stants calculated by the method of nonlinear least squares[7] and presented in Table II have standard deviations of 6%. Product analysis by glpc–proportional-flow counting showed that III was the only peak to contain radioactivity.

Table II. Kinetic Data for Tritium Incorporation Rates into 1H-Undecafluorobicyclo[2.2.1]heptane in Sodium Methoxide–Methanol Solution

Run no.	[NaOMe] × 10^2, M^a	Temp,^{b} °C	$10k_2$, M^{-1} $sec^{-1\,c}$
149	0.10	−23.0	*d*
167	0.24	−44.7	5.7
180	0.25	−44.9	9.1
228	1.1	−52.9	2.89
222	5.3	−63.5	0.80
190	5.2	−63.5	0.93
218	5.3	−74.1	0.124

[a] Substrate concentration 0.003 to 0.021 *M*. [b] ±0.2°. [c] ±6%; corrected for the variation of the density of methanol with temperature. [d] Complete isotopic equilibration in less than 3.3 min.

The extreme reactivity of compound III is shown by complete isotopic exchange in less than 4 min at −23° with 0.001 *N* base. Least-squares activation parameters calculated to be $\Delta H^* = 12.4 \pm 0.2$ kcal/mole and $\Delta S^* = -3.7 \pm 1.1$ eu allow comparison with the exchange rates determined by Andreades.[4] From the results summarized in Table I it is to be noted that compound III is some five times *more* reactive than tris(trifluoromethyl)methane.[8] This comparison provides important evidence that carbon–fluorine no-bond resonance does not provide significant stabilization in tris(trifluoromethyl)methyl anion and, consequently, that such hyperconjugation is probably without significance in the other systems to which the concept has been applied. The relative stability of these fluorinated carbanions undoubtedly derives largely from an inductive field effect.[9] This comparison also suggests that tris(trifluoromethyl)methyl anion has a pyramidal rather than a planar structure; it is noteworthy that tris(trifluoromethyl)amine has a pyramidal structure about the nitrogen.[10]

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(7) We are indebted to Professor D. F. DeTar, Florida State University, for making available to us a copy of his LSKIN1 computer program.

(8) Tritium was used in the present study. Andreades employed deuterium. Isotope effects do not alter the significance of the arguments presented.

(9) A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **89**, 693 (1967).

(10) R. L. Livingston and G. Vaughan, *ibid.*, **78**, 4866 (1956).

(11) Woodrow Wilson Fellow, 1964–1965; National Science Foundation Predoctoral Cooperative Fellow, 1965–1967; Eastman Kodak Science Award, 1966.

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Acidity of Hydrocarbons. XXIV. Proton Exchange of 9-Substituted Fluorenes with Methanolic Sodium Methoxide. Stabilization of 9-Trifluoromethylfluorenyl Anion by Inductive Effects

Sir:

Interaction mechanisms of fluorine substituents are of particular interest. In the accompanying paper[1] we have presented evidence that hyperconjugation effects are not important in stabilizing fluoroalkyl anions. In the present paper we demonstrate that normal inductive field effects suffice to rationalize the relative stability of 9-trifluoromethylfluorenyl anion. Protodetritiation kinetics were run in methanolic sodium methoxide of several 9-substituted 9-tritiated fluorenes including that from 9-trifluoromethylfluorene (I). This compound is reported in the literature as the product in 7.5% yield from the treatment of diphenyltrifluoromethylcarbinol with sulfuric acid at room temperature,[2] but this product was characterized only by a melting point, 170.5–171°. We find the cyclodehydration to be more satisfactory in polyphosphoric acid at 120–130° for 1.5 hr, but the product recrystallized in quantitative yield from petroleum ether has mp 95.5–96.5°.[3] The nmr spectrum (CCl_4) shows a complex multiplet in the aromatic region, τ 2.25–3.00 (8 H), and a well-defined quartet at τ 5.66 with $J_{HF} = 9$ cps (1 H). This evidence together with the molecular weight (calcd, 234; found (osmometry), 222) confirms the structure of I; the compound isolated by Kaluszyner and Cohen[2] is something else. Tritium was incorporated into the 9 position to give I-*t* by treatment with pyridine containing tritium-enriched water. The product of a similar reaction with D_2O showed the aromatic multiplet of the nmr unchanged but the methine quartet was absent.

The exchange reaction of I-*t* with methanolic sodium methoxide was self-quenching; from the reaction mixture there was isolated 9-trimethoxymethylfluorene, colorless needles, mp 130.0–131.5°,[3] but only if the reaction mixture was rigorously anhydrous. With traces of water the reaction product was methyl 9-fluorenecarboxylate. Protodetritiation kinetics were obtained by using excess base (pseudo zero order in sodium methoxide) at low temperature with the experimental conditions of the preceding paper.[1] The following reaction mechanism is indicated, but only the rate of the first step is important in the present context. The results summarized in Table I lead to the activation parameters, $\Delta H^* = 12.3 \pm 0.2$ kcal/mole and $\Delta S^* = -15.6 \pm 0.9$ eu.

Protodetritiation kinetics of the other 9-substituted fluorenes were normal and were followed by conventional liquid scintillation counting methods. The relative rates are summarized in Table II.

The logarithms of the relative rates for the 9-substituted fluorenes are plotted against the p*K*'s of the corresponding acetic acids in Figure 1. An equivalent plot can be constructed *vs.* σ_I of the substituents with the same results. Only the compounds with tertiary hydrogens are plotted; fluorene itself, in which the exchangeable hydrogens are secondary, is omitted but

(1) A. Streitwieser, Jr., and D. Holtz, *J. Am. Chem. Soc.*, **89**, 692 (1967).

(2) A. Kaluszyner and S. Cohen, *Tetrahedron*, **11**, 252 (1960).

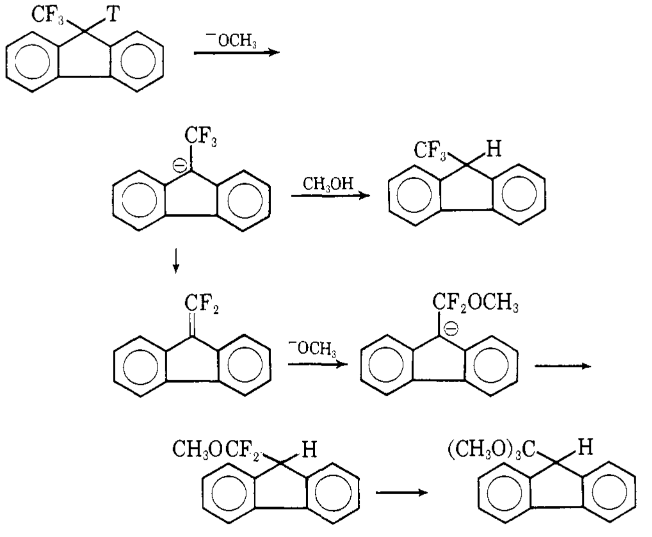
(3) All new compounds in this paper have satisfactory analyses.

Table I. Protodetritiation of 9-Trifluoromethylfluorene-9-*t*

[I-t], N	[NaOMe], N	Temp, °C	10^4k_1, sec^{-1}	10^3k_2,[a] l. mole^{-1} sec^{-1}
0.00421	0.143	−31.5 ± 0.3	20.9 ± 0.3	14.6 ± 0.2.
0.00421	0.262	−31.0 ± 0.1	44.2 ± 0.6	16.9 ± 0.2
0.00427	0.145	−45.3 ± 0.4	4.55 ± 0.02	3.13 ± 0.11
0.00427	0.266	−45.0 ± 0.1	9.02 ± 0.10	3.39 ± 0.37
		45		9700[b]

[a] At the reaction temperature; that is, k_2 is corrected for solvent contraction from room temperature. [b] Extrapolated from data at lower temperatures.

its inclusion would not alter the conclusions. A line drawn through the hydrocarbon substituents passes rather close to the point for the trifluoromethyl substituent. Because of the reactivity differences long extrapolations are required. The methoxymethyl group deviates significantly from the line, but this value is the result of a single kinetic run. The present conclusion does not change significantly if we draw the best line to include the methoxymethyl group. Because of the importance of the correlation line in defining the magnitude of inductive effects in the exchange reactions of 9-substituted fluorenes, we expect to define it more precisely with additional compounds and measurements. Nevertheless, the present data suffice to establish that the trifluoromethyl group does not produce reactivity significantly in excess of that expected from inductive effects alone. In particular, there is no room in these results for any significant contribution from C–F anionic hyperconjugation.



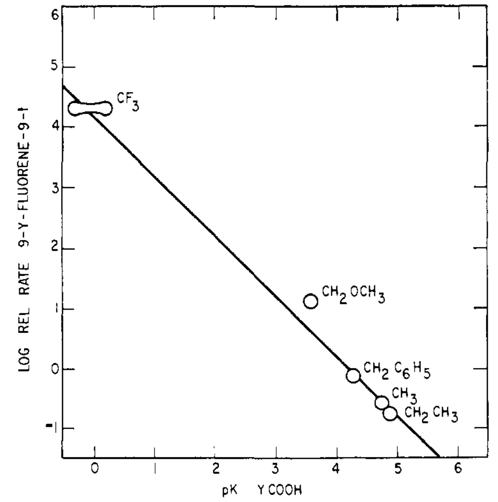


Figure 1. Comparison of kinetic acidities of 9-substituted fluorenes with the acidities of the corresponding substituted acetic acids.

Table II. Protodetritiation of 9-Substituted Fluorenes in Methanolic Sodium Methoxide at 45°

9-Substituent, Y	k_{rel}[a]	pK[b] YCOOH
H	1.00	...
CH_3	0.26	4.76
CH_3CH_2	0.18	4.88
$CH_2C_6H_5$	0.72	4.31
CH_2OCH_3	12.9	3.57[c]
CF_3	2 × 10^4	−0.26, + 0.23

[a] k_2 for fluorene-9-*t* is (43.2 ± 1.5) × 10^{-5} l. mole^{-1} sec^{-1}. We are indebted to R. A. MacQuarrie, R. I. Sadayasu, J. S. Wright, and Dr. T. L. Kruger for individual kinetic runs. [b] J. F. King in "Technique of Organic Chemistry," Vol. XI, Part 1, K. W. Bentley, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 317. [c] E. J. King, *J. Am. Chem. Soc.*, **82**, 3575 (1960).

This study and that of the preceding paper[1] are independent and involve different assumptions and logic, but lead to the same conclusion; taken together they provide compelling evidence for the absence of fluorine hyperconjugation as a significant stabilizing phenomenon in fluoroalkyl anions.

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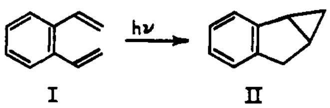
Photochemical Rearrangement of *o*-Divinylbenzene

Sir:

As a result of our interest in $C_{10}H_{10}$ compounds containing an aromatic ring fused to a system containing a small ring[1] we decided to examine a possible route to one or more of these by a photochemical rearrangement of *o*-divinylbenzene (I). When a solution of I, pre-



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(1) M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966).