the alkylation must have occurred with little or no loss of optical purity.

That the reaction of anion formation and alkylation occurred at the syn carbon was demonstrated by determining the absolute configuration of the (−)-1,3-dimethyl-2,6-diphenyl-4-piperidone (**3**) formed by hydrolysis of **2**. Reaction of **2** with pyridinium chlorochromate[11] gave a 56% yield of 1:1 mixture of the two epimers of **3a** and **3b**. This mixture gave a negative Cotton effect at 296 nm which by the ketone sector rule[12] confirmed the absolute configuration to be (−)-(2*R*,3*R*,3*S*,6*S*)-1,3-dimethyl-2,6-diphenyl-4-piperidone (**3a** and **3b**). The optical purity of the ketones was estimated to be 75% by ^1H NMR analysis using Eu(Tfc)$_3$.[10] The loss in chirality on hydrolysis of the oxime probably reflects the error in the determination of optical purity of the ketones (**3a** and **3b**).

These results clearly show the regiospecificity of the alkylation of the oximino dianion to be syn to the oximino oxygen and conformationally specific giving an axially substituted oxime. This series of reactions also provides a unique approach to stereochemical control of synthesis of substituted ketones via a chiral oxime.

Experimental Section

Stereospecific Alkylation of (*Z*)-2,6-Diphenyl-1-methyl-4-piperidone Oxime (1). A 0.5 M solution of 1.658 g (5.92 mmol) of (*Z*)-(+)-2,6-diphenyl-1-methyl-4-piperidone oxime, $[\alpha]_D$ +26.34°,[6] in anhydrous tetrahydrofuran was cooled to −80 °C under a stream of dry nitrogen. To the solution was added rapidly 5.918 mL (13.02 mmol) of 2.2 M *n*-butyllithium in hexane. The resulting solution was stirred under nitrogen at −10 °C for 45 min. The solution was cooled again to −80 °C, followed by the rapid addition of 0.379 mL (6.1 mmol) of iodomethane, and stirred between 0 and 5 °C for 2 h. The reaction mixture was hydrolyzed with 20 mL of water, the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were dried over sodium sulfate and filtered through magnesium sulfate. Evaporation of the solvent furnished 1.8 g of **1** as a yellow solid. The product was recrystallized from aqueous ethanol to give 1.5 g (88%) of (*Z*)-(−)-(2*R*,3*R*,6*S*)-1,3-dimethyl-2,6-diphenyl-4-piperidone oxime (**2**): mp 187.9 °C; IR ($CHCl_3$) 3750, 3300, 1650, 1660 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (d, 3 H), 1.85 (s, 3 H), 2.30 (q, 1 H), 2.56 (t, 1 H), 3.5 (br, 1 H), 3.1–3.3 (m, 2 H); $[\alpha]^{25}_D$ −30.76° (*c* 0.331 g/100 mL, 95% EtOH). Only the product containing the axially oriented 3-methyl was observed.

Anal. Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.68; H, 7.82; N, 9.55.

(−)-(2*R*,3*R*,3*S*,6*S*)-1,3-Dimethyl-2,6-diphenyl-4-piperidone (3a and 3b). To a suspension of 582 mg (2.7 mmol) of pyridinium chlorochromate in 6 mL of methylene chloride was added finely powdered sodium acetate and a solution of **2** in 15 mL of methylene chloride. The mixture started to turn black within a few seconds, but stirring was continued at room temperature for 35 h. The mixture was diluted with 100 mL of ether and filtered through Florisil. Evaporation of the solvent gave 200 mg of an oily residue. The crude product was chromatographed through silica gel to give 168 mg (56%) of 1:1 **3a** and **3b** as a yellow oil which crystallized: mp 131–132 °C; IR (neat) 1710^{-1}; NMR ($CDCl_3$) δ 0.74 (d, axial C-Me), 1.08 (d, equatorial C-Me), 1.75 (s) and 1.85 (s) (3 H, *N*-methyl), 2.3–3.6 (m, 5 H, Ar), 7.4 (m, 10 H); $[\alpha]^{25}_D$ −34.8° (*c* 0.775 g/100 mL; 95% ethanol), CD [Θ] −853° cm^2/g at 296 nm (*c* 0.00755 g/cm^3 in 95% EtOH).

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 82.07; H, 7.66; N, 5.00.

The picrate was prepared in ethanol to give a yellow solid, mp 170–171 °C.

Anal. Calcd for $C_{25}H_{24}N_4O_8$: C, 58.99; H, 4.82; N, 11.00. Found: C, 58.25; H, 4.72; N, 11.01.

Determination of the Optical Purity of 1, 2, and 3. To 51 mL of a 0.5 M solution (0.17 mmol) of the amine in deuteriochloroform was added 0.05 mL (0.005 mmol) of tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III), Eu(tfc)$_3$, as a 0.1 M solution of deuteriochloroform. The NMR spectra of these solutions exhibited an NCH_3 singlet for the one isomer at δ 2.19 and a singlet at δ 2.00 for the other isomer. The intensities of the peaks showed a composition of 87 and 13% for **1** and 86 and 14% for **2**. The 3-methyl group for the (−)-isomer of **2** appeared as a doublet at δ 1.65 and a doublet at δ 1.85 for the (+)-isomer at a ratio of 80:20% (−:+). The original solution of oxime (**2**), now with 0.2 mL (0.002 mmol) of Eu(tfc)$_3$ in $CDCl_3$ (0.1 M), gave a broad singlet at δ 2.7 for the 3-methyl group of the (−)-isomer and a similar absorption at δ 3.1 for the (+)-isomer. A ratio of 4:1 (−:+) was calculated. The two *N*-methyl groups had collapsed into one broad singlet.

The NMR of the mixture of **3a** and **3b** showed no separation of the signal for the N methyl and the C methyl of **3b**. The axial methyl groups of the isomers of **3a** separated into two collapsed doublets at about δ 0.8. The optical purity was estimated from this ratio to be about 75%. This value is subject to considerable error due to problems in integration. Since **3b** was formed from **3a**, the optical purity of **3b** must be the same as **3a**.

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Registry No.—**1**, 64912-36-3; (−)-**2**, 64912-37-4; (+)-**2**, 64912-38-5; **3a**, 64912-39-6; **3b**, 64912-40-9; **3** picrate, 57162-51-3.

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Reactions of Dichlorobenzenes with Solvated Electrons in Liquid Ammonia[1a]

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Halobenzenes and other monosubstituted benzenes react with solvated electrons from alkali metals in liquid ammonia to give a phenyl radical and the anion of the leaving group.[2] Phenyl radicals can react with another electron and be further reduced to phenyl anions, which upon abstracting protons from ammonia gives, ultimately, benzene.[3]

Dichlorobenzenes were expected to react with solvated electrons step by step as halobenzenes do, and that would imply the formation of *o*-, *m*-, and *p*-chlorophenyl anions at some stage of the reaction. The *o*-chlorophenyl anion generated by other means in liquid ammonia has been shown to eliminate the chloride ion leading to benzyne, but no similar elimination of the chloride ion from the *m*- or *p*-chlorophenyl

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Table I. Reaction of Halobenzenes with Alkali Metals in Liquid Ammonia

Expt no.	Halobenzene	Concn, M	Metal	Concn, M[a]	Benzene	Aniline yield, %[b]	Solid products
1	C_6H_5Cl[p]	0.11	K	0.24	79	11	
2	C_6H_5Cl[p]	0.11	Na	0.26	80	12	
3	C_6H_5Cl[p]	0.16	Li	0.43	86	2	
4[c]	C_6H_5Cl[p]	0.070	Na	0.21	96		
5[d]	o-$C_6H_4Cl_2$[q]	0.053	K	0.24	70	11	
6[d]	o-$C_6H_4Cl_2$[q]	0.080	Na	0.39	54	19	
7[d]	o-$C_6H_4Cl_2$[q]	0.076	Li	0.38	86	7	
8[d,e]	o-$C_6H_4Cl_2$[q]	0.040	Na	0.23	88	1	
9[f]	o-$C_6H_4Cl_2$[q]	0.20	Li	0.14	21[g]	1	
			Li	0.36	69[h]	2	
			Li	0.55	72[i]	5	
			Li	0.70	80[j]	6	
10	m-$C_6H_4Cl_2$[r]	0.070	K	0.11	23	27	32
11	m-$C_6H_4Cl_2$[r]	0.053	Na	0.22	22	18	44
12	m-$C_6H_4Cl_2$[r]	0.070	Li	0.36	27		53
13[d]	p-$C_6H_4Cl_2$[s]	0.019	K	0.11	25	10	54
14[d]	p-$C_6H_4Cl_2$[s]	0.056	Na	0.26	27	4[k]	51
15[d]	p-$C_6H_4Cl_2$[s]	0.059	Li	0.36	37		52
16[l]	p-$C_6H_4Cl_2$[s]	0.041	Na	0.19	80		5
17[m]	p-$C_6H_4Cl_2$[s]	0.028	Na	0.09	74		3
18[n]	p-$C_6H_4Cl_2$[s]	0.032	Na	0.14	41	[o]	58

[a] The metal was added bit by bit, and the concentration is stated as if it had not reacted. [b] Benzene and aniline were determined by GLC and the solid products by weighing. Biphenylamine and 2- and 4-aminobiphenyls were detected in small yields but were not quantified. [c] 0.35 M water was added. [d] The yield is the average of two concordant runs. [e] 0.33 M water was added. [f] Samples were taken after each addition of metal. [g] 78% of the unreacted o-DCB was determined. [h] 22% of the unreacted o-DCB was determined. [i] 9% of the unreacted o-DCB was determined. [j] Biphenylamine and 2- and 4-aminobiphenyls in ca. 10% yield. [k] In another run aniline was distilled and isolated (6.5% yield by weighing). [l] 0.40 M water was added. [m] 0.20 M methanol was added. [n] 0.14 M toluene was added. [o] Not quantified. [p] Registry no.: 108-90-7. [q] Registry no.: 95-50-1. [r] Registry no.: 541-73-1. [s] Registry no.: 106-46-7.

anion has been reported, although these anions have been generated in several solvents.[4,5]

Results and Discussion

The reaction of chlorobenzene (CB) with Na or K metal in liquid ammonia gives benzene (ca. 80%) as the major product, together with aniline (ca. 12%), and very small amounts of diphenylamine and aminobiphenyls (experiments 1 and 2). These results can be explained by the reaction of CB with a solvated electron to give the phenyl radical,[2] which does not react with ammonia to give benzene, at least in competitive reactions with nucleophiles or solvated electrons.[6] As the reaction proceeds, the concentration of amide ions builds up, and the amide ions can react with phenyl radicals by the $S_{RN}1$ mechanism to give, ultimately, aniline.[7] Some aniline could also be formed via benzyne by the reaction of CB with amide ions.

When Li metal was used as the electron source, the yield of aniline dropped to 2% (experiment 3). This result is attributed to the low solubility of $LiNH_2$ in liquid ammonia[8] which severely limits the rate of reaction with the phenyl radical.

When CB reacted with Na metal in liquid ammonia containing water as the proton source to neutralize amide ions, benzene was the only product formed (experiment 4).

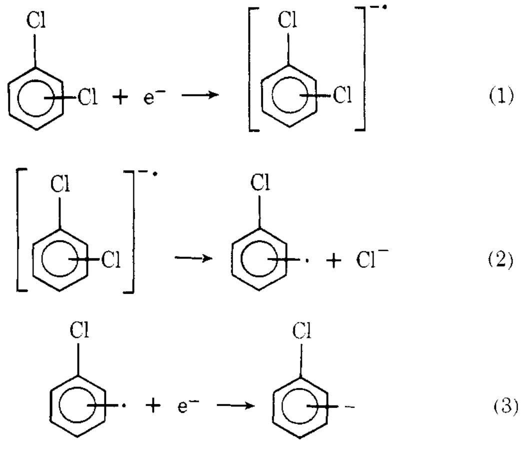
The reaction of o-dichlorobenzene (o-DCB) with Na or K metal in liquid ammonia yielded benzene (54–70%) and aniline (19–11%). With Li metal as the electron source, there was a slight decrease in the yield of aniline (experiment 7).

The reactions of m-dichlorobenzene (m-DCB) and p-dichlorobenzene (p-DCB) with Na or K metal in liquid ammonia gave small yields of benzene and aniline (experiments 10–14).[9] The remaining organic product was a complex mixture of saturated, unsaturated, and aromatic hydrocarbons. Attempts to isolate a pure fraction by column chromatography, GLC, TLC, or recrystallization were unsuccessful because the products decomposed during the process. NMR analyses of the crude product or samples obtained by column chromatography or by recrystallization indicated the presence of $-CH_2-$ and $=CH-$ absorption, together with aromatic protons. The relative amount of each was highly dependent upon the metal used. After catalytic hydrogenation over Pt/C, the product from the reaction with any of the three metals showed only aromatic and $-CH_2-$ protons in a ratio of ca. 1:1.4.

Our results can be explained as shown in Scheme I. Steps 1 and 2 are straightforward in analogy with the reaction of CB. Inasmuch as the phenyl radical does not abstract hydrogen from ammonia, it is reasonable to assume that o-, m-, and p-chlorophenyl radicals do not abstract hydrogen either. However, they can take another electron, giving the corresponding o-, m-, and p-chlorophenyl anions (step 3).

o-Chlorophenyl anion has been generated by other means, and it has been shown to eject chloride ion, giving benzyne.[11] The o-chlorophenyl anion can also be protonated, giving CB, and the ratio of protonation–elimination is 7.6 in 60% ammonia–40% diethyl ether.[12] Benzyne can further react with

Scheme I



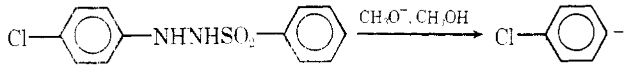
electrons and protons to be reduced to benzene, or it can react with ammonia or amide ion, forming aniline.

In order to see whether any CB can be obtained from the reaction of *o*-DCB with Li metal when there are electrons in deficiency, we carried out an experiment in which we took samples after each small addition of the metal to the reaction solution and analyzed the reaction mixture by GLC (experiment 9). Even when large amounts of *o*-DCB remained unreacted, CB could not be detected. In order to have an estimate of the relative reactivities of CB and *o*-DCB, equimolecular amounts of each substrate were treated with Na metal in liquid ammonia, and it was found that both reacted at about the same rate, in agreement with similar results found earlier with related substrates.[13]

The fact that no CB was found may be attributed to the reaction of CB with electrons in an electron-rich zone (electrons in high local concentration, with the rate of reaction being greater than the rate of mixing).

Similar pathways can be expected for *m*- and *p*-chlorophenyl radicals, which can take an electron giving *m*- and *p*-chlorophenyl anions. However, protonation of these anions seems not to be the main reaction pathway, because in such a case the ultimate product should be benzene as with CB. The reaction of *p*-DCB in the presence of good proton donors led mainly to benzene (experiments 16 and 17).

It is known that the *p*-chlorophenyl anion is an intermediate in the basic decomposition of 1-(*p*-chlorophenyl)-2-benzenesulfonyl hydrazide in methanol[4,5] (eq 4).



(4)

When we treated this substrate with KCH_3O in liquid ammonia, we found 25–30% of the chloride elimination, together with 30–40% of CB, and therefore estimate the ratio of the proton capture rate to the chloride elimination rate to be 1–1.4.[14]

Elimination of the chloride ion from *m*- and *p*-chlorophenyl anions should form *m*- and *p*-benzyne-like intermediates, which may give rise to the polymeric material; *m*- and *p*-benzynes have been postulated as intermediates in several reactions.[15]

In the reaction of *p*-DCB with solvated electrons from Na metal in liquid ammonia containing toluene as hydrogen donor, the yield of benzene was slightly increased (experiment 18). In the same reaction in the presence of methanol (experiment 17) or water (experiment 16) as proton donors, a large increase in the benzene yield was found.

These results are consistent with the mechanism sketched in Scheme I and indicate that the rate of hydrogen abstraction of the *m*- and *p*-chlorophenyl radicals from toluene does not compete with its reaction with electrons; however, protonation of the *m*- and *p*-chlorophenyl anions is the major reaction pathway in the presence of good proton donors such as water or methanol.

Experimental Section

General. Reagents were all commercially available materials except for 1-(*p*-chlorophenyl)-2-benzenesulfonyl hydrazide, which was prepared by the procedure of Hoffmann,[16] mp 136–137 °C dec, from aqueous ethanol (lit.[4] 136–137 °C dec). Solvents were purified by standard procedures. NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrophotometer with CCl_4 as solvent, and all spectra are reported in parts per million relative to Me_4Si (δ). Potentiometric titrations were carried out with a Metrohm Herisau pH Meter Model E 396 B, using a combined silver–calomel electrode (Metrohm Herisau). TLC was performed on silica gel plates. Column chromatography was performed on neutral aluminum oxide (Merck). Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with a flame ionization detector. Peak areas were corrected by the detector response using internal standards (toluene to quantify benzene, biphenyl to quantify aniline, anthracene to quantify aminobiphenyls and diphenylamine, and bromobenzene to quantify chlorobenzene). A 1.8 × 3 mm column packed with 10% Carbowax 20M on Chromosorb P was used. Alkali metals were cut in small pieces and washed free of oil with dried diethyl ether or pentane immediately before addition to the reaction mixtures. Liquid ammonia was dried over sodium metal and distilled, under nitrogen, into the reaction flask.

Reaction of Chlorobenzene and Alkali Metals. A procedure for the reaction of Na metal with CB is representative. The reaction was performed in a three-neck round-bottom flask fitted with a dry ice–isopropyl alcohol condenser, stirred by a magnetic stirrer, and constantly swept by a slow stream of dry nitrogen. To distilled liquid ammonia (220 mL), CB (0.025 mol) was added, and then Na metal (0.057 mol) was added bit by bit. In the reactions in which water (or another proton donor) was used, it was added before the alkali metal. After all the alkali metal had been introduced, solid ammonium chloride was added to quench the reaction, followed by 150 mL of diethyl ether with the internal standards, and the ammonia was allowed to evaporate. The ether extract was washed with water, dried over anhydrous Na_2SO_4, and analyzed by GLC.

Reaction of *o*-Dichlorobenzene with Alkali Metals. The procedure was the same that as for CB. In experiment 9, where samples were taken after each addition of metal, a J-shaped tube was used to take liquid ammonia from the reaction flask and added to water, extracted with ether, and analyzed by GLC.

Reaction of *m*- and *p*-Dichlorobenzenes with Alkali Metals. The reactions were performed as before. When the ether from the ether extract was evaporated in vacuo, a waxy solid was found. With Na or K metal as the electron source, and after removal of aniline by distillation in vacuo, the NMR spectrum had peaks centered at δ 1.2, a complex group of peaks in δ 1.3–3.2, a small multiplet at δ 5.6, and a peak at δ 7.2. With Li metal as the electron source, all these peaks remained, but aniline was not formed. After catalytic hydrogenation (atmospheric pressure with 10% Pt/C, 48 h), only the olefinic peaks disappeared (δ 5.6).

Reaction of 1-(*p*-Chlorophenyl)-2-benzenesulfonyl Hydrazide with Potassium Methoxide. After the addition of 1.24 g of K metal (31.8 mmol) to 100 mL of distilled liquid ammonia, 1.29 mL of anhydrous methyl alcohol (31.8 mmol) was slowly added dropwise. A crystal of ferric chloride was added to catalyze the formation of $KOCH_3$, and then solid 1-(*p*-chlorophenyl)-2-benzenesulfonyl hydrazide (1.45 mmol) was added slowly. After 30 min the reaction was quenched with excess redistilled water and then processed as in the previous experiments. The water layer was acidified with nitric acid and diluted to standard volume, and aliquots of the dilute solution were titrated potentiometrically with silver nitrate to quantify the chloride ion. In a blank reaction with everything the same but without the 1-(*p*-chlorophenyl)-2-benzenesulfonyl hydrazide, the chloride ion yield was determined to be less than 1%.

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Registry No.—Benzene, 71-43-2; aniline, 62-53-3; ammonia, 7664-41-7; biphenylamine, 122-39-4; 2-aminobiphenyl, 90-41-5; 4-aminobiphenyl, 92-67-1; 1-(*p*-chlorophenyl)-2-benzenesulfonyl hydrazide, 21857-36-3.

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A Stereospecific Route to Trisubstituted Olefins via Organoboranes

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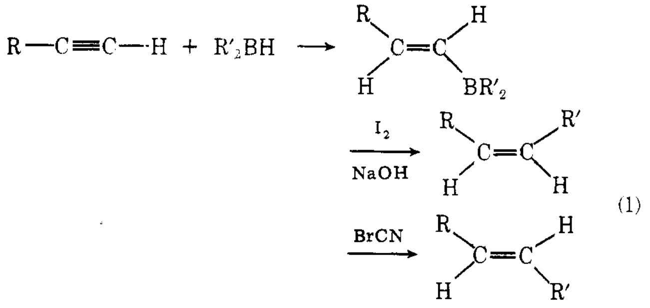
The Zweifel syntheses of cis[1] and trans[2] olefins (eq 1) via vinylboranes have found limited applications in organic synthesis in large part because of the limited availability of stable dialkylboranes.[3] A further limitation is the requirement imposed by hydroboration that a hydrogen be cis to boron in the initial borane, thus limiting the applicability of this reaction to cis and trans disubstituted olefins.



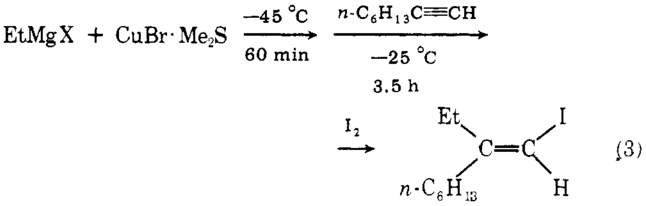
Since the common intermediate in these reactions appears to be a vinyl-substituted borate salt, it appeared reasonable to investigate alternative methods of obtaining the intermediates. In analogy with the lithium alkynyltrialkylborate complexes,[4] formation of a vinyltrialkylborate complex[5] from a vinyllithium and a trialkylborane followed by iodination should lead to olefins. Herein, we report the utility of this sequence in the synthesis of stereospecifically defined trisubstituted olefins[6,7] and the somewhat surprising stereochemistry of this reaction.

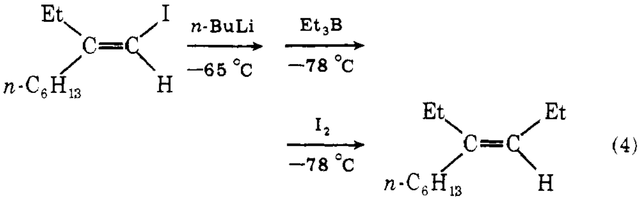
Initially, we found that treatment of tri-n-hexylborane with vinyllithium or vinylmagnesium bromide followed by iodination gives moderate yields of 1-octene[8] (eq 2). In order to ascertain the overall stereochemistry and the potential synthetic applications to stereospecifically defined olefins, we undertook a systematic study of this reaction using 2,2-disubstituted vinyl iodides as precursors of stereospecifically defined vinyllithiums.

$$(n\text{-}C_6H_{13})_3B + MCH{=}CH_2 \longrightarrow \xrightarrow{I_2} n\text{-}C_6H_{13}CH{=}CH_2 \qquad (2)$$

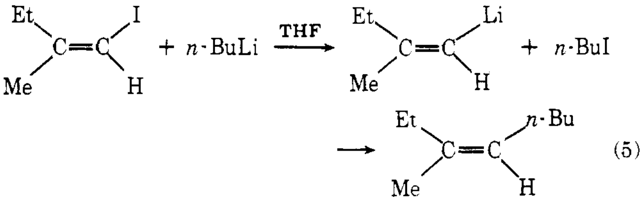
M = Li 60–65%
M = MgBr 40–50%

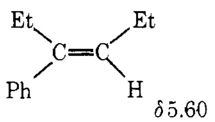
Reaction of ethylmagnesium bromide in the presence of $CuBr{\cdot}Me_2S$ with 1-octyne leads upon iodination to a 63% yield of (E)-2-ethyl-1-iodo-1-octene (eq 3).[9] Sequential treatment of the iodide with n-butyllithium, triethylborane, and iodine at low temperature leads to a 75% yield of (E)-4-ethyl-3-decene (eq 4).[10] In view of these encouraging results, a number of the iodides were synthesized by the Normant procedure. From these derivatives the corresponding trisubstituted olefins **1a–j** were prepared. The results are summarized in Table I.



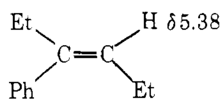


Comparison of the proton-decoupled ^{13}C NMR spectra of Z and E isomers **1g** and **1h** clearly indicates that the two isomers are different. The stereochemistry of the products was determined in two ways. Treatment of (Z)-2-methyl-1-iodo-1-butene with n-butyllithium in THF at −78 °C leads to halogen-metal exchange. Subsequent displacement of the iodide with retention at the vinyl carbon[11] gives (Z)-3-methyl-3-octene (eq 5), identical in all respects with **1i.** Further support for this stereochemical assignment comes from the proton NMR spectrum of **1j**. Comparison of the vinyl proton's adsorption at δ 5.56 in **1j** with those reported for (Z)- and (E)-3-phenyl-3-hexene[12] (**2a,b**) confirms the stereochemical assignment of **1j** as the E isomer.





2a



2b

The stereochemical purity of the resultant trisubstituted olefins remains a difficult problem. In all cases, by proton-decoupled ^{13}C NMR spectroscopy we appear to have only one isomer. In the case of **1g** and **1h**, each isomer is clearly different, uncontaminated by detectable amounts of the opposite isomer. Furthermore, in the proton NMR of **1j** we cannot detect any of the opposite isomer. Based on careful NMR analysis of **1j**, we have determined this isomer to be at least 97% stereochemically pure. Unfortunately, preliminary attempts to analyze **1g** and **1h** by capillary gas chromatography have failed to separate the isomers.[13] However, the ^{13}C NMR spectra indicate each isomer to be at least 95% stereochemically pure.

Presumably, this reaction involves a mechanism similar to the halogenation reactions of vinylboranes. Initial complexation of the vinyllithium with the trialkylborane gives an "ate" complex (eq 6). Subsequent formation of the iodonium ion

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