C_6H_6, $(C_2H_5)_3N$, Et_2S, etc., either the degree of aggregation is not very large or the enthalpy of solvation is slight. These are the systems where similar enthalpies are measured in CCl_4 and hexane. One word of caution: low enthalpies are obtained for pyridine adducts in CCl_4 as solvent because of extensive solvation (0.5 kcal mole^{-1}) of pyridine by CCl_4.[13–15]

It is desirable to extend the range of solvents that can be employed in these studies. In previous work, problems associated with the use of CH_2Cl_2 and benzene were pointed out.[16] It was of interest to investigate *o*-dichlorobenzene as a solvent for measuring enthalpies because of its desirable solubility properties. After making the appropriate correction for the heat of solution of the acid, the measured enthalpy of adduct formation between dimethylacetamide and *m*-trifluorophenol in *o*-dichlorobenzene was found to be nearly the same as that measured in carbon tetrachloride. Unfortunately the low vapor pressure of *o*-dichlorobenzene prevented a molecular weight determination of dimethylacetamide in this solvent since it would further test the model presented above. However, it appears that *o*-dichlorobenzene may be a good solvent for determination of enthalpies of adduct formation. More data are desirable to test the general applicability of this conclusion since *o*-dichlorobenzene is probably a more polar and a more basic solvent than either carbon tetrachloride or cyclohexane.

Acknowledgment. The authors acknowledge the generous support of the Paint Research Institute and National Science Foundation through Grant GP-5498.

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(13) K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, **62**, 2063 (1966).

(14) P. Datta and G. M. Barrow, *J. Am. Chem. Soc.*, **87**, 3053 (1965).

(15) S. G. W. Ginn and J. L. Wood, *Spectrochim. Acta*, **23A**, 611 (1967).

(16) R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Am. Chem. Soc.*, **88**, 2717 (1966).

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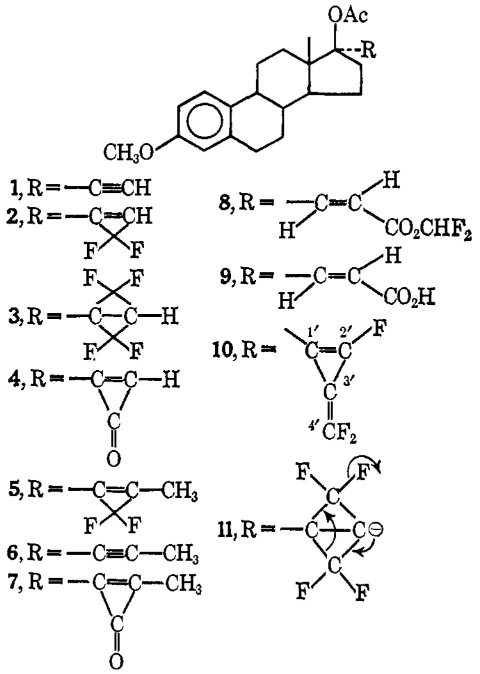
Chemistry of Difluorocarbene Adducts to Sterically Hindered Acetylenes[1]

Sir:

We wish to report the addition of difluorocarbene to the 17α-acetylenic side chain of ethynylestradiol 3-methyl ether and to describe a variety of novel transformations of the adducts.

Treatment of **1** with difluorocarbene (generated by decomposition of the sodium salt of chlorodifluoroacetic acid[2] in diglyme) afforded 48% of the difluorocyclopropene **2** [mp 122–123°; $[\alpha]_D$ −10°; λ_{max} 278 and 287 mμ (log ε 3.29 and 3.26); ν_{max} 3070 cm^{-1};[3] pmr 1.00 (18-H), 2.10 (acetate), and 7.33 ppm (*t*, $J_{H,F}$ = 2 cps, cyclopropene H). *Anal.* Found: C, 71.86; H, 6.97; F, 9.14] and 7% of the tetrafluorobicyclo[1.1.0]butane[4] **3** [mp 131–132°, $[\alpha]_D$ +19°; λ_{max} 278 and 287 mμ (log ε 3.33 and 3.30); ν_{max} 1770 and 1695 cm^{-1} (weak); pmr 0.92 (18-H) and 2.15 ppm (acetate); ^{19}F nmr 139, 150 ($J_{F,F\,gem}$ = 178 cps), *gem*-difluoromethylene, and 140.5, 151.5 ppm ($J_{F,F\,gem}$ = 178 cps), *gem*-difluoromethylene;[5] m/e 452 (M^+). *Anal.* Found: C, 66.54; H, 6.23; F, 16.05].



Formic or sulfuric acid hydrolysis of the difluorocyclopropene **2** gave the cyclopropenone **4** [mp 147–148°; $[\alpha]_D$ −37°; λ_{max} 278 and 287 mμ (log ε 3.30 and 3.34); ν_{max} 1830 and 1740 cm^{-1}; pmr 0.98 (18-H), 2.11 (acetate), and 8.29 ppm (vinylic H). *Anal.* Found: C, 76.32; H, 7.45]. Hydrolysis of unstable dihalocyclopropene intermediates to give cyclopropenones has also been reported by Breslow and his coworkers.[6]

The vinylic proton of **2** was removed with sodium hydride and the resultant anion alkylated with methyl iodide to yield **5** [mp 131–132°; $[\alpha]_D$ −13°; λ_{max} 278 and 287 mμ (log ε 3.34 and 3.30); ν_{max} 1810 and 1745 cm^{-1}; pmr 0.97 (18-H), 2.02 (*t*, $J_{H,F}$ = 2.5 cps, vinylic methyl), and 2.07 ppm (acetate). *Anal.* Found: C, 72.50; H, 7.33; F, 8.84]. This result was confirmed by addition of difluorocarbene to the 17α-propynyl steroid **6** which also afforded **5**. In the latter experiment there was formed a substantial amount of the methylated cyclopropenone **7** [mp 169–170°, $[\alpha]_D$ −27°, λ_{max} 278 and 287 mμ (log ε 3.29 and 3.26), ν_{max} 1845 and 1745 cm^{-1}; pmr 0.99 (18-H), 2.11 (acetate), and 2.18 ppm (vinylic methyl). *Anal.* Found: C, 76.53; H, 7.28]. It was noted that the rate of hydrolysis of **5** to **7** is qualitatively much faster than

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(1) Publication No. 314 from the Syntex Institute of Steroid Chemistry.

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

(3) 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, dd = pair of doublets. The ^{19}F nmr spectra were run in chloroform containing trichlorofluoromethane as an internal reference, and all chemical shifts reported are positive (upfield from $CFCl_3$ resonance). These determinations were made on a Varian HA 100 spectrometer operating at 100 and 94.1 Mcps, respectively. The ^{19}F nmr spectra were calibrated using an audio side-band technique.

(4) *Cf.* W. Mahler, *J. Am. Chem. Soc.*, **84**, 4600 (1962).

(5) The nonequivalence of all four fluorine nuclei is attributed to the location of the bicyclobutane system on an asymmetric center. Careful examination of the spectrum revealed that one of each pair of geminal fluorine nuclei is coupled with the proton at the ring junction ($J_{H,F}$ = 20 cps); long-range coupling of 5 and 8 cps was also apparent. A detailed analysis of this spectrum will be presented in the ensuing full paper.

(6) (a) R. Breslow and G. Ryan, *J. Am. Chem. Soc.*, **89**, 3073 (1967); (b) R. Breslow and L. Altman, *ibid.*, **88**, 504 (1966). We wish to thank Professor Breslow for an exchange of results concerning monosubstituted cyclopropenones prior to publication.

in the case of the conversion of **2** to **4**. This enhancement in the rate of hydrolysis is attributed to the +I effect of the cyclopropenyl methyl group in **5**.

Reaction of difluorocarbene with the cyclopropenone **4** under strictly anhydrous conditions provided, besides some starting material, 50% of the ethynyl derivative **1**. However, in the presence of water this transformation took a different course to yield (in 20%) the unsaturated ester **8** [mp 111–112°; $[\alpha]_D$ +58°; λ_{max} 222–224, 278, and 287 mμ (log ε 4.23, 3.24, and 3.20); ν_{max} 1760 and 1750 cm^{-1}; pmr 1.00 (18-H), 2.05 (acetate), 5.74 (d, J_{trans} = 16 cps, 21-H), 7.19 (d, J_{trans} = 16 cps, 20-H), and 7.09 ppm (t, $J_{H,F}$ = 71 cps, O–CHF_2). *Anal.* Found: C, 66.47; H, 6.72; F, 8.37]. The ethynyl derivative **1** is probably formed by simple thermal decomposition of the cyclopropenone since, when heated in diglyme in the absence of sodium chlorodifluoroacetate, the cyclopropenone **4** affords compound **1** in 49% yield.[6,7]

Ester **8** formation probably proceeds *via* attack by difluorocarbene[8] on the free α,β-unsaturated acid **9** [mp 175–177°; $[\alpha]_D$ +73°; λ_{max} 278 and 287 mμ (log ε 3.31 and 3.27); ν_{max} 3420, 3190, 1732, and 1713 cm^{-1}; pmr 1.00 (18-H), 2.06 (acetate), 5.78 (d, J_{trans} = 16 cps, 21-H), 7.15 (d, J_{trans} = 16 cps, 20-H), and 9.83 ppm (carboxyl H, exchanged with D_2O). *Anal.* Found: C, 71.78; H, 7.59]. When this reaction is run in the presence of water the yield of difluoromethyl ester[8] rises to 48%.

Reaction of **3** with sodium hydride in benzene solution afforded the difluoromethylene cyclopropene **10** [mp 109–111°; $[\alpha]_D$ +31°; λ_{max} 232, 278, and 287 mμ (log ε 4.46, 3.33, and 3.29); ν_{max} 1855 and 1775 cm^{-1}; pmr 0.95 (18-H) and 2.20 (acetate); ^{19}F nmr 92.4 (dd, $J_{4'F,4'F}$ = 117 cps, $J_{2'F,4'F}$ = 43 cps), 94 (dd, $J_{4'F,4'F}$ = 117 cps, $J_{2'F,4'F}$ = 43 cps, 4,4′-difluoromethylene), 140 ppm (*t*, $J_{2'F,4'cF} = J_{2IF,4'tF}$ = 43 cps, 2′F), *m/e* 432 (M^+). *Anal.* Found: C, 69.49; H, 6.43; F, 14.00]. The structure of **10** is supported by its physical properties[9] and represents the first example of a methylenecyclopropene not stabilized by electron-delocalizing substituents.

The formation of **10** can be rationalized as resulting from the C-21 anion[10] which undergoes bond cleavage and expulsion of fluoride ion as indicated in **11**.

Acknowledgment. We wish to thank Miss J. Tremble and Drs. T. Toube, L. Throop, and L. T kes for the determination of physical properties of compounds here reported.

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[7] This observation has some precedent; *cf.* R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965); R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965).

[8] R. A. Mitsch and J. E. Robertson, *J. Heterocyclic Chem.*, **2**, 152 (1965).

[9] A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963); M. A. Battiste, *ibid.*, **86**, 942 (1964); W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964); E. D. Bergmann and I. Agronat, *ibid.*, **86**, 3587 (1964); A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964); T. Eicher and A. Loschner, *Z. Naturforsch.*, **21b**, 899 (1966), and references cited.

[10] It was neither possible to exchange the C-21 proton with D_2O nor to intercept this anion with methyl iodide, since attempted alkylation afforded **10**. These observations support the concerted mechanism shown in **11**.

[11] Syntex Postdoctoral Fellow, 1966–1967.

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[13] Deceased, Jan 6, 1966.

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The Formation and Reactivity of Benzocyclobutenone Anion

Sir:

The benzocyclobutadiene character of the enolate anion of benzocyclobutenone (**1a**) might lead to the prediction of an unusually low acidity of the methylene hydrogens of this compound. An unsuccessful attempt to observe base-catalyzed hydrogen–deuterium exchange as a probe in evaluating this prediction has been reported.[1,2] These data have demonstrated that the carbonyl of benzocyclobutenone is highly reactive toward nucleophiles and that the four-membered ring cleaves with great facility, but have not provided an answer to this interesting question. Since the acidity of the methylene hydrogens of benzocyclobutenone is of interest from both a synthetic as well as theoretical standpoint, we have investigated some base-catalyzed reactions of this compound.

Addition of **1a**[3] or **1b**[1] to a suspension of NaH in DMF results in a moderately rapid evolution of hydrogen gas (reaction time ~30 min at 25°). Acidic workup of the reaction mixture yields as the major products (~50%) dimers **2a**[4] and **2b** derived from the original ketones. The dimeric nature of these products could be verified by their mass spectral molecular weights (**2a** *m/e* 236 ($C_{16}H_{12}O_2$), **2b**, *m/e* 292 ($C_{20}H_{20}O_2$)). The infrared spectra of **2a** and **2b** show carbonyl bands at 1690 cm^{-1} characteristic of an open-chain or nonstrained ketone. Both products contain four enolizable hydrogens, as evidenced by rapid acid-catalyzed hydrogen–deuterium exchange which could be detected by nmr spectroscopy. The nmr spectrum of **2a** (τ 2.15–3.0 m and 5.41 s; relative intensities 2:1) and **2b** (τ 3.1 s, 3.22 s, 6.0 s, and 7.79 s; relative intensities 1:1:2:6) combined with the above data are consistent with the dibenzo[*a*,*e*]cycloocta-3,7-dione and 3′,5′,8′,10′-tetramethyldibenzo[*a*,*e*]cycloocta-3,7-dione[5] structures indicated. The structure of **2a** can be conclusively demonstrated by comparison of its physical properties to those reported for this compound.[6] The origin of **2a** and **2b** can readily be accounted for according to Scheme I.[7]

Addition of **1a** or **1b** to a suspension of NaH in DMF containing 1 equiv of benzaldehyde yields as the major

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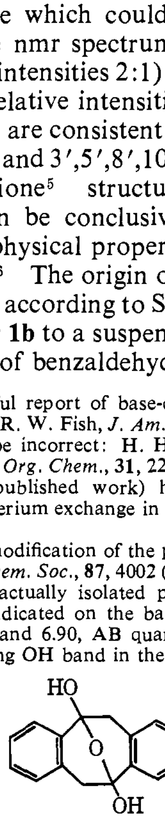
[1] An initial successful report of base-catalyzed exchange for this compound (H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 749 (1960)) has recently proven to be incorrect: H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966).

[2] M. P. Cava (unpublished work) has observed partial base-catalyzed hydrogen–deuterium exchange in 2-carbomethoxybenzocyclobutenone.

[3] Synthesized by a modification of the procedure of H. Wasserman and J. Solodar, *J. Am. Chem. Soc.*, **87**, 4002 (1965).

[4] Compound **2a** is actually isolated primarily as a hydrate (**2c**) assigned the structure indicated on the basis of the nmr spectrum (τ 2.2–3.2 m, 6.25 s, 6.85, and 6.90, AB quartet, *J* = 16.5 cps; relative intensities 4:1:2), a strong OH band in the infrared, and a correct elemental analysis. Heating this hydrate above its melting point for a short period converts it to the ketone described in the text.



2c

[5] This compound gave a satisfactory elemental analysis.

[6] S. Wawzonek, *J. Am. Chem. Soc.*, **62**, 745 (1940); A. Cope and S. W. Fenton, *ibid.*, 73, 1671 (1951).

[7] This scheme is not intended to represent a detailed mechanism, but rather a plausible reaction sequence.