

hexane afforded colorless crystals, mp 109–111 °C.

Anal. Calcd for C₁₅H₁₂BrCl₃O₃S: C, 39.28; H, 2.63. Found: C, 39.20; H, 2.80.

Isopropyl Tosylate. The compound was prepared as previously described.¹¹

Isopropyl Brosylate. The compound was prepared by the usual method.¹²

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Registry No.—CF₃CO₂H, 76-05-1; H₂SO₄, 7664-93-9; 1-(*o*-chlorophenyl)-2,2-dichloro-1-propanol, 355996-56-6.

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Equilibria in Reactions of Fluorocarbon Olefins, Imines, and Ketones with Fluoride Ion

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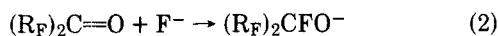
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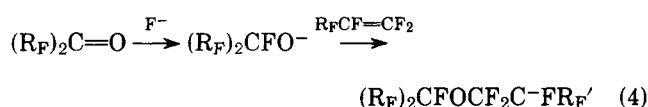
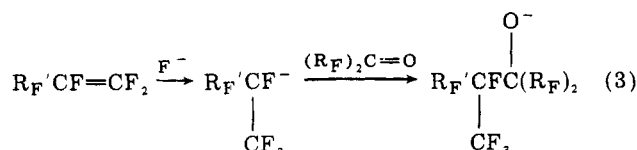
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Rate and enthalpy measurements indicate that fluoride ion adds more easily to the C=O bond in H(CF₂)₆COCF₃ than to the C=C bond in H(CF₂)₇OCF=CF₂, at near ambient temperatures in a polar aprotic solvent. When both are present, however, there can be rapid fluoride exchange from the kinetically more favored to the less favored anion; the initial composition thus has little importance. In fluoride-catalyzed dimerization of C=C, C=O, and C=N compounds at 170–180 °C under equilibrium conditions, the final product will be the most thermodynamically stable one and can be predicted on the basis of relative acidities. The codimerization reaction is highly product specific.

Fluoride ion adds to highly fluorinated olefins and carbonyl compounds to form respectively carbanions and alkoxide ions which undergo many of the characteristic reactions of their nonfluorinated analogues.¹



In a mixed system containing olefin, carbonyl compound, and fluoride ion, two reaction possibilities exist: alkylation of the carbonyl compound or alkoxylation of the olefin



The first of these reactions has often been reported and the second never. Broadly speaking the question somewhat resembles the addition of an enolate ion to C=O in classical base-catalyzed carbonyl condensations, in which the new bond formed is C–C rather than C–O. The fluorinated carbanion and alkoxide ions are not ambident, as is the enolate ion, but

it has heretofore been assumed that they are in some way interconvertible. The present work shows that this interconvertibility is real, that the overall reaction is apt to be thermodynamically rather than kinetically controlled, and that the product can be predicted in terms of relative acidities.

In order to study the C=O/C=C system shown in eq 3 and 4, two compounds of medium chain length, H(CF₂)₆COCF₃ (1) and H(CF₂)₇OCF=CF₂ (2), were prepared. A vinyl ether rather than an α -olefin was chosen since a terminal *F*-olefin² undergoes very facile double-bond migration in the presence of fluoride ion and this reaction would have interfered with the kinetic studies. A schematic diagram of the two syntheses is shown in Scheme I. No unusual difficulties were encountered. During identification of the vinyl iodide, an unexpected fragmentation pattern in the mass spectrum of the compound

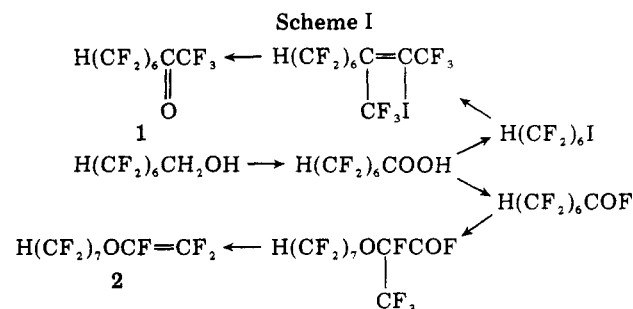


Table I. Variation of K_{eq} with Temperature for the Addition of Fluoride Ion to $H(CF_2)_6COCF_3$ and $H(CF_2)_7OCF=CF_2$

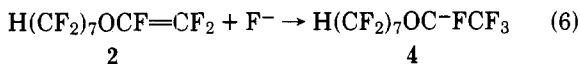
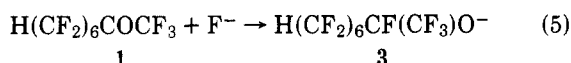
Substrate	Temp, °C	% anion	K_{eq}
$H(CF_2)_6COCF_3$	30	77.3	3.4
	10	56.8	1.4
	-10	45.5	0.8
$H(CF_2)_7OCF=CF_2$	30	50	1.0
	25	38	0.6
	5	25	0.3
	-15	0	

revealed a rearrangement rather similar to the McLafferty rearrangement. Details and supporting evidence for this phenomenon have been reported elsewhere.³

Preliminary tests of an infrared method for following the reaction of fluoride ion with substrate were carried out on a more easily accessible model compound, *F*-1-heptene, using potassium fluoride as fluoride source since cesium fluoride was found to react with ketones inconveniently rapidly for kinetic purposes. As followed by the disappearance of the terminal C=C infrared absorption, the reaction between *F*-1-heptene and fluoride ion always went to completion, even when the fluoride:olefin ratio was less than 1:1. This can be ascribed to fluoride-catalyzed rearrangement of the olefin, since with compounds 1 and 2, which are incapable of rearranging, complete disappearance of the original IR band was not observed. Moreover, in the mass spectrum of the product recovered from the treatment of *F*-1-heptene with KF, fragments were noted (*m/e* 181, 212) which indicated respectively a cleavage β to the third carbon in the chain and a loss of two CF_3 groups, processes which would occur in *F*-2-heptene but not in the original *F*-1-heptene. It has been observed previously that rearrangement is a very facile process when it can occur.^{1,4}

Plots of concentration vs. time showed zero-order kinetics. This fact and the large surface area effect noted with excess KF indicated that the reaction occurs on the crystal surface rather than in solution. Graham found a similar rate acceleration in the case of tetrafluoroethylene with fluoride ion.⁵

The reactions of the two principal test compounds with fluoride ion are shown below.

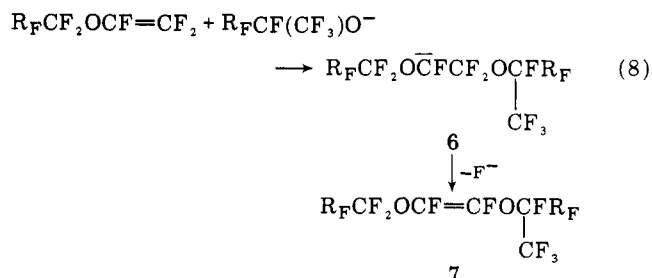
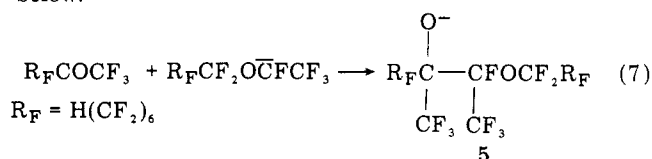


Kinetic studies on these systems were run in diglyme at 30 °C with KF, using either IR or NMR to follow the reaction; the two methods gave fair agreement. In view of the heterogeneity of the reactions, rate constants are no more than relative, but since the same batch of KF was used throughout the average values should be significant for comparing the relative reaction velocities of the two compounds under those specific conditions. Average values for $t_{1/2}$ and K_{eq} respectively were 0.53 h and 4.1 for the ketone and 1.1 h and 1.3 for the vinyl ether, when followed by IR. Equilibrium constants at various temperatures, as found by NMR, are shown in Table I.

By plotting $\ln K_{eq}$ vs. T^{-1} , an approximate value for the enthalpy of anion formation was obtained. For the ketone $\Delta H = -5$ kcal/mol and for the vinyl ether $\Delta H = -9$ kcal/mol.

Competition for fluoride ion between vinyl ether and ketone was investigated by NMR for three cases: case I, preformed vinyl ether anion (carbanion) plus excess free ketone; case II, preformed ketone anion (alkoxide) plus excess free vinyl ether; case III, approximately equimolar quantities of ketone and vinyl ether, plus potassium fluoride in half this total molar

quantity. The anions were prepared in diglyme as usual, the other reactant and $CFCl_3$ as internal standard were added in vacuo at -180 °C, and the tubes were sealed and stored at -80 °C until use. Each was then warmed rapidly to room temperature, spectra being taken immediately after warm-up and again after 1 and 2 h of mixing at room temperature. The two possible reactions of alkylation and alkoxylation are shown below.



Although interpretation of the NMR spectra was difficult because of the possible presence of six different species and because differences in the chemical shift values of the various CF_3 groups were within or very near to the limits of reproducibility from sample to sample, the following conclusions seemed clear. In case I, the preformed carbanion originally present was absent even in the earliest spectrum taken. Free vinyl ether appeared in this spectrum but disappeared rapidly and was completely gone in the final spectrum. In case II, carbanion was detected in the first spectrum taken and persisted thereafter since vinyl ether was in excess. Since the carbanion disappears in the presence of free ketone, as shown by case I, the ketone formed in case II must have been consumed by reaction with the carbanion. In case III, neither the ether nor its carbanion was detected at any time. The final spectrum was virtually identical with that of case I.

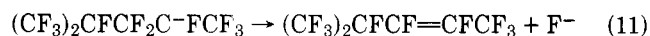
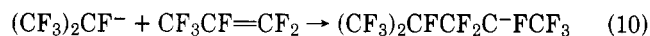
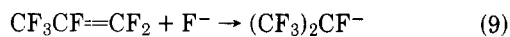
These results are in accord with the reaction pattern vinyl ether 2 + alkoxide 3 \rightleftharpoons carbanion 4 + ketone 1 \rightarrow condensation product 5. Initial conditions are of minimal importance; in any system composed of the ketone, the vinyl ether, fluoride ion, and the respective anions, whether any of these be potential or real, the only end result is the formation of the carbanion and its addition to the ketone. Transfer of fluoride ion from the alkoxide ion 3 to the vinyl ether 2 is rapid and quantitative; the carbanion is apparently formed more effectively by this process than by simple addition of fluoride ion to the ether. In other words, the ketone acts as a very efficient carrier of fluoride ion.

The reaction pattern can be rationalized in terms of the relative strengths of the conjugate acids and bases involved. The alkoxide 3 is a weaker base than the carbanion 4 (i.e., $(R_F)_2CFOH$ is a stronger acid than $R_FOCH_2CF_3$), therefore the ketone reacts more easily than the vinyl ether with fluoride ion. The alkoxide does not attack the C=C double bond as such an attack would lead to the more highly basic carbanion 6, but the carbanion 4 can attack the C=O double bond to give 5, the weakest base of all since it is the anion of a tertiary *F*-alcohol, with $pK_a \approx 5$.

Considerations of equilibrium, anion stability, and relative acidity have similarly been found to be product determining in the fluoride-catalyzed codimerization of *F*-olefins and *F*-imines. When the three reactants $CF_3N=CF_2$, $CF_3CF=CF_2$, and $(CF_3)_2C=CF_2$ are treated separately with cesium fluoride the first dimerizes at 50 °C or less, the second dimerizes at 150 °C, and the third does not react. Presumably the lack of re-

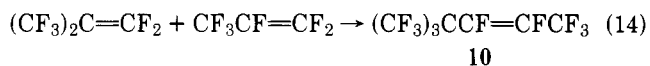
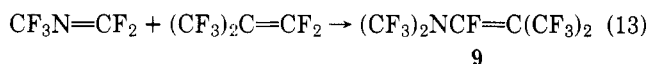
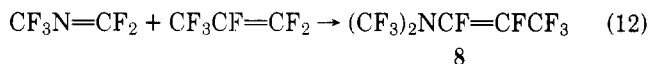
action of $(CF_3)_2C=CF_2$ is due to poor accommodation of this bulky molecule or the related $(CF_3)_3C^-$ ion on the crystal surface, since the olefin can be dimerized by CsF at $-20^\circ C$ even in diethyl ether.⁶

The dimerization or codimerization presumably occurs in three steps: (1) addition of fluoride ion to an olefin to form the anion, (2) addition of this anion to a second molecule of olefin to form a larger anion, and (3) expulsion of fluoride ion to form the most stable (i.e., most highly substituted) olefin.

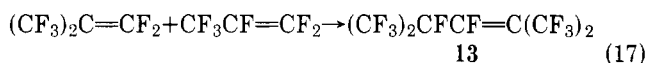
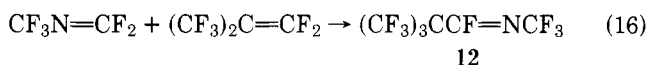
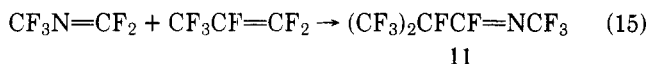


In the presence of two different olefins, it would be expected that the more reactive of the pair should add fluoride ion to form an anion and that this anion would then attack a second molecule to give the codimer or the homodimer of the more reactive species. In short, the more reactive olefin should serve as addend and the less active (ignoring homodimerization) as receptor.

Given the aforementioned reactivities, crossed reactions of the three compounds should give the products predicted below, with possibly one homodimer in each case.



The actual results were exactly the opposite of those predicted. In every case, the less reactive species served as addend and the more reactive as receptor, to give high yields of the codimer and none of the homodimer. Results obtained are shown below.

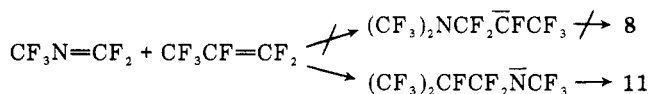


Furthermore, the intervention of an equilibrium involving monomer, dimer, and anions was shown by heating the imine homodimer $(CF_3)_2NCF=NCF_3$ with $CF_3CF=CF_2$ and fluoride ion. The codimer 11 was produced.

The results show that the reaction is subject to thermodynamic rather than kinetic control. They can be rationalized on the same basis (anion stability and conjugate acid strength) as the preceding results on C=O vs. C=C activity. In the pair of reactions 12 and 15, the anionic intermediate is a conjugate base of either a C-H or an N-H acid. The latter is the stronger acid and therefore leads to the observed product.⁷

The same considerations hold for reactions 13 and 16. In the pair 14 and 17 the choice is between a secondary carbanion $(CF_3)_3CCF_2C^-FCF_3$ and a tertiary carbanion $(CF_3)_2CFCF_2C^-(CF_3)_2$. Since a tertiary C-H bond in a hydrofluorocarbon is about 10^5 times as acidic as a secondary C-H,⁸ the tertiary carbanion is the one which leads to product. In this last case the reluctance of $(CF_3)_2C=CF_2$ to add fluoride ion may also be a contributing factor, but it should be noted that the $(CF_3)_3C^-$ does form in reaction 16, possibly by a fluoride transfer mechanism such as that observed previously with the vinyl ether/ketone pair.

Scheme II



It is sometimes possible to change a regime of thermodynamic control to one of kinetic control by moderating the reaction conditions, as in the classic case of naphthalene sulfonation. In this regard, it is interesting to note that in the $(CF_3)_2C=CF_2/CF_3CF=CF_2$ reaction, only the kinetic dimer is obtained when the reaction is run at room temperature in a polar aprotic solvent.⁹

Experimental Section

General. The compounds $CF_3(CF_2)_4CF=CF_2$, $H(CF_2)_6CH_2OH$, $(CF_3)_2C=O$, $CF_3CF=CF_2$, and $CF_3C=CCF_3$ were obtained from PCR, Inc. and used as received; $(CF_3)_2C=CF_2$ was made by reformation of $CF_3CF=CF_2$ ¹⁰ and $CF_3N=CF_2$ by pyrolysis of $(CF_3)_2NCOF$.¹¹ Before use, the water content of the solvents glyme and diglyme was checked at 10 ppm or below, and CsF and KF were dried in vacuo at $50^\circ C$ for 10–15 h. Mass spectra were recorded on an AEI-MS12 instrument using 8 kV, 100 μA , source temperature $70^\circ C$, inlet temperature $120^\circ C$. NMR measurements were made using a Varian DP-60 at 56.4 MHz with $CFCl_3$ as internal standard.

Preparation of $H(CF_2)_6COCF_3$, 8-Hydril-F-2-octanone, Compound 1. $H(CF_2)_6COOH$ was prepared by oxidation of $H(CF_2)_6CH_2OH$.¹² Reaction of its sodium salt with iodine was best carried out at 180 – $200^\circ C$ in sulfolane to give a 65% yield of $H(CF_2)_6I$: bp $109^\circ C$ (630 mm); mass spectrum [m/e (rel intensity)] 428 (19), 301 (38), 231 (69), 177 (61), 131 (100). The iodide was added to hexafluorobut-2-yne by heating in a sealed Pyrex tube at $250^\circ C$ for 12–14 h to give $H(CF_2)_6C(CF_3)=CICF_3$, bp 72 – $73^\circ C$ (7.5 mm), in 66% conversion and >90% yield: IR (C=C) 1580 cm^{-1} ; mass spectrum 590 (12), 325 (64), 213 (78), 212 (100), 193 (32), 143 (52), 131 (42), 127 (34), 113 (36), 101 (26), 93 (64). The substituted vinyl iodide was oxidized with 2.2 mol of $KMnO_4$ in 1:1 acetone-water at $30^\circ C$, treated with SO_2 , separated, dried with P_2O_5 , and fractionated to give 70% $H(CF_2)_6COCF_3$: bp $115^\circ C$ (630 mm); IR (C=O) 1790 cm^{-1} ; mass spectrum 398 (2), 329 (12), 301 (24), 281 (24), 263 (28), 231 (52), 203 (14), 181 (34), 169 (50), 163 (28), 151 (24), 131 (100), 119 (75), 113 (74), 102 (62), 97 (35), 93 (46); NMR [ϕ^* (splitting, area)] 139.2 (d, 2 F), 131.1 (s, 2 F), 124.5 (s, 2 F), 122.4 (s, 4 F), 119.2 (s, 2 F), 76.4 (s, 3 F).

Preparation of $H(CF_2)_7OCF=CF_2$, 10-Hydril-F-3-oxadecene, Compound 2. $H(CF_2)_6COOH$ was refluxed with excess benzoyl chloride for 3 h and fractionated to give 88% $H(CF_2)_6COCl$: bp $67^\circ C$ (70 mm); IR (C=O) 1780 cm^{-1} . The acid chloride was refluxed with NaF in diglyme and fractionated to give 78% $H(CF_2)_6COF$, bp $91^\circ C$ (630 mm) (lit. 88 – $91^\circ C$ (760 mm)¹³). Hexafluoropropylene epoxide, 0.020 mol, prepared by reaction of $CF_3CF=CF_2$ with alkaline hydrogen peroxide,¹⁴ was added slowly to 0.017 mol of $H(CF_2)_6COF$ stirred with 0.01 mol of CsF in 25 mL of triglyme, followed by 5–6 h of reflux. Fractionation gave $H(CF_2)_7OCF(CF_3)COF$, bp $69^\circ C$ (30 mm), IR (C=O) 1870 cm^{-1} , in 22% average yield. The ether acid fluoride was converted to the sodium salt, which was pyrolyzed in vacuo at $250^\circ C$ over 3–5 h to give 81% yield $H(CF_2)_7OCF=CF_2$: bp $82^\circ C$ (88 mm); IR (C=O) 1830 cm^{-1} ; mass spectrum 448 (3), 131 (48), 119 (20), 101 (28), 100 (19), 97 (16), 78 (100); NMR 138 (d, 2 F), 127.6 (s, 2 F), 123.5 (s, 2 F), 121.1 (s, 6 F), 84.1 (s, 2 F), 116 (m, 1 F), 122.8 (m, 1 F), 137.4 (m, 1 F). The ϕ^* values agreed well with those of a similar F-(vinyl ether) prepared by others.¹⁵ All liquid intermediates and final products showed >98% purity by GC.

Utilization of NMR. The ϕ^* values for CF_3 in diglyme solution were surprisingly little affected by complex formation, $CF_3C(=O)O^-$ 77, $CF_3CF(O^-)$ 78, CF_3C^-FO 82; a similarly slight change of about 2 ppm was noted for CF_3 in $(CF_3)_2CO$ and $(CF_3)_2CFO^-$. Spin-spin splitting was not observed except for that of the CHF_2 doublet and that among the vinyl fluorine atoms of the ether. The most reliable identification data were (1) distortion of the CHF_2 doublet due to superposition of the vinyl fluorine α to oxygen, which identified the free ether, and (2) a new peak at 54 ppm which appeared on treatment of the vinyl ether with fluoride ion, presumably OC^-FCF_3 .

Codimerizations. Equimolar quantities (0.4–0.1 mol) each of the two reactants were heated in a steel bomb with 50 g of CsF for 6 days at 170 – $180^\circ C$. After cooling, the bomb was evacuated for several hours and the condensate (dry ice trap) was fractionated. Chromatographic purity of all products was at least 99%. $(CF_3)_2CFCF=NCF_3$ (11), 4-(F-methyl)-F-2-aza-2-pentene: bp 28 – $31^\circ C$ (630 mm) (bp

(CF₃N=CF₂)₂ 34 °C (630 mm), bp (CF₃CF=CF₂)₂ 30 °C (630 mm); conversion 79%; IR (C=N) 1765 cm⁻¹ (C=N in (CF₃)₂NCF=NCF₃ 1760, C=C in (CF₃)₂CFCF=CFCF₃ 1750); NMR (φ*, area) CF₃C (74.5, 6 F), CF₃N (59.9, 3 F), CF=N (17.3, 1 F), CFC (191, 1 F). (CF₃)₃CCF=NCF₃ (12), 4,4-di(*F*-methyl)-*F*-2-aza-2-pentene: bp 51–53 °C (630 mm); yield 95%; conversion 69%; mol wt 326 (calcd for C₄F₈: CF₃N=CF₂ 333); IR (C=N) 1760 cm⁻¹; NMR CF₃C (62.1, 9 F), CF₃N (56.4, 3 F), CF=N (5.6, 1 F). (CF₃)₂CFCF=C(CF₃)₂ (13), 2,4-di(*F*-methyl)-*F*-2-pentene: bp 63–64 °C (630 mm); yield 95%; conversion 83%; IR (C=C) 1680 cm⁻¹ (C=C in (CF₃)₂C=CFCF₂F₅ 1690, in *cis*-(CF₃)₂CFCF=CFCF₃ 1750); NMR CF₃OC (74.4, 6 F), CF₃C= (59.4, 3 F), CFC (55.3, 1 F), CF=C (183, 1 F).

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Registry No.—1, 63703-12-8; 2, 63703-13-9; 11, 63703-14-0; 12, 58599-97-6; 13, 63703-15-1; H(CF₂)₆COONa, 2264-25-7; H(CF₂)₃I, 63703-16-2; H(CF₂)₆C(CF₃)=CFCF₃, 6307-17-3; H(CF₂)₆COOH, 1546-95-8; H(CF₂)₆COCl, 41405-35-0; H(CF₂)₆COF, 5927-65-1; H(CF₂)₇OCF(CF₃)COF, 63703-18-4; F⁻, 16984-48-8; hexafluoropro-

pene, 116-15-4; benzoyl chloride, 98-88-4; hexafluoropropylene epoxide, 428-59-1.

References and Notes

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Reactivity of Benzylic Carbanions. 4. Kinetic Studies of Reactions of Alkyl Halides with 9-Alkyl-10-lithio-9,10-dihydroanthracenes and Diphenylmethyl lithium. The Relationship of Reaction Rates to Product Stereochemistry

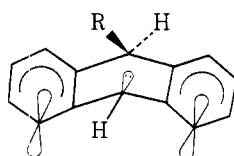
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The kinetic measurements of a series of highly reactive anion reactions with primary and secondary halides were made and related to the stereochemistry of the products. There is evidence for a change of factors affecting the reactivity between the primary and secondary systems.

The stereochemistry of reactions of 9-alkyl-10-lithio-9,10-dihydroanthracene and alkylanthracene has been studied extensively with interesting and sometimes inconsistent results.² The crux of these apparent inconsistencies involves the stereochemistry and mechanistic implications of the anion, I, as a flattened boat conformer with preferred axial orienta-



- Ia, R = H
 b, R = Et
 c, R = *i*-Pr
 d, R = *t*-Bu

tions of the alkyl substituent in the lithio derivative.^{2b,c} This conformational preference is determined by two factors. First, the anion in the axial position permits maximum interaction with the π orbitals on the neighboring rings, thus stabilizing the charge by delocalization. Most of this delocalization is

unavailable when the anion is in an equatorial conformation. Second, the alkyl group in the axial position has minimum steric interaction with the peri hydrogens of the neighboring rings. That this conformer is of lower energy than the equatorial is substantiated by NMR studies, which indicate for the series 9-alkyl-9,10-dihydroanthracenes that the orientation of the 9-ethyl, 9-isopropyl, and 9-*tert*-butyl groups is essentially 100% pseudoequatorial.³ If these were the only factors, then alkylation reactions should lead to products with *cis* stereochemistry. Interestingly, while there are many reactions that do give mainly *cis* products, there are many that give predominantly the *trans* isomer.^{2a,4-6} Moreover, there does not appear to be a simple explanation based on steric factors. For example, ethyl bromide reacts with Ic to give product mixtures of 74% *cis* and 26% *trans* isomers.^{2a} Similar results were obtained with methyl and isopropyl iodide.⁶ The wide range of stereoselectivity appears not to be confined to alkylation reactions, as deuteration of the anion^{7,5} and reduction of alkyl anthracene^{8,9} can lead to widely varying ratios of *cis* to *trans* isomer by changing reaction conditions.

The variation in reaction parameters such as temperature, solvent, leaving group, and anion structure has in general led