

The product, α, α' -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene, bp 104–108° (29 mm), was obtained in 50–80% yield.

Anal. Calcd for $C_8H_4F_4Br_2$: C, 28.60; H, 1.20; F, 22.62; Br, 47.58. Found: C, 28.85; H, 1.34; F, 22.87; Br, 47.85.

α, α' -Bis(ethylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIa).—To a solution of 2.53 g (0.11 mol) of sodium in 40 ml of methanol was added 6.2 g (0.1 mol) of ethyl mercaptan. The solution was then diluted with 100 ml of dimethyl sulfoxide. After 15.1 g (0.045 mol) of α, α' -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was added, the solution was heated at 50–60° for 2 hr, stirred at room temperature for 16 hr, and poured into ca. 750 ml of water. The product separated and was isolated from the aqueous mixture by extraction with three 300-ml portions of methylene chloride. Removal of methylene chloride by evaporation followed by distillation gave 10.2 g (75%) of the thio ether: bp 90–110° (0.2 mm); mp 70–78°.

α, α' -Bis(propylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIb).—This compound was prepared by the same procedure described for VIa.

From 7.6 g (0.1 mol) of propyl mercaptan and 15.1 g (0.045 mol) of α, α' -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 11.8 g (76%) of the thio ether, bp 123–140° (0.5–1 mm).

α, α' -Bis(butylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIc).—This compound was prepared by the same procedure described for VIa.

From 10.0 g (0.1 mol) of butyl mercaptan and 15.1 g (0.045 mol) of α, α' -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 12.0 g (75%) of this ether, bp 130–140° (0.2 mm).

α, α' -Bis(ethylsulfonyl)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (IIIa).—To a stirred solution of 24.8 g (0.083 mol) of α, α' -bis(ethylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (VIa) in 300 ml of 1:1 acetic acid–acetic anhydride cooled at 0–5° was added dropwise 57 ml

(0.5 mol) of H_2O_2 of 30% hydrogen peroxide over 1–2 hr. The reaction mixture was allowed to warm to room temperature gradually over 3–4 hr, stirred for 24 hr, and poured into water (ca. 500 ml). The bissulfone separated and was filtered and washed successively with water, 5% sodium carbonate, and water. Recrystallization from chloroform–hexane gave 24 g (80%) of the bissulfone, mp 163–164°.

Anal. Calcd for $C_{12}H_{14}F_4S_2O_4$: C, 39.77; H, 3.89; F, 20.97; S, 17.7. Found: C, 39.73; H, 3.91; F, 20.74; S, 17.50.

α, α' -Bis(propylsulfonyl)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (IIIb).—This compound was prepared by the procedure described for IIIa.

From 26.2 g (0.08 mol) of α, α' -bis(propylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 20.2 g (65%) of the sulfone, mp 162–163°.

Anal. Calcd for $C_{14}H_{18}F_4S_2O_4$: C, 43.11; H, 4.65; F, 19.48; S, 16.44. Found: C, 43.16; H, 4.91; F, 19.78; S, 16.25.

α, α' -Bis(butylsulfonyl)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene (IIIc).—This compound is prepared by the procedure described for IIIa.

From 35.4 g (0.1 mol) of α, α' -bis(butylthio)- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene was obtained 21 g (50%) of the sulfone IIIc, mp 163–166°.

Anal. Calcd for $C_{16}H_{22}F_4S_2O_4$: C, 45.02; H, 5.32; F, 18.16; S, 15.32. Found: C, 45.28; H, 5.33; F, 18.36; S, 15.58.

Registry No.—II, 3345-29-7; IIIa, 3200-21-3; IIIb, 3200-22-4; IIIc, 3200-23-5; IVa, 651-12-7; IVb, 2629-68-7; VIa, 3200-26-8; VIb, 3200-28-0; VIc, 3200-13-3.

Stereospecific Coupling Reactions between Organolithium Reagents and Secondary Halides¹

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In sharp contrast to simple alkylolithium reagents, which give largely racemized products in their coupling reactions with optically active organic halides, the present study shows that charge-delocalized organolithium reagents couple with optically active secondary halides with predominant inversion of configuration. The organolithium reagents studied were benzyl-, allyl-, and benzhydryllithium. Optically active secondary halides studied were 2-bromobutane, 2-bromooctane, 2-chlorooctane, and α -phenylethyl chloride. It is of considerable interest for dynamic stereochemistry that the present finding of good inversion stereospecificity for reactions of charge-delocalized RLi reagents parallels the situation for certain poor leaving groups on asymmetric silicon, which actually give retention of configuration with simple alkylolithium reagents. The tendency for charge-delocalized RLi to give inversion thus appears to be fairly general.

Reaction of an optically active secondary halide with an alkylolithium reagent gives a low yield of coupled product and proceeds with predominant racemization (98%) of the asymmetric center.³ Analogous reactions utilizing organosodium^{4,5} and Grignard reagents^{5–8} show considerable variation in stereospecificity and yield. In several cases, condensation reactions using charge-delocalized organosodium and Grignard reagents, where the charge on the carbanion is partially dispersed through a π system, proceed with almost 100% inversion of configuration at the asymmetric

carbon bearing the halogen. Both pyrrolylmagnesium bromide⁷ and benzyllithium^{4,9} coupled with 2-bromobutane without apparent loss of optical activity.¹⁰

The latter results and the observation that the stereochemical pathway in organosilicon coupling reactions is influenced to a great extent by the degree of charge delocalization in organometallic reagents¹² indicated that some types of organolithium reagents might couple with optically active organic halides with a high degree of stereospecificity.

Results

Charge-delocalized organolithium reagents coupled with optically active secondary halides with a stereo-

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TABLE I
 COUPLING REACTIONS OF ORGANOLITHIUM REAGENTS WITH OPTICALLY ACTIVE SECONDARY HALIDES

R'X reactant	$[\alpha]^{25D}$, deg	Optical purity, %	RLi reagent	R'R product	$[\alpha]^{25D}$, ^a deg	Optical purity, %	Stereo speci- ficity, ^b % inversion	Yield, %
2-BrC ₄ H ₉	+6.2	15.7 ^c	C ₆ H ₅ CH ₂ Li	C ₂ H ₅ CH(CH ₃)CH ₂ C ₆ H ₅	-1.98	17.8 ^d	100 ^e	58
2-BrC ₈ H ₁₇	-33.5	82 ^f	C ₆ H ₅ CH ₂ Li	C ₆ H ₁₃ CH(CH ₃)CH ₂ C ₆ H ₅	-5.03	85
2-BrC ₈ H ₁₇	+27.3	66.8 ^f	CH ₂ =CHCH ₂ Li ^h	C ₆ H ₁₃ CH(CH ₃)CH ₂ CH=CH ₂	+5.30	76.6 ^f	100 ^e	68
2-ClC ₈ H ₁₇	-30.8	85.5 ^f	CH ₂ =CHCH ₂ Li ^h	C ₆ H ₁₃ CH(CH ₃)CH ₂ CH=CH ₂	-5.50	78.5 ^f	92	59
C ₆ H ₅ (CH ₃)CHCl	+88.5 ^g	70.3 ⁱ	CH ₂ =CHCH ₂ Li ^h	C ₆ H ₅ CH(CH ₃)CH ₂ CH=CH ₂	-4.25 ^k	26.5 ⁱ	38	34
C ₆ H ₅ (CH ₃)CHCl	-24.3	19.3 ⁱ	CH ₂ =CHCH ₂ Li ^m	C ₆ H ₅ CH(CH ₃)CH ₂ CH=CH ₂	+0.90 ^k	5.6 ⁿ	29	39
C ₆ H ₅ (CH ₃)CHCl	-59.3	47.0 ⁱ	(C ₆ H ₅) ₂ CHLi	C ₆ H ₅ CH(CH ₃)CH(C ₆ H ₅) ₂	-11.7 ^o	54 ^p	100 ^{e,q}	48

^a Measured neat in a 1-dm tube unless otherwise noted. ^b A stereospecificity of, say, 90% means that the product was 90% optically pure (10% racemic) if optically pure reactant was used. ^c Based on a calculated maximum value of $[\alpha]^{25D}$ 39.4°. ^d Based on a calculated value of $[\alpha]^{25D}$ 11.6°. ^e The actual value is >100%. The deviation from 100% is outside experimental error and indicates the use of a valve either too high for optically pure halide or too low for optically pure product. ^f Based on the experimental value of $[\alpha]^{25D}$ 42.0°. See W. Gerrard and H. R. Hudson, *J. Chem. Soc.*, 2310 (1964). ^g The value for optically pure product has not been determined. ^h Prepared from tetraallyltin and *n*-butyllithium in pentane solvent. ⁱ Based on a calculated value of $[\alpha]_D$ 7.0°. ^j Based on the experimental value of $[\alpha]^{25D}$ 36.1°. See H. Brauns, *Rec. Trav. Chem. Pays-Bas*, 65, 799 (1946). ^k Reported as observed rotation α_D rather than specific rotation $[\alpha]_D$. ^l Based on a calculated maximum value of α_D 126°. ^m Prepared by lithium metal cleavage of allyl phenyl ether. ⁿ Based on a calculated value of α_D 16.1°. ^o In acetone solvent. ^p Based on the experimental maximum value of $[\alpha]_D$ 2.17° (*c* 1.2, acetone). ^q The stereochemistry of this reaction has not been rigorously determined. See text for discussion of assigned stereospecificity.

specificity comparable in all but one case with that obtained from reactions with similar organosodium reagents. In five reactions where the configurations of the halides and the hydrocarbon products had been related, the predominant stereochemical pathway was inversion of configuration. The results are summarized in Table I.

Benzyl lithium and allyllithium coupled with secondary bromoalkanes with essentially 100% inversion of configuration. The per cent optical purity of the products from the coupling reaction was based on values obtained by an alternate synthetic sequence which did not involve the asymmetric center and which utilized high-purity 2-methylbutanol.⁴ *Inversion* of configuration is indicated because the configurations of (+)-2-bromobutane and (+)-2-bromooctane have been related to (+)-1-phenyl-2-methylbutane and (-)-4-methyl-1-decene.⁴ Using the maximum values for the bromides found in the literature, $[\alpha]^{25D}$ 39.4° for 2-bromobutane¹¹ and $[\alpha]^{20D}$ 42.0° for 2-bromooctane,¹³ as values for the optically pure halides, a stereospecificity in excess of 100% was calculated. This inconsistency may reflect slight inaccuracies of the maximum specific rotations of the halides and hydrocarbons used.

The reaction between the chloride, (-)-2-chlorooctane which has the same configuration as (-)-2-bromooctane,¹⁴ and allyllithium proceeded with a slightly lower stereospecificity, 92% inversion of configuration. This decrease again may indicate an inaccuracy in the values assumed for optically pure materials, rather than a difference in reactivity between the chloride and the bromide.

Reaction of (+)- α -phenylethyl chloride with allyllithium prepared from reaction of tetraallyltin and *n*-butyllithium gave (-)-2-phenyl-1-pentene with 38% inversion of configuration and 62% racemization. The stereospecificity is based on the theoretical maximum value of α_D 126° for α -phenylethyl chloride.⁵ (-)-2-Phenyl-1-pentene and (-)-2-phenylpentane have the

same configuration and have been related to (-)- α -phenylethyl chloride.¹⁵ Since the stereospecificity and yield were low compared with that observed in the analogous reaction with allylsodium,⁵ the reagent was prepared by a second method, cleavage of allyl phenyl ether with lithium metal in ethyl ether solvent. A slightly lower stereospecificity, 29% inversion of configuration, and 71% racemization was obtained in the second reaction. Although excellent stereospecificity in the reaction of allylsodium with α -phenylethyl chloride (>85%)⁵ tends to discount such a possibility, we agree with the point made by a referee that the lowered stereospecificity in the reaction of allyllithium with α -phenylethyl chloride might reflect fast metalation of the formed product, 2-phenyl-1-pentene, followed by racemization of the derived benzylic carbanion.

When benzhydryllithium was coupled with (-)- α -phenylethyl chloride, α_D -59.3°, 47% optically pure, the fractionally distilled product had $[\alpha]_D$ -11.7°. Repeated recrystallization from methanol, which did not change the infrared spectrum, increased the specific rotation to a maximum value of -21.7° (*c* 1.2, acetone). On the classical (but nonrigorous) assumption that the latter value *approximates* that of the optically pure hydrocarbon, the reaction can be assigned a high stereospecificity. Based on starting chloride of 47% optical purity and the optimistic view that optically pure product has $[\alpha]_D$ -21.7°, this assumption gives a value of 100% for the stereospecificity, but the latter should be regarded with caution.

Even though the configuration of (+)-1,1,2-triphenylpropane has not been rigorously related to (-)- α -phenylethyl chloride,¹⁶ the assumption that inversion of configuration obtains for the coupling of benzhydryllithium with α -phenylethyl chloride seems reasonable, because, in all five cases where the configurations have been related, charge-delocalized organolithium reagents condensed with secondary halides with inversion of configuration.

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recrystallizations from methanol, 0.22 g of product was recovered: $[\alpha]^{25}_D -21.7^\circ$ (*c* 1.2, acetone); mp $75-76^\circ$ [lit.¹⁶ mp $76-77^\circ$; $[\alpha]_D +6.67^\circ$ (*c* 14.8, acetone)]. The infrared spectrum did not change with recrystallization.

A second reaction performed under very similar conditions gave (-)-1,1,2-triphenylpropane, $[\alpha]_D -3.38^\circ$ (*c* 27.8, acetone), in 93% yield from (-)- α -phenylethyl chloride, $[\alpha]^{24}_D -15.0^\circ$ (neat, *l* = 1 dm).

Registry No.—(+)-2-Bromobutane, 5787-32-6; (-)-2-bromooctane, 5798-55-2; (+)-2-bromooctane, 1191-24-8; (-)-2-chlorooctane, 18651-57-5; (+)- α -phenylethyl chloride, 1459-15-0; (-)- α -phenylethyl chloride, 3756-41-0; benzyl lithium, 766-04-1; allyllithium, 3052-45-7; benzhydryllithium, 881-42-5.

Metal-Ammonia Reduction. VII. Stereospecific Reduction in the Phenanthrene Series^{1,2}

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Phenanthrene and its 9-alkyl- and 9,10-dialkyl derivatives are efficiently reduced in the 9,10 position by lithium in ammonia in the presence of colloidal iron. 9,10-Dimethyl- and 9,10-diethylphenanthrene undergo stereospecific *cis* reduction under these conditions. The corresponding *trans* diastereomers required for comparison by variable-temperature nmr were synthesized *via* alkylation of the corresponding 9-alkyl-10-lithio-9,10-dihydrophenanthrenes. The unstable second-stage reduction product of phenanthrene was assigned the 2,4a,9,10-tetrahydrophenanthrene structure on the basis of nmr and uv data, and comparison with its 4a-methyl homolog obtained through reductive methylation of phenanthrene. Stereospecific *cis* reduction and *trans* alkylation are explicable in terms of the conformational properties of the respective monoanionic intermediates and preferential axial attack during final protonation and alkylation, respectively.

Efficient single-stage reduction of a series of representative polycyclic aromatic hydrocarbons (anthracene, naphthalene, benz[*a*]anthracene, dibenz[*a,h*]anthracene, 3-methylcholanthrene, and pyrene) by lithium dissolved in liquid ammonia was described in parts I–IV of this series.³ The structures of the dihydro products accorded, in general, with predictions⁴ based upon molecular orbital calculations of the positions of highest electron density in the anionic intermediates. Also, stepwise reduction (of anthracene and benz[*a*]anthracene^{3b}) provided products whose structures at each stage were in accord with qualitative prediction of relative anionic stabilities. The steric course of reduction also proved highly specific;^{3a} 9,10-dialkylanthracene and 7,12-dimethylbenz[*a*]anthracene furnished the corresponding *trans*-dialkyldihydro derivatives exclusively.⁵

The present paper reports detailed investigation of reduction in the phenanthrene series. Evidence is presented concerning the stereochemistry of reduction of 9,10-dialkylphenanthrene, the structures of secondary products, and the effects of reaction variables on the course of reaction.

Previous investigations have been confined to phenanthrene itself. Hückel and Bretschneider⁶ reported treatment of phenanthrene in liquid ammonia with 2 g-atoms of sodium to provide small quantities of 9,10-dihydrophenanthrene; 4 equiv of the metal gave a mixture believed to contain 1,2,3,4-tetrahydrophenanthrene. Analogous reduction in the presence of alcohol

furnished, according to Mejer,⁷ 1,2,3,4,4a 9,10,10a-octahydrophenanthrene as the sole product.

Results

Phenanthrene, in accord with theoretical prediction,⁴ underwent preferential lithium-ammonia reduction at the 9,10 position.^{3a} However, under conditions previously demonstrated to provide efficient transformation of acene hydrocarbons to dihydro derivatives,³ reduction of phenanthrene and 9-methylphenanthrene was incomplete and accompanied by secondary products (Table I, experiments 1, 2, and 9).

A brief investigation of reaction conditions led to an improved procedure which provided 9,10-dihydro derivatives of phenanthrene (**1a**), 9-alkylphenanthrene (**1b** and **1c**), and 9,10-dialkylphenanthrene (**1d** and **1e**) (Chart I) with yields generally of 70–80% (Table I). The beneficial effects of colloidal iron on limiting further reduction^{3b} were evident in the transformation of **1b** to **2b** [74–82% in the presence of catalytic quantities of iron (experiments 10 and 11) and only 17% in its absence (experiment 9)]. In the case of phenanthrene itself, the corresponding percentages of 9,10-dihydrophenanthrene were 80% (experiment 5) and 57% (experiment 6), respectively. In 20 min, conversion of phenanthrene was essentially complete in the absence of iron (experiment 8) and 85% in its presence (experiment 7). Thus, phenanthrene tends to undergo over-reduction in the absence of iron and under-reduction in its presence; adjustment of the ratio of lithium to hydrocarbon appears to only partially compensate these tendencies. This "iron effect" appears to involve, as suggested earlier,^{3b} iron-catalyzed consumption of surplus lithium. In practice, it is convenient to employ excess lithium (3.5 g-atoms) and conduct reactions in the presence of iron (0.05 g-atom), taking advantage of the fact that the dihydrophenanthrenes are more

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