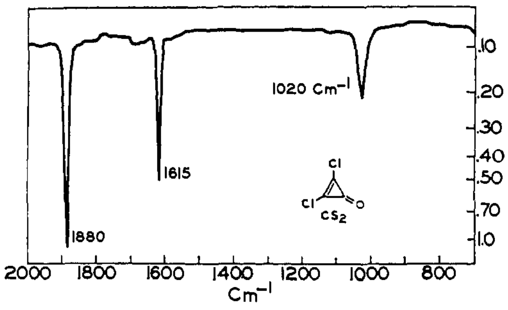
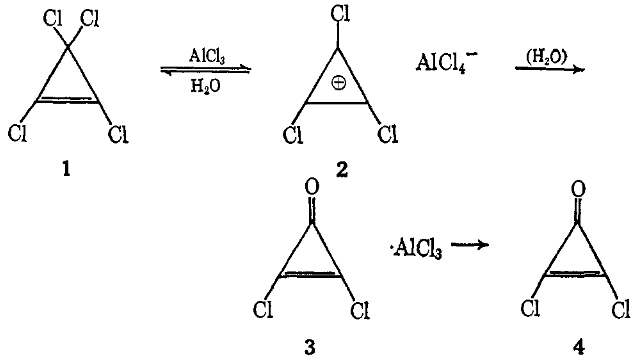


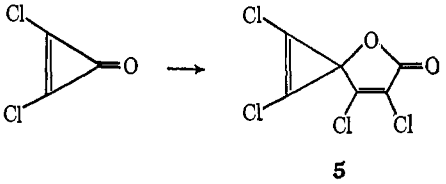
Figure 1. Infrared spectrum of dichlorocyclopropenone in CS_2.

to 0–5°, and shaken for a few seconds with ice water. The organic layer was separated, dried over calcium chloride and magnesium sulfate at 0°, and then concentrated under vacuum. Molecular distillation of the residue (0°, 0.05 mm) under nitrogen followed by repeated crystallization from pentane at −40° gave pure colorless dichlorocyclopropenone: mp −6°; m/e 122. Calcd for 2Cl: P + 2, 65.3%; P + 4, 10.6%. Found: P + 2, 62.5%; P + 4, 10.1%.[3] Besides the parent peak, five major fragment peaks appeared in the mass spectrum of **4**, corresponding to loss of Cl, Cl_2, CO, COCl, and C_2ClO. No proton resonance appeared in the nmr spectrum. The infrared spectrum (Figure 1) contained strong bands at 1880 and 1615 cm^{-1} in the region characteristic of substituted cyclopropenones.[4,5] An additional band at 1020 cm^{-1} is probably due to C–Cl modes of the vinylic chlorine.[2]



On one occasion a large sample of **4** *(~40 g), after being crudely distilled and stored overnight at −78°, underwent detonation while being warmed to room temperature prior to further purification. Preparation of* **4** *only in quantities less than 1 g and use of appropriate shielding is recommended.* Amounts of **4** up to 1 g have been prepared repeatedly and have never decomposed explosively at temperatures below 0°. Dilute solutions of **4** in CH_2Cl_2 can be handled at room temperature, where they appear to have a decomposition half-time of a few hours.

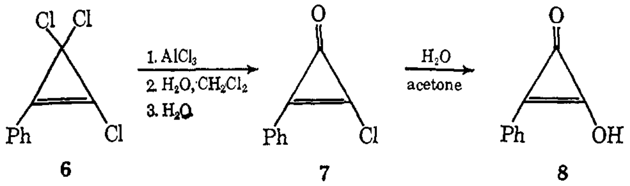
The neat liquid decomposes rapidly, and sometimes explosively, at room temperature. Molecular distillation of the dark residue after decomposition gave about 20% of a crystalline dimer: mp 75–76°; ν_{max} (CS_2) 1820, 1795, 1625, 1005, and 930 cm^{-1}. *Anal.* Calcd for $(C_3Cl_2O)_2$: C, 29.31; Cl, 57.68%; mol wt, 244. C, 29.34; Cl, 57.67, m/e 244. Calcd for 4Cl: P + 2, 131%; P + 4, 63.9%. Found: P + 2, 126%; P + 4, 63.3%. The dimer is believed to have the spirolactone formula **5**. Thermal dimerization of cyclopropenones to spirolactones of this type is well known.[4]



5

Further hydrolysis of **4** with 65% aqueous sulfuric acid leads to α,β-dichloroacrylic acid, isolated in high yield and identical with that obtained earlier by aqueous hydrolysis of **1**.[2]

The generality of the slow hydrolysis reaction as it pertains to the synthesis of other cyclopropenones is shown by the conversion of phenyltrichlorocyclopropene (**6**)[6] to chlorophenylcyclopropenone (**7**): mp 40–43 dec; ν_{max} (CS_2) 1865, 1640, and 1220 cm^{-1}; nmr multiplet centered at τ 2.3; m/e 164. Calcd for 1Cl: P + 2, 32.6%. Found: P + 2, 34.2%. Hydrolysis of **7** in aqueous acetone afforded the known compound[4d] hydroxyphenylcyclopropenone (**8**) in high yield. Hydrolysis of other chlorocyclopropenones is under investigation.



Acknowledgment. This research was supported by a grant from the Public Health Service.

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[3] R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p 17.

[4] (a) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965); (b) R. Breslow, L. Altman, A. Krebs, E. Mohacsi, I. Murata, R. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320, 1326 (1965); (c) R. Breslow and L. Altman, *ibid.*, **88**, 504 (1966); (d) D. Farnum, J. Chickos, and P. Thurston, *ibid.*, **88**, 3075 (1966).

[5] The parent compound, cyclopropenone, exhibits absorptions at 1835 and 1870 cm^{-1}: R. Breslow and G. Ryan, *ibid.*, **89**, 3073 (1967).

[6] S. Tobey and R. West, *ibid.*, **86**, 4215 (1964); J. Chickos, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1966; D. Zecher, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1967.

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Solvent Effects on the Values Measured for Enthalpies of Adduct Formation

Sir:

We have been interested in obtaining and interpreting thermodynamic data for the formation of 1:1 Lewis acid–base adducts.[1] Linear relationships have been shown to exist between the measured enthalpies and parameters obtained from infrared and nmr data[2–4] for certain systems. Ideally these enthalpies of adduct formation should involve unsolvated, monomolecular species which would be best approximated by gas-phase

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[1] For a review and discussion of previous work, see R. S. Drago, *Chem. Brit.*, 3516 (1967).

[2] T. D. Epley and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 5770 (1967).

[3] M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962).

[4] T. F. Bolles and R. S. Drago, *ibid.*, **88**, 5730 (1966).

conditions. In a limited number of cases it has been found that the enthalpies of adduct formation measured in "inert" solvents, such as carbon tetrachloride and saturated hydrocarbons, are nearly the same as those in the gas phase.[5,6] It has been assumed, therefore, that enthalpies measured in such inert solvents do approximate the gas phase.[2] However, we now report the very surprising result that for some acid–base systems the enthalpy of adduct formation measured in cyclohexane is significantly different from that measured in carbon tetrachloride.

Table I gives the relevant thermodynamic data. The determination and calculation of the enthalpies and equilibrium constants were accomplished simultaneously from calorimetric data.[2] A new program has been developed using the minimum seeking method[7] that has been incorporated into a general minimization routine, SIMPLEX.[8]

Table I[a]

Acid	Solvent	ΔH, kcal mole^{-1}	K, l. mole^{-1}
$CF_3C_6H_4OH$	CCl_4	7.3 ± 0.1	768 ± 166
	C_6H_{12}	9.8 ± 0.1	971 ± 339
$C_4H_9C_6H_4OH$	CCl_4	6.4 ± 0.1	78.9 ± 2.7
	C_6H_{12}	8.1 ± 0.2	274 ± 46
$CF_3C_6H_4OH$	o-$C_6H_4Cl_2$	6.9 ± 0.1	347 ± 114

[a] The base used in all cases was dimethylacetamide.

The measured enthalpy of reaction, ΔH, of phenol with various bases has been shown[2] to be linearly related to the shift of the phenolic infrared stretching frequency, $\Delta\nu_{OH}$. This series has been extended to include substituted phenols and it has been found that eq 1 closely correlates the enthalpies and phenolic infrared frequency shifts.

$$-\Delta H\,(\text{kcal mole}^{-1}) = 0.103\Delta\nu_{OH}\,(\text{cm}^{-1}) + 3.08 \qquad (1)$$

The observed phenolic frequency shift in carbon tetrachloride of *m*-trifluoromethylphenol upon addition of dimethylacetamide (DMA) was found to be 391 ± 8 cm^{-1}. The resultant enthalpy using eq 1 is 7.1 kcal mole^{-1} which is nearly that obtained in carbon tetrachloride but not in cyclohexane. Similarly for *p*-*t*-butylphenol with dimethylacetamide, the observed phenolic shift of 320 cm^{-1} predicts an enthalpy of reaction of 6.38 kcal mole^{-1} which is close to the observed value in carbon tetrachloride but not in cyclohexane. Thus for these two systems, eq 1 correlates rather well with those enthalpies measured in carbon tetrachloride but not in cyclohexane.

The four-parameter, linear enthalpy relation[9] allows the calculation of the enthalpy of formation of adducts

$$-\Delta H = C_AC_B + E_AE_B \qquad (2)$$

where C_A and E_A represent constants assigned to a given Lewis acid, and C_B and E_B are the corresponding values for the Lewis base. Present values of the E and C parameters[9–11] predict values of enthalpies for the dimethylacetamide-*m*-trifluorophenol and dimethylacetamide-*p*-*t*-butylphenol pairs of 7.23 and 6.30 kcal mole^{-1}, respectively. Again these values are close to the enthalpies measured in carbon tetrachloride.

In an attempt to arrive at the source of the difficulty, molecular weight measurements of dimethylacetamide in carbon tetrachloride and cyclohexane were made. The measured molecular weight of dimethylacetamide (0.05 mole l.$^{-1}$) in carbon tetrachloride was found to be 230 (formula weight of dimethylacetamide, 87), while the molecular weight determined for a similar concentration of dimethylacetamide in cyclohexane was approximately 1000, averaging approximately 12 molecules of dimethylacetamide per group. In order that the equilibrium constant data fit a 1:1 expression, the degree of association in the adduct must equal the association of the base. These measurements are usually made in excess base.

For the observed enthalpy measured in an "inert" solvent to approximate that measured in the gas phase, the enthalpy of solvation of the reactants and products should be quite small so that the sum of the energies of solvation of the reactants may be nearly equal to that of the product.[1] The reaction of an acid with dimethylacetamide in carbon tetrachloride occurs between one molecule of acid reacting with a base molecule which is in turn solvated with about two other base molecules. The situation is similar in cyclohexane except that much larger aggregates of base are present. The adduct can be partially or wholly solvated by the additional base molecules present in the aggregate. Since the adduct is more polar than a base molecule, the enthalpy of solvation of the product can be considerably greater than that of the reactants. This solvation energy would be smaller in CCl_4 than in hexane because there are fewer molecules in the aggregate in the former solvent. This would account for the disparity of the measured enthalpies in carbon tetrachloride and cyclohexane.

Both the higher enthalpy and equilibrium constants observed in cyclohexane than in carbon tetrachloride are consistent with the solvation of the acid–base adduct into the associated base aggregate. The additional solvation would act as a driving force for adduct formation and as a source of additional heat. In view of the very extensive size of the aggregate in cyclohexane, one could conceive of the reaction of dimethylacetamide and *p*-*t*-butylphenol in cyclohexane to approach the conditions of the reaction of *p*-*t*-butylphenol in pure base. The reaction of *p*-*t*-butylphenol with DMA in pure DMA has been measured and reported having a value of 7.94 kcal mole^{-1}.[12] Interestingly, and in strong support of our proposal, this is nearly the value of the enthalpy of this acid–base pair in cyclohexane. The additional enthalpy of solvation of the adduct thus corresponds to -1.6 kcal mole^{-1}. We thus find the unexpected result that a very nonpolar solvent is not ideal for the systems described here, but instead one desires a solvent that interacts with the polar base strongly enough to dissociate aggregates and weak enough to make an insignificant (0.1–0.2 kcal mole^{-1}) contribution to the enthalpy (corresponding to usual experimental error).

When the donor is not very polar, *e.g.*, Et_2O, C_5H_5N,

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(5) J. M. Goodenow and M. Tamres, *J. Chem. Phys.*, **43**, 3393 (1965).

(6) F. T. Long and R. L. Strong, *J. Am. Chem. Soc* , **87**, 2345 (1965).

(7) J. A. Nelder and R. Mead, *Computer J.*, **8**, 308 (1965).

(8) The general minimization routine, SIMPLEX, has been copyrighted by J. P. Chandler of the University of Indiana, Physics Department, 1965.

(9) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

(10) T. F. Bolles and R. S. Drago, *ibid.*, **88**, 3921 (1966).

(11) T. F. Bolles and R. S. Drago, *ibid.*, **88**, 5730 (1966).

(12) T. S. S. K. Murty, Doctoral Dissertation, University of Pittsburgh, 1967.

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.

[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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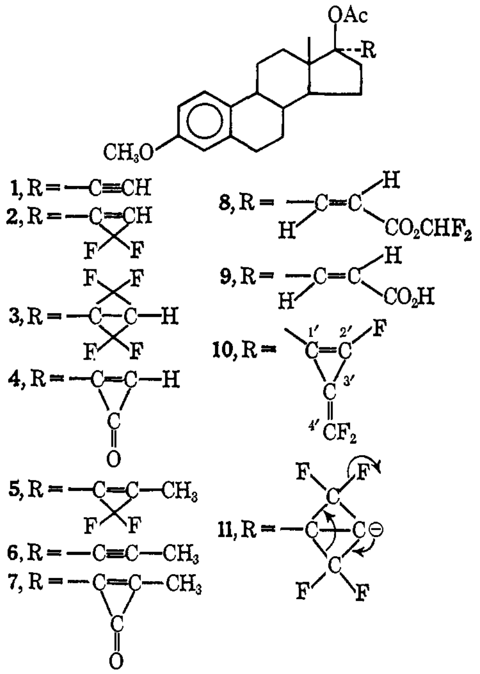
Chemistry of Difluorocarbene Adducts to Sterically Hindered Acetylenes[1]

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.