to the 9 position on either face of I without ever becoming completely detached from the anion. A similar *conducted tour mechanism* was previously formulated for isoracemization of certain carbon acids by amines through ion-pair intermediates in nondissociating solvents.[6]

A k_e/k_α value of 1.00 ± 0.05 was found for the partial racemization and exchange of I-D_+ in *t*-butyl alcohol and potassium phenoxide under the conditions reported in Table I. Since isoinversion (k_3) is a contributor to the mechanism, exchange must have taken place with a small amount of net retention to balance fortuitously the isoinversion and give over-all lack of stereospecificity. In both solvent–base systems studied, only a small fraction of I may be said to react by distinctly stereospecific processes. Most of the reaction proceeds either by a delicate balance between exchange with retention and inversion or more likely by nonstereospecific processes of exchange with total racemization.

These results and the attendant hypotheses point to the possibility that in many cases of base-catalyzed hydrogen–deuterium exchange experiments of carbon acids, k_e/k_α values may reflect blends of isoracemization and exchange with retention, total racemization, or even inversion. The techniques described in these communications provide methods for differentiation. The present results leave undemonstrated an unambiguous case where inversion with exchange exceeds retention with exchange.

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[6] D. J. Cram and L. Gosser, *J. Am. Chem. Soc.*, **86**, 2950, 5457 (1964).

[7] National Science Foundation Trainee at UCLA, 1965–1966.

Warren T. Ford,[7] Edward W. Graham, Donald J. Cram
Contribution No. 2014, Department of Chemistry
University of California at Los Angeles
Los Angeles, California 90024
Received December 1, 1966

Acidity of Hydrocarbons. XXIII. Base-Catalyzed Proton Exchange of 1H-Undecafluorobicyclo[2.2.1]heptane and the Role of Carbon–Fluorine No-Bond Resonance

Sir:

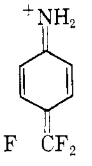
The relatively large effect of perfluoroalkyl groups on chemical reactivity has long been appreciated by numerous workers. In addition to a normal electron-attracting inductive field effect, a conjugative interaction mechanism involving carbon–fluorine no-bond resonance (hyperconjugation) has been invoked frequently. Roberts[1] has suggested that I is an important contributing resonance structure of *p*-trifluoromethylaniline on the basis of dipole moment and p*K* data. Pauling[2] and Hine[3] have used related concepts in interpreting various bond lengths and solvolytic reactivities of polyhalogenated compounds. Andreades[4] obtained the relative rates in Table I for hydrogen–deuterium exchange of polyfluoroalkanes with sodium methoxide in methanol-*d*.

Inductive effects alone were considered to be insufficient to account for the large differences in reactivity; these differences were rationalized instead in terms of stabilization of the intermediate carbanion by a hyperconjugative effect, II.

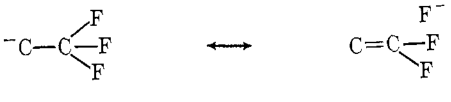
Table I. Relative Rates for Isotopic Exchange[a]

Substrate	Relative rate
CF_3H[b]	1
$CF_3(CF_2)_6H$[b]	6
$(CF_3)_2CFH$[b]	2×10^5
$(CF_3)_3CH$[b]	10^9
1H-Undecafluorobicyclo-[2.2.1]heptane (III)	5×10^9

[a] In sodium methoxide–methanol solution. [b] Reference 4.

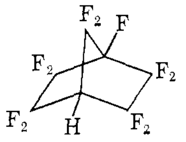


I



II

One operational criterion for testing the presence of such hyperconjugation is the conformational requirement that the C–F bond overlap significantly with the orbital to which it is to be hyperconjugated. Andreades[4] has suggested the use of a bridgehead system to test the importance of hyperconjugation; one useful molecule of this type, 1H-undecafluorobicyclo[2.2.1]heptane (III), has recently been synthesized.[5] The carbanion intermediate in base-catalyzed exchange of the bridgehead proton is forced to remain pyramidal, and hyperconjugation of the type in II is greatly reduced by Bredt's rule. Consequently, the role of inductive effects is enhanced, and if such hyperconjugation is an *important* factor is stabilizing tris(trifluoromethyl)methyl anion, base-catalyzed proton exchange of tris(trifluoromethyl)methane should be orders of magnitude faster than that of III.[6]



III

The base-catalyzed exchange rates for the replacement of hydrogen for tritium in III were measured in methanol-*t* with sodium methoxide as catalyst in the temperature range −23 to −74°. Each kinetic point was a separate experiment performed in a 3-ml test tube by smashing a fragile bulb containing methanol-*t* into the temperature-equilibrated solution of III in methanolic sodium methoxide. At an appropriate time the kinetic point was quenched with a precooled solution of toluenesulfonic acid in methanol, worked up, and analyzed by normal liquid scintillation counting techniques. Usually four points plus two infinity determinations were made for each run. Rate con-

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[1] J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, 72, 408 (1950).

[2] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 314–316.

[3] J. Hine and R. J. Rosscup, *J. Am. Chem. Soc.*, **82**, 6115 (1960).

[4] S. Andreades, *ibid.*, **86**, 2003 (1964).

[5] S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 21, 2997 (1965). Note that these authors have shown that the bridgehead anion can be generated from III and used synthetically.

[6] The most serious weakness of this argument is that III may have enhanced acidity because of increased s character in the C–H bond derived from ring strain effects on the norbornane structure. A correlation between kinetic acidity and $J_{C^{13}-H}$ in this laboratory indicates that the bridgehead hydrogen of norbornane itself has enhanced reactivity by two orders of magnitude.

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] $\times 10^2$, 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.

A. Streitwieser, Jr., David Holtz[11]
Department of Chemistry, University of California
Berkeley, California 94720

Received September 24, 1966

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

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[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.