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Alkylations of 9-Lithio-9,10-dihydroanthracenes by Alkyl Halides, Alkyl Sulfates, and Alkylolithium Compounds. The Trapping of Radicals Generated by Lithium-Halogen Exchange Reactions

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Abstract: 10-*tert*-Butyl-9-lithio-9-methyl-9,10-dihydroanthracene (**1**) is alkylated stereospecifically *trans* to the 10-*tert*-butyl group by *n*-alkyl bromides, iodides, and sulfates. The protons on the β carbon of the new 9-alkyl group in these hydrocarbons appear upfield of tetramethylsilane as a result of diamagnetic anisotropic effects of the aromatic rings. Methylation of the 9-ethyl analog of **1** also occurs stereospecifically *trans* to the 10-*tert*-butyl group to yield the other diastereomer of the product obtained on ethylation of **1**. The relative reactivities of alkyl iodides (Me > Et > *n*-Bu) and dialkyl sulfates (Me > Et) toward **1** are consistent with an S_N2 mechanism for alkylation. Alkyl iodides can stimulate the alkylation of **1** by alkylolithium compounds. These indirect alkylations also occur stereospecifically *trans* to the 10-*tert*-butyl group. They occur only under conditions conducive for lithium-halogen exchange reactions, and the yields of indirect alkylation product increase with increasing temperatures. The concentration, temperature, and alkyl group effects on these reactions are consistent with a mechanism involving trapping of radical intermediates in the lithium-halogen exchange reaction by **1**. These effects are not consistent with pathways in which the iodide derived from **1** or the alkylolithium compound by lithium-halogen exchange reaction is an important intermediate. The ethylations of 10-ethyl-9-lithio-9,10-dihydroanthracene by ethyl bromide and iodide and ethyllithium-methyl iodide all have *cis* stereoselectivity (99%).

The stereoselectivity of alkylation of 10-alkyl-9-lithio-9,10-dihydroanthracenes in tetrahydrofuran (THF) solution by alkyl iodides is a function of the size of both the 10-alkyl group and the iodide alkyl group.¹ When both groups are small, *e.g.*, methyl or ethyl, the *cis* hydrocarbon is the major or exclusive product,² and, when both groups are large, *e.g.*, isopropyl, the *trans* hydrocarbon is the major product.^{1,3} The same alkylation stereoselectivity is obtained using alkyl bromides^{2a,c,3b} and in liquid ammonia solution.^{2a,c}

As part of a systematic study of solvent effects on the reactions of carbanions, we report here our studies on the stereoselectivity of alkylation of 10-*tert*-butyl-9-lithio-9-methyl-9,10-dihydroanthracene (**1**) and 10-*tert*-butyl-9-ethyl-9-lithio-9,10-dihydroanthracene (**2**). We have previously shown that the predominant ion-pair solvation complex of **1** and **2** present is different in diethyl ether, THF, and hexamethylphosphoramide (HMPA) solutions.⁴ Unlike the protonation reactions of **1** and **2**⁴ or of 10-alkyl-9-lithio-9,10-dihydroanthracenes,⁵ the solvent, temperature, or alkylating agent had no effect on the stereospecificity of alkylation. We have discovered that in reactions of mixtures of **1** and primary alkylolithium compounds with methyl iodide, the major product contains the alkyl group derived from the alkylolithium compound (indirect alkylations). The stereoselectivity of the direct and indirect alkylations of **1** are identical. The direct and indirect ethylations of 10-

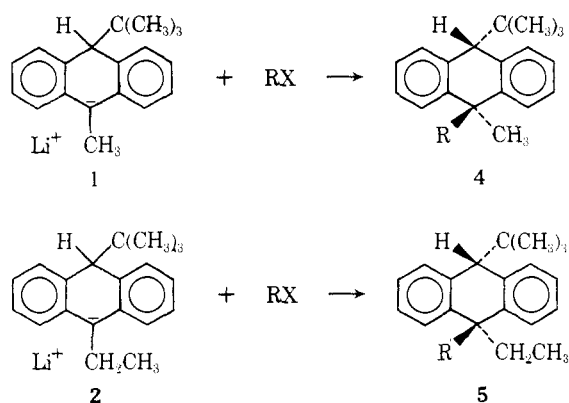
ethyl-9-lithio-9,10-dihydroanthracene (**3**) also have identical stereoselectivity.

It has been proposed that the mechanism of reaction of alkyl iodides with these carbanions may be a S_N2 displacement or may be a two-step sequence.¹ The first step is lithium-halogen exchange between the carbanion and the alkyl iodide. This is followed by coupling of the iodide derived from the carbanion and the alkylolithium compound formed in the first step. The relative reactivities of methyl, ethyl, and *n*-butyl iodide and dimethyl and diethyl sulfate toward **1** have been determined to distinguish between these possible mechanisms. The sulfates cannot react by a two-step sequence analogous to that proposed for the iodides. Similar relative reactivities for the iodides and sulfates will indicate that they react by the same mechanism. The relative reactivities in S_N2 displacements are methyl > ethyl > *n*-butyl.⁶ The relative reactivities expected for the two-step sequence would be difficult to predict. Possible mechanisms for the indirect alkylation reactions and their relation to the direct alkylation reactions are discussed.

Results

Alkylation Reactions. The carbanions **1** and **2** were prepared by reaction of *n*-butyl- or ethyllithium with diethyl ether, THF, HMPA, or 2,5,8,11-tetraoxadodecane (triglyme) solutions of *cis*- or *trans*-10-*tert*-butyl-9-methyl- or 10-*tert*-butyl-9-ethyl-9,10-dihydroanthracene, respec-

Scheme I

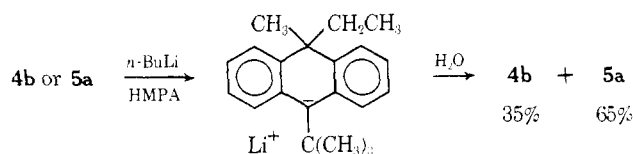


a, R = Me; b, R = Et; c, R = *n*-Pr; d, R = *n*-Bu

tively.⁴ Reaction of **1** with ethyl iodide or diethyl sulfate in diethyl ether or THF solutions at 23 or -78° proceeded virtually quantitatively to afford the ethyl compound **4b** (Scheme I). The configuration was established by nmr (see below). None of the other diastereomer, **5a**, could be detected by glpc in these reaction mixtures. Diastereomer **4b** is also the only product detected in the reactions of **1** with ethyl bromide in THF solution at 23° , diethyl sulfate in HMPA solution at 23° , ethyl iodide in triglyme solution at 23° , and triethyloxonium tetrafluoroborate in THF and HMPA solutions at 23° . Reactions of **2** with methyl iodide or dimethyl sulfate in diethyl ether or THF solutions at 23 or -78° or in HMPA solutions at 23° yield **5a** as the only detected product. Since the new alkyl group enters **1** and **2** stereospecifically trans to the 10-*tert*-butyl group, these alkylation reactions are kinetically controlled.

The stereospecificity observed above is maintained on alkylation with *n*-propyl or *n*-butyl halides. The only product detected from reaction of **1** with *n*-propyl bromide in THF or HMPA solutions at 23° is **4c**. Similarly, reaction of **1** with *n*-butyl bromide in THF solution or *n*-butyl iodide in THF or HMPA solutions at 23° yields **4d**.

The interconversion of **4b** and **5a** was effected by lithiation at C₁₀ with *n*-butyllithium in HMPA solution followed



by protonation with water. No C₁₀ protons were detected in the nmr spectrum of a reaction mixture protonated with deuterium oxide. Thus virtually complete lithiation occurred. Compounds **4b** and **5a** were not lithiated by *n*-butyllithium in THF or diethyl ether solutions. Therefore solvent effects on the protonation and spectra could not be studied.

Configurations of the Alkylation Products. Several striking patterns in the proton chemical shifts can be used to readily assign the configurations shown in Scheme I (Table I). The use of compounds **4a** and **5b** as reference points greatly facilitates the analysis. In all compounds with a *cis*-9-methyl-10-*tert*-butyl substructure (**4a-d**), the methyl group absorbs at *ca.* 1.82 ppm, and the *tert*-butyl absorbs at *ca.* 0.71 ppm. When the 10-*tert*-butyl is *cis* to a 9-ethyl (**5a,b**), the *tert*-butyl absorbs at *ca.* 0.80 ppm, and when a 9-methyl is trans to the 10-*tert*-butyl (**4a, 5a**), the methyl absorbs at *ca.* 1.46 ppm.

The pronounced upfield shifts of the β protons on 9-alkyl groups trans to the 10-*tert*-butyl (**4b-d, 5b**) compared with

Table I. Nuclear Magnetic Resonance Spectral Data for the 9,9-Dialkyl-10-*tert*-butyl-9,10-dihydroanthracenes^a

Compd	Chemical shifts, ppm (coupling constant, Hz)					
	CH ₃	CH _α ^b	CH _β ^b	CH _γ ^b	CH _δ ^b	H C ₁₀ -C(CH ₃) ₃
4a	1.85 1.44					3.76 0.72
4b	1.82	1.92	-0.24 (t, 7.0)			3.63 0.72
4c	1.80	1.82 (t, 7.0)	0.0	0.44 (t, 6.6)		3.60 0.70
4d	1.80	1.84 (t, 8.0)	0.0	0.84 (t, 6.6)	0.52	3.61 0.71
5a	1.49	2.04	1.10 (t, 7.4)			3.78 0.80
5b		2.18 2.02	1.13 (t, 7.4) -0.12 (t, 7.1)			3.75 0.81

^a Spectra run as carbon tetrachloride solutions at 100 MHz. Chemical shifts relative to internal tetramethylsilane. Aromatic protons in all compounds are two multiplets: 7.4 (2 H), 7.1 (6 H). ^b Refers to the protons on the alkyl group greater than methyl, e.g., for an ethyl group the CH₂ = CH_α and the CH₃ = CH_β.

the β protons on 9-ethyl groups *cis* to the 10-*tert*-butyl are consistent with previous observations for related compounds. For example, the methyl protons of the ethyl groups of *trans*- and *cis*-10-*tert*-butyl-9-ethyl-9,10-dihydroanthracene absorb at 0.63 and 1.24 ppm, respectively.^{4,7} The upfield shifts of the β protons are related to the ease with which the alkyl group can get into or the amount of time it spends in conformations where the β protons are in the shielding region over the aromatic rings.^{8,9} 9,10-Dihydroanthracenes can adopt either a planar or a boat-shaped (which need not be rigid) conformation.^{4,7,9} Assuming that the *tert*-butyl group will retain its strong preference for a pseudo-axial orientation in a boat-shaped conformation for **5b**, the *trans* ethyl group will be in a pseudo-equatorial orientation. The vertical and horizontal distances from the center of the plane of an aromatic ring to the methyl protons of an ethyl group in a pseudo-equatorial orientation in a boat-shaped conformation and in a planar conformation were measured on a Drieding model.⁸ A higher field chemical shift is predicted for the methyl protons of the ethyl group in the planar molecule for all conformations of the ethyl group compared.^{8,10} The larger upfield shifts of the β protons on the 9-alkyl groups of **4b-d** and **5b** compared with the methyl protons of the ethyl group of *trans*-10-*tert*-butyl-9-ethyl-9,10-dihydroanthracene indicates that these trialkyl dihydroanthracenes are much flatter than similar dialkyl dihydroanthracenes.

Competitive Alkylation Reactions. All these reactions were extremely rapid and were done under conditions picked to minimize local mixing effects. The carbanion solution was added slowly as drops by cannula under a nitrogen atmosphere to a vigorously stirred solution containing an excess of the two reagents (Table II). The relative reactivities were calculated assuming second-order reactions and pseudo-first-order reactions (when applicable).¹¹ The calculated relative rates agreed within $\pm 10\%$ for each series. The relative reactivities [methyl iodide, 1.8; ethyl iodide, 1.0; *n*-butyl iodide, 0.75; ethanol, 5.5; dimethyl sulfate, 2.5; diethyl sulfate, 1.0 (assuming only one alkyl group reacts)] are in the expected order for S_N2 reactions. They are compressed compared to Streitwieser's average relative reactivities: methyl, 30; ethyl, 1.0; *n*-butyl, 0.4.⁶ This compression may be due to different solvation and ion pairing effects for **1** and the simpler nucleophiles used for determination of the average relative reactivities,¹² and/or it may

Table II. Competitive Alkylation Reactions of **1** in THF Solution^a

Series ^b	Reagents, mmol		Yield, % ^c			
	A	B	4a	4b	4d	RH ^d
1	3.21	2.50	67	33		
	3.21	3.75	60	40		
	3.21	5.00	54	46		
	3.21	6.25	50	50		
2	1.61	0.88	75		25	
	1.61	1.75	66		34	
	1.61	1.75	72		28	
	0.80	1.75	62		38	
3	1.06	1.91	58	42		
	1.06	1.53	60	40		
4	1.06	1.71	18			82
	1.06	0.85	36			64
	1.06	0.34	59			41

^a Reactions done at 23° using 0.1 mmol of **1**. ^b Series 1: A = methyl iodide; B = ethyl iodide. Series 2: A = methyl iodide; B = *n*-butyl iodide. Series 3: A = dimethyl sulfate; B = diethyl sulfate. Series 4: A = dimethyl sulfate; B = ethanol. ^c Relative yields corrected for response factors obtained by glpc analysis. ^d RH = 10-*tert*-butyl-9-methyl-9,10-dihydroanthracene (87% *cis*, 13% *trans*).

reflect the greater reactivity of **1**.¹³ The similarity of the relative reactivities of the iodides and sulfates suggests that reaction of **1** with both substrates occur by simple S_N2 displacement. The reactions of less hindered resonance stabilized carbanions with optically active secondary chlorides, bromides, iodides, and tosylates also proceed by a S_N2 mechanism.¹⁴

A brief study of *steric effects* confirmed earlier observations that the 10-alkyl group of the carbanion and the entering alkyl group have an influence on alkylation stereoselectivity.¹⁻³ Reaction of **3** with 2-chloro-2-methylpropane in THF solution at 23° yields 14% *trans*-9-*tert*-butyl-10-ethyl-9,10-dihydroanthracene and 86% 9-ethyl-9,10-dihydroanthracene. No *cis* diastereomer is detected in this reaction, whereas 14% *trans*- and 86% *cis*-10-ethyl-9-methyl-9,10-dihydroanthracene are formed on reaction of **3** with methyl iodide at 23°. The 10-methyl group of 9,10-dimethyl-9-lithio-9,10-dihydroanthracene does not affect direct alkylation *trans* to it to the same extent that the 10-*tert*-butyl group of **1** and **2** does. Equal amounts of *cis*- and *trans*-9,10-dimethyl-9-ethyl-9,10-dihydroanthracene are formed on reaction of this carbanion with ethyl bromide in THF solution at -78, 0, and 23°. Thus the bulk of the 10-*tert*-butyl group in **1** and **2** inhibits *cis* alkylation.

Indirect Alkylations. The product yields obtained on reaction of THF solutions containing mixtures of **1** and methyl-, ethyl-, or *n*-butyllithium with methyl, ethyl, or *n*-butyl iodide (different alkyl groups were combined) are summarized in Table III. The yield of alkylation product derived from the alkyllithium compound increases with increasing temperature (expt 1-5) and with increasing alkyllithium to alkyl iodide ratio (compare expt 6-8, 11-13, and 14-16). The only product formed by indirect alkylation of **1** with ethyllithium is **4b**. Thus the direct and indirect alkylations of **1** yield the same diastereomer.

The same yields of **4a** (30%) and **4d** (70%) are obtained whether methyl iodide (1.6 mmol) is rapidly added to a THF solution containing **1** (0.1 mmol) and *n*-butyllithium (0.32 mmol) (expt 7), or a THF solution containing **1** (0.1 mmol) and *n*-butyllithium (0.32 mmol) is rapidly added to methyl iodide (1.6 mmol) neat or as a THF solution. Thus the relative yields of alkylation products are not influenced by the order of addition when the addition, and the mixing, is rapid. There is competition between the direct alkylation

Table III. Product Yields of Indirect Alkylations of **1**^a

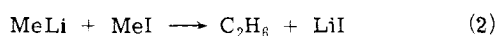
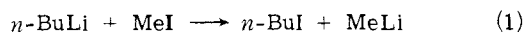
Expt ^b	RLi, mmol	R'I, mmol	Temp, °C	Yield, % ^c			
				4a	4b	4d	5a
1	0.25	0.8	-78	82		18	
2	0.25	0.8	-22	46		54	
3	0.25	0.8	23	27		73	
4	0.25	10.0	-78	96		4	
5	0.25	10.0	23	56		44	
6	0.16	1.6	23	41		59	
7	0.32	1.6	23	30		70	
8	0.32	0.6	23	15		85	
9	0.20	1.3	23	1		99	
10	0.40	1.8	23	1		99	
11	0.16	1.6	23		62	38	<i>d</i>
12	0.32	1.6	23		43	57	<i>d</i>
13	0.16	0.4	23		56	44	<i>d</i>
14	0.13	1.6	23		40	60	<i>d</i>
15	0.30	1.6	23		54	46	<i>d</i>
16	0.13	0.4	23		44	56	<i>d</i>
17	0.13	1.6	23	45	55		<i>d</i>

^a The reactions are in THF solutions (1.0 ml) containing 0.1 mmol of **1**. The alkyl iodide was rapidly added to the solution containing **1** and the alkyllithium compound. Experiments 1-3 and 6-8 are duplicates; the rest are singles. ^b Experiments 1-8 involved *n*-butyllithium and methyl iodide; 9 and 10 involved methyllithium and *n*-butyl iodide; 11-13 involved *n*-butyllithium and ethyl iodide; 14-16 involved ethyllithium and *n*-butyl iodide; and 17 involved ethyllithium and methyl iodide. ^c Relative yields corrected for response factors obtained by glpc analysis. ^d Not detected (<0.5%).

by the alkyl iodide and the indirect alkylation by the alkyllithium compound initiated by the iodide. More direct alkylation occurs when more iodide is added or if a higher concentration of iodide is maintained in the experiment. For example, slow dropwise addition of a THF solution containing **1** (0.1 mmol) and *n*-butyllithium (0.32 mmol) to a THF solution of methyl iodide (1.6 mmol) yields 50% **4a** and 50% **4d**.

Reaction of THF solutions containing methyllithium and **1** with *n*-butyl iodide yielded only 1% **4a** (expt 9 and 10). Thus methyllithium does not participate in the indirect alkylation reactions to the same extent that ethyl- and *n*-butyllithium do. No indirect alkylation product is detected in reactions of mixtures of **1** and ethyl- or *n*-butyllithium with alkyl bromides or dimethyl sulfate. These observations suggest that the indirect alkylation reactions are related to the lithium-halogen exchange reaction. Methyllithium participates in this reaction only with activated halides,¹⁵ and this reaction does not occur readily between alkyl bromides and alkyllithium compounds.¹⁶

One obvious pathway for alkylation by the alkyllithium compound is *via* its iodide formed in the lithium-halogen exchange reaction. A study of the reaction between *n*-butyllithium and methyl iodide ruled out this pathway as a major source of the **4d** formed in reactions of methyl iodide with mixtures of *n*-butyllithium and **1**. In this study, THF solutions containing 0.16 and 0.32 mmol of *n*-butyllithium were allowed to react with 1.6 mmol of methyl iodide at 23 and -78°. No alkyllithium compounds were detected by nmr in these solutions immediately after mixing. Analysis of the solutions by glpc showed only *n*-butyl iodide and excess methyl iodide were present (*n*-pentane and *n*-octane were not detected) in the -78° reactions, and only a small amount of *n*-octane in addition to the iodides was present in the 23° reactions. The methyl iodide to *n*-butyl iodide mole ratios for the reactions of 0.32 mmol of *n*-butyllithium are 3.0 (-78°) and 2.9 (23°) and for the 0.16 mmol reactions are 7.7. These ratios and the products formed are consistent with eq 1 and 2 as the major reactions. The maximum amount of **4d** expected in reactions of **1** and *n*-butyllithium



with methyl iodide can be calculated if the *n*-butyl iodide formed by eq 1 is its major source. Combination of the mole ratios and the relative reactivities of methyl and *n*-butyl iodide obtained above predicts only 12% **4d** should be formed in the reaction of **1** and 0.32 mmol of *n*-butyllithium with 1.6 mmol of methyl iodide, and only 5% **4d** should be formed in the corresponding reaction in the presence of 0.16 mmol of *n*-butyllithium. These calculations contrast with the yields of **4d** observed, 70 and 59%, in expt 7 and 6. The calculations were tested by reacting 0.1 mmol of **1** with the THF solution resulting from the reaction of 0.32 mmol of *n*-butyllithium and 1.6 mmol of methyl iodide at 23°. Only 10% **4d** is formed in this reaction. This result and the results of the inverse addition experiments described above indicate that the *n*-butyl iodide formed by lithium-halogen exchange reaction is not a major source of the **4d** formed by indirect alkylation of **1** with *n*-butyllithium.

The stereoselectivity of the direct and indirect ethylations of the less sterically demanding carbanion 10-ethyl-9-lithio-9,10-dihydroanthracene (**3**) is the same. Reaction of a THF solution containing 0.5 mmol of **3** and 1.0 mmol of ethyllithium with 1.6 mmol of methyl iodide at -78° yields 18% *cis*-10-ethyl-9-methyl-9,10-dihydroanthracene and 1% *trans*- and 80% *cis*-9,10-diethyl-9,10-dihydroanthracene. The relative amounts of *trans*- and *cis*-9,10-diethyl-9,10-dihydroanthracene obtained in this reaction (2:98) are essentially the same as those obtained on reaction of **3** with ethyl bromide or iodide in THF solution at -78° (1:99).

No *cis*- or *trans*-9-*tert*-butyl-10-ethyl-9,10-dihydroanthracene is formed in reactions at -78° of THF solutions containing 0.5 mmol of **3** and 1.7 mmol of *tert*-butyllithium with 2.4 mmol of methyl or ethyl iodide. The only products detected are 10-ethyl-9-methyl-9,10-dihydroanthracene (99% *cis*) and 9,10-diethyl-9,10-dihydroanthracene (99% *cis*), respectively. When a THF solution containing 0.5 mmol of **3** and 1.7 mmol of *tert*-butyllithium was allowed to warm to 23° before reaction with 2.4 mmol of methyl iodide, 8% *trans*- and 46% *cis*-10-ethyl-9-methyl-9,10-dihydroanthracene and 46% 10-ethyl-9-neohexyl-9,10-dihydroanthracene (tentatively identified by nmr) are formed. The cleavage of THF to ethylene and the enolate of acetaldehyde by *tert*-butyllithium is so rapid there might not have been any *tert*-butyllithium present when the methyl iodide was added.¹⁷ The *tert*-butyllithium also reacts rapidly with the ethylene to yield neohexyllithium,¹⁸ which then indirectly alkylates **3**. Neohexyl halides undergo S_N2 displacements at very slow rates.¹⁹ Thus the apparent incorporation of the neohexyl group is also strong evidence against indirect alkylation occurring *via* the iodide of the alkyllithium compound formed in the lithium-halogen exchange reaction.

Indirect alkylation reactions also occur when mixtures of **1** and *n*-butyllithium are allowed to react with methyl or ethyl iodide in diethyl ether or triglyme solutions. The reactions in these solvents have the same characteristics as the more extensively studied reactions in THF solution.

Discussion

The stereospecific direct and indirect alkylations of **1** and **2** *trans* to the 10-*tert*-butyl group in diethyl ether, THF, triglyme, and HMPA solutions indicate that these reactions are not a function of the predominant ion pair present. Alkylation of **1** and **2** by alkyl iodides *via* the two-step mechanism involving a lithium-halogen exchange reaction should yield a mixture of products.¹ The observed identical stereo-

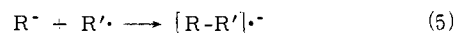
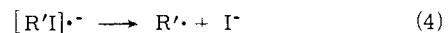
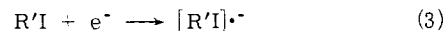
specificities for the alkyl iodides and other alkylating agents as well as the relative reactivities obtained in the competitive alkylation experiments are consistent with a S_N2 mechanism and rule out the two-step mechanism.

The alkylation reactions of **1**, **2**, and **3** seem to be controlled mainly by steric interactions. Others^{1-3,5} have discussed protonation and alkylation stereoselectivities of 9-lithio-9,10-dihydroanthracenes in terms of bent carbanions that exist as equilibrium mixtures of *cis* and *trans* diastereomers (10-alkyl group relative to anion electron pair). Our results are consistent with this analysis as well as one based on a planar carbanion. The latter hypothesis has the advantage of not requiring that either the 10-alkyl group of the carbanion or the entering alkyl group assumes a pseudo-equatorial position along the reaction pathway for alkylation *trans* to the 10-alkyl group.

The results of the reactions of mixtures of **1** or **3** and alkyllithium compounds with alkyl iodides are also not consistent with the iodide derived from the carbanion as an intermediate. The stereoselectivities of indirect alkylation by *n*-butyl- and ethyllithium are not what would be expected. Moreover the temperature effect and the ineffectiveness of methyl- and *tert*-butyllithium at indirect alkylation are not readily explained by this pathway. Although the relative reactivities of alkyllithium compounds are a function of concentration and reaction type,²⁰ *tert*-butyllithium in particular should have reacted with the iodide derived from **3**. The iodides derived from **1** and **2** are tertiary. Thus elimination should be a major reaction with the alkyllithium compounds.^{21,22} Neither the elimination products nor the products expected from further reaction with alkyllithium compounds²³ and alkyl iodides were detected in the reaction mixtures.

Indirect alkylations of **1** and **3** by alkyllithium compounds occur only under conditions when the lithium-halogen exchange reaction can occur. We have established that the alkyl iodide derived from the alkyllithium compound and the iodide derived from the carbanion by lithium-halogen exchange reaction are not important intermediates in these reactions. A mechanism which is consistent with our observations has as its key step trapping of the free radical intermediates in the lithium-halogen exchange reaction²⁴ by the carbanion.

Nitro compound anions, enolate anions, and resonance stabilized carbanions can participate in alkylation²⁷ or arylation²⁸ reactions which have as a key step coupling of the anion with a radical. These reactions are usually short^{27a} chain reactions (eq 4-6) initiated by light or the addition of an electron donor (eq 3). (R[•] = **1** or **3**; R' is the alkyl group



of the iodide or the lithium compound.) The radical anion of the coupled product formed in eq 5 can donate an electron to the alkyl iodide (eq 6) or an alkyl radical (eq 7). The initiation step in our reactions is formation of free radicals intermediates in lithium-halogen exchange reactions.

The observed preference of methylithium for coupling rather than lithium-halogen exchange reactions implies no radicals will be formed in reactions of methylithium with *n*-butyl iodide. The low yields of **4a** formed in reactions of mixtures of methylithium and **1** with *n*-butyl iodide are consistent with this. The nonradical nature of some lithium-

halogen exchange reactions at low temperature^{14a,29} could explain the temperature dependence of the indirect alkylations and the lack of indirect alkylation by *tert*-butyllithium at -78° . The preferential incorporation of ethyl or *n*-butyl groups in indirect alkylations by ethyl- or *n*-butyllithium initiated by methyl iodide imply the formation of more ethyl or *n*-butyl radicals than methyl radicals. Several factors which could contribute to this are: (1) reduction of an alkyl radical (eq 7) is more rapid than reduction of methyl iodide (eq 6); (2) radical forming lithium-halogen exchange reactions are occurring between *n*-butyllithium and *n*-butyl iodide or ethyllithium and ethyl iodide; or (3) iodine atom transfer from *n*-butyl or ethyl iodide to methyl radical is occurring to form *n*-butyl or ethyl radicals and methyl iodide.³⁰ The radical trapping mechanism for indirect alkylations is consistent with the observed identical stereospecificities for direct and indirect alkylations since the bond forming step in both cases involves nucleophilic attack by the carbanion.

The scope of these indirect alkylation reactions will be explored with a variety of resonance stabilized carbanions in order to determine their efficacies as radical traps. The use of this technique to introduce hindered alkyl groups, *e.g.*, neopentyl and neohexyl, will also be studied.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under atmospheres of prepurified nitrogen. Ether was distilled from lithium aluminum hydride under a nitrogen atmosphere immediately before use. THF was distilled from a dark purple solution of sodium benzophenone dianion under a nitrogen atmosphere immediately before use. HMPA and triglyme were vacuum distilled from sodium twice before use. Melting points were obtained using a Laboratory Devices Mel-Temp capillary melting point apparatus and are uncorrected. Nmr spectra were run as carbon tetrachloride solutions on a JEOL MH-100 spectrometer; chemical shifts are reported in parts per million downfield from internal tetramethylsilane and coupling constants in hertz. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Analytical glpc analyses were performed on a Gow-Mac Model 750 instrument (flame ionization detector). The components in reaction mixtures from **1** were analyzed using a 6-ft 10% DEGS on 80-100 mesh Chromosorb W(AW) column operating at 155° . The components in reaction mixtures from **2** and **3** were analyzed using a 10-ft 10% SE-30 on 80-100 mesh Chromosorb W column operating at 210° . Response factors for the hydrocarbons were determined relative to **4a**. Compounds could be identified by nmr spectra of the crude reaction mixtures since the reactions were so clean. The components in the reactions of methyl iodide and *n*-butyllithium were analyzed on the DEGS column at ambient temperature. The response factor of *n*-butyl iodide was determined relative to methyl iodide.

Materials. Methylithium (from methyl chloride) was purchased as an ether solution from Foote. Ethyllithium was synthesized from ethyl bromide and lithium metal (low sodium) in ether solution.¹⁵ *tert*-Butyl- and *n*-butyllithium were purchased from Lithium Corporation of America as hydrocarbon solutions. Concentrations of organolithium reagent solutions were determined by the Gilman double-titration method with 1,2-dibromoethane.³¹ Solutions of **1** and **2** were prepared as described previously,⁴ and **3** was prepared by the reaction of anthracene with ethyllithium in THF solution.^{2,5}

The *cis*- and *trans*-9,10-dimethyl-, 9,10-diethyl-, 10-ethyl-9-methyl-, 10-*tert*-butyl-9-ethyl-, and 10-*tert*-butyl-9-methyl-9,10-dihydroanthracenes were synthesized by literature procedures.¹⁻⁴ The alkyl halides and sulfates were purified by distillation. Professor M. Y. Darensbourg of this department supplied the triethyloxonium tetrafluoroborate.

10-*tert*-Butyl-9,9-dialkyl-9,10-dihydroanthracene (4a-d, 5a,b). All these compounds were synthesized in high yield by the procedure given for **5b** from **1** (**4a-d**) or **2** (**5a-b**). The nmr spectra are given in Table I, and analytical data are given in Table IV.

Table IV. 9,9,10-Trialkyl-9,10-dihydroanthracenes (**4** and **5**)

Compd	Mp, $^{\circ}$ C	Calcd, %		Found, %	
		C	H	C	H
4a	54-55	90.85	9.15	90.75	9.29
4b	94-96	90.59	9.41	90.38	9.56
4c	96-98	90.35	9.66	90.16	9.64
4d	97.5-99	90.13	9.87	90.18	9.70
5a	Oil	90.59	9.41	90.48	9.29
5b	84-86	90.35	9.66	90.40	9.60

To a solution of 10-*tert*-butyl-9-ethyl-9,10-dihydroanthracene (0.408 g, 1.55 mmol) in THF (15 ml) at 0° was added to a solution of *n*-butyllithium (3.2 mmol) in hexane. The resulting red solution of **2** was stirred for 6 hr before quenching with ethyl bromide. Addition of water and ether followed by conventional work-up afforded **5b** (0.5 g). Recrystallization from ethanol provided the analytical sample (0.32 g), mp $84-86^{\circ}$.

The direct and indirect alkylation reactions were usually done by adding the alkylating agent by microliter syringe to 1-ml aliquots of *ca* 0.1 *N* solutions of **1**, **2**, and **3**. The mixture solutions for the indirect alkylations of **1** were prepared by adding a solution of the alkylolithium compound by microliter syringe to 0.5 ml of a 0.2 *N* solution of **1**. This solution was then diluted to 1.0 ml. The mixture solutions for the indirect alkylations of **3** were prepared the same way but on a larger scale. All these solutions were prepared in centrifuge tubes that were oven dried (160°), flushed with dry nitrogen, and capped with No-Air stoppers.

The solutions for *competitive alkylation reactions* were prepared by adding 0.4 ml of THF and measured quantities of two alkylating agents by microliter syringe to a dry, nitrogen flushed centrifuge tube capped with a No-Air stopper and equipped with a magnetic stirring bar. The centrifuge tube was immersed in an ambient temperature (23°) water bath, and the quench solution was vigorously stirred while 0.5 ml of a 0.2 *N* THF solution of **1** was added dropwise by cannula. Water (10 ml) and hexane (2 ml) were added to the tube, and the upper layer was analyzed by glpc.

The inverse addition indirect alkylation reactions were done in a similar fashion.

Reaction of *n*-Butyllithium and Methyl Iodide. THF solutions (0.5 ml) of *n*-butyllithium containing 0.32 and 0.16 mmol were prepared at -78° in dry, nitrogen flushed centrifuge tubes capped with No-Air stoppers. Methyl iodide (100 μ l, 1.6 mmol) was added to one solution of each concentration at -78° and one solution containing 0.16 mmol of *n*-butyllithium and two solutions containing 0.32 mmol at 23° . One of the latter solutions was transferred to a dry, nitrogen flushed nmr tube capped by No-Air stopper by cannula. The remaining solutions were quenched with 6 ml of water and 0.5 ml of *n*-hexane before glpc analysis. One solution of 0.32 mmol of *n*-butyllithium was allowed to warm to 23° and was quenched with 6 ml of water and 0.5 ml of *n*-hexane. This served as a blank for glpc analysis.

10-Ethyl-9-neohexyl-9,10-dihydroanthracene was isolated from a reaction of **3** (0.5 mmol) and *tert*-butyllithium (1.7 mmol) with methyl iodide (2.4 mmol) in THF solution at 23° by collection from a 10 ft \times 0.25 in. 10% SE-30 glpc column at 200° as a colorless oil. The nmr [(CCl₄) δ 0.80 (s, 9 H), 1.05 (t, $J = 7.0$ Hz, 3 H), 1.20-1.40 (m, 2 H), 1.50-1.85 (overlapping q, m, $J = 7.2$ Hz, 4 H), 3.67 (t, $J = 7.2$ Hz, 2 H), 7.13 (s, 8 H)] is consistent with the assigned compound and suggests that the compound collected is the *cis* diastereomer.

Acknowledgment. The Tulane University Chemistry Department is thanked for its support. The nmr spectrometers were purchased with funds supplied mainly by the Gulf Foundation.

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Partial Photoresolution. IV. *cis*- and *trans*-Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) Photoisomerization and Inversion at 5461 Å in Chlorobenzene Solution

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Abstract: The partial resolution of both *cis*- and *trans*-tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) was accomplished in chlorobenzene solution by irradiation with circularly polarized light at 5461 Å. Because photoisomerization accompanied inversion, the *cis* and *trans* isomers were separated by tlc. The circular dichroism spectra, normalized to optically pure enantiomer, yielded maxima at 615 and 430 nm and a minimum at 545 nm. The only significant difference between the CD spectra is that the values of ($\epsilon_l - \epsilon_r$) at the 545- and 615-nm bands are more positive for the *trans* isomer. This discrepancy is justified stereochemically. Quantum yields were obtained for the six possible transformations in the *cis*-*trans* system, *i.e.*, inversion of either geometrical isomer without isomerization, inversion of either isomer with isomerization, and isomerization of either isomer without inversion. The results indicate that all processes occur, suggesting that both bond-rupture and twisting mechanisms are present.

Partial photoresolution or the process of inducing optical activity in a racemic mixture by causing a photolytic inversion of enantiomers has been applied successfully to Cr(III) complexes with oxalato,¹⁻³ ethylenediamine,⁴ 1,10-phenanthroline, and 2,2'-bipyridine,⁵ and acetylacetonato⁶ ligands. In the Cr(acac)₃ case, the reaction quantum yields in various organic solvents were smaller than for Cr(ox)₃³⁻ in aqueous solution by factors of 50 or so,⁶ suggesting perhaps that the photolysis mechanism of the former is quite different from that of the latter, which is assumed to invert through a water catalyzed bond-rupture process.⁷

The tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III), or Cr(tfa)₃, system, while being chemically very similar to Cr(acac)₃, should yield more information concerning the mechanism(s) of inversion because of the fact that a geometrical isomerization may occur simultaneously with the optical inversion as a result of the unsymmetrical ligand. This gives rise to the photokinetic system shown in Figure 1. Because certain mechanisms, *e.g.*, trigonal twist, rhombic twist, bond rupture with trigonal-bipyramid intermediate, etc., are allowed by only certain pathways, **1** through **6**, a knowledge of values of the six quantum yields

should give some insight into the preferred mechanism(s).

In addition to photokinetic information, a photoresolution yields the ORD and CD spectra of optically pure enantiomers, which have not been hitherto obtained by other workers. Sometimes it is assumed in studies of systems of complexes like this one that the *cis* and *trans* isomers have the same rotational strengths, and so another reason for this study was to test the validity of such an assumption.

Experimental Section

The compound Cr(tfa)₃ was prepared according to an established procedure.⁸ The *cis* and *trans* isomers were completely separated on 1000- μ , 20 × 20 cm, tlc plates (Analtech silica gel G) using 50:50 v/v benzene-hexane for the developing solvent. The slower moving fraction, which was less abundant, was assumed to be the *cis* isomer because of similar results obtained by Fay and Piper on liquid columns.⁹ The *R_f* factors are about 0.33 and 0.16 for the *trans* and *cis* isomers, respectively. In order to increase the amount of *cis* isomer, the purified *trans* isomer was dissolved in *o*-dichlorobenzene and refluxed for several hours after which the tlc fractionation procedure was repeated. *Anal.* Calcd for Cr(CF₃COCHCOCH₃)₃: C, 35.22; H, 2.35; F, 33.46. Found: