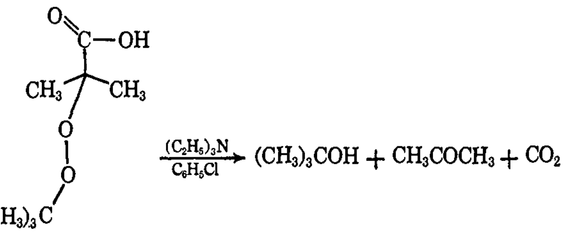
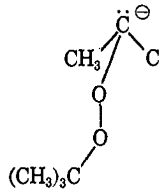


$\xrightarrow[C_6H_5Cl]{(C_2H_5)_3N} (CH_3)_3COH + CH_3COCH_3 + CO_2$ (1)

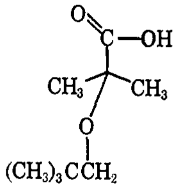
I

25°, acetone and *t*-butyl alcohol were produced in quantitative yield along with carbon dioxide. Acetone and *t*-butyl alcohol were identified by comparison of gas–liquid partition chromatography (glpc) retention times with authentic samples. In addition, the infrared spectra of fractions collected by glpc were identical with those of acetone and *t*-butyl alcohol. The structure of I was established by its infrared (carboxyl group: 2570, 2670, 1730 cm^{-1}; peroxide group, tentative: 875, 1175 cm^{-1}) and nmr (α-methyl protons: 1.45 ppm, singlet, area = 6; *t*-butyl protons: 1.23 ppm, singlet, area = 9; carboxyl proton: 11.6 ppm, singlet, area = 1) spectra along with analytical data. *Anal.* Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.86; H, 9.34. Acid I was prepared by the following synthetic sequence: isobutylenechlorohydrin[2] was converted to isobutylene oxide;[3] the oxide was treated with *t*-butyl hydroperoxide in the presence of acid to give 2-methyl-2-*t*-butylperoxy-1-propanol; finally acid I was obtained by chromic acid oxidation of the alcohol. Details of the preparation of I will be reported later.

The closest analogy to the decarboxylative fragmentation reaction (1) is found in the fragmentation reactions of β-halo acids.[4] Data have been presented for two types of fragmentation mechanisms for the β-halo acids: one, a concerted elimination of bromide ion and carbon dioxide, and the other, a two-step process where ionization of the carbon–bromine bond occurs initially, followed by loss of carbon dioxide. The analogous mechanisms may be considered for I where *t*-butoxide is the leaving group rather than bromide. In addition, a third mechanism is possible where carbon dioxide is lost to give II. Subsequent reaction of II will give *t*-butoxide and acetone. Of these three mechanisms, the concerted process from the amine salt of I is most likely. Unassisted heterolytic or homolytic rupture of the peroxide bond at 25° will be insignificant. For example, di-*t*-butyl peroxide has a half-life of 239 hr at 100° in benzene.[5]



II



III

Kinetic data are inconsistent with a two-step mechanism to give II as an intermediate. At 25° in chlorobenzene, the triethylamine salt of I has a half-life of about 25 min. In contrast, 2-methyl-2-neopentoxypropionic acid III is inert under identical conditions. The rates of decarboxylation of acids I or III to a carbanion intermediate should not differ greatly.

The structure of III was established by its infrared (carboxyl group: 2560, 2670, 1710 cm^{-1}; ether group: 1078, 1175 cm^{-1}) and nmr (α-methyl protons: 1.43 ppm, singlet, area = 6; *t*-butyl protons: 0.91 ppm, singlet, area = 9; methylene protons: 3.06 ppm, singlet, area = 2; carboxyl proton: 12.0 ppm, singlet, area = 1) spectra along with analysis of the methyl ester of III. *Anal.* Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.70. Found: C, 63.48; H, 11.07. Acid III was prepared by chromic acid oxidation of 2-methyl-2-neopentoxy-1-propanol. This alcohol was obtained from the acid-catalyzed reaction of isobutylene oxide[3] and neopentyl alcohol. The details of the synthesis will be presented later.

The 1,2-elimination reaction of peroxides with base has been reported.[6] Thus, benzyl *t*-butyl peroxide undergoes reaction with base to produce benzaldehyde and *t*-butyl alcohol.[6a] Similarly, 1-phenylethyl *t*-butyl peroxide gives acetophenone and *t*-butyl alcohol.[6b] Ionic rupture of the peroxide bond according to fragmentation reaction 1 finds analogy in these 1,2-elimination reactions.

Acknowledgment. We thank the U. S. Army Research Office, Durham, for support of this work and Robert Castro for experimental help.

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A Novel Type of Valence Tautomerism in Organometallic Complexes

Sir:

The occurrence of intramolecular rearrangements in organometallic complexes is well documented. The species which display the phenomenon largely fall into one of two categories. The first involves complexes in which a σ-bonded metal–carbon linkage is broken and re-formed in the rearrangement as in allylmagnesium systems and various σ-cyclopentadienyl–metal complexes.[1] The second class involves rearrangement of π-type complexes in which a metal atom is attached to three or more carbon atoms of a conjugated framework of sp^2 carbon atoms, most commonly fully conjugated cyclic systems; examples of this latter type include the valence tautomerism exhibited by cyclooctatetraene–Fe(CO)$_3$ and –Fe$_2$(CO)$_6$ complexes and cycloheptatrienyl–metal complexes.[2] We wish now to report a novel

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[1] See, for example, G. M. Whitesides, J. E. Norlander, and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 2010 (1962); T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Moorhouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966); H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.* (Amsterdam), **4**, 313 (1965).

[2] See, for example, B. Dickens and W. M. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962); C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966); F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966); C. E.

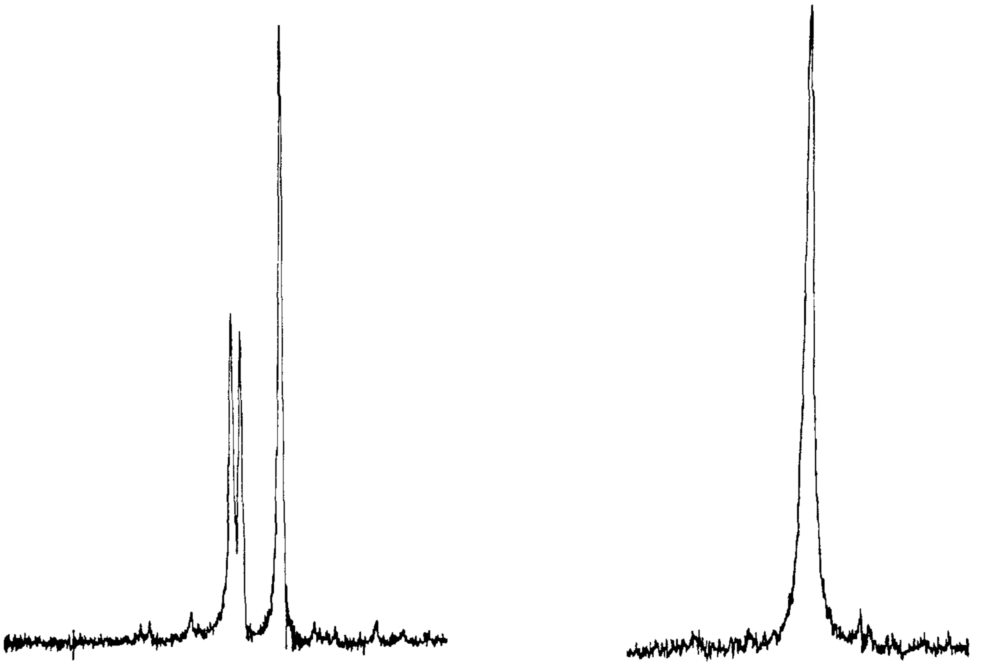
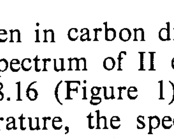


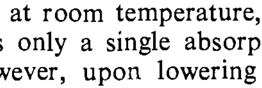
Figure 1. Nmr spectrum of $C_7H_{12}Fe(CO)_4$ taken in CS_2 at −60° (left) and + 30° (right).

case of degenerate valence tautomerism in an allene complex in which the ligand–metal interaction alternates between the two orthogonal π molecular orbitals of the allene system.

Reaction of tetramethylallene with $Fe_2(CO)_9$ produces two complexes having the molecular formulas $C_7H_{12}Fe(CO)_4$ (A) and $C_7H_{12}Fe(CO)_3$ (B).[3,4] Compound A, which is formed in predominant amount when limited quantities of $Fe_2(CO)_9$ are employed, is converted upon prolonged heating or, more rapidly, by reaction with $Fe_2(CO)_9$ into the substance B. Compound B is identified as 2,4-dimethyl-1,3-pentadiene-iron tricarbonyl (I) by its nmr spectrum and by oxidative degradation which liberates a hydrocarbon identical with authentic 2,4-dimethyl-1,3-pentadiene. Compound A gives mainly tetramethylallene upon oxidative degradation and is assigned the olefin–$Fe(CO)_4$ formulation II analogous to other monoolefin–$Fe(CO)_4$ complexes.



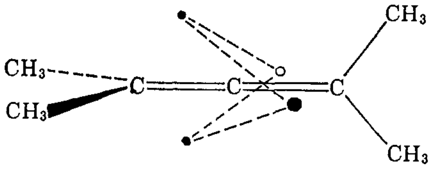
I



$$(CH_3)_2C{=}\underset{\substack{|\\ Fe(CO)_4}}{C}{=}C(CH_3)_2$$

II

Taken in carbon disulfide at room temperature, the nmr spectrum of II exhibits only a single absorption at τ 8.16 (Figure 1). However, upon lowering the temperature, the spectrum changes until at −60° it involves three single bands at τ 7.97, 8.02, and 8.23, having areas 1:1:2; this latter pattern is now consistent with a structure involving coordination of the allene to the iron by means of one double bond as in II.



III

The nature of this temperature dependence indicates that the $Fe(CO)_4$ unit is rapidly moving from one π molecular orbital to the second orthogonal one and at room temperature it is tracing a path indicated by the dotted lines in formula III. The activation energy for the process is determined to be 9.0 ± 2.0 kcal.[5] The intramolecular character of the rearrangement is indicated by the appearance of two singlets in the room-temperature nmr spectrum of a mixture of the complex and tetramethylallene.

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(3) Determined by elemental and mass spectrometric analysis. Compound A produces triphenylphosphine–$Fe(CO)_4$ upon reaction with triphenylphosphine.

(4) The compound $C_6H_8Fe_2(CO)_6$ produced in the reaction between allene and $Fe_3(CO)_{12}$ is also reported to exhibit valence tautomerism [A. Nakamura, *Bull. Chem. Soc. Japan*, **39**, 543 (1966)]. We have prepared this same material from allene and $Fe_2(CO)_9$ but have been unable to demonstrate that the very small change in nmr chemical shifts displayed upon varying the temperature requires such an interpretation.

(5) We thank Mr. A. Liles for the determination of this value.

(6) The authors thank the U. S. Army Research Office (Durham) and the Robert A. Welch Foundation for financial assistance. We also thank General Aniline and Film Corp. for a generous gift of iron carbonyl.

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Sensitized Photolyses of 3-Sulfolenes. Mechanism of Photochemical Sulfur Dioxide Extrusion from Sulfones

Sir:

It has been proposed that photochemical SO_2 extrusion from sulfones occurs by concerted fragmentation of a vibrationally excited ground state, $S^0{}_n$, produced by internal conversion from S^1 or intersystem crossing from T^1.[1] We present evidence which suggests that in the case of sensitized photolyses of 3-

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