treatment of these plots gave slopes of 234 and 206 Hz/mol % Eu(fod)$_3$, respectively.

(12) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, $J.$ $Amer.$ $Chem.$ $Soc.,$ **92**, 5734 (1970).

(13) R is here taken as the vector distance from oxirane oxygen to the most proximate hydrogen of the given methyl group. In this way, we are neglecting the important orientation of Eu, which is of course undefinable in the present instance.

(14) For instance, if a single, configurationally unique, methyl group in **1** and **9** were undergoing the shift to C_4 in **2** and **10**, respectively.

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8-Oxoheptafulvene

$Sir:$

Heptafulvenes having electron-attracting groups at the 8 position are stabilized by the contribution of dipolar structures[1] relative to the ground state in contrast to heptafulvene itself.[2] Polar structures can also be considered for the previously unknown 8-oxoheptafulvene (**1**) which contains a seven-membered unsatu-

(1) T. Nozoe, T. Mukai, K. Osaka, and N. Shishido, $Bull.$ $Chem.$ $Soc.$ $Jap.,$ **34**, 1384 (1961); M. Yamanaka, H. Watanabe, T. Mukai, T. Nozoe, and M. Kubo, $J.$ $Amer.$ $Chem.$ $Soc.,$ **82**, 5665 (1960); H. Shimanouchi, T. Ashida, T. Sasada, M. Kakudo, I. Murata, and Y. Kitahara, $Bull.$ $Chem.$ $Soc.$ $Jap.,$ **38**, 1230 (1965); **39**, 2322 (1966).

(2) W. von E. Doering and D. W. Wiley, $Tetrahedron,$ **11**, 183 (1960).
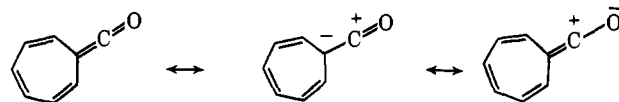
rated ring and ketene moiety. We have been interested in the properties of compound **1**, and now wish to report our results on its formation and some reactions.

Dropwise addition of 1.4 equiv of NEt$_3$ to a stirred solution of tropyl-7-carboxylic acid chloride (**2**) and cyclopentadiene in anhydrous ether or n-hexane at $ca.$ $-20°$ immediately afforded triethylamine hydrochloride. The mixture was stirred at room temperature for 1 hr, and chromatography of the ether extract on silicic acid gave about 60% of an adduct **3** as a colorless liquid.[3] Compound **3** exhibits infrared bands (neat) at 1778 (four-membered cyclic ketone) and 1600, 723, and 695 cm^{-1} (tropilidene moiety); the nmr spectrum ($CDCl_3$) at 100 MHz includes signals at δ 2.33 (1 H, d, d, q, $J = 17, 9, 2$ Hz, exo H-5′), 2.66 (1 H, d, d, m, $J = 17, 2$ Hz, endo H-5′), 2.94 (1 H, d, m, $J = 8$ Hz, H-2′), 3.83 (1 H, d, d, d, $J = 9, 8, 2$ Hz, H-6′), 5.09 (1 H, d, m, $J = 9$ Hz, H-2 or H-7), 5.22 (1 H, d, m, $J = 9$ Hz, H-7 or H-2), 5.29 and 5.70 (2 H, m, H-3′ and H-4′), 6.23 (2 H, m, H-3 and H-6), and 6.58 (2 H, m, H-4 and H-5). The chemical-shift assignments and couplings were verified by double and triple resonance experiments and by comparison with the spectra of tropilidene[4] and the adducts of cyclopentadiene with ketenes.[5] Adduct **3** also exhibits $\lambda_{max}^{cyclohexane}$ 274 nm (ϵ 2610) as expected for a tropilidene chromophore, and a mass spectral parent ion at m/e 184 (relative intensity 41) as well as major fragment ions at 156 (19), 155 (19), 141 (27), 118 (84), 115 (23), 91 (22), 90 (100), and 89 (22).

A similar reaction in the presence of indene instead of cyclopentadiene gave 24% of crystalline adduct **4**, mp 95–97.5°. Compound **4** showed an infrared band (KBr) at 1770 cm^{-1}; $\lambda_{max}^{isooctane}$ 264 nm (ϵ 3720), 269 (4200), 275 (3730); nmr ($CDCl_3$), δ 2.96 (1 H, d, d, $J = 16.8, 9.2$ Hz, exo H-7′), 3.31 (1 H, br d, $J = 16.8$ Hz, endo H-7′), 3.46 (1 H, d, $J = 8$ Hz, H-2′), 4.14 (1 H, d, d, d, $J = 9.2, 8, 2$ Hz, H-8′), 5.01 (1 H, d, m, $J = 9.2$ Hz, H-2 or H-7), 5.43 (1 H, d, m, $J = 9.2$ Hz, H-7 or H-2), 6.15–6.45 (2 H, m, H-3 and H-6), and 6.6–7.2 (6 H, m, H-4, -5, -3′-6′); mass spectral parent ion at m/e 234 (1.4), and fragment ions at 206 (1), 205 (1.4), 119 (9), 118 (49), 116 (100), 115 (90), 91 (17), 90 (84), 89 (30), and 63 (24). The chemical-shift assignments and couplings were also confirmed by double resonance technique and by comparison with the spectra of tropilidene derivatives[4] and the adduct of indene and dichloroketene.[6]

Hydrogenation of **3** over palladium/charcoal led to the uptake of 4 mol of hydrogen and afforded oily tricyclic saturated ketone **5**: mol wt 192 (mass spectrum); ir (neat) 1770 cm^{-1}; dinitrophenylhydrazone mp 91–92°.

The formation of the adducts **3** and **4** can be explained by a cycloaddition reaction of olefins with 8-oxohepta-

(3) All new compounds gave satisfactory elemental analyses.

(4) G. Fraenkel, R. E. Carter, A. McLachlar, and J. H. Richard, $J.$ $Amer.$ $Chem.$ $Soc.,$ **82**, 5846 (1960); H. Günther, M. Görlitz, and H. H. Hinrichs, $Tetrahedron,$ **24**, 5665 (1968).

(5) M. R. S. Roberts, A. Dieffenbacher, and A. S. Dreiding, $Helv.$ $Chim.$ $Acta,$ **53**, 417 (1970), and references cited therein.

(6) R. W. Turner and T. Seden, $Chem.$ $Commun.,$ 399 (1966).

fulvene (1) formed *in situ* by elimination of hydrogen chloride from 2 with NEt₃. The intermediacy of 1 was further confirmed by the following experiment. After the addition of NEt₃ to a solution of 2 in ether at −60°, CH₃OD was added to the resultant reddish solution. Work-up of the reaction mixture afforded methyl tropyl-7-carboxylate-7-*d* (6), the structure of which was determined by ir, nmr, and mass spectra. Only a small amount of deuterium exchange at the 7 position was observed for methyl tropyl-7-carboxylate in the presence of NEt₃, hydrogen chloride, and an excess of CH₃OD, even after the mixture was stirred at room temperature for 1 day. Therefore, it must be concluded that compound 6 was formed by the reaction of 1 and CH₃OD. These reaction patterns are analogous to those of ketenes[7] rather than hepta-fulvenes with eight-π-electron systems.

Although a multiplet around 6 ppm in the nmr of a mixture of 2 and NEt₃ can be ascribed to 1, attempted isolation of 1 has been unsuccessful to date.
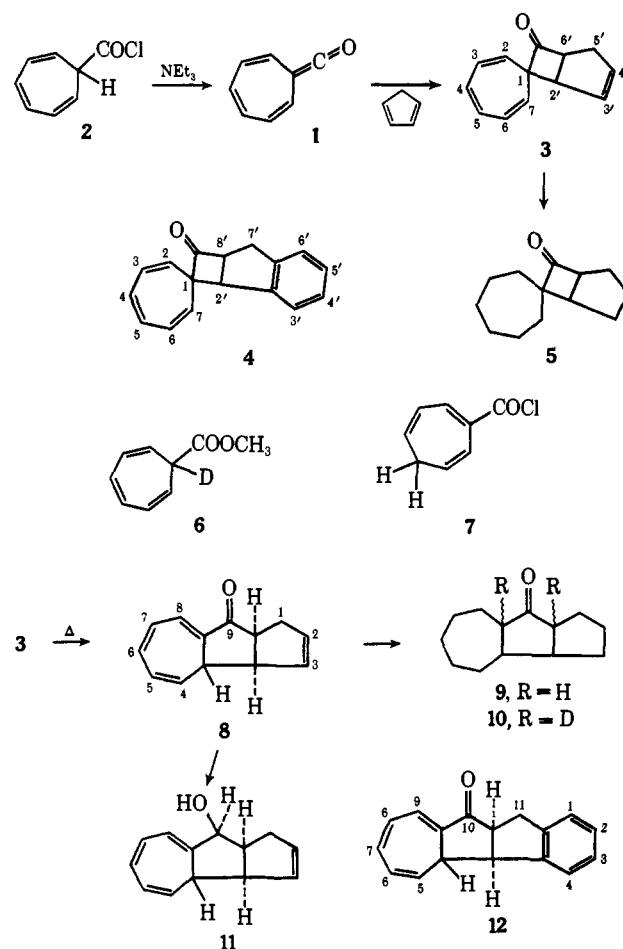
The reaction of tropyl-3-carboxylic acid chloride 7 with NEt₃ in the presence of cyclopentadiene did not occur and the starting materials were recovered.

The attempted distillation of the adduct 3, or standing a solution of 3 at room temperature for 1 week or so, afforded isomeric 3a,3b,9,9a-tetrahydro-1*H*-cyclopent-[*a*]azulen-9-one (8), bp 100° (2 mm), in good yield. Compound 8 gave a dinitrophenylhydrazone, mp 191–193° dec, and showed an infrared band (neat) at 1700 cm⁻¹; nmr (CDCl₃) δ 2.22 (1 H, m, H-3b), 2.71 (2 H, m, H-1), 2.95 (1 H, m, H-9a), 3.56 (1 H, d, m, J = 8 Hz, H-3a), 5.33 (1 H, d, d, J = 9.5, 4.1 Hz, H-4), 5.60 and 5.73 (2 H, m, H-2 and H-3), 6.20 (1 H, d, m, J = 9.5 Hz, H-5), 6.76 (2 H, m, H-6 and H-7), and 6.96 (1 H, m, H-8). The chemical-shift assignments and coupling constants were verified by an application of shift reagent, Eu(DPM)₃, as well as by decoupling experiments. Compound 8 also exhibits $\lambda_{max}^{isooctane}$ 224.5 nm (ϵ 12,500), 303.5 (4500) as expected for the conjugated carbonyl chromophore in 8. The coupling constant, $J_{3a,3b}$ = *ca.* 1 Hz, suggests that the configuration of H-3a and H-3b is trans. The mass spectrum of 8 was super-imposable with that of compound 3.[8] Compound 8 absorbed 4 mol of hydrogen by catalytic hydrogenation to give oily ketone 9: mol wt 192 (mass spectrum); ir (neat) 1728 cm⁻¹; dinitrophenylhydrazone mp 177–177.5°. The deuterium exchange reaction of 9 in CH₃ONa–CH₃OD afforded a dideuterio derivative 10, mol wt 194 (mass spectrum).

Reduction of 8 with NaBH₄ afforded an alcohol 11, whose nmr (assigned by a decoupling technique and application of shift reagent) [δ 1.82 (s, O*H*), 2.17 (1 H, m, H-3b), 2.35 (1 H, d, d, m, J = 16, 7.1 Hz, exo H-1), 2.60 (1 H, d, d, m, 16, 4.2 Hz, endo H-1), 3.05 (1 H, d, d, d, d, J = 7.1, 7.1, 7.1, 4.2 Hz, H-9a), 3.28 (1 H, m, H-3a), 4.65 (1 H, br d, J = 7.1 Hz, H-9), 5.10 (1 H, d, d, J = 9.5, 4.6 Hz, H-5), 5.75 (1 H, m, H-2 and -3), 6.02 (1 H, d, m, J = 9.5 Hz, H-14), 6.27 (1 H, m, H-8), and 6.55 (2 H, m, H-6 and -7)] is consistent with the structure shown in Scheme I.

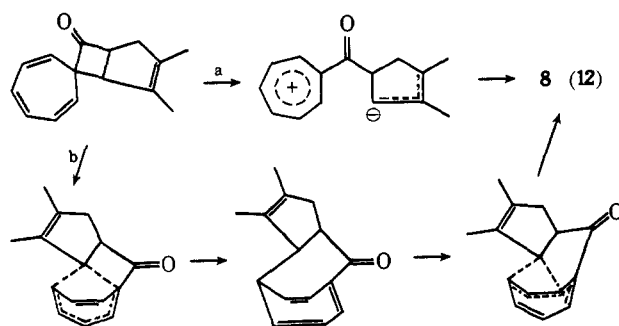Furthermore, compound 4 was also isomerized by heating in refluxing benzene to give 4b,4c,10,10a-tetra-

(7) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, p 38.

(8) It is expected that 3 would rearrange to 8 under the measurement conditions.

Scheme I

hydro-11*H*-indeno[1,2-*a*]azulen-10-one (12): mp 97–98°; ir (KBr) 1659 cm⁻¹; $\lambda_{max}^{cyclohexane}$ 217 nm (ϵ 17,400), 228 (15,900), 177–286 (7320), 310 (sh) (6210); nmr (CDCl₃) showing a similar pattern with that of 8, δ 2.56 (1 H, m, H-4c), 3.15–3.5 (3 H, m, H-10a and 11), 4.09 (1 H, d, m, J = 5.5 Hz, H-4b), 5.56 (1 H, d, d, J = 9.5, 4.5 Hz, H-5), 6.32 (1 H, m, H-6), 6.75 (2 H, m, H-7 and -8), 6.95 (1 H, m, H-9), and 7.15 (4 H, m, H-1-4).

The mechanism of the formation of 8 and 12 from 3 and 4, respectively, is interesting in light of the well-known orbital symmetry selection rules.[9]

The fact that the isomerization of 4 in the presence of an excess of indene-*1-d* gave 12 having no deuterium shows that the rearrangement is intramolecular. We tentatively propose two pathways for this rearrange-

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

ment; one is an ionic mechanism (a)[10] and the other (b) involves two consecutive sigmatropic 1,5 shifts. A mechanistic study is now underway.

Acknowledgment. We thank Mr. K. Sasaki for performing the double resonance experiments.

(10) The similar ionic mechanism has been postulated for the isomerization of the spiro[2.6]nona-2,4,6-triene derivative to the indane derivative: T. Mukai, T. Nakazawa, and K. Isobe, *Tetrahedron Lett.*, 565 (1968); W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, 92, 6391 (1969).

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Stereoelectronic Dependence of Metallomethyl Substituent Effects by Fluorine-19 Nuclear Magnetic Resonance

Sir:

Fluorine-19 substituent chemical shifts (scs) indicate that metallomethyl groups are electron releasing relative to the methyl group when disposed para to fluorine in the benzene ring system,[1,2] a phenomenon which was first revealed by chemical reactivity and spectroscopic studies.[2,3] This metallomethyl substituent effect has been explained in essentially three different ways, either by: (i) an inductive effect, (ii) hyperconjugation, or (iii) a combination of i and ii.

Since it is expected that $\sigma-\pi$ conjugation would have similar stereoelectronic requirements to p–π conjugation[3,4] we have sought to evaluate the relative importance of the two mechanisms in the ground state by determining whether fluorine-19 chemical shifts show any dependence on the geometrical relationship of the carbon–metal bond and the π system of the aromatic substrate. Accordingly, we have synthesized three bicyclic silicon compounds (I, II, and III), together with the appropriate carbon analogs (5-fluoroindan and 6-fluorotetralin), in which the C–Si bond is constrained to a varying degree to the nodal plane of the adjacent π system.

If the inductive effect is more important, then the chemical shift for I and II relative to 5-fluoroindan and 6-fluorotetralin, respectively, should be comparable to the shift observed for IV relative to p-fluorotoluene (+1.57 ppm in cyclohexane; +1.75 ppm in DMF),[1c] while if the hyperconjugative mechanism is predominant then the relative chemical shifts for I and II

(1) (a) W. Adcock, B. F. Hegarty, W. Kitching, and A. J. Smith, *J. Organometal. Chem.*, 12, 21 (1968); (b) W. Kitching, W. Adcock, and B. F. Hegarty, *Aust. J. Chem.*, 21, 2411 (1968); (c) A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, 92, 6140 (1970).
(2) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometal. Chem.*, 20, 49 (1969), and references therein.
(3) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 92, 7476 (1970), and references therein; (b) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, 93, 5715 (1971); (c) J. M. Jerkunica and T. G. Traylor, *ibid.*, 93, 6278 (1971).
(4) (a) R. S. Mulliken, *J. Chem. Phys.*, 7, 339 (1939); R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, 63, 41 (1941); (b) A. N. Nesmeyanov and I. I. Kritskaya, *Dokl. Akad. Nauk SSSR*, 121, 447 (1958); (c) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

I   II

III   IV
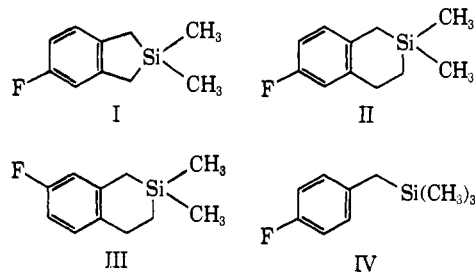
should be significantly less positive (C–Si σ bond less electron donating) than +1.57 or +1.75 ppm in the appropriate solvent.[5,6]

The results shown in Table I seem to provide a fairly definite answer to the problem. First of all, it can be seen from the chemical shifts of I and II relative to the shifts of the appropriate carbon analogs (+0.24 and +0.84 ppm in cyclohexane; +0.21 and +1.16 ppm in DMF) that the electron-donating ability of the C–Si

Table I. [19]F Chemical Shifts in Hz and (ppm) Relative to TCTFB in Cyclohexane and DMF

| Compound | Solvent[a] | |
	Cyclohexane	DMF
I[b]	+236 (+4.19)	+318 (+5.64)
II[b]	+283 (+5.02)	+377 (+6.69)
III[b]	+198 (+3.51)	+288 (+5.10)
5-Fluoroindan[c]	+223 (+3.95)	+306 (+5.43)
6-Fluorotetralin[c]	+236 (+4.18)	+312 (+5.53)

[a] The fluorine nmr spectra were measured with a Varian A56/60 operating at 56.4 MHz using solutions containing 15% (w/w) of the fluoro compound, together with 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB). [b] I, II, and III gave satisfactory analyses and their proton nmr spectra were in accordance with the assigned structures; details will be given in a main paper. [c] Available from another investigation (see ref 9 and W. Adcock, P. D. Bettess, and S. Q. A. Rizvi, *Aust. J. Chem.*, 23, 1921 (1970).

bond (indicated by the degree of shielding of the fluorine nucleus) is conformationally dependent. Since the π-inductive effect is expected to be insensitive to angular effects of this type, these results are clearly in accord with a predominant $\sigma-\pi$ interaction. It is of interest to note that the relative shift of II (+1.16 ppm in DMF) is approximately what one would expect on the basis that the hyperconjugative interaction is a function of cos θ, where θ is the angle of twist (cos 40° $\simeq$ 0.76).[6–8]

(5) This assumes, to a first approximation, that the relative importance of CH and CC hyperconjugation is indistinguishable. Since no definitive experimental distinction has yet been made this seems reasonable.
(6) An examination of Dreiding models shows that to a first approximation it can be assumed that I and 5-fluoroindan are planar molecules and that the C–Si bond in the former does not interact significantly with the π system. In II, III, and 6-fluorotetralin the alicyclic ring is conformationally mobile, there being two freely interconvertible conformations. However, whereas in 6-fluorotetralin the interconversion is between two half-chair conformations, both II and III seem to favor half-boat forms. In fact, the models for II and III cannot be maintained in a half-chair conformation. The dihedral angle between the C–C–Si plane and the aromatic ring in the half-boat arrangement is ~50° for II and III suggesting that any hyperconjugative interaction between the C–Si bond and the π system should be significantly reduced compared to IV, but greater than in I where the dihedral angle is = 0°.
(7) M. J. S. Dewar, *J. Amer. Chem. Soc.*, 74, 3345 (1952). The resonance integral β^θ is given approximately by $\beta^\theta \simeq \beta^0 \cos \theta$, where θ is the angle of twist.
(8) Eaborn and coworkers (see ref 2) have indicated that a maximum C–Si hyperconjugative interaction is achieved in the phenyl system with the (Me₃Si)₂CH group which has a scs 2.13 ppm (CCl₄) upfield from the scs of the CH₃ substituent.