The reaction of phenyllithium with *n*-butyl chloride in butyl ether to give *n*-butylbenzene proceeds with an activation energy of 21.2 kcal./mole; that with *t*-butyl chloride to give benzene and isobutylene proceeds at a rate 1.6 times faster than with the primary chloride at 80°, but with an activation energy of 22.7 kcal./mole.

The data with methyllithium were rather peculiar. Each run gave good agreement with the second-order rate equation and consistent with other runs using the *same preparation* of methyllithium; however, different batches of methyllithium gave rate constants differing from each other by as much as one order of magnitude. What catalyst was present in the various preparations is not known. Only one batch was prepared in a sufficiently large quantity for the estimation of activation energies. This was Batch II, where data at three temperatures are available. The plots of log *k* *vs.* $1/T$ are given in Fig. 5, and the data show good consistency. The reaction of methyllithium with *n*-butyl chloride gives a mixture of elimination and substitution, hence the calculated value of the activation energy of 18.9 kcal./mole has no precise meaning. The reaction of methyllithium with *t*-butyl chloride to give methane and isobutylene proceeds at a rate approximately ten times faster than the total second-order reaction with the primary chloride at 80°, but with a higher activation energy of 20.8 kcal./mole.

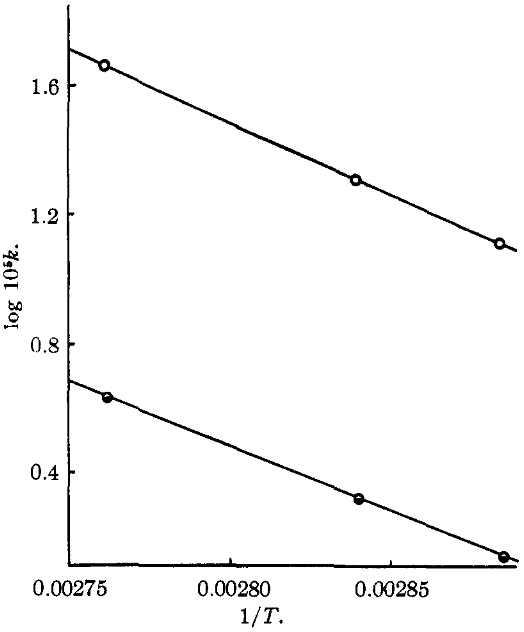

Fig. 5.—Plots for calculation of activation energies for methyllithium (Batch II) and ○—○, *t*-BuCl; ◒—◒, *n*-butyl chloride.

Summary

The reactions of phenyllithium and of methyllithium with *n*- and *t*-butyl chlorides in butyl ether have been studied. Phenyllithium gave principally *n*-butylbenzene with *n*-butyl chloride and isobutylene and benzene with *t*-butyl chloride, whereas methyllithium gave predominantly elimination with either halide. Kinetic data indicated that both the substitution and elimination reactions were first order in organolithium compound and first order in alkyl halide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Reactions of Organometallic Compounds. II. The Reactions of Phenyllithium and of *n*-Butyllithium with α- and γ-Methylallyl Chlorides[1]

BY STANLEY J. CRISTOL, WENDELL C. OVERHULTS AND JOHN S. MEEK

α- and γ-methylallyl chlorides were reacted with phenyllithium in ethyl ether to give substantially identical mixtures comprising 90–95% of crotylbenzene and 5–10% of α-methylallylbenzene. Analogous results were obtained with *n*-butyllithium. The results are interpreted in terms of a carbonium-ion process. It is suggested that the coupling reactions of alkyl halides with organometallic compounds and with sodium can be understood in terms of a duality of mechanism—that is, both direct and carbonium-ion displacement mechanisms are available for these systems.

Although the mechanisms of the coupling reactions of organosodium and organomagnesium compounds with alkyl halides have been studied in some detail, less work has been reported on analogous studies with organolithium compounds. The reactions between organolithium compounds and alkyl halides are of interest because of similarities to the second part of the postulated path for the Wurtz–Fittig reaction[2,3,4]

$$\text{R-Metal} + \text{R'X} \longrightarrow \text{R—R'} + \text{Metal-X} \qquad (1)$$

In a previous paper[5] we showed that the reactions of phenyllithium and methyllithium with *n*-butyl and *t*-butyl chlorides in butyl ether were of the second order, first order with respect to organolithium compound and first order with respect to alkyl halide.[6] As these data can be accommodated to a direct displacement or to a carbonium-ion mechanism, further study of reactions of organolithium compounds with alkyl halides seemed warranted.

We have, therefore, undertaken a study of the products of the reactions of phenyllithium and of *n*-butyllithium with α-methylallyl (methylvinylcarbinyl) and crotyl (γ-methylallyl) chlorides.

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(1) This work was reported, in part, before the Division of Organic Chemistry at the Spring, 1950, Meeting of the American Chemical Society, Philadelphia, Pennsylvania.

(2) A. A. Morton and G. M. Richardson, THIS JOURNAL, **62**, 123 (1940); A. A. Morton, J. B. Davidson and B. L. Hakan, *ibid.*, **64**, 2242, (1942).

(3) G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941).

(4) F. C. Whitmore and H. D. Zook, THIS JOURNAL, **64**, 1783 (1942).

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(6) Reactions with *n*-butyl chloride gave coupling and elimination, whereas with *t*-butyl chloride only elimination was observed.

The coupling reactions occur in approximately 60% yield in each case.

As the properties and reactions of organolithium compounds are generally intermediate between those of organosodium compounds and Grignard reagents,[7] it is of interest to mention reactions reported between the butenyl chlorides and compounds of these types. Levy and Cope[8] have shown that crotyl chloride and α-methylallyl chloride react with the sodio derivative of allylbenzene in liquid ammonia without rearrangement, that is, the primary chloride gave 3-phenyl-1,5-heptadiene and the secondary chloride gave 3-methyl-4-phenyl-1,5-hexadiene. On the other hand, Henne, Chanan and Turk,[9] and Young and his co-workers[10] have shown that rearrangement does occur in the reactions of the allylic halides with Grignard reagents. Thus, when either crotyl chloride or α-methylallyl chloride was allowed to react in ether with allylmagnesium chloride,[10a] butenylmagnesium chloride,[10a] phenylmagnesium bromide[10b] or *n*-butylmagnesium chloride,[9] mixtures of coupled hydrocarbons were obtained, and in each case the coupled product related to the primary chloride predominated. In the last two cases, the mixtures were substantially identical.

Our results with organolithium compounds are comparable to those with Grignard reagents, giving approximately identical mixtures with both butenyl chlorides, the product resulting from the primary butenyl radical being formed in large excess. Thus, when either chloride was added to a solution of phenyllithium in ether and the resulting product analyzed in a fractionating column rated at 60 theoretical plates, the butenylbenzene fraction was shown to comprise 90–95% of crotylbenzene and 5–10% of α-methylallylbenzene; similarly, when either chloride was allowed to react with *n*-butyllithium, the octene fraction was shown to comprise 90–95% of 2-octene and 5–10% of 3-methyl-1-heptene. In addition, in the latter reaction, a small amount (<0.5%) of 3-methyl-1,5-heptadiene was found, presumably being formed as a result of metal exchange between the butyllithium and the butenyl chloride, followed by coupling with another mole of the butenyl chloride. The product observed is the one expected on the basis of Young's experience with Grignard reagents.[10a]

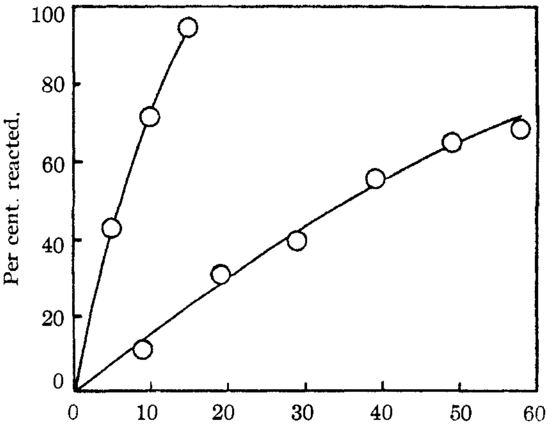

Fig. 1.—Relative reactivities of butenyl chloride isomers with phenyllithium at 27°: upper curve, α-methylallyl chloride; lower curve, crotyl chloride.

Our results are best explained by a mechanism similar to that proposed by Wilson, Roberts and Young[10b] for the Grignard system. Here a carbonium-ion intermediate is involved,[11] with its formation facilitated by a preliminary coördination of the chlorine atom with the lithium of the organolithium compound. After the (presumably rate-determining) separation into ions, the positive ion coördinates with a phenyl group from either the coördinated molecule of phenyllithium or from another molecule. This mechanism is consistent with the products observed, and we plan kinetic experiments to determine the molecularity of the reaction. Preliminary experiments (see Fig. 1) indicate that α-methylallyl chloride reacts with phenyllithium somewhat more rapidly than does crotyl chloride, a fact not inconsistent with the carbonium-ion mechanism.[12] The reactions proceed rapidly and exothermically at room temperature.

The data thus suggest the availability of the carbonium-ion intermediate (S_N1-type) process for the reaction of organolithium compounds with alkyl halides. On the other hand, the relative reactivities of *n*-butyl chloride and *t*-butyl chloride, which reacted at comparable rates with phenyllithium,[5] can best be explained by assuming reactions of the direct-displacement (S_N2) type or direct-elimination (E2) type. A carbonium-ion process would lead to predictions of rates for the tertiary halide several orders of magnitude greater than for the primary halide.[15] It thus appears that either displacement mechanisms[15] of the S_N1 or S_N2 types are available for the reaction of organolithium compounds with alkyl halides, and also as well for the second part of the Wurtz reaction.[16] Although the

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[7] F. Runge, "Organometallverbindungen," Wissenschaftliche Verlag., Stuttgart, 1944, p. 3.

[8] H. Levy and A. C. Cope, THIS JOURNAL, **66**, 1684 (1944).

[9] A. L. Henne, H. Chanan and A. Turk, *ibid.*, **63**, 3474 (1941).

[10] (a) W. G. Young, J. D. Roberts and H. Wax, *ibid.*, **67**, 841 (1945); (b) K. W. Wilson, J. D. Roberts and W. G. Young, *ibid.*, **71**, 2019 (1949).

[11] Experiments such as these give no indication regarding the "degree of freedom" of the carbonium-ion intermediate nor of the intimate details of its formation, but it seems clear that the carbonium-ion intermediate is one in which the carbon–chlorine covalent bond is substantially converted to an ionic bond prior to formation of the new covalent carbon–phenyl bond, irrespective of other ionic or solvation bonds.

[12] We are indebted to Professor John F. Lane of Rutgers University for pointing out to us that one would not expect large differences in reactivity of the two ismeric halides in carbonium-ion processes, as each leads to the identical hybrid ion, so that the ionic bond strengths would be approximately equal. Experimental data indicate the validity of this argument.[13,14] Our results, which indicate a somewhat greater reactivity for the secondary isomer in the carbonium-ion process, seem to be the first ones in which a definitely greater reactivity has been observed for the secondary over the primary isomer. Under solvolysis conditions, the greater reactivity of the primary isomer has been presumed to be due to the incursion of a direct-displacement process with solvent.[14]

[13] J. F. Lane and W. G. Young, THIS JOURNAL, **60**, 847 (1938).

[14] W. G. Young and L. J. Andrews, *ibid.*, **66**, 421 (1944).

[15] See, for example: (a) L. C. Bateman, K. A. Cooper, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 925 (1940); (b) E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[16] Experiments in this Laboratory indicate that phenylsodium, suspended in petroleum ether, reacts with butenyl chlorides with rearrangement, in contradistinction to the results of Levy and Cope[8] with sodioallylbenzene in liquid ammonia (Cristol and Overhults, unpublished work).

reactions are conducted in non-ionizing solvents, it is clear that coördination of the halogen atom with the metal portion of the organometallic compound is analogous to the effect of solvent on the halogen atom in the solvolytic process. The assumption of a duality of mechanism for such reactions will explain the inconsistency of results observed in the reactions of optically active alkyl halides with sodium and with sodium alkides, where certain systems lead to substantially complete racemization,[17,18,19] and others lead to Wurtz-type products with small to substantial optical activity,[19,20,21] and with inversion in the displacement of halogen by the alkyl group.[21] The first type may perhaps be considered as examples of the S_N1 process and the second, examples of the S_N2 process or of mixed processes.

Acknowledgment.—The authors are indebted to the Office of Naval Research for support of this work and to Mr. L. H. Cummings for the preparation of crotyl alcohol.

Experimental

Materials.—The organolithium solutions were prepared in anhydrous ethyl ether according to previously described methods.[22,23] Crotyl chloride [b.p. 78° (630 mm.), $n^{20}\text{D}$ 1.4346-1.4354] was prepared from crotyl alcohol[24] by treatment with concentrated hydrochloric acid and converted to α-methylallyl chloride [b.p. 57° (630 mm.), $n^{20}\text{D}$ 1.4150-1.4156] by refluxing with 2 mole per cent. of ferric chloride.[25] Each chloride was distilled carefully through a center-rod column (rated at 60 theoretical plates at maximum efficiency) and center fractions were used.

Crotyl Chloride with Phenyllithium.—Crotyl chloride (45.3 g., 0.5 mole) was added dropwise to 0.55 to 0.60 mole of phenyllithium in 500 ml. of ether, after which the solution was refluxed for 2 hours, then hydrolyzed by careful addition of water. The ether layer was dried over magnesium sulfate. A center-rod column (rated at 60 theoretical plates at maximum efficiency) was used to separate the mixture to give a 60% yield of which 90-95% was crotylbenzene, b.p. 172° (630 mm.), and 5-10% α-methylallylbenzene, b.p. 157-162° (630 mm.). The crotylbenzene was identified in the following manner: (1) by catalytic hydrogenation to *n*-butylbenzene which gave a 2,4-diacetamido derivative[26] [m.p. 212-213°, reported 213-214°]; and (2) by ozonolysis, followed by identification of the aldehydes formed, which were (a) acetaldehyde (methone derivative, m.p. 141-142°, reported 141-142°[27]) and (b) phenylacetaldehyde [2,4-dinitrophenylhydrazone, m.p. 119-120°, semicarbazone, m.p. 154-155°; reported 121°,[28] 156°,[29] respectively]. Each of these four derivatives, when mixed with an authentic sample, showed no depression of melting point. The α-methylallylbenzene fraction was found to be contaminated with bromobenzene so that the 2,4-diacetamido derivative of the hydrogenation product could not be obtained as a solid. Ozonolysis gave formaldehyde identified by its methone derivative (m.p. 189-190°, identical with an authentic sample, reported 191-191.5°) and hydratropaldehyde as shown by its semicarbazone (m.p. 153-154°, reported 153-154°[30]). The m.p. was not depressed when this material was mixed with an authentic sample.[30]

α-Methylallyl Chloride with Phenyllithium.—The reaction was carried out as described above for crotyl chloride, using 0.5 mole of chloride, to obtain a 50-60% yield of the butenylbenzenes in the same ratios, identified in the same manner.

Crotyl Chloride with *n*-Butyllithium.—One-half mole of chloride when added to 0.55 to 0.6 mole of *n*-butyllithium in 500 ml. of ether in a similar manner gave a 60% yield of which 90-95% was octene-2, 5-10% 3-methyl-1-heptene, and 0.2 to 0.5% 3-methyl-1,5-heptadiene. Octene-2 was identified by its physical constants: b.p. 118° (633 mm.), d^{20}_4 0.7251, $n^{20}\text{D}$ 1.4141; reported[31] b.p. 121° (760 mm.), d^{20}_4 0.7193-0.7284, $n^{20}\text{D}$ 1.4148. The 3-methyl-1-heptene and 3-methyl-1,5-heptadiene, which had almost identical boiling points, could not be separated by fractional distillation, but were estimated by quantitative catalytic hydrogenation measurements and by refractive index ratios.

α-Methylallyl Chloride with *n*-Butyllithium.—The reaction was carried out as before, with similar results. The constants found for octene-2 were b.p. 118° (629 mm.), d^{20}_4 0.7218, $n^{20}\text{D}$ 1.4149.

Relative Reactivities.—Weighed samples (0.048 g., 0.5 mmole) of crotyl and of α-methylallyl chlorides were added to 50 ml. of a 0.08 *M* solution of phenyllithium in ether. The reaction rates at 27° were followed by pipetting samples into alcohol and titrating the base with standard acid. The half-life for the reaction of crotyl chloride with phenyllithium under these conditions was 35 minutes, while that for α-methylallyl chloride was 6 minutes. The data are plotted in Fig. 1.

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