serve to diminish both the rate of dehydration of the carbinol and the intensity of the main absorption band of the olefin, the latter effect is not nearly as large as the effect of *o*-methyl groups located on the aromatic ring. A review of the evidence, therefore, indicates that the effect of neighboring methyl groups on the ultraviolet absorption spectra of 1-phenylcyclohexenes is primarily a steric one, but that other forces are superimposed upon steric ones in determining the influence of the methyl groups on the dehydration rates of the 1-phenylcyclohexanols.

Any effort to identify and appraise the forces other than steric ones which are exerted by neighboring methyl groups on the dehydration rates of the 1-phenylcyclohexanols must be relegated to the realm of speculation until far more elaborate studies on these compounds and their rates of dehydration can be carried out. A rational interpretation of dehydration rate studies requires detailed knowledge of (a) the reaction mechanism, (b) the steric configurations of the 1-phenylcyclohexanols and (c) the position of the double bond in the phenylcyclohexenes. Even if the El mechanism can be assumed for the acid-catalyzed dehydration of these tertiary carbinols, the structures of the olefins cannot be predicted when the carbinol structure includes an *o*-methyl group on the aliphatic ring. In such cases complications must be taken into account by such factors as probable *trans* elimination, influences which operate to determine whether the Hofmann or the Saytzeff rule governs the direction of elimination, and stabilization of the transition state of elimination through the interaction of the aromatic ring unsaturation with the developing double bond, which requires co-planarity. These factors are not independent of each other. For example, both the configuration of 1-phenyl-2-methylcyclohexanol (II) and the stereochemical course of the dehydration reaction (*cis* or *trans*) must be known in order that it be possible to postulate whether the product will be 1-phenyl-2-methylcyclohexene (Saytzeff rule) or 1-phenyl-6-methylcyclohexene (Hofmann rule) or a mixture of both. Furthermore, if both *cis* and *trans* elimination can occur, the conclusions from recent investigations indicate that if the direction of elimination is governed by electromeric forces the Saytzeff rule will be followed[15] while direction of the reaction by steric effects leads to elimination in accordance with the Hofmann rule.[16] Experiments which are now being planned should yield evidence relating to the sensitive interplay among the factors of reaction mechanism, stereochemistry of the carbinols and the structures of the olefins.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Coupling of Lithium Alkyls and Alkyl Halides. Metal–Halogen Exchange Reactions

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1-Butyllithium and (+)2-bromobutane react with inversion of configuration to give (−)3-methylheptane. Extensive racemization accompanies the inversion. The results are compared with those reported for sodium alkyls and are explained on the basis of the ionic character of the reagents. Metal–halogen exchange reactions occur prior to coupling of lithium alkyls and secondary chlorides but do not take place at slightly lower temperatures in the absence of coupling.

From a comparison of *n*-hexyl and neopentyl chlorides in the reaction with ethylsodium, it was suggested that coupling occurs by a metathetical reaction of the Walden type.[2]

$$C_2H_5Na + RX \longrightarrow RC_2H_5 + NaX$$

Studies with optically active secondary halides have furnished excellent evidence for this mechanism in certain displacement reactions.[3] However, almost complete racemization occurs in the reaction of sodium alkyls with secondary bromides. Displacement reactions involving the more covalent lithium alkyls have been studied kinetically and have been interpreted in terms of either a direct or an ionic mechanism.[4]

A study of this displacement on optically active secondary halides was undertaken several years ago in this Laboratory in the hope that less racemization would occur with lithium alkyls than with the more ionic sodium compounds. This result was not realized. For example, 1-butyllithium reacts with (+)2-bromobutane, $[\alpha]^{25}\text{D}$ 15.82, in dodecane at 65° to give a 37% yield of (−)3-methylheptane, $[\alpha]^{25}\text{D}$ −0.12, along with butane and butene. An inversion of configuration is indicated in the coupling process, because the configurations of (+)2-bromobutane and (+)3-methylheptane can be related.[5] From the maximum values of the rotations of the halide and hydrocarbon, racemization to the extent of 98% is calculated.

These results are of interest in connection with the recent theory of Lane and Ulrich, whereby optical activity is retained more readily when the organometallic compound is essentially ionic and

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TABLE I

REACTION OF LITHIUM ALKYLS WITH ALKYL HALIDES

Li alkyls		Halides		Sol-vent,[a]	Time,	Temp.,		B.p.		
R	Mole	R'X	Mole	ml.	hr.	°C.	Products and yields	°C.	Mm.	n^{20}_D
1-C_4H_9	0.18	2-C_4H_9Br	0.18	50 D	18	75	3-Methylheptane (37%)	117	740	1.3985–1.3987
							Butane (61%), butene (22%)			
1-C_4H_9	.18	2-C_4H_9Br	.18	30 D	15	65	3-Methylheptane (24%)			
							Butane (53%), butene (20%)			
1-C_4H_9	.18	(+)2-C_4H_9Br[b]	.18	10 D	12	65	(−)-3-Methylheptane[c] (37%)	117–118	745	1.3990
							Butane (43%), butene (25%)			
1-C_4H_9	.17	2-C_4H_9Cl	.22	30 D	72	55	Mixture of octanes	117–119	747	1.4012–1.4025
1-C_4H_9	.52	2-$C_8H_{17}Cl$	.50	280 P	6	36	*n*-Valeric acid[d] (16%)	88–89	20	
							2-Chlorooöctane (93%)	58–59	19	1.4266–1.4267
							Di-*n*-butyl ketone[e] (27%)	75	19	1.4197
							Tri-*n*-butylcarbinol (19%)	138	19	1.4449
2-C_8H_{17}	.45	1-C_4H_9Cl	.45	600 P	5	40	*n*-Valeric acid (0%)			
							2-Methyloctanoic acid[f] (32%)	86–90	4	
							High-boiling neutral compounds			
1-C_3H_7	.50	2-C_4H_9Cl	.50	230 D	11[g]	42	3-Methylhexane (14%)	90	742	1.3878–1.3881
							3,4-Dimethylhexane (27%)	117	742	1.4035–1.4037
1-C_5H_{11}	.64	2-C_4H_9Cl	.64	175 D	72	55	3,4-Dimethylhexane (33%)	117	742	1.4037
							3-Methyloctane (14%)	144	738	1.4071–1.4072
							Decane (15%)	173	738	1.4109–1.4121

[a] D = dodecane, P = pentane. [b] Prepared as described by P. A. Levene and R. E. Marker, *J. Biol. Chem.*, 91, 412 (1931), b.p. 89.5° at 736 mm., $n^{21.5}_D$ 1.4360, $[\alpha]^{25}_D$ (homogeneous) +15.82. [c] $[\alpha]^{25}_D$ (homogeneous) −0.12, no precipitate with silver nitrate solution. The maximal rotation of 3-methylheptane is −10°. [d] Neut. equiv., 106, anilide, m.p. 63°. [e] Semicarbazone, m.p. 89.5°. [f] Neut. equiv., 159, amide, m.p. 79.5°. [g] Propyllithium remained. Two liters of gas was evolved upon addition of water. The aqueous layer contained only 0.37 mole of soluble chloride (Volhard).

the halide is not easily ionized.[6] Thus, racemization in the coupling of (+)2-bromobutane and benzylsodium occurs to the extent of only 26%, whereas sodium alkyls in which the carbanions are not stabilized by resonance give nearly complete racemization.[3,7] The low activity of the 3-methylheptane in this work reflects the covalent character of the lithium alkyl and the ease of ionization of the secondary bromide.

The less easily ionizable secondary chlorides underwent an unexpected metal–halogen interchange prior to coupling and led to mixtures of hydrocarbons. Heretofore, interchange reactions involving alkyllithium compounds

$$RLi + R'X \rightleftarrows RX + R'Li$$

have been observed only with bromides, iodides, and certain reactive benzyl-type chlorides.[8] The 3-methylheptane from the reaction of 1-butyllithium and 2-chlorobutane contained isomeric octanes from which it could not be separated. The exchange reaction was demonstrated conclusively by varying the alkyl groups in order to permit separation of the products. The results are summarized in Table I. Carbonation experiments show that metal–halogen exchange does not take place in hydrocarbon solvents at 36–40°. However, at 40–55°, coupling occurs to give a mixture of hydrocarbons the composition of which can be explained only by extensive metal–halogen interchange.

Experimental

Purification of Solvents.—Commercial dodecane[9] was found to absorb bromine in glacial acetic acid. The unsaturated material could not be removed by adsorption on a silica-gel column. Catalytic hydrogenation (PtO_2) at 45 p.s.i. followed by fractionation through an 18-plate column gave the pure hydrocarbon, b.p. 132° at 65 mm., n^{20}_D 1.4215. Pentane was shaken with three portions of concentrated sulfuric acid, washed, dried and distilled.

Lithium Alkyls in Dodecane.—Pentane solutions of lithium alkyls were prepared from the corresponding chlorides in the conventional manner.[10] A 20% excess of lithium was used to ensure reaction of all of the halide. The clear, filtered pentane solutions were concentrated at 20 mm. and room temperature, and the remainder of the pentane was distilled at 1 mm. into a trap cooled in liquid air. Additional pentane or hexane was added and the distillation repeated to sweep out any unreacted halide. Purified dodecane was then added and the solutions stored in an atmosphere of nitrogen. Aliquot samples were decomposed with absolute ethanol for titration and halogen analysis (Stepanoff). Halides could not be detected in these solutions.

Reactions of Lithium Alkyls with Halides.—Data for these experiments are summarized in Table I. The lithium alkyl solution was added dropwise with stirring to the halide over a period of three to six hours at a temperature sufficiently high to ensure reaction. Heating was then continued for an additional time. Gases were led from the column to a liquid-air trap or suitable gas measuring device. A nitrogen atmosphere was maintained throughout the reaction.

Carbonations were effected by pouring the solutions onto excess powdered Dry Ice. The product was separated by suitable extractions into neutral and acidic fractions before distillation.

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