

(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=CFC₂F₅ 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

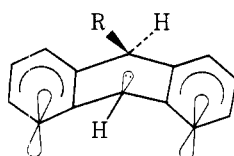
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The kinetic measurements of a series of highly reactive anion reactions with primary and secondary halides were made and related to the stereochemistry of the products. There is evidence for a change of factors affecting the reactivity between the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

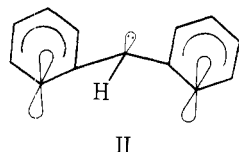
The variation in reaction parameters such as temperature, solvent, leaving group, and anion structure has in general led

Table I. Second-Order Rate Constants for Reactions of Anions with Alkyl Halides^a

R/X	Registry no.	Anion ^b	Registry no.	$k_1, M^{-1} s^{-1c}$	% cis isomer ^d
HexCl	544-10-5	Ph ₂ CH	881-42-5	1.0×10^1	
		HAnth	17228-13-6	1.0×10^1	
EtCl	79-00-3	EtAnth	17228-12-5	6.0	92
		<i>i</i> -PrAnth	35150-61-9	4.1	75
HexCl				2.3	
HexBr	111-25-1	<i>t</i> -BuAnth	35150-62-0	1.0	
		Ph ₂ CH		2.7×10^3	
		HAnth		2.7×10^3	
		EtAnth		1.5×10^3	92
		<i>i</i> -PrAnth		5.9×10^2	74
<i>i</i> -PrBr	75-26-3	<i>t</i> -BuAnth		3.3×10^2	
		Ph ₂ CH		1.9×10^2	
		HAnth		6.2×10^1	
		EtAnth		4.3×10^1	30
		<i>i</i> -PrAnth		4.0×10^1	15
<i>i</i> -PrI	75-30-9	<i>t</i> -BuAnth		4.0×10^1	2 ^e
		Ph ₂ CH		4.9×10^3	
		HAnth		3.4×10^3	
		EtAnth		1.7×10^3	30
		<i>i</i> -PrAnth		1.4×10^3	12

^a In THF at 20 °C. ^b Lithium counterion. ^c The average of at least three determinations at three different concentrations. The absolute values are within 10% variation. ^d See ref 7. ^e See ref 2c.

to changes in product yields and composition.^{2a,c} We have sought further and definitive mechanistic information by bringing the powerful and quantitative techniques of kinetics to this study. We have now studied the effect of reaction variables upon the absolute reaction rates. We have used rapid-mixing stopped flow techniques for a systematic kinetic study of I with alkyl halides. Further, we have included in our study reactions of diphenylmethyl lithium, II, which serves



II

as a model having maximum electronic interaction but none of the steric factors present in I. Thus by comparing the absolute reaction rates of these compounds we have attempted to assess directly the structural effects that result in product mixtures of cis and trans isomers.

Whereas product studies have indicated reaction differences, kinetic studies can differentiate between the possibilities that the decrease in formation of the cis isomer is a consequence of a reaction being slowed or of another reaction being accelerated. Equally important, this study is novel in that heretofore absolute rates have not been reported for these highly reactive, air- and moisture-sensitive anions. We report the kinetic data for the substitution reactions of perhaps the most reactive nucleophiles that have been studied to date.

Results and Discussion

The kinetics were measured with a rapid-mixing stopped flow apparatus previously described¹⁰ by monitoring the decay of the highly colored anions at 500 nm. The reactions were overall second order, with first-order dependence on both the anion and the alkyl halide. This was demonstrated by observing the first-order decay of the anions when reacted with an excess of the halide and by determining first-order behavior of the halide over a concentration range of 10^{-2} to 10^{-1} M. The second-order rate constants are summarized in Table I. Inspection of the table reveals that, for each halide reaction, there is a decrease in rate as the size of substituent increases, going from Ia to Ic. Also, there is a concomitant decrease in the amount of cis product. Of greater interest, the log of the

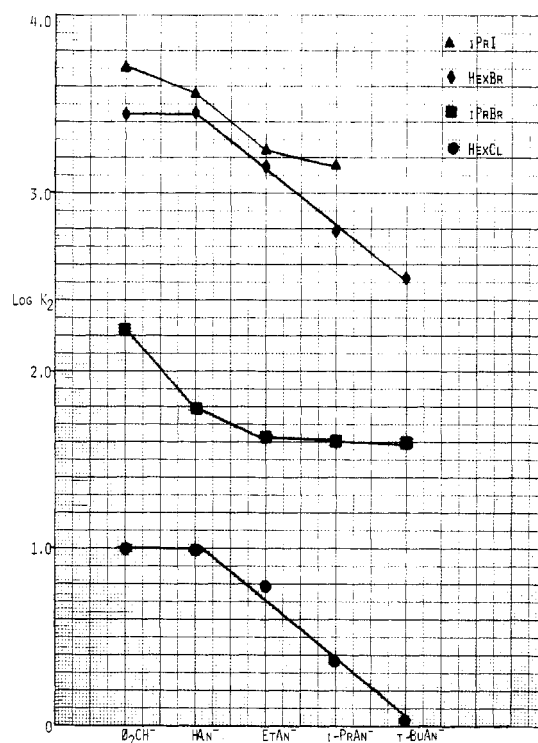


Figure 1.

absolute rate constant is related to the energy of the reaction, and therefore a plot of these values vs. the degree of substitution in the anions indicates the relationship of the alkylation reaction to the steric requirements of the anions. As seen in Figure 1, there appear to be two different relationships operating that depend on the nature of the halide. When alkylation involves a primary bromide or chloride, the rates are equal for II and Ia, and equally important there is a monotonic decrease in rate with increase in steric bulk of the anions. In contrast, when reaction involves a secondary bromide or iodide, there is a large decrease in rate of reaction of II compared to Ia. Also, significantly the decrease in rate of Ib-d is not monotonic and in fact the differences are quite small in the case of the bromide.

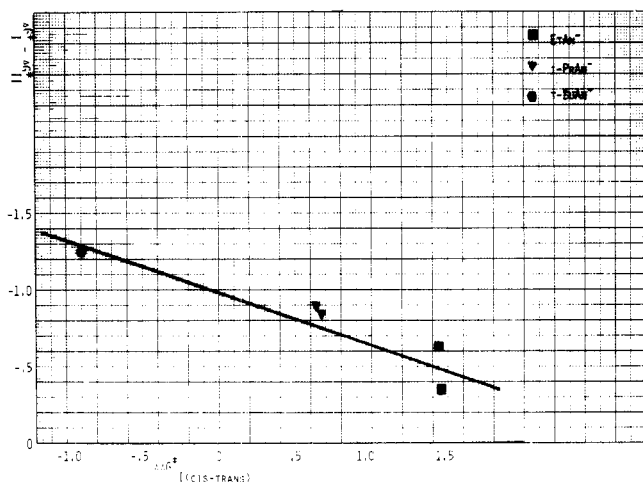


Figure 2.

Therefore it appears that there is a relationship between the rates of reaction of the anions with primary halides and the steric properties of the anion. That there is a similar and quantitative relationship between reaction rates and product stereochemistry is shown in Figure 2. The relationship of the free energies of activation relative to II to the differences in activation energies leading to cis and trans products for primary halides is plotted in Figure 2. Inspection of the plot suggests that the factors producing the overall rate retardation and the decrease in amounts of cis compound are quantitatively related over an extended range of reactivities. In contrast, for secondary halides the absence of a relationship is indicated by the comparable plot for the same anions. In this case the factors producing the decrease in cis compound and overall rates do not appear to correlate as shown by Figure 3.

The emerging pattern is that the kinetic and product studies are related and fall into two distinct sets. For the first (with primary halides), the incursion of a steric effect is seen with substitution at the 9 position and increases as the size of the group increases. Importantly, this is confirmed by the pattern of rate decrease ($\text{Et} > i\text{-Pr} > t\text{-Bu}$) with a greater effect in going from *i*-Pr to *t*-Bu. This pattern is characteristic of a classical steric effect and is ascribed to the spherical symmetry of the *tert*-butyl group. In this regard the similarity of the rates of Ia and II signal an absence of important steric differences between these compounds.

In the second set (with secondary halides), a significant rate difference is seen before substitution at the 9 position and increases in the size of the group have a surprisingly small effect on the reaction rate with the bromide. The rate difference of 3 to 1 between Ia and II signals an important difference between the two anions. Moreover the rate ratio of primary to secondary bromide for II is 14, typical of anion values, whereas the rate ratio for Ia is 44.

The possibility that a dominant elimination reaction with the secondary halides obscures the comparison with the primary can be shown to be unimportant by the following considerations. First, while the reported yields of alkylated products vary considerably, yields of 90% or greater have been obtained in preparations of 9-isopropyl-9,10-dihydroanthracene,^{2c} 9-isopropyl-10-ethyl-9,10-dihydroanthracene,^{2a} and 9-isopropyl-10-*tert*-butyl-9,10-dihydroanthracene^{2c} using secondary halides. Second, in all cases comparisons are made between the rate of the dihydroanthracenyl anion and the diphenylmethyl anion with the same halide. In related systems there are data that show that the amount of elimination with the two types of anions is comparable.¹¹ Finally, in reactions of related "naked anions" with 2-chloro- and 2-bromooctane,

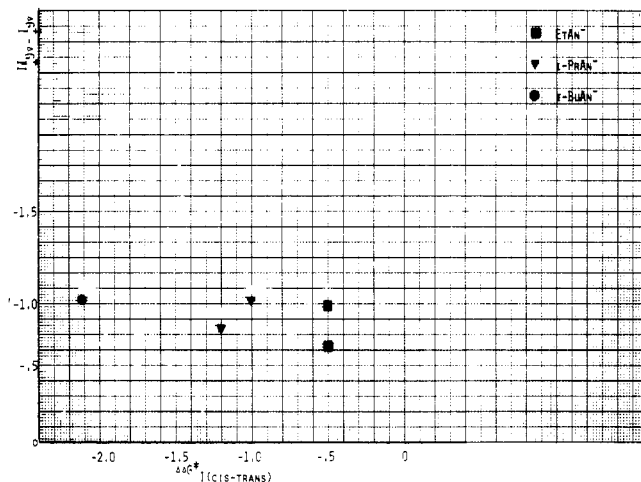


Figure 3.

the amount of elimination products was determined to be 3 and 17%, respectively.¹² Thus it is unlikely that the amount of elimination in the several systems is either substantial or that it differs significantly from that of the reference anion.¹³

Conclusion

For reaction with the primary halides, the results can be accommodated in a straightforward manner. The preponderant attack by anion is in the preferred conformer of axial-axial orientation (I). This is true whatever the exact nature of the anion in the absence of halide, whether quasiplanar, pseudoaxial, rapidly equilibrating, or a complex mixture of ion-pair equilibria.^{2c} There is little difference in the steric effect of the model compound and that with a hydrogen in the 9 position. With increasing size of the substituent in the 9 position two effects are noted, the overall rate decreases and increasing amounts of the trans compound are formed. Thus the 9-alkyl group in an axial position hinders axial attack as would be expected.

Reaction with secondary halides, accompanied by both slower reaction rates and product compositions of mainly trans stereochemistry, can be explained by two different schemes. First, there is an increasing and dominant attack of anion in the conformer with the lithio derivative in the equatorial orientation. This allows the alkyl group to remain in the more favorable axial orientation but provides less charge delocalization. Or second, attack is by the conformer with increasing amounts of the alkyl group in the equatorial position, thus allowing the anion to maintain the favorable axial orientation. It is possible that both schemes contribute depending on the reactants. In the present study, the pattern of a rate difference between the model compound and the unsubstituted anion, together with a dampened steric effect, is more consistent with the scheme of quasiequatorial anion attack.¹⁴

Experimental Section

Materials. The alkyl halides were obtained from Eastman Organic Chemical, purified by trap-to-trap transfer through calcium hydride, and stored over calcium hydride. Chromoquality THF from Matheson Coleman and Bell was distilled from benzophenone ketyl immediately before using. *n*-Butyllithium (1.6 M in hexane) was obtained from Aldrich Chemical Co., Inc. Diphenylmethane was obtained from Matheson Coleman and Bell and distilled before using (fraction bp 255–265 °C collected (lit.¹⁵ bp 262 °C)).

Kinetic Procedures. Kinetic measurements were determined as follows. THF (50 mL) was distilled from sodium benzophenone ketyl into a side-arm flask, fitted with a septum stopper and containing I or II (0.5 mmol) under an argon atmosphere. To the stirred solution an equimolar amount of *n*-butyllithium was added dropwise by sy-

ring through the septum to give the characteristic deep red color of the anion. THF (50 mL) was distilled into another side-arm flask containing a carefully weighed amount of halide (1.0 to 10.0 mmol) also under an argon atmosphere.

The rapid-mixing stopped flow apparatus, thermostated at 20 °C, was flushed with several aliquots of dry THF and then with the anion solution until the effluent in the stop syringe maintained the anion color. Solutions of anion and halide were transferred to the apparatus by gas-tight syringes in a manner that excluded air or moisture. After several flushes of the respective chambers by the anion and halide solutions, oscilloscope traces of multiple runs were photographed. Each photograph was analyzed by measuring the intensities at various times and obtaining the pseudo-first-order slope by computer analysis.

9,10-Dihydroanthracene. To a solution of anthracene (36 g, 20 mmol) in THF (300 mL) and an excess of sodium (20 g) was added methanol (75 mL) over a period of 3 h. The product was isolated and recrystallized twice from ethanol to give 27 g, mp 107–108 °C (lit.^{10b} mp 108 °C).

Alkylation of 9-Alkyl-9,10-dihydroanthracene. All the reactions were conducted in the following way. To the 9-alkyl (5 mmol) dissolved in 100 mL of THF and maintained under an atmosphere of argon at –40 °C was added over 30 min *n*-butyl lithium (5 mmol, 2.3 M in hexane). The solution turned red immediately. After 30 min of stirring, the alkyl halide (2 mL in 40 mL of THF) was added drop by drop. After decolorization and extraction with ether, the reaction products were analyzed by gas chromatography (3 m, 10% silicon QF, on Varaport 100–120, at 130 °C). The products were separated by chromatography on an activated aluminum column. The isomers were first collected together and the purity was checked by mass spectroscopy. A second chromatography using petroleum ether eluted first the trans isomer, next the cis isomer, and finally 9-alkyl-9,10-dihydroanthracene.

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Registry No.—9,10-Dihydroanthracene, 613-31-0; anthracene, 120-12-7.

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Oxidative Cleavage of α -Ketols and Related Ketones with Alkaline Hydrogen Peroxide¹

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The oxidative C–C cleavage of α -ketols $R_1COC(OH)R_2R_3$ (1) has been found to proceed smoothly with alkaline hydrogen peroxide in aqueous methanol affording high yields of ketones $R_2R_3C=O$ and carboxylic acids R_1CO_2H . The reaction obeys second-order kinetics: $v = k_2[R'OO^-][ketol]$, where $R'OO^-$ may be t -BuOO⁻ or $PhCO_3^-$ in place of HOO^- . The cleavage of aromatic ketones ($R_1 = Ph$) is much faster than that of aliphatic ketones ($R_1 = Me$). The relative rate with $PhCO_3^-$ (a stronger oxidant) vs. HOO^- varies from 0.14 to 2.8 with changing ketols. These results are explained by the rate-determining concerted fragmentation of the $C=O$ adduct 6 (Scheme I). Acylolins (1, $R_2 = H$) were cleaved to carboxylic acids and aldehydes R_3CHO , which were further oxidized to acids. α -Amino ketones 3 were cleaved to ketimine or ketone. α -Methoxy- α,α -diphenylacetophenone (2) is also cleaved, the rate being only $1/2000$ that of the corresponding α -ketol 1a ($R_1 = R_2 = R_3 = Ph$), to benzophenone dimethyl acetal and α -hydroperoxy- α -methoxydiphenylmethane, suggesting an intermediacy of α -alkoxy carbonium ion. Alkaline hydrogen peroxide is advantageous in the selective cleavage of α -ketols in comparison with the other ordinary oxidants.

Ordinary reagents for the oxidative cleavage of α -hydroxy ketones (α -ketols) are periodic acid in aqueous solution and lead tetraacetate in organic solvents.² The other known reagents are bromine,³ peracids,⁴ and nickel peroxide.⁵ We wish to report here that alkaline hydrogen peroxide is a mild and effective oxidant for the cleavage of α -ketols and related ketones. This reagent is inactive to 1,2-glycols, contrary to the

case with periodic acid or lead tetraacetate, and hence may cleave α -ketols selectively even in the presence of a 1,2-dihydroxy group.

Results and Discussion

Oxidative Cleavage of α -Phenylbenzoins. α -Phenylbenzoin 1a ($R_1 = R_2 = R_3 = Ph$) can be easily oxidized by al-