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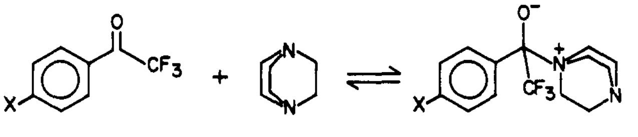
Zwitterionic Adducts between a Strongly Electrophilic Ketone and Tertiary Amines

Sir:

We report evidence for the existence of zwitterionic adducts, e.g. **3**, between electrophilic ketones, such as α,α,α-trifluoroacetophenone (**1**), and tertiary amines, such as 1,4-diazabicyclo[2.2.2]octane (Dabco, **2**). This report complements the observation of adducts between ketones and strong electrophiles such as boron trifluoride,[1] which have weak boron-oxygen bonds.



1 a,X = H
b,X = F

2

3 a,X = H
b,X = F

The interactions between carbonyl compounds and nucleophilic reagents such as amines are well documented both in the ground state[2] and in the excited state.[3] The excited-state reactions are dominated by electron transfer and hydrogen abstraction, whereas the ground-state interactions, with few exceptions,[4] involve addition. Primary and secondary amines add to the carbonyl double bond giving rise to hemiaminals which may lose water to form imines or enamines or react with a second molecule of amine to form the more stable aminals. Zwitterions may be short-lived intermediates in these reactions.[5] Ground-state interactions between carbonyl groups and tertiary amine moieties have been inferred from weakened carbonyl stretching frequencies[6] and from transannular N···C=O distances in medium-sized ring compounds.[7] Interactions between ketones and amines, whether of the charge-transfer type or due to nucleophilic approach of the amine, are expected to be particularly strong for ketones whose electron affinity (and electrophilic nature) is enhanced by electron-withdrawing substituents. This prediction is confirmed by the spectroscopic data observed in solutions containing trifluoroacetophenone and tertiary amines.

The addition of tertiary amines to acetonitrile solutions containing trifluoroacetophenone or its derivatives results in characteristic changes in the IR, UV, and NMR spectra. For example, addition of a fivefold excess of Dabco causes the complete disappearance of the carbonyl stretching band at 1791 cm^{-1}. Similarly, the UV absorption bands at 255 and 290 nm decrease with increasing Dabco concentration. Even more significant changes are observed in the NMR spectra: the reaction of Dabco with *p*-fluorotrifluoroacetophenone results in the observation of a new ^{19}F signal, nearly 9 ppm upfield of the CF_3 signal of the ketone, and in a new set of ^{13}C resonances as well. The most dramatic ^{13}C shift is observed for the quartet representing the carbon bonded to oxygen: this resonance is shifted upfield by ~105 ppm. Substantial downfield shifts are observed for the trifluoromethyl and for the ipso carbons, ~8 and ~7 ppm, respectively, whereas the remaining aromatic carbons show minor upfield shifts (Figure 1, Table I).

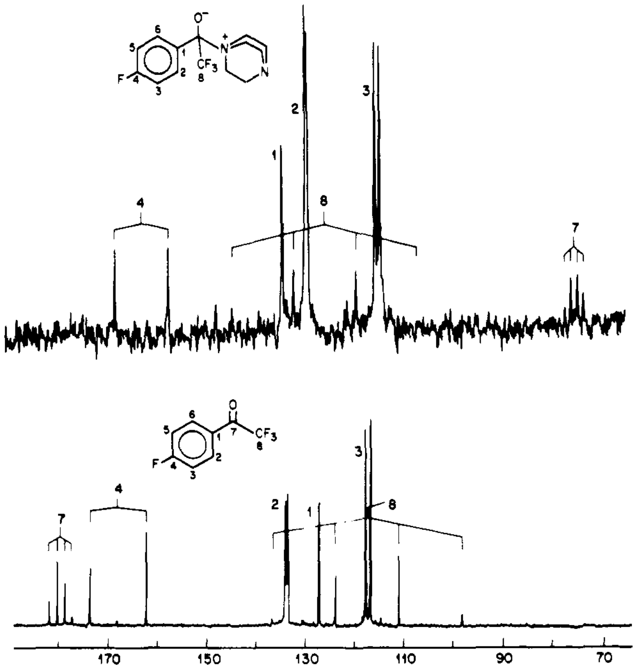


Figure 1. Proton decoupled ^{13}C NMR spectrum of 1.0 M *p*-fluoro-α,α,α-trifluoroacetophenone in acetone-d_6 (bottom) and of its Dabco adduct recorded in an acetone-d_6 solution containing 0.2 M *p*-fluorotrifluoroacetophenone and 1.0 M Dabco (top).

These results document significant changes in the vicinity of the carbonyl carbon, whereas only minor changes are indicated for the para and meta positions of the benzene ring. Accordingly, we propose that the new species is formed by nucleophilic attack of the amine on the carbonyl group and that it is zwitterionic in nature. The ^{13}C NMR chemical shift is a particularly sensitive tool to monitor such a change. For example, the transannular interaction of a tertiary amino group with a carbonyl function in a ten-membered ring, where the N···C distance lies between 2.56 and 2.58 Å,[8] results in an upfield shift of the carbonyl resonance (by 11 ppm)[9] and in a

Table I. ^{19}F and ^{13}C Chemical Shifts[a] and Coupling Constants[b] of *p*-Fluorotrifluoroacetophenone and Selected Adducts

	p-F-TFA	DABCO Adduct	Hydrate	Methanolate
$C^{19}F_3$ (s)[c]	+5.9	-2.7	-6.4	-5.8
$^{13}CF_3$ (q)[c]	117.8 (291)	126.3 (285)	126.1 ( )	124.2 (287)
C-O (q)	180.3 (35)	75.8 (28)	93.9 (31)	97.5 (32)
ipso-C (d)[c]	127.6 (3)	135.0 (3)	135.4 (3)	132.1 (3)
ortho-C (d)	134.2 (9)	130.0 (9)	130.7 (9)	131.4 (9)
meta-C (d)	117.6 (22)	115.6 (22)	115.4 (22)	115.9 (22)
para-C (d)	168.2 (257)	163.7 (246)	164.2 (243)	164.7 (247)

[a] In parts per million relative to trifluoroacetic acid and to Me_4Si, respectively; downfield shifts are denoted as positive. [b] In hertz in parentheses. [c] s = singlet; q = quartet; d = doublet.

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change of the carbonyl stretching frequency (by up to 40 cm^{-1}),[10] whereas the formation of a bicyclic hemiaminal ether with an N—C bond length of 1.50 Å[11] results in an additional upfield shift of 84 ppm.[12] Within this frame of reference, the 105-ppm upfield shift observed for the adducts, e.g., **3**, indicates that one of the Dabco nitrogen atoms has moved to within bonding distance. This assignment is further supported by a comparison with the corresponding hydrate and methanolate[13] which have very similar chemical shifts (Table I).

The interaction between ketone and amine does not result in quantitative adduct formation as documented, for example, by the observation of two distinct ^{19}F resonances. The ratio of ketone to adduct signals shows the concentration and temperature dependence typical for an equilibrium. The NMR data gave a considerably better fit for the 1:1 adduct than for a species with other than 1:1 stoichiometry. These results may not completely eliminate the possibility of 2:1 adducts, particularly not for very high concentrations of one of the reactants, but they render them unlikely under the conditions of our experiments.

For the pair, trifluoroacetophenone-Dabco, the observed ratio of CF_3 resonances indicates an equilibrium constant, $K_{292} = 1.5$ L/mol, and the temperature dependence of the equilibrium constant between 257 and 337 K yields the thermodynamic parameters, $\Delta H^\circ = -9.3$ kcal/mol and $\Delta S^\circ = -32$ eu. The adducts of trifluoroacetophenone with 1-azabicyclo[2.2.2]octane (Abco) and triethylamine (TEA) are less stable than the adduct with Dabco, with equilibrium constants, $K_{292} = 0.6$ L/mol for the abco adduct and $K_{292} = 0.07$ L/mol for the TEA adduct. The reduced stabilities of these complexes precluded accurate determinations of ΔH° and ΔS° by the NMR method.

Thermodynamic parameters for all three adducts were determined calorimetrically by thermometric titration procedures[14] in acetonitrile solution.[15] The results follow: Dabco adduct, $K_{298.2} = 0.893$, $\Delta H^\circ = -9.03$ kcal/mol, $\Delta S^\circ = -30.5$ eu; Abco adduct, $K_{298.2} = 0.362$, $\Delta H^\circ = -8.73$ kcal/mol, $\Delta S^\circ = -31.3$ eu; TEA adduct, $K_{298.2} = 0.037$, $\Delta H^\circ = -8.66$ kcal/mol, $\Delta S^\circ = -35.6$ eu. On the basis of these results, an electronic stabilizing factor involving lone-pair interactions[16] in the Dabco complex is not discernible. The relative equilibrium constants of the Dabco and Abco adducts can be attributed to a statistical factor, whereas the much lower stability of the TEA complex can be ascribed to unfavorable steric factors.

Although the thermodynamic stabilities of the zwitterionic adducts are similar to those of molecular complexes such as the π complexes between aromatic hydrocarbons and ketones,[17] the NMR spectra of the two types of adducts reveal fundamental differences. The π molecular complexes show weighted averages of the chemical shifts of free and complexed reactants indicating that the barrier between the reactants and the complex is low and that the rate of equilibration is fast on the NMR time scale. In contrast, the observation of separate signals for the ketone and the zwitterionic adducts indicates that, in these systems, the rate of exchange is slow and the barrier between reactants and adduct is high. Further experiments are being carried out to investigate similar adducts in related systems and to determine the time scale of the association/dissociation processes.[18]

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Experimental Evidence for Nonsquare Cyclobutadiene as a Chemically Significant Intermediate in Solution

Sir:

After decades of dispute[1] most experimentalists and theoreticians now seem to agree on a D_{2h} (rectangular) singlet description for the ground state of cyclobutadiene. A crucial experiment leading to the new accord was the matrix isolation infrared study of Masamune et al.[1z] This work showed that cyclobutadiene and cyclobutadiene-d_4, prepared from a variety of precursors, had infrared spectra which were inconsistent with a D_{4h} equilibrium geometry but were consistent with a D_{2h} structure.

We felt that it would be desirable to obtain independent experimental support for nonsquare cyclobutadiene as a chemically significant[2] intermediate in solution. Such an experiment might be a progenitor to the determination of the energy difference between D_{2h} and D_{4h} geometries of singlet cyclobutadiene as well as serving to demonstrate that non-