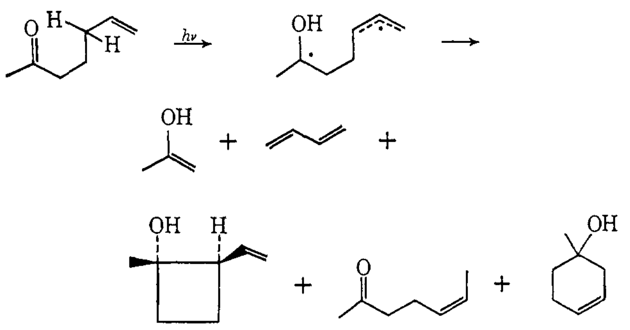

photolysis of 2-hexanone-5,5-d_2 is enhanced over 2-hexanone.[10] The quantum yield from the triplet state (ϕ_t) increases from 0.23 to 0.37, while that from the singlet state (ϕ_s) decreases from 0.10 to 0.05. Since the γ hydrogen is 2.7 times more reactive than the γ deuterium in the reactions from the singlet state, deuteration may also decrease the k_{-s} in the deuterated ketone. The ϕ_{st} will increase as the k_s and k_{-s} decrease, and ϕ_t for 2-hexanone-5,5-d_2 increases over that of 2-hexanone due to the increase in ϕ_{st}.

In conclusion, we wish to report that the rate for nonradiative decay from the singlet state (k_{-s}) of alkanones with γ hydrogens increases as the nature of the γ hydrogen changes from primary to secondary to tertiary and that the nonradiative process may involve the reverse chemical reaction from the singlet biradical intermediate. The results of this investigation and our earlier work constitute a complete analysis of the behavior of photoexcited 2-alkanones with γ hydrogens.[10a]

(10) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

(10a) NOTE ADDED IN PROOF. Recent theoretical work by A. Heller, *Mol. Photochem.*, **1**, 257 (1969), suggests that chemical reactions may well be involved in the nonradiative relaxation of excited states. We reach the same conclusion independently and our work is in complete agreement with his theory.

(11) The authors wish to acknowledge the National Science Foundation and the U. S. Public Health Service for the support of this work.

(12) National Science Foundation Trainee, 1966–1968; National Institutes of Health Predoctoral Fellow, 1968–1970.

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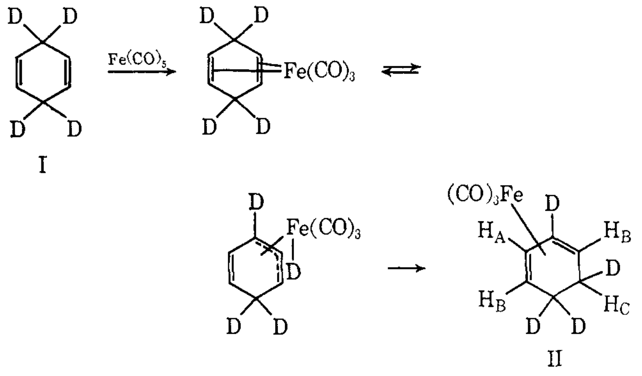
Mechanism of Formation of Conjugated Diene–Iron Tricarbonyl Complexes from Nonconjugated Dienes

Sir:

Reactions of monoolefins with a catalytic amount of iron pentacarbonyl leads to isomerization.[1] Two mechanisms have been proposed for this reaction: an addition–elimination mechanism and a mechanism involving allylic hydrogen abstraction. The iron carbonyl catalyzed isomerization of allylic alcohols to carbonyl compounds has recently been shown to proceed *via* the allylic hydrogen abstraction mechanism.[2,3] To our knowledge, no results have appeared concerning the mechanism of formation of conjugated diene–iron tricarbonyl complexes from nonconjugated dienes, a synthetically important *noncatalytic* reaction.[4,5] This communication reports a mechanistic investigation of the reaction of one such diene, cyclohexa-1,4-diene, with iron pentacarbonyl.

Cyclohexa-1,4-diene reacts with iron pentacarbonyl or triiron dodecacarbonyl to give cyclohexa-1,3-diene-iron tricarbonyl.[4,6] An allylic hydrogen abstraction mechanism has been proposed for this type of reaction.[5,7] A simple approach to this mechanistic problem involves labeling the methylene groups of the diene with deuterium and analyzing for deuterium in the product. 3,3,6,6-Tetradeuteriocyclohexa-1,4-diene (I) was prepared as previously described.[8] A mixture of the deuterated diene and iron pentacarbonyl in anhydrous benzene was photolyzed under conditions identical with those described for the nondeuterated compound.[4] The product, identified as II (described below), was obtained as a yellow oil (bp 77° (0.8 mm)) in 46% yield.



The infrared spectrum (neat) of II showed terminal metal carbonyl stretching bands at 2062 and 1976 cm^{-1} and carbon–deuterium stretching at 2210 and 2190 cm^{-1}. The nuclear magnetic resonance spectrum, recorded in carbon tetrachloride solution with tetramethylsilane as internal standard, gave signals at 1.58, 3.26, and 5.38 ppm in the ratio of 1.0:1.8:1.0 for H_C, H_B, and H_A, respectively. The mass spectrum of cyclohexa-1,3-dieneiron tricarbonyl has been reported.[9] We recorded the mass spectra of both the nondeuterated and deuterated complexes (at 70 eV). The mass spectrum of cyclohexa-1,3-dieneiron tricarbonyl was in agreement with the results of Winters and Kiser, giving a parent molecular ion peak at *m/e* 220. The molecular ion peak of the deuterated complex appeared at *m/e* 224 and the fragmentation pattern, like that of the corresponding nondeuterated complex, was characterized by successive loss of carbon monoxide units from $C_6H_4D_4Fe(CO)_3^+$ to give the ions $C_6H_4D_4Fe(CO)_2^+$ and $C_6H_4D_4Fe(CO)^+$ at *m/e* 196 and 168, respectively. No ion of composition $C_6H_4D_4Fe^+$ was observed (the nondeuterated analog $C_6H_8Fe^+$ was also not detected[9]). However, as $C_6H_6Fe^+$ was abundant in the spectrum of the nondeuterated compound, $C_6H_4D_2Fe(CO)^+$ (*m/e* 164) was in large abundance in the mass spectrum of II (the ion $C_6H_3D_3Fe(CO)^+$ was present in low abundance). Loss of carbon monoxide from $C_6H_4D_2Fe$-

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(1) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

(2) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968).

(3) F. G. Cowherd and J. L. von Rosenberg, *J. Am. Chem. Soc.*, **91**, 2157 (1969).

(4) A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc., A*, 332 (1968).

(5) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, 1, 1 (1964).

(6) J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, 83, 2954 (1961).

(7) R. Pettit, G. F. Emerson, and J. Mahler, *J. Chem. Educ.*, 40, 175 (1963).

(8) J. R. Campbell, Ph.D. Thesis, Queen's University, 1969; see S. Wolfe and J. R. Campbell, *Chem. Commun.*, 877 (1967).

(9) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, 69, 3198 (1965).

(CO)$^+$ gave $C_6H_4D_2Fe^+$ (m/e 136). The mass spectra of both the nondeuterated and deuterated complexes exhibited bands at m/e 112 for $Fe(CO)_2^+$ and 84 for $Fe(CO)^+$ and the most intense band in both spectra was due to Fe^+ (m/e 56).

These results clearly indicate that the formation of conjugated diene–iron tricarbonyl complexes, by reaction of nonconjugated dienes with iron carbonyls, occurs *via* a π-allylhydroiron tricarbonyl intermediate. In addition it may be suggested that the mechanisms for complex formation and for catalytic isomerization of allylic alcohols are similar. An alternative mechanism involving hydrogen migration through a suprafacial pathway is also possible, but this alternative has been ruled out in the allylic alcohol–carbonyl isomerization reaction.[3]

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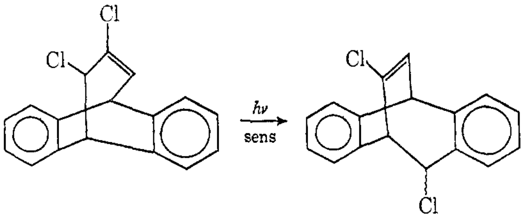
Photochemical Transformations. V. Allylic Rearrangements and Rearrangement of Allylic Halides to Cyclopropyl Halides[1]

Sir:

We recently reported[1c] the photosensitized rearrangement of 3,4-dichloro-6,7:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (**1**) to a mixture of *exo* and *endo* epimers of 4,6-dichloro-2,3:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (**2**). As the reaction **1** → **2** is formally related to a Wagner–Meerwein isomerization, we suggested that other systems, which (a) are capable of accepting triplet photosensitization and (b) may have formal analogy to carbonium ion rearrangements, may be amenable to rearrangement.



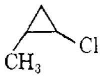
1 **2**

Preliminary work has suggested that a number of such processes do occur. These will be reported as data satisfactory for publication accumulate. The first experiments which we wish to report involve sensitized photorearrangements of α-methylallyl chloride (**3**), γ-methylallyl (crotyl) chloride (**4**), allyl chloride, and allyl bromide. Allylic systems represent reasonable choices to study, in view of the voluminous and important contributions which work on such compounds has led to in our understanding of anionotropic rearrangements.[2]

When crotyl chloride (**4**) was irradiated[3] in acetone, the expected isomerization to **3** occurred rapidly, with 16% of **3** formed in 8 hr. Continued irradiation slowly gave rise to two new and unexpected products. After 56 hr, the reaction mixture[4] consisted of 13% **3**, 25% **4**, 13% **5**, and 15% **6**.[5] Similarly, when a 75:25 mixture of **3**:**4** was irradiated in acetone for 30 hr, the product mixture contained 20% **3**, 33% **4**, 6% **5**, and 10% **6**; **5** and **6** do not appear to be photolabile (60-hr irradiation). Benzene and *m*-xylene were also found to be satisfactory solvent–sensitizers. Irradiation (λ >2700 Å) of **4** in pentane produced no **5** or **6** and only extremely slow conversion to **3**. **3** and **4** were stable in the dark when subjected to otherwise similar conditions. It should be noted that the irradiated solutions have a higher ratio of **3**:**4** than results from thermodynamic equilibration,[7] and the formation of **5** and **6** from **3** or **4** is also opposite to that observed in ground-state chemistry.[8]

$CH_2{=}CHCHClCH_3$ **3**

$CH_3CH{=}CHCH_2Cl$ **4**



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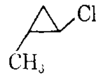

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As the formation of the cyclopropanes was of substantial theoretical and practical interest, offering the possibility of a new synthetic procedure for cyclopropyl halides, we have looked briefly at photoreactions of allyl chloride and bromide. The chloride was irradiated in methyl ethyl ketone and gave 19% yield of chlorocyclopropane[9] in 24 hr, while the bromide in acetone gave 11% of bromocyclopropane[9] after 16 hr.

Volman and Phillips[10] have noted that at least 18 volatile compounds are formed by the unsensitized irradiation with 2537-Å light of liquid allyl chloride; chlorocyclopropane was not found. They suggest that the (*unsensitized*) primary photochemical process is homolytic cleavage of the carbon–chlorine bond. Our results, which are so different from Volman's, are consistent with the idea suggested earlier[1c] that such photochemical processes proceed through vibrationally excited carbonium ion–halide ion ion pairs which combine to give thermodynamically unstable (or stable)

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[1] Previous papers in series: (a) S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, **76**, 5000 (1954); (b) *ibid.*, **80**, 1950 (1958); (c) S. J. Cristol, G. O. Mayo, and G. A. Lee, *ibid.*, **91**, 214 (1969); (d) S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).

[2] R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

[3] A Hanovia 450-W high-pressure mercury vapor lamp (type L) was used with a water-jacketed quartz immersion well. Approximately 0.1–0.3 M solutions of the allylic halide in solvent–sensitizer were degassed and irradiated in thin-wall Pyrex tubes.

[4] Reaction progress was monitored by gas chromatography (gc) using a Aerograph Model 90-P instrument. Product mixtures were satisfactorily analyzed using a 15-ft × 0.25 in. column packed with 25% SE-30 on 60–80 mesh Chromosorb W and a 10 ft × 0.25 in. column packed with 18% SE-30 on 60–80 mesh Chromosorb W.

[5] Compounds **5** and **6** were isolated from photoreaction mixtures by preparative gc and the assigned structures were consistent with the following spectral data: (**5**) pmr (CCl_4), H-1 τ 8.8 (m), H-2 6.96 (m), H-3_{syn} 9.64 (d, J = 3.4 Hz), H-3_{anti} 8.98 (m), 1-CH_3 8.8; ir (CCl_4)[6] 1032 cm^{-1} (w); m/e (70 eV) 90 (3), 92 (1); (**6**) pmr (CCl_4), H-1 τ 9.0 (m), H-2 7.4 (m), two H-3 9.38 and 9.14 (b-m), 1 CH_3 8.9 (d, J = 1.1 Hz); ir (CCl_4)[6] 1029 (m), 1060 cm^{-1} (w); m/e (70 eV) 90 (3), 92 (1).

[6] Analogous to the corresponding bromides reported by H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

[7] J. F. Lane, J. Fentress, and L. T. Sherwood, Jr., *J. Amer. Chem. Soc.*, 66, 545 (1944).

[8] J. D. Roberts and V. C. Chambers, *ibid.*, 73, 5034 (1951).

[9] These products were identified by comparison of retention volumes and ir spectra with authentic compounds.

[10] (a) D. H. Volman and R. W. Phillips, *Ber. Bunsenges Phys. Chem.*, 72, 242 (1968); (b) R. W. Phillips and D. H. Volman, *J. Amer. Chem. Soc.*, 91, 3418 (1969).