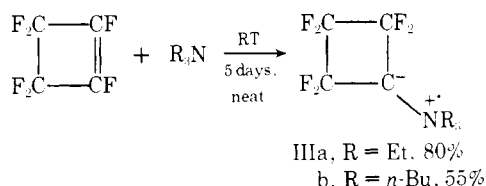
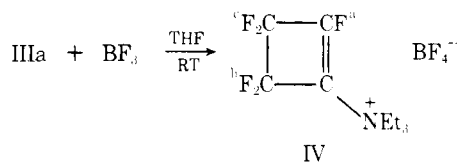


adjacent difluoromethylene groups toward stabilization of I.

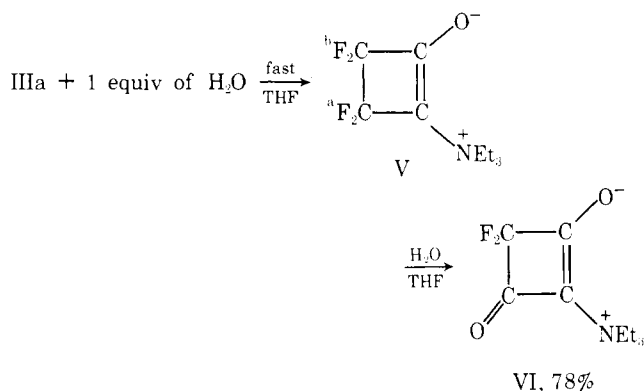
We now wish to report the first example of an isolable fluorinated carbanion uncomplicated by $d\pi-p\pi$ types of interactions. When I is allowed to react with trialkylamines, the stable polyfluorinated carbanion, the trialkylammonium-2,2,3,3,4,4-hexafluorocyclobutane ylide (III), is formed. Ylide



IIIa is a pale yellow, moisture-sensitive solid, which, except for the one missing doublet splitting (due to phosphorus), shows a ^{19}F NMR spectrum similar to that of I.⁷ It exhibits two sets of multiplets at ϕ^* 85.5 (rel area 2) and 122.4 ppm (rel area 1).⁸ The spectroscopic data is only consistent with the ylide structure III. It is totally inconsistent with the earlier suggested ammonium salt structures for the products of these reactions.⁹ A derivative of the cyclobutenylammonium structure was prepared for spectroscopic comparison purposes. For example, when IIIa was treated with boron trifluoride etherate, 1-(pentafluorocyclobutenyl)triethylammonium tetrafluoroborate (IV) was formed in quantitative yield. Salt IV is a moisture-sensitive solid which exhibits the following ^{19}F NMR spectrum, ϕ^* 95.8 (rel area 1, F^a), 112.4 (rel area 2, F^b), 119.2 (rel area 2, F^c), and 153.3 ppm (rel area 4, BF₄⁻), in agreement with the postulated structure.



The hydrolysis of IIIa can be carried out sequentially to give either a mono (V)¹⁰ or bis (VI)¹¹ hydrolysis product. Compound VI is identical with the hydrolysis product isolated by Rapp,¹² providing corroborative evidence that our compound III is the same as reported earlier.



Confirmation of our spectroscopic conclusions above has been recently provided by an x-ray structural determination of IIIb.¹³ The x-ray determination unequivocally shows the ylidic structure, rather than the ammonium salt, to be the correct representation of III. To our knowledge, III is the first reported example of a stable halogenated nitrogen ylide and the first example of a stable fluorinated carbanion system stabilized only by inductive effects.

The ease of formation and stability of III suggests that other related polyfluorinated carbanion systems may be similarly formed and exhibit inherent stability, even in the absence of

any $d\pi-p\pi$ stabilization.¹⁴ Sufficient inductive stabilization can decrease the ease of the usually favored β -elimination process and permit the formation and isolation and study of unusual carbanion systems. Our work continues to explore these unusual elusive carbanions.

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- (6) The phosphorus-carbon bond length of 1.713 Å² was indicative of $d\pi-p\pi$ overlap. When halogens other than fluorine were substituted at the position α to the ylide carbon, the stability of the ylide decreased, suggesting that partial stabilization came from the α -difluoromethylene groups.
- (7) Ylide I exhibits two sets of signals in the ^{19}F NMR at ϕ^* 86.9 (4 F) and 124.6 ppm (2 F).
- (8) Ylide IIIb shows a similar ^{19}F NMR pattern at ϕ^* 84.1 (4 F) and 122.8 ppm (2 F).
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Received March 29, 1977

Comments on Entropy Change in Ion-Molecule Equilibria

Sir:

In recent years, many investigators have reported quantitative information about the thermochemistry of ion-molecule reactions based on the observation of ion-molecule equilibria in high pressure or ion cyclotron resonance mass spectrometers. Such equilibria have been observed in systems in which hydride transfer,¹ proton transfer,² and charge transfer³ reactions occur reversibly. In some of these investigations, the equilibrium constant is determined as a function of temperature, thus giving an experimental determination of the entropy change for the reaction. Thus a value for the enthalpy can be obtained:

$$-RT \ln K_{\text{eq}} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

However, in many studies, K_{eq} is determined at a single temperature only. In many such investigations the results are interpreted in terms of enthalpy changes by making the assumption that the entropy change is zero, or can be estimated entirely on the basis of the differences in symmetry, moments of inertia, vibrational frequencies, and degeneracies of the electronic states of the reactant and product species. On this basis, scales of "proton affinities" and scales of "adiabatic ionization potentials" have been reported which often have an estimated accuracy of ± 0.1 or 0.2 kcal/mol (1 kcal/mol = 4.18 kJ = 0.043 eV). In this communication, it will be shown that, when eq 1 is used for the derivation of thermodynamic information from ion-molecule equilibrium constants, terms must be included to account for the effects of the intermolecular forces experienced by the ions and molecules which undergo reaction. The contribution to the entropy change due to the

Table I. Rate Constants of Charge Transfer in the Exothermic Direction in Charge-Transfer Equilibria

	cm ³ /molecule s × 10 ¹⁰				Ref
	<i>K</i> _{eq}	<i>k</i> _f	<i>Z</i> _f ^a	<i>T</i> , °C	
NO ⁺ + C ₆ D ₆ ⇌ C ₆ D ₆ ⁺ + NO	119.0	14.3	16.0	350	This work ^b
C ₆ H ₆ ⁺ + C ₆ H ₅ Cl ⇌ C ₆ H ₅ Cl ⁺ + C ₆ H ₆	28	17	15	410	3d
c-C ₄ H ₄ O ⁺ + C ₆ H ₅ CH ₃ ⇌ C ₆ H ₅ CH ₃ ⁺ + C ₄ H ₄ O	12.6	12.8	13.2	350	This work ^b
C ₆ H ₅ CH ₃ ⁺ + C ₆ H ₅ C ₂ H ₅ ⇌ C ₆ H ₅ C ₂ H ₅ ⁺ + C ₆ H ₅ CH ₃	5.3	12.8	12.6	350	This work ^b
C ₆ H ₅ CF ₃ ⁺ + C ₆ F ₅ H ⇌ C ₆ F ₅ H ⁺ + C ₆ H ₅ CF ₃	3.5	11.6	11.1	350	This work ^b
C ₆ H ₅ F ⁺ + <i>p</i> -C ₆ H ₄ F ₂ ⇌ C ₆ H ₄ F ₂ ⁺ + C ₆ H ₅ F	3.5	10.2	10.4	350	This work ^b

^a Calculated from equations listed in ref 6. Values of α and μ_D taken from ref 8. ^b Determined in the NBS pulsed ICR mass spectrometer using the double-resonance ion-ejection technique. Accuracy: $\pm 15\%$.

Table II. Rate Constants of Charge Transfer in the Endothermic Direction in Charge-Transfer Equilibria

	cm ³ /molecule s × 10 ¹⁰			kcal/mol ^a	
	<i>k</i> _r ^b	<i>Z</i> _r ^c	<i>k</i> _r = <i>Z</i> _r <i>e</i> ^{−ΔH(Lit.)/<i>RT</i>}	$\Delta H = RT \ln (k_f/Z_r)$	ΔH , lit. ^d
c-C ₄ H ₄ O ⁺ + C ₆ H ₅ CH ₃ ⇌ C ₆ H ₅ CH ₃ ⁺ + c-C ₄ H ₄ O	1.0	9.8	0.9	−1.4	−1.4
C ₆ H ₅ F ⁺ + <i>p</i> -C ₆ H ₄ F ₂ ⇌ <i>p</i> -C ₆ H ₄ F ₂ ⁺ + C ₆ H ₅ F	2.4	13.6	2.0	−1.0	−1.1
1,2,4,5-C ₆ H ₂ F ₄ ⁺ + NO ⇌ NO ⁺ + 1,2,4,5-C ₆ H ₂ F ₄	1.3	15.0	1.2	−1.5	−1.5
C ₆ H ₅ CH ₃ ⁺ + C ₆ H ₅ C ₂ H ₅ ⇌ C ₆ H ₅ C ₂ H ₅ ⁺ + C ₆ H ₅ CH ₃	2.0	11.8	1.7	−1.1	−1.1
C ₆ H ₅ CH ₃ ⁺ + 4-FC ₆ H ₄ CH ₃ ⇌ 4-FC ₆ H ₄ CH ₃ ⁺ + C ₆ H ₅ CH ₃	2.8	11.7	3.0	−0.86	−0.81

^a 1 kcal/mol = 4.18 kJ = 0.043 eV. ^b Determined in the NBS pulsed ICR mass spectrometer using the double-resonance ion-ejection technique. Accuracy: $\pm 15\%$. ^c Calculated from equations listed in ref 6. Values of α and μ_D taken from ref 8. ^d Reference 9.

Table III. Comparison of Experimentally Determined Entropy Changes with Those Calculated from $\Delta S_{\text{coll}} = R \ln (Z_f/Z_r)$

	ΔS_{exp} , eu	ΔS_{coll} , ^a eu	Ref
C ₆ H ₅ Br ⁺ + C ₆ H ₅ I ⇌ C ₆ H ₅ I ⁺ + C ₆ H ₅ Br	−0.7	0.0	3d
C ₆ H ₅ Br ⁺ + C ₆ H ₅ CH ₃ ⇌ C ₆ H ₅ CH ₃ ⁺ + C ₆ H ₅ Br	−2	−0.5	3d
C ₆ H ₅ CH ₃ ⁺ + 1,2-C ₆ H ₄ (CH ₃) ₂ ⇌ 1,2-C ₆ H ₄ (CH ₃) ₂ ⁺ + C ₆ H ₅ CH ₃	+2	+0.2	3d
1,2-C ₆ H ₄ (CH ₃) ₂ + C ₆ H ₅ OCH ₃ ⇌ C ₆ H ₅ OCH ₃ ⁺ + 1,2-C ₆ H ₄ (CH ₃) ₂	+2	+0.2	3d
1,3,5-C ₆ H ₃ (CH ₃) ₃ ⁺ + C ₆ H ₅ OCH ₃ ⇌ C ₆ H ₅ OCH ₃ ⁺ + 1,3,5-C ₆ H ₃ (CH ₃) ₃	+2	+0.2	3d
CS ₂ ⁺ + C ₆ H ₅ CN ⇌ C ₆ H ₅ CN ⁺ + CS ₂	+2	+2.0	3d
H ₃ O ⁺ + H ₂ S ⇌ H ₃ S ⁺ + H ₂ O	−1.0 ± 0.4	−0.4	2a
C ₂ H ₅ OH ₂ ⁺ + HCO ₂ CH ₃ ⇌ H ₂ CO ₂ CH ₃ ⁺ + C ₂ H ₅ OH	+0.1 ± 0.4	+0.1	2a

^a Calcd: $\Delta S_{\text{coll}} = R \ln (Z_f/Z_r)$. *Z*_f and *Z*_r were calculated using equations listed in ref 6. Values of α and μ_D taken from ref 8.

intermolecular interactions can be estimated from the ratio of the ion–molecule collision rates in the forward and reverse directions. This contribution is small (≤ 3 eu), but is usually ignored and often results in a net change in the calculated enthalpy which is greater than the claimed accuracy.

The existence of such a term in the entropy is inevitable if one expresses the forward and reverse rate constants in terms of collision theory, as is noted in many textbooks.⁴ That is, if the rate constant of a bimolecular reaction is

$$k = ZPe^{-E/RT} \quad (2)$$

where *Z* is the rate constant for collision of the reacting pair, *P* is a probability that a collision will be reactive when the exponential terms approaches unity, and *E* is an energy barrier, then the equilibrium constant, *K*_{eq}, must be equal to

$$K_{\text{eq}} = \frac{k_f}{k_r} = \frac{Z_f P_f e^{-E_f/RT}}{Z_r P_r e^{-E_r/RT}} = \frac{Z_f P_f}{Z_r P_r} e^{-(E_f - E_r)/RT} = e^{\Delta S/R} e^{-\Delta H/RT} \quad (3)$$

(where the subscript f refers to the forward or exothermic direction of reaction, and the subscript r refers to the reverse or endothermic direction). Then, since $e^{-(E_f - E_r)/RT}$ can be equated to $e^{-\Delta H/RT}$ (for ion–molecule reactions, *E*_f is usually

zero and *E*_r is just $-\Delta H$), it follows that

$$\Delta S = R \left[\ln \frac{Z_f}{Z_r} + \ln \frac{P_f}{P_r} \right] \quad (4)$$

In the case of ion–molecule reactions, there are numerous examples in the literature⁵ of reactions for which *P* is close to unity. That is, for many exothermic ion–molecule reactions *k*_f = *Z*_f, within experimental error. For ion–molecule collisions, the collision rate constants, *Z*, can be readily calculated.⁶ Table I shows that, even under conditions such that the reaction in the reverse direction can occur, *P* may be unity. Table II shows that *P* may be unity in the endothermic direction also, so that in many ion–molecule equilibria the enthalpy of reaction may be predicted simply from the rate constant of the reverse reaction.

This implies that eq 4 is valid for ion–molecule reactions. The results given in Tables I and II demonstrate that it is not the case that the mechanism of the equilibrium might include some compensating occurrence such that the ratio *Z*_f/*Z*_r in eq 3 and 4 would be effectively cancelled by components of the ratio *P*_f/*P*_r.

Thus it can be concluded from these results that, in any ion–molecule equilibrium in which the entropy is not experimentally determined, the estimation of the intermolecular

entropy term can be based on the term $R \ln (Z_f/Z_r)$. Most calculations of entropy changes in ion-molecule equilibria have been based on ratios of partition functions expressing the distributions of internal energy in the separated reactant and product species. These partition functions are derived from a model of the system which assumes that interactions, such as those taken into account in calculating Z_f and Z_r , do not exist. The inclusion of a term $R \ln (Z_f/Z_r)$ in the entropy merely reflects the fact that, in the particular case of equilibria involving ions, such interactions do play a role. According to thermodynamics, the calculation of ΔS from statistical mechanics involves two parts, that arising from the ratios of internal partition functions (the "ideal" contribution) and that arising from the effects of the intermolecular forces on the configuration integral. The latter contribution is generally expressed in terms of the fugacity, which is usually derived from the experimentally observed pressure-volume-temperature relationships of a gas or from van der Waals constants. Obviously the fugacities of ions are not experimentally accessible in these ways. However, a calculation⁷ of the contribution to ΔG° by intermolecular interactions is based on a consideration of the same potential functions which are the basis for the calculation of Z . Hence, it is to be expected that a statistical mechanical derivation of ΔS for ion-molecule equilibria would result in expressions which are equivalent to those derived here from kinetic considerations.

Table III lists some values of ΔS which are derived from the results of Meot-Ner and Field,^{3d} who determined ΔG° for charge-transfer equilibria in aromatic systems at 450 and 600 K. Since the changes in ΔG° over this temperature range are small (± 0.3 kcal/mol), these authors concluded that the entropy change for charge-transfer equilibria in these systems is zero. The comparisons shown in Table III demonstrate that, for all the reaction pairs studied by those authors in which there should be no other contributions to the entropy, the sign of the entropy change is always correctly predicted from the collision contribution. (In these measurements the experimental error is of approximately the same magnitude as the entropy change being determined.) Table III also shows the only entropy determinations in the literature^{2a} for proton-transfer equilibria in which it is predicted there should be no other contributions to the entropy change. The collision contribution correctly predicts the sign and approximately the magnitude of the measured entropy change.

Acknowledgment. The authors would like to acknowledge helpful conversations with Dr. Robert N. Goldberg, Mr. Donald D. Wagman, Dr. David Garvin, Dr. J. L. Beauchamp, Dr. C. E. Klotz, and Dr. William Saunders. They would also like to thank Drs. M. Meot-Ner and F. Field for access to their data before publication.

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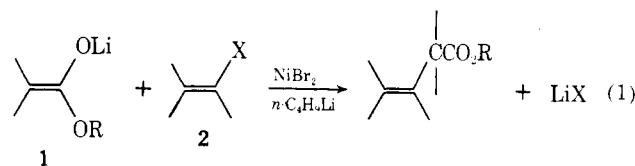
Received February 21, 1977

A Nickel Catalyst for the Arylation and Vinylation of Lithium Ester Enolates

Sir:

α -Aryl and α -vinyl carbonyl groupings are structural features of a large number of biologically important molecules. A method for the direct arylation or vinylation of enolate anions would greatly simplify the synthesis of such molecules. Progress to this goal has been reported by a number of workers,¹ with perhaps the most promising approach to date being the trapping of photogenerated aryl radicals with ketone enolates (the $S_{RN}1$ reaction).²

We wish to report that the addition of *n*-butyllithium to suspensions of nickel(II) bromide in tetrahydrofuran (THF) at dry ice temperature forms material which catalyzes an efficient substitution reaction of lithium ester enolates (**1**) with aryl or vinyl halides (**2**) (eq 1). The reaction occurs with clean



retention of stereochemistry at the halogen-bearing carbon, as judged from results obtained with the configurational isomers of β -bromostyrene (eq 2, 3).³

The reaction with the lithium enolate of ethyl crotonate (**5**) occurs at the γ carbon to give chain extended vinylation or

