very different substituent effect on carbon–carbon cleavage. For the hydrogen-transfer step alone, if it is dependent upon positive charge or radical character at the reaction sites on the ring,[9,10] *meta* isomers (which are *ortho* and *para* to the transfer sites) might be expected to exhibit more certain effects, through resonance, upon the reaction and the Z/Z_0 ratios than would *para* isomers. In fact, it can be seen in Table I that at 12-eV ionizing voltage electron-withdrawing (+X) *meta* substituents generally enhance the reaction rates relative to butylbenzene, whereas $-X$ groups usually decrease the rates somewhat.

The McLafferty rearrangement in *n*-butylbenzene itself has been written as in **a** with hydrogen transfer to a radical site,[6] although in this formalism an alternative representation (**b**), in which hydrogen is transferred to a positively charged site, might also be considered. The relative importance of radical character or positive
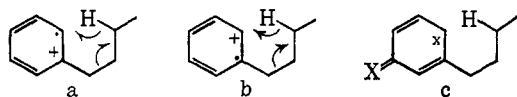
charge at the transfer site should depend on the nature and position of a substituent; thus, in the resonance-structure formalism, the effect of a *m*-amino or *m*-nitro substituent would be depicted in **c** as X = $^+NH_2$, x = · or X = $\cdot NO_2$, x = +. Similar structures for *para* substituents do not appear to establish either radical character or positive charge at the transfer site. Accordingly, the observed difference in behavior of any pair of isomers is in qualitative agreement with the greater Z/Z_0 ratio being associated with greater radical character or positive charge at the transfer site.

However, interrelating the data of Table I using the above argument is not nearly so straightforward, and the relative importance of positive charge *vs.* radical character is difficult to assess from resonance structures. For, although +X groups do not induce the Z/Z_0 ratios to vary too far from unity, what differences are observed seem to be unrelated to the calculated π-electron positive charge (essentially zero) at the transfer site of the molecular ion.[11] At best, the larger Z/Z_0 value of a pair of isomers is in congruence with the lower π-electron density at the transfer site. Parallel correlations between +X and $-X$ substituents are not obvious, except perhaps for *meta*-substituted compounds; *i.e.*, positive charge at the transfer site appears to decrease the probability of transfer.[11]

Whatever the implications of the above discussion, it may be shown that there is a reasonably good correlation with the Hammett equation[12] for the effect of *meta* substituents on the abundance of the M − 42 ions.[7] Plots of log Z/Z_0 *vs.* σ^+ or σ for *meta* substituents treated as *para* (to the transfer site) give $\rho \approx +0.2$.

Similar plots with *para* substituents show wide scattering.

R. Nicoletti,[13] D. A. Lightner
Contribution No. 2205, Department of Chemistry
University of California, Los Angeles, California 90024
Received January 22, 1968

Additions of Difluorocarbene to an Ene–Yne System in a Steroid Molecule[1]

Sir:

We wish to report the first addition of difluorocarbene to an ene–yne systems[2] and to describe some chemical and spectral properties of the resulting adducts.

Addition of a large excess of difluorocarbene (generated by decomposition of the sodium salt of chlorodifluoroacetic acid in diglyme)[3] to 1[4] afforded six new substances (separated by preparative silica gel thin layer chromatoplates) in addition to some recovered starting material.

The first three compounds were assigned structures **2a** [mp 237–238°; $[\alpha]_D$ +161°; λ_{max} 224, 278, and 287 mμ (log ϵ 4.32, 3.30, and 3.26); ν_{max} 3430, 2225, and 1663 cm^{-1}; nmr 1.01 (poorly resolved d, $J \cong 1$ cps, 18-H), 2.05 (d, $J = 1.5$ cps, vinylic CH₃), and ~ 4.35 ppm (unresolved m, 16β-H); mass spectra 354 (M$^+$). *Anal.* Found: C, 78.08; H, 7.82; F, 4.76], **2b** [mp 169–170°; $[\alpha]_D$ +136°; λ_{max} 226, 278, and 287 mμ (log ϵ 4.32, 3.32, and 3.29); ν_{max} 2220, 1662, and 1612 cm^{-1}; nmr 0.91 (unresolved d, 18-H), 2.04 (d, $J = 1.5$ cps, vinylic CH₃), and 5.01 ppm (d, $J_{HF} \cong 50$ cps, 16β-H); mass spectra 356 (M$^+$). *Anal.* Found: C, 77.80; H, 7.27; F, 10.82], and **3** [mp 177°; $[\alpha]_D$ −100°; λ_{max} 288 mμ (log ϵ 4.05); ν_{max} 1640 cm^{-1}; nmr 0.91 (poorly resolved d, $J \cong 1$ cps, 18-H), 2.04 (d, $J = 1.5$ cps, vinylic CH₃), and 5.97, 6.08 ppm (15-, 16-H, $J = 7$ cps). *Anal.* Found: C, 81.64; H, 7.67; F, 5.14].

The formation of compounds **2a** and **2b**, characterized by their ultraviolet absorption in the 225-mμ region, can be rationalized as resulting from the attack of OH and F, respectively, at C-16 in **4**, followed by bond migration and fluorine loss, as depicted in **5**.[6] Structure **2a** was further confirmed by oxidation[7] to

(1) Publication No. 330 from the Syntex Institute of Steroid Chemistry.

(2) The addition of dichlorocarbene to an ene–yne system has been carried out; *cf.* (a) L. Vo-Quang and P. Cadiot, *Compt. Rend.*, **252**, 3827 (1961); (b) L. Vo-Quang and P. Cadiot, *Bull. Soc. Chim. France*, 1518 (1965); (c) I. A. D'yakonov and L. P. Danilkina, *Zh. Obshch. Khim.*, **32**, 1008 (1962); **34**, 738 (1964); (d) E. V. Dehmlow, *Tetrahedron Letters*, 3763 (1966), and references therein.

(3) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959); J. M. Birchall, G. W. Cross, and R. N. Hazeldine, *ibid.*, 81 (1960).

(4) Prepared by treatment of 3,17β-dihydroxy-17α-propionylestra-1,3,5(10)-triene 3-methyl ether with acetic anhydride in the presence of *p*-toluenesulfonic acid; mp 156–157°; $[\alpha]_D$ +59°; λ_{max} 229–230, 278, 287 mμ (log ϵ 4.24, 3.37, and 3.31); ν_{max} 1608 and 1575 cm^{-1}; nmr 0.86 (18-H), 2.0 (acetylenic CH₃), and 5.95 ppm (16-vinylic H).[5] *Anal.* Found: C, 85.98; H, 8.33.

(5) Infrared spectra were determined in potassium bromide disks and the pmr spectra in deuteriochloroform solution containing tetramethylsilane as an internal reference; chemical shifts are reported in parts per million on the δ scale; d = doublet, t = triplet, m = multiplet. These determinations were made on a Varian A-60 spectrometer. We wish to thank Miss J. Tremble and Drs. T. Toube, L. Throop, and L. Tökes for the determination of the physical properties of compounds here reported.

(6) We wish to thank Professor G. Stork, Columbia University, and Dr. J. H. Fried, Syntex Laboratories, for helpful suggestions.

(7) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(9) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 8.

(10) F. W. McLafferty and T. Wachs, *J. Am. Chem. Soc.*, **89**, 5043 (1967).

(11) D. A. Lightner, unpublished data. Calculated from LCAO-SCF wave functions of aniline and nitrobenzene, the respective radical-cation π-electron densities at C-4 are 0.876 and 0.968, at C-3 are 0.983 and 0.997, and at C-2 are 0.938 and 0.991. Similarly, the positive charge per cents at C-4 are 15.5 and 0.0, at C-3 are 1.5 and 0.5, and at C-2 are 10.0 and 0.2.

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter 7.

the corresponding 16-ketone 2c [mp 195–196°; [α]D +136°; λmax 278 mμ (log ε 4.17); νmax 2215 and 1685 cm⁻¹; nmr 1.20 (18-H) and 2.15 ppm (d, J = 1.5 cps, vinylic CH₃) (at 100-cps, sweep width $J_{18H,F}$ = 1.2 cps and $J_{21H,F}$ = 1.4 cps). *Anal.* Found: C, 78.08; H, 7.39; F, 5.46], which exhibits a strong chromophore at 278 mμ. The unresolved doublet, characterizing the protons at C-18 in alcohol 2a, in the 16-fluoro derivative 2b, as well as in triene 3, indicates long-range coupling with fluorine, hence supporting the geometry indicated for the substituent at C-17 in these compounds.[8] Finally the α configuration is assigned to the hydroxyl at C-16 in alcohol 2a and to the fluorine atom in 2b, since approach of the anion presumably takes place from the less hindered α side of the molecule.
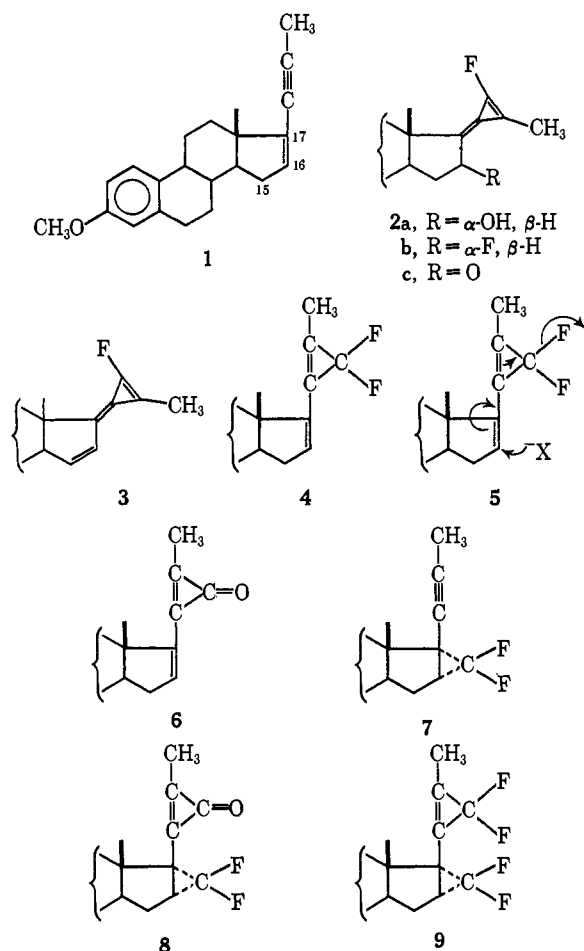
2a, R = α-OH, β-H
b, R = α-F, β-H
c, R = O

characteristic triple maximum in the ultraviolet spectrum, was identified as the cyclopropenone derivative 6 [mp 139–141°; [α]D +21°; λmax 231, 249–250, and 287 mμ (log ε 4.13, 4.17, and 3.35); νmax 1855 and 1640 cm⁻¹; nmr 0.93 (18-H), 2.31 (cyclopropene methyl), and 6.63 ppm (16-H); mass spectra 334 (M⁺). *Anal.* Found: C, 83.05; H, 7.81].

The last two compounds were assigned structures 7 [mp 148–150°; [α]D +122°; λmax 219, 278, and 287 mμ (log ε 3.95, 3.33, and 3.28); νmax 1612 cm⁻¹; nmr 1.05 (18-H) and 1.85 ppm (acetylenic CH₃). *Anal.* Found: C, 78.02; H, 7.60; F, 10.92] and 8 [mp 165°; [α]D +153°; λmax 278 and 287 mμ (log ε 3.23 and 3.18); νmax 1855 and 1720 cm⁻¹; nmr 1.17 (18-H), 2.20, and 2.23 ppm (cyclopropenone CH₃). *Anal.* Found: C, 74.48; H, 6.95; F, 9.85].

The difluorocyclopropene derivative 4 was not isolated probably due to rapid hydrolysis to the cyclopropenone 6, since the +I effect of the methyl group is known to increase the rate of hydrolysis of difluorocyclopropene.[9] Moreover, the substantial amount (27%) of starting material 1 recovered at the end of the reaction can be attributed to regeneration of the triple bond by subsequent decomposition of cyclopropenone 6, an observation which has some precedent.[9,10] Indeed, recrystallization of the cyclopropenone derivative 6 from acetone solution afforded mainly the acetylenic steroid 1.

The difluorocyclopropenone derivative 8 results from initial addition of 2 equiv of difluorocarbene to the ene–yne system of 1 to give the unstable tetrafluoro compound 9 which was not isolated, because of facile hydrolysis to the corresponding cyclopropenone 8 (*vide supra*).

The monoadduct 7 can be the product of monoaddition or the result of thermal decomposition of the initially formed cyclopropenone 8. The latter conclusion is supported by the observation that 8 is decarbonylated to give 7 in boiling diglyme.

The α stereochemistry assigned to the difluoromethylene grouping in compounds 7 and 8 is based on the absence of long-range coupling with the protons at C-18 which would be expected for the 16β,17β adduct.[8]

(9) P. Anderson, P. Crabbé, A. D. Cross, J. H. Fried, L. H. Knox, J. Murphy, and E. Velarde, submitted for publication.
(10) R. Breslow and L. Altman, *J. Am. Chem. Soc.*, **88**, 504 (1966), and references cited therein.
(11) Syntex Postdoctoral Fellow, 1966–1967.

The major compound (isolated in 11% yield), from the difluorocarbene addition reaction, which presents a

(8) (a) A. D. Cross and P. W. Landis, *J. Am. Chem. Soc.*, **84**, 1736, 3784 (1962); **86**, 4005 (1964); (b) A. D. Cross, *ibid.*, **86**, 4011 (1964).

Pierre Crabbé, Paul Anderson,[11] **Esperanza Velarde**
Research Laboratories, Syntex S.A.
Mexico, D.F., Mexico