adducts of triiodide, I_3^-, to linear polymer matrices. The properties and structures of these species were thoroughly discussed during the last years.[5-8] In Pd(dpg)$_2$I the matrix is built by the regularily arranged phenyl groups. The binding of I_3^- to this linear array seems to be much stronger than in the iodine–starch species. This is caused by the resulting positive charge on the linear chain of palladium ions—leading to a shortened palladium–palladium distance—and the negative charge of the linear I_3^- chain. The visible spectrum of the solid palladium complex resembles in all respects those found for the mentioned triiodide compounds.

There is one analytical proof of the suggested structure. The amounts of iodine and iodide can be determined by dissolving the complex Pd(dpg)$_2$I in hydrochloric acid. In this way the compound is decomposed without redox reactions. It is found by using copper(II) and thiosulfate in the conventional titrimetric method that these species actually contain iodide and that elementary iodine molecules and iodide ions are present in almost the same amount. This means the stoichiometry of I_3^- units can be established analytically.

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Concerning Contrasting Effects of Base Structure on Hydrogen-Bonded Ion-Pair and Hydrogen-Bonded Complex Formation[1]

Sir:

We have utilized the fluorine nuclear magnetic resonance (F nmr) shift, Δ, of the *p*-fluorobenzenesulfonate ion, measured in the polar aprotic solvent CH_2Cl_2, to scale (approximately) the electron densities with which the proton interacts in the conjugate acids of general bases (BH^+). The approximate scale of electron densities in general bases (B), at the site of hydrogen-bonded complex formation, has been previously obtained using the F nmr shifts of *p*-fluorophenol in CCl_4 solution.[2] The assumption is made that, in either our series of hydrogen-bonded ion pairs ($A^- \cdots {}^+HB$)[3] with *p*-FC$_6$H$_4$SO$_3^-$ or the corresponding series of hydrogen-bonded complexes ($AH \cdots B$)[3] with *p*-F$_6$H$_4$OH, the hydrogen bonding does not appreciably polarize or distort the scales of electron densities applicable for free BH^+ or B, respectively. This assumption, which is necessarily approximate, is based upon the relatively weak strength of the hydrogen-bonding interaction compared to the strength of covalent bonding. Our results indicate that there is a remarkable dependence of the potential energy gradient of the proton between $A\text{–}H \cdots B$ and $A^- \cdots HB^+_{(\text{solvated})}$ upon base structure.

Employing a variety of oxygen and nitrogen bases (similar to those for which critical differences were obtained in the work with *p*-FC$_6$H$_4$OH), the F nmr shifts of the 1:1 ion pair of the base with *p*-FC$_6$H$_4$SO$_3$H have been measured at 0.02 *M* concentration in CH_2Cl_2 solution at 25°. The shift of *p*-FC$_6$H$_4$SO$_3^-$ under the same conditions has been obtained using the crown ether complex[4] of the Na^+ salt. The hydrogen-bonded ion pairs are shifted 1.2–3.8 ppm to lower field strength than this *p*-FC$_6$H$_5$SO$_3^-$ salt. This magnitude of shifts is essentially the same as that observed in the formation of 1:1 hydrogen-bonded complexes with *p*-FC$_6$H$_4$OH.[2] However, the scale of bases for the F nmr shifts for the hydrogen-bonded ion-pair system is markedly different than that for the hydrogen-bonded complex system (for example, the former tends to give amine > pyridine > carbonyl compound, whereas the latter gives the reverse order[2]). Table I lists typical results for both systems.

Table I. *p*-Fluorobenzenesulfonic Acid Hydrogen-Bonded Ion Pairs

		Ion-pair formation		*p*-FC$_6$H$_4$-OH···B
Base	pK_A, H_2O	$-\Delta H°$, kcal	Δ,[a] ppm	Δ,[b] ppm
sym-Tetramethylguanidine	13.9	27.3	7.78	3.70
(*n*-Bu)$_3$N	10.9	25.8	7.36	2.50
Et$_3$N	10.8	24.9	7.25	2.66
4-Dimethylaminopyridine	9.6	23.3	7.46	3.37
C$_6$H$_5$CH$_2$NMe$_2$	8.9	21.5	6.96	2.34
(Allyl)$_3$N	8.3	21.4	6.94	2.10
4-Methylpyridine	6.0	16.6	6.92	2.70
CF$_3$CH$_2$NEt$_2$	(5.8)	16.1	6.62	(1.5)[d]
Pyridine	5.2	15.4	6.68	2.49
C$_6$H$_5$NMe$_2$	5.1	14.7	6.71	1.75
p-BrC$_6$H$_4$NMe$_2$	4.2	(13.7)	6.52	(1.6)[d]
3-Bromopyridine	2.8	11.7	6.18	1.99
m-NO$_2$C$_6$H$_4$NMe$_2$	2.6	(10.5)[c]	6.15	(1.1)[d]
Guaiazulene	1.4		(5.6)[e]	(1.2)[d]
p-NO$_2$C$_6$H$_4$NMe$_2$	0.6	(7.6)[c]	5.79	(0.7)
2,6-Dimethyl-γ-pyrone	0.4	5.5	5.83	2.98
Tetramethylurea	~0	6.4	5.68	3.00
N,*N*-Dimethylacetamide	−0.2	5.4	5.21	2.86

[a] Shifts relative to 0.02 *M* *p*-FC$_6$H$_4$SO$_3$Et in CH_2Cl_2 at 25°, which may be taken as essentially equal to those for internal *p*-FC$_6$H$_4$SO$_3$H. Shift for crown ether Na^+ complex of *p*-FC$_6$H$_4$SO$_3^-$ in CH_2Cl_2 is 8.8 ppm; "apparent per cent proton transfer" obtained for each ion pair as 100Δ/8.8. [b] *Cf.* ref 2. [c] Value estimated from the relationship $-\Delta H° = 0.82[-\Delta H°_{\text{TFA}}] - 5.9$, where $\Delta H°_{\text{TFA}}$ is the heat of ion-pair formation with trifluoroacetic acid in CH_2Cl_2 solution. This relationship has been confirmed in unpublished results for the other bases of this table. [d] Value estimated from results for analog compounds; *cf.* ref 2. [e] Obtained at −40° with excess base; value uncertain.

The upfield F nmr shifts (given in Table I) for the formation of the *p*-FC$_6$H$_4$SO$_3^-$ ion pairs from *p*-FC$_6$H$_4$SO$_3$H parallel quite closely the aqueous pK_A of the base (for bases with pK_A > 0, *cf.* Table I), whereas the shifts for formation of the *p*-FC$_6$H$_4$OH hydrogen-bonded complexes bear no simple correspondence to the pK_A values.[2] However, these latter shifts are well correlated[2] by pK_{HB} values, standard free-energy parameters

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(1) This work was supported in part by the Public Health Service. We also gratefully acknowledge the support of the National Science Foundation which made available the nmr spectrometer to the Chemistry Department.
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measuring the relative stabilities of the hydrogen-bonded complexes.[5] This empirical relationship (called the linear SEE equation) has been observed for a variety of kinds of chemical change in which the reaction centers are tagged by a p-FC_6H_4 group.[2] The relationship is interpreted as involving approximately linear relationships between the relative electron density changes at the reaction center and the corresponding changes in potential energy.[2]

To the extent that aqueous pK_A values may be taken as measures of the relative potential energies for nearly complete proton transfer to base in polar aprotic solvent,[6] the shifts for ion-pair formation with p-$FC_6H_4SO_3H$ may be anticipated (and are observed) to be parallel to pK_A values. Another estimator of the relative potential energy for nearly complete proton transfer is provided by the $\overline{\Delta H}^\circ$ value of the following reaction carried out in CH_2Cl_2 solution (the use of the ethyl acetate complex is needed to obtain solubility of the acid).

$$p\text{-}FC_6H_4SO_3H\cdots EtOAc + B \rightleftharpoons p\text{-}FC_6H_4SO_3^-\cdots HB^+ + EtOAc$$

We have measured $\overline{\Delta H}^\circ$ values utilizing the method of Arnett,[7] in which dilute base solution is injected into a solution with approximately a 20-fold excess of acid. The $\overline{\Delta H}^\circ$ value obtained does depend upon the acid–base ratio since this influences the solvation of the ion pair (by hydrogen bonding and other solvation interactions).[8] However, relative values of $\overline{\Delta H}^\circ$ obtained under essentially identical conditions may be accepted as approximately quantitative measures of the relative potential energy changes. Table I shows that $\overline{\Delta H}^\circ$, pK_A, and ion-pair Δ values are all three quite parallel.

We believe the results of Table I support strongly the premise[5] that the markedly different extents of apparent proton transfer[9] in the hydrogen-bonded complexes ($<\sim 30\%$) and the hydrogen-bonded ion pairs ($>\sim 65\%$) are predominantly responsible for different base scales against proton donors (*i.e.*, the different extents of proton transfer introduce important differences in the effective nuclear charges acting on the bonding electrons). This interpretation is indicated by the fact that the close parallelism between pK_A, $\overline{\Delta H}^\circ$, and Δ values for our hydrogen-bonded ion-pair systems is not upset by the presence of hydration effects in pK_A values. It therefore is unlikely that the hydration effects on pK_A are the predominant cause for the lack of any single generalized correlation of Δ and pK_{AB} values for the corresponding p-$FC_6H_4OH\cdots B$ complexes with pK_A values.[10] Studies on the role of solvation on the mobile equilibria between hydrogen-bonded complexes and hydrogen-bonded ion pairs are in progress, as well as applications of these equilibria to proton-transfer kinetics.[11]

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[10] The alternate interpretation is also inconsistent with the observation that the F nmr shifts of 0.01 M p-FC_6H_4OH in binary H_2O mixtures of either 0.70- or 0.50-mol fractions of H_2O are in the same unique (non-pK_A) order as the Δ values in CCl_4 solution,[2] *i.e.*, pyridine < DMA < HMPA (unpublished results of Dr. L. Joris. We are indebted to Professor V. Gold for suggesting this experiment).

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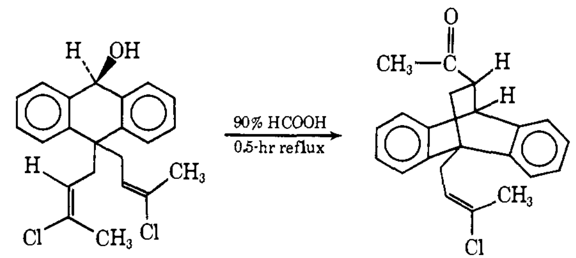
Intramolecular Alkylation of Internal Chloro Olefins. A Facile Route to the D Ring in 20-Keto Steroids

Sir:

We recently demonstrated that intramolecular electrophilic attack upon 2-chloro-1-ene side chains constitutes a general method for cycloalkanone synthesis[1] and also noted that internal chloro olefins provide entry to cycloalkyl ketones.[1] This report illustrates how acetylcycloalkanes can be quickly assembled from 1,3-dichloro-2-butene and the homologous 2,5-dichloro-2-pentenes.[2] A particularly relevant illustration of the power of this approach in organic synthesis is the direct assembly of the trans-fused 1-acetyl-8-methylhydrindan system, exemplified in the transformation **11** → **12** below, which promises to have broad utility in construction of the C/D hydrindan system of steroids.[3]

Typical of the value of 1,3-dichloro-2-butene (**1**) as an annelating agent is the efficient cyclization of **2**,[4,5] mp 104–106°, prepared by alkylation of anthrone with excess **1** and subsequent lithium aluminum hydride reduction, to **3**[4] in 92% yield. A noteworthy feature of this reaction[6] is retention in **3** of an *un-*



2 **3**

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[4] Characterized fully by (a) satisfactory nmr, ir, uv, and mass spectral analyses where appropriate and (b) elemental analysis.

[5] Most vinyl chlorides used in this work are a cis–trans mixture, which can be used without separation since neither geometric isomer derived therefrom offers any substantial advantages in the ring-forming step.

[6] Vicinal coupling of the bridgehead proton (δ 4.6 ppm, J = 2.5 Hz) in **3**, which disappears upon deuteration with base, confirms that a transannular allylic shift (from C_9 to C_{10}) did *not* preceed cyclization. Had this been the case (interchange bridgehead groups in structure **3**), the bridgehead proton would be split at least into a triplet, with no