The product, α, α' -dibromo- $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoro-*p*-xylene, bp

104-108° (29 mm), was obtained in 50-80% yield. *Anal.* Caled 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 chlo-ride. 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 H₂O₂ 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 Recrystallization from chloroform-hexane gave 24 g water.

(80%) of the bissulfone, mp 163-164°.
Anal. Calcd for C₁₂H₁₄F₄S₂O₄: 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 C14H18F4S2O4: 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 C16H22F4S2O4: 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; VĨc. 3200-13-3.

Stereospecific Coupling Reactions between Organolithium Reagents and Secondary Halides¹

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Received June 5, 1969

In sharp contrast to simple alkyllithium 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 alkyllithium reagents. The tendency for chargedelocalized RLi to give inversion thus appears to be fairly general.

Reaction of an optically active secondary halide with an alkyllithium 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 reagents⁵⁻⁸ 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

(1) We acknowledge the generous support of the Dow Corning Corp. and a NSF Summer Fellowship to W. K.

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(5) R. L. Burwell, A. D. Shields, and H. Hart, J. Amer. Chem. Soc., 76, 908 (1954).

(6) R. L. Letsinger and J. G. Traynham, ibid., 72, 849 (1950).

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(8) P. A. Levene and R. E. Marker, J. Biol. Chem., **97**, 563 (1932).

carbon bearing the halogen. Both pyrrylmagnesium bromide⁷ and benzylsodium^{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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(12) L. H. Sommer, W. D. Korte, and P. G. Rodewald, ibid., 89, 862 (1967).

⁽⁹⁾ R. L. Letsinger, J. Amer. Chem. Soc., 70, 406 (1948).

⁽¹⁰⁾ Letsinger⁹ originally estimated that the reaction proceeded with approximately 74% inversion (26% racemization) using a maximum value for 2-bromobutane which was too low.11

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

R'X reactant	[α] ²⁴ D, deg	Optical purity, %	RLi reagent	R'R product	[α] ²⁴ D, ^α deg	Optical purity, %	Stereo speci- ficity, ^b % inversion	Yield, %
2-BrC4H9	+6.2	15.7	$C_6H_5CH_2Li$	$C_2H_5CH(CH_3)CH_2C_6H_5$	-1.98	17.84	100*	58
$2\text{-BrC}_8\text{H}_{17}$	-33.5	821	$C_6H_5CH_2Li$	$C_6H_{13}CH(CH_3)CH_2C_6H_5$	-5.03	• • • •		85
$2\text{-BrC}_8\text{H}_{17}$	+27.3	66.8^{f}	$CH_2 = CHCH_2Li^h$	$C_6H_{13}CH(CH_3)CH_2CH=CH_2$	+5.30	76.6^i	100°	68
2-ClC ₈ H ₁₇	-30.8	85.5^{i}	$CH_2 = CHCH_2Li^h$	$C_6H_{13}CH(CH_3)CH_2CH=CH_2$	-5.50	78.5^{i}	92	59
C ₆ H ₅ (CH ₃)CHCl	$+88.5^{k}$	70.3^{i}	$CH_2 = CHCH_2Li^h$	$C_6H_5CH(CH_3)CH_2CH=-CH_2$	-4.25^{k}	26.5^{\imath}	38	34
C ₆ H ₅ (CH ₃)CHCl	-24.3	19.3^{i}	$CH_2 = CHCH_2Li^m$	$C_6H_5CH(CH_3)CH_2CH=CH_2$	$+0.90^{k}$	5.6^n	29	39
C ₆ H ₅ (CH ₃)CHCl	-59.3	47.0^{i}	$(C_6H_5)_2CHLi$	$C_6H_5CH(CH_3)CH(C_6H_5)_2$	-11.70	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 $[\alpha]^{25}D$ 39.4[°].¹¹ ^d Based on a calculated value of $[\alpha]^{25}D$ 11.6[°].⁴ ^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 $[\alpha]^{25}D$ 42.0°. See W. Gerrard and H. R. Hudson, J. Chem. Soc., 2310 (1964). ^e The value for optically pure product has not been determined. ^h Prepared from tetraallyltin and n-butyllithium in pentane solvent. ^c Based on a calculated value of $[\alpha]D$ 7.0^e ^f Based on the experimental value of $[\alpha]^{25}D$ 36.1°. See H. Brauns, Rec. Trav. Chem. Pays-Bas, 65, 799 (1946). ^k Reported as observed rotation αD rather than specific rotation $[\alpha]D$. ^f Based on a calculated walue of αD 126^{°, f} ^m Prepared by lithium metal cleavage of allyl phenyl ether. ⁿ Based on a calculated value of αD 16.1°.⁵ ^o In acetone solvent. ^p Based on the experimental 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.

Benzyllithium 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-bromoctane 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, $[\alpha]^{25}D$ 39.4° for 2-bromobutane¹¹ and [a]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 tetrallyltin 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 $(-)-\alpha$ 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, $\alpha p -59.3^{\circ}$, 47% optically pure, the fractionally distilled product had $[\alpha]p -11.7^{\circ}$. Repeated recrystallization from methanol, which did not change the infrared spectrum, increased the specific rotation to a miximum 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 $[\alpha]p -21.7^{\circ}$, 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.

⁽¹³⁾ J. G. Traynham, J. Chem. Educ., 41, 617 (1964). See also W. Gerrard and H. R. Hudson, J. Chem. Soc., 2310 (1964).

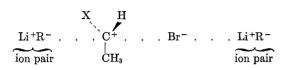
⁽¹⁴⁾ A. J. Houssa, J. Kenyon, and H. Phillips, ibid., 1700 (1929).

⁽¹⁵⁾ J. H. Brewster, J. Amer. Chem. Soc., 81, 5475 (1959), and references cited therein.

⁽¹⁶⁾ E. Bergmann, Helv. Chim. Acta, 20, 611 (1937).

Discussion

A transition state similar to that proposed by Eastham and Gibson¹⁷ for the coupling reaction of n-butyllithium with 1-bromooctane in hexane-ether solvent also seems reasonable for the reactions with chargedelocalized organolithium reagents. Donor solvent molecules are not shown in the transition state given below.



When the attacking organolithium reagent has considerable ionic character due to charge delocalization, such as the benzyl-type RLi compounds,^{18,19} and when X is an alkyl group, the reaction could be considered a one-step displacement which does not involve an intermediate and proceeds with complete Walden inversion. The electrophilic portion of a second organolithium molecule may be necessary for assistance in the breaking of the carbon-bromine bond, particularly since the reaction solvent, ethyl ether, is relatively nonpolar.

Increased stability of the incipient carbonium ion through delocalization when X is a phenyl group may lead to appreciable racemization in the coupling reaction due to the formation of a planar intermediate with some ion-pair character. However, since the strength of a nucleophile can influence the energy of the transition state,²⁰ slight changes in the nucleophilic strength of the organolithium reagent could lead to variations in the stereochemistry. Even though benzhydryllithium and allyllithium are both chargedelocalized reagents, the former nucleophile displaced the halogen from α -phenylethyl chloride with essentially 100% inversion of configuration, while reaction with the latter nucleophile led to 30% inversion and 70% racemization. The increased inversion stereochemistry may indicate that the more highly chargedelocalized benzhydryllithium¹⁹ is a stronger nucleophile than allyllithium under these reaction conditions.²¹ A previous study has shown that benzhydryllithium couples with both an asymmetric silane and methoxysilane with greater inversion stereochemistry than allyllithium²²

Experimental Section

Analysis using vapor phase chromatography showed that the hydrocarbon products were free from unreacted halides. An Aerograph A-90-P chromatograph equipped with a column packed with 5% Se-30 on Chromosorb W was used.

Previously described methods were used for the synthesis of following compounds: (+)- and (-)-2-bromooctane,^{23,24} (-)-2-

- (18) V. R. Sandel and H. H. Freedman, *ibid.*, **85**, 2328 (1963).
- (19) R. Waack and M. A. Doran, ibid., 85, 1651 (1963).
- (20) S. Winstein, E. Grunwald, and H. W. Jones, ibid., 73, 2700
- (1951).

(21) R. Waack and P. West, ibid., 86, 4495 (1964), have indicated that benzyllithium is a stronger nucleophile than allyllithium in the metalation or triphenylmethane by organolithium compounds.

- (22) L. H. Sommer and W. D. Korte, ibid., 89, 5802 (1967).
- (23) R. L. Shriner and J. H. Young, ibid., 52, 3332 (1930).
- (24) We thank Dr. Richard Smetana for the generous gift of resolved 2-octanol.

chlorooctane,²⁵ (+)-2-bromobutane,²⁶ and (+)- and (-)- α phenylethyl chloride.5

Reaction of Benzyllithium with (+)-2-Bromobutane.-Benzyllithium was prepared from benzyl ether (17.0 g, 0.085 mol) and lithium metal wire (ca. 6 g) in ethyl ether solvent according to a procedure described previously.¹² To the benzyllithium solution was added, dropwise over a period of 5 min, a solution of 3.38 g (0.025 mol) of (+)-2-bromobutane, $[\alpha]^{34}p$ +6.18° (neat), in 25 ml of ethyl ether. After 1 hr, the reaction mixture was added to ice-water, washed five additional times with water, and then dried over sodium sulfate. The ethyl ether was removed by heating on a steam bath and the residue was chromatographed over a 26 \times 1 in. column of silica gel with a 50% benzene-pentane solvent blend. Fractional distillation gave 2.10 g (0.014 mol) of 1-phenyl-2-methylbutane: $[\alpha]^{24}_{D} - 1.98^{\circ}$ (neat); bp 100-101° (34 mm); n^{25}_{D} 1.4875 [lit.⁶ bp 95° (30 mm); n^{25}_{D} 1.4856].

Reaction of Benzyllithium with (-)-2-Bromooctane.—By the same procedure as described above, reaction of 6.25 g (0.033 mol) of (-)-2-bromooctane, $[\alpha]^{24}D - 33.5^{\circ}$ (neat), with benzyllithium (0.087 mol) gave, after fractional distillation, 5.87 g (0.029 mol) of 1-phenyl-2-methyloctane: $[\alpha]^{26}D - 5.03^{\circ}$ (neat); bp 107-108° (1.7 mm); $n^{26}D$ 1.4882 [lit.⁶ bp 135-136° (15 mm); n²⁵D 1.4823].

Reaction of Allyllithium with (+)-2-Bromooctane.-Allyllithium was prepared as a white solid from the reaction of tetraallyltin (11.4 g) and 0.5 N n-butyllithium (200 ml) in pentane solvent.²⁷ The supernatant liquid was removed by means of nitrogen pressure and the solid was washed three times with 100-ml portions of pentane. Dissolving the solid in 100 ml of dry ethyl ether gave 0.040 mol of allyllithium by titration with hydrochloric acid. A solution of 4.72 g (0.024 mol) of (+)-2bromooctane, $[\alpha]^{25}D + 27.3^{\circ}$ (neat), in 25 ml of ethyl ether was slowly added, with stirring, to the allyllithium solution cooled with an ice bath. After 4 hr the ethereal solution was added to ice-water, washed four times with cold water, and dried over sodium sulfate. Fractional distillation gave 2.5 g (0.0163 mol) of 4-methyl-1-decene: $[\alpha]^{25}D + 5.30^{\circ}$ (neat); bp 74-75° (10 mm); $n^{25}D 1.4242$ [lit.⁶ bp 70° (12 mm); $n^{25}D 1.4246$]. Reaction of Allyllithium with (-)-2-Chlorooctane.—By a

procedure similar to that described for the previous experiment except that the reaction mixture was stirred for 8 hr at room temperature, reaction of 5.23 g (0.035 mol) of (-)-2-chlorooctane, $[\alpha]^{24}D$ -30.8° (neat), with allyllithium (0.060 mol) gave 3.25 g (0.021 mol) of 4-methyl-1-decene: $[\alpha]^{24}D - 5.50^{\circ}$ (neat); bp 74-75° (16 mm); n²⁵D 1.4246.

Reaction of Allyllithium with α -Phenylethyl Chloride.—By a procedure similar to that described above except that the reaction mixture was stirred for 30 min at ca. 20°, reaction of 3.86 g (0.028 mol) of (+)- α -phenylethyl chloride, α^{25} D +88.5° (neat, l = 1 dm), with allyllithium (0.40 mol) gave 1.37 g (0.009 mol) of 4-phenyl-1-pentene: $[\alpha]^{25}$ D -4.25° (neat, l = 1 dm); bp 82-84° (16 mm); n^{25} D 1.4994 [lit.⁵ bp 187-189° (uncorrected); n^{25} D 1.5020].

Since the stereospecificity of the previous reaction was rather low, the reaction was performed again using allyllithium pre-pared from an alternate procedure.²⁸ Reaction of 5.44 g (0.039 mol) of $(-)-\alpha$ -phenylethyl chloride, α^{24} D -24.3° (neat, l = 1dm), with allyllithium (0.060 mol) prepared by the cleavage of allyl phenyl ether (12.5 g) with lithium metal wire (6.0 g) gave, after a reaction period of 3 hr at room temperature, 2.22 g (0.015 mol) of 4-phenyl-1-pentene: $[\alpha]^{24}D + 0.90^{\circ}(\text{neat}, l = 1 \text{ dm});$ bp 84° (16 mm); $n^{25}D$ 1.5031.

Reaction of Benzhydryllithium with $(-)-\alpha$ -Phenylethyl Chloride.29-Benzhydryllithium was prepared by metalation of diphenylmethane (32 g) with 1.75 N n-butyllithium by refluxing the mixture for 18 hr in a mixture of ethyl ether and hexane. A solution of 3.57 g (0.027 mol) of (-)- α -phenylethyl chloride, $[\alpha]^{25}D$ -59.3° (neat, l = 1 dm), in 20 ml of ether was added dropwise to the organolithium reagent at room temperature. The mixture was stirred for 4 hr. After hydrolysis with dilute hydrochloric acid, the organic layer was washed four times with water and dried over sodium sulfate. Fractional distillation gave 3.64 g (0.013 mol) of (-)-1,1,2-triphenylpropane: $[\alpha]^{24}D$ -11.7° (c 6.1, acetone); bp 172-174° (2.5 mm). After five

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⁽²⁵⁾ A. McKenzie and T. M. A. Tudhope, J. Biol. Chem., 62, 551 (1924). (26) G. K. Helmkamp, C. D. Joel, and H. Sharman, J. Org. Chem., 21, 845 (1956)

recrystallizations from methanol, 0.22 g of product was recovered: $[\alpha]^{26}D - 21.7^{\circ}$ (c 1.2, acetone); mp 75-76° [lit.¹⁶ mp 76-77°; $[\alpha]D + 6.67^{\circ}$ (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; benzyllithium, 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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Received April 28, 1969

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, naphthacene, 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 thecorresponding 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 9,10dihydrophenanthrene; 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 9,10,10aoctahydrophenanthrene 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-dihydro-phenanthrene 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 overreduction in the absence of iron and underreduction 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

(7) S. Mejer, Bull. Acad. Polon. Sci., Chim., 9, 773 (1961).

⁽¹⁾ This investigation was supported in part by Public Health Grant CA-8674 from the National Cancer Institute.

⁽²⁾ Part VI: R. G. Harvey and C. C. Davis, J. Org. Chem., 34, 3607 (1969).

 ^{(3) (}a) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, J. Amer.
 Chem. Soc., 91, 4545 (1969); (b) R. G. Harvey and K. Urberg, J. Org.
 Chem., 33, 2206, 2570 (1968); (c) R. G. Harvey, *ibid.*, 32, 238 (1967).

⁽⁴⁾ A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 425.

^{(5) 9,10-}Dimethylanthracene was a notable exception in that cis and trans diastereomers were formed in equal proportion.

⁽⁶⁾ W. Hückel and H. Bretschneider, Ann., 540, 157 (1939).