Anal. Calcd. for $C_{13}H_{19}ClO_4$: C, 59.0; H, 3.4; Cl, 13.4. Found[15]: C, 58.9; H, 3.5; Cl, 13.3.

Reduction of XIII with Lithium Aluminum Hydride.—To a slurry of 175 mg. (4.62 mmoles) of lithium aluminum hydride in 20 ml. of ether was added 281 mg. (0.993 mmoles) of XIII in several portions. The mixture was heated to reflux when hydrogen evolution ceased. After 18 hr. at reflux, the cooled mixture was treated with saturated ammonium chloride solution and acidified with 20% sulfuric acid. After the usual work-up, the resulting colorless oil could not be crystallized, but was undoubtedly mainly the diol XIV, as indicated by n.m.r. analysis. The oil was converted to the di-*p*-nitrobenzoate which was a solid, m.p. 128–129°, in high yield.

Anal. Calcd. for $C_{27}H_{21}ClN_2O_9$: C, 58.7; H, 3.8; Cl, 6.4; N, 5.1. Found[b]: C, 58.7; H, 3.9; Cl, 6.6; N, 5.2.

3,6-Dichloro-4-(2-phenyl-2-hydroxyethylamino)coumarin (XXI).—A refluxing solution of 2.50 g. (10.0 mmoles) of III in 100 ml. of ethanol was treated with a solution of 2.77 g. (20.2 mmoles) of 2-hydroxyphenethylamine in 10 ml. of ethanol at reflux for 2.5 hr. After cooling, the resulting precipitate was washed with several portions of distilled water and dried to yield 2.99 g. (86%) of XV: m.p. 193–195°; infrared bands (KBr) at 2.87 (m), 2.99 (m), 6.01 μ (s); $\lambda_{\max}$, mμ (log ε), 220 (4.57), 250 (sh) (4.09), 312 (4.09), 325 (4.09), 337 (sh) (4.00); $\lambda_{\min}$, mμ (log ε), 276 (3.34), 320 (4.07).

Anal. Calcd. for $C_{17}H_{13}Cl_2NO_3$: C, 58.3; H, 3.7; Cl, 20.3; N, 4.0. Found[a]: C, 58.4; H, 3.9; Cl, 20.2; N, 4.0.

2-Phenyl-9-chloro-2,3-dihydro[1]benzopyrano[3,4–6][1,4]oxazin-5(1H)-one (XXII).—A refluxing solution of 2.72 g. (7.77 mmoles) of XXI in 85 ml. of 1,2-dimethoxyethane was treated with 389 mg. of a 53% dispersion of sodium hydride (8.58 mmoles) in mineral oil. The reaction mixture was maintained under a nitrogen atmosphere and held at reflux for 3 hr. The cooled reaction mixture was filtered and the precipitate was washed with several portions of water and dried to yield 2.24 g. (92%) of XXII, m.p. 305–310° dec. Recrystallization from acetone yielded the analytical sample: m.p. 310–312° dec.; infrared bands (KBr) at 2.99 (m), 3.04 (w), 6.02 μ (s); $\lambda_{\max}$, mμ (log ε), 210 (4.38), 230 (4.19), 251 (4.05), 290 (sh) (3.66), 298 (3.87), 302 (3.90), 309 (4.02), 341 (3.91); $\lambda_{\min}$, mμ (log ε), 277 (3.28), 319 (3.75).

Anal. Calcd. for $C_{17}H_{12}ClNO_3$: C, 65.1; H, 3.9; Cl, 11.3; N, 4.5. Found[b]: C, 65.0; H, 4.2; Cl, 11.4; N, 4.4.

3,6-Dichloro-4-anilinocoumarin (XV).—A mixture of 2.55 g. (10.2 mmoles) of III, 1.96 g. (21.0 mmoles) of aniline, and 20 ml. of N,N-dimethylformamide was heated on a steam bath for 30 min. The cooled reaction mixture was poured into 500 ml. of water and filtered. The precipitate was dried and recrystallized from benzene to yield 2.43 g. (78%) of XV: m.p. 222–224°; infrared bands at 2.92 (w), 5.83 μ (s); $\lambda_{\max}$, mμ (log ε), 220 (4.27), 228 (4.30), 254 (4.14), 278 (3.89), 333 (4.08); $\lambda_{\min}$ mμ (log ε), 244 (4.11), 295 (3.79).

Anal. Calcd. for $C_{15}H_9Cl_2NO_2$: C, 58.9; H, 3.0; Cl, 23.2; N, 4.6. Found[b]: C, 59.1; H, 2.9; Cl, 23.3; N, 4.5.

3-Ethoxy-4-anilino-6-chlorocoumarin (XVI).—To a refluxing solution of 650 mg. (2.12 mmoles) of 3,6-dichloro-4-anilinocoumarin in 10 ml. of ethanol was added 20 ml. of 0.1 *N* sodium ethoxide in ethanol during 10 min. The resulting mixture was held at reflux for an additional 60 min., diluted with water, and cooled. There was obtained 544 mg. (85%) of XVI, m.p. 115–117°. Crystallization from 95% ethanol afforded the analytical sample: m.p. 116–117°; infrared bands at 3.03 (w), 5.97 μ (s); $\lambda_{\max}$, mμ (log ε), 208 (4.42), 220 (sh) (4.34), 260 (4.36), 304 (3.97), 313 (4.04), 350 (4.05); $\lambda_{\min}$, mμ (log ε), 232 (4.03), 287 (3.78), 321 (3.80).

Anal. Calcd. for $C_{17}H_{14}ClNO_3$: C, 64.7; H, 4.5; Cl, 11.2; N, 4.4. Found[a]: C, 64.7; H, 4.7; Cl, 11.3; N, 4.4.

6-Chloro-3-ethoxy-4-(1-propylamino)coumarin (XVIII).—A refluxing solution of 543 mg. (1.99 mmoles) of 3,6-dichloro-4-(*n*-propylamino)coumarin[4] in 10 ml. of ethanol was treated with 20 ml. of a 0.1 *N* sodium ethoxide solution during 13 min. The reaction mixture was held at reflux for 30 min., cooled to room temperature, and filtered. The filtrate was evaporated to dryness, and the residue was washed with water and dried to yield 536 mg. (96%) of colorless XVIII: m.p. 70–71°; infrared bands at 3.00 (w), 6.00 μ (s); $\lambda_{\max}$, mμ (log ε), 208 (4.41), 234 (4.19), 262 (4.02), 303 (3.88), 311 (3.95), 347 (3.98); $\lambda_{\min}$, mμ (log ε), 223 (4.09), 255 (3.99), 281 (3.45), 320 (3.78).

Anal. Calcd. for $C_{14}H_{16}ClNO_3$: C, 59.7; H, 5.7; Cl, 12.6; N, 5.0. Found[a]: C, 59.7; H, 5.7; Cl, 12.6; N, 5.2.

3-Ethoxy-4-(*o*-aminoanilino)-6-chlorocoumarin (XX).—A refluxing solution of 653 mg. (2.03 mmoles) of 3,6-dichloro-4-(*o*-aminoanilino)coumarin (XIX)[4] in 10 ml. of ethanol was treated with 20 ml. of a 0.1 *N* sodium ethoxide in ethanol during 21 min. The reaction mixture was held at reflux for an additional 30 min. and cooled to room temperature. The precipitate was collected, washed with several portions of ethanol and with water, and dried to yield 408 mg. of XX as yellow needles, m.p. 146–148°. An additional 188 mg. of XX (total yield 89%) was obtained from the filtrate. Recrystallization from ethanol afforded the analytical sample: m.p. 146–148°; infrared bands at 3.00 (w), 5.98 μ (s); $\lambda_{\max}$, mμ (log ε), 210 (4.19), 240 (4.03), 255 (3.98), 299 (4.12), 303 (4.12), 310 (4.11), 345 (4.04); $\lambda_{\min}$, mμ (log ε), 277 (3.91), 301 (4.11), 306 (4.09), 321 (3.91).

Anal. Calcd. for $C_{17}H_{15}ClN_2O_3$: C, 61.7; H, 4.6; Cl, 10.7; N, 8.5. Found[a]: C, 61.9; H, 4.8; Cl, 10.8; N, 8.5.

Reactions of Alkyl Allyl and Alkyl Propenyl Ethers with *n*-Butyllithium

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The reaction of alkyl allyl ethers with *n*-butyllithium in hydrocarbon solvent has been found to be quite temperature dependent. At −33° isomerization to the more stable alkyl *cis*-propenyl isomer occurs. At 70° a cleavage reaction produces an *n*-alkyl alcohol and heptene-1, and, at intermediate temperatures, mixtures of products are obtained. The alkyl *cis*-propenyl ethers were shown to be stable to the reaction conditions.

Reactions of ethers with alkyllithium reagents have received considerable study and various mechanistic pathways have been described for these rather complex reaction systems. Among these are displacement,[1] metalation adjacent to the oxygen atom,[2] ring metalation *ortho* to an ether substituent,[3] α elimination,[4] Wittig rearrangement,[5] and β elimination reactions.[6] In the special case of ethers which are capable of producing a resonance-stabilized anionic intermediate, benzyl compounds have been the most thoroughly studied, with Wittig rearrangement being the most commonly reported reaction. The corresponding reactions of allyl and vinyl ethers are relatively unexplored although

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(1) K. Ziegler and H.-G. Gellert, *Ann.*, **567**, 185 (1950).

(2) See H. Hoberg, *ibid.*, **656**, 1 (1962), for leading references.

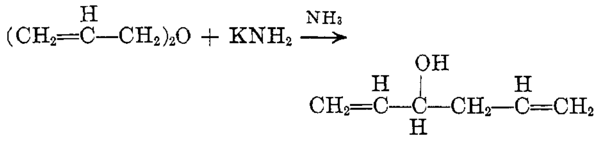
(3) H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

(4) U. Schöllkopf and M. Eisert, *Angew. Chem.*, **72**, 349 (1960); *Ann.*, **664**, 76 (1963).

(5) P. T. Lansbury and V. A. Pattison, *J. Org. Chem.*, **27**, 1933 (1962), and references therein.

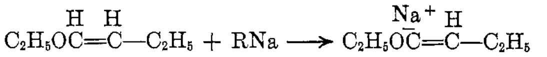
(6) R. L. Letsinger and E. Bobko, *J. Am. Chem. Soc.*, **75**, 2649 (1953); R. L. Letsinger and D. F. Pollart, *ibid.*, **78**, 6079 (1956).

apparently quite complex. Thus, Hauser[7] has shown that diallyl ether undergoes the Wittig rearrangement when treated with potassium amide in liquid ammonia (reaction 1). The course of the reaction is indicated



$$(CH_2{=}\overset{H}{C}{-}CH_2)_2O + KNH_2 \xrightarrow{NH_3} CH_2{=}\overset{H}{C}{-}\underset{H}{\overset{OH}{C}}{-}CH_2{-}\overset{H}{C}{=}CH_2 \quad (1)$$

to be initial proton abstraction at an allylic position followed by either a concerted[7] rearrangement or an elimination–addition sequence.[5] Potassium *t*-butoxide causes isomerization of allyl to *cis*-propenyl ethers, again quite probably by initial allylic proton removal.[8] Furthermore, it has been established that the allyl isomer undergoes more rapid proton loss than does the *cis*-propenyl isomer.[8,9] With the more strongly basic alkylsodium reagents, acyclic vinyl ethers are reported[10] to undergo metalation exclusively at the sp^2 carbon adjacent to oxygen[11] (reaction 2).



$$C_2H_5O\overset{H}{C}{=}\overset{H}{C}{-}C_2H_5 + RNa \longrightarrow C_2H_5O\overset{Na^+}{\bar{C}}{=}\overset{H}{C}{-}C_2H_5 \quad (2)$$

It was then of interest to study some of the factors involved in reaction of allyl and propenyl ethers with alkyllithium reagents.

Results

Reaction of Alkyl Allyl Ethers with *n*-Butyllithium in Hydrocarbon Solvent.—The dropwise addition of *n*-butyllithium in hexane to *n*-alkyl allyl ethers at room temperature resulted in an exothermic reaction. Maintaining the temperature at reflux (72°) by adjusting the drop rate gave, upon hydrolysis, high yields of *n*-alkyl alcohols and heptene-1. *n*-Hexyl, *n*-octyl, and *n*-dodecyl allyl ethers were used, giving *n*-hexyl, *n*-octyl, and *n*-dodecyl alcohols, respectively. The alcohols were identified by infrared and gas chromatographic (g.l.p.c.) comparisons with authentic samples. Heptene-1 was identified by n.m.r., infrared, and mass spectral analyses, as well as by boiling point.

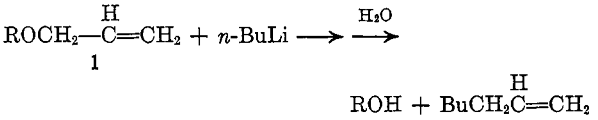
A possible reaction path for formation of the cleavage products, *n*-alkyl alcohol and heptene-1, was α elimination followed by reaction of vinylcarbene with *n*-butyllithium. Experiments were performed which militate against this possibility. Thus, quenching a reaction mixture with deuterium oxide provided heptene-1 which had not incorporated deuterium by n.m.r. and mass spectral analyses.[4] Conducting the reaction in the presence of excess cyclohexene again provided heptene-1 with no evidence for the formation of norcarane derivatives.

An experiment with *n*-octyl allyl ether, in which the reaction temperature was maintained between 30 and 40° by cooling, resulted in a 23% yield of octyl *cis*-propenyl ether in addition to *n*-octyl alcohol and, presumably, heptene-1. This ether was identified by g.l.p.c. and infrared comparison to a sample prepared by the method of Prosser.[8a] Other experiments, in which hexane solutions of alkyl allyl ethers were precooled in a liquid ammonia bath before the slow addition of *n*-butyllithium, returned only starting material and the corresponding alkyl *cis*-propenyl ether. Since isomerization reactions of this nature presumably proceed through an allyl carbanionic intermediate,[12] trapping experiments were performed. Carbonation of a reaction mixture of octyl allyl ether and *n*-butyllithium at −33° provided octyl *cis*-propenyl ether and an acidic product which was shown to be *n*-pentanoic acid by infrared spectral analysis. Quenching a similar reaction mixture of dodecyl allyl ether with deuterium oxide gave dodecyl *cis*-propenyl ether with no incorporation of deuterium by n.m.r. analysis.

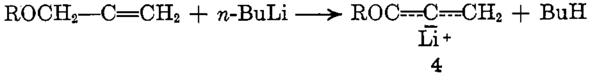
Attempted Reaction of Alkyl *cis*-Propenyl Ethers with Butyllithium in Hydrocarbon Solvent.—Dropwise addition of *n*-butyllithium in hexane to octyl *cis*-propenyl ether in hexane at room temperature gave no evidence of exothermicity. Hydrolysis after stirring for 1 hr. gave only recovered starting material. Similarly, addition of deuterium oxide to a reaction mixture gave octyl *cis*-propenyl ether containing no deuterium by n.m.r. analysis. Carbonation, following a 1-hr. stirring period, resulted in the predominant formation of pentanoic acid.[13]

Discussion

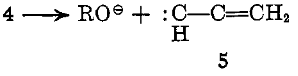
It is evident that the predominant course for reaction of *n*-butyllithium and alkyl allyl ethers in refluxing hexane is the production of alcohols and 1-olefin (reaction 3). At least two reaction paths can be postulated for this process, *i.e.*, α elimination and displacement. An α elimination sequence would involve proton abstraction at the allylic position, elimination of a vinylcarbene (**5**), followed by reaction with *n*-butyllithium, and finally hydrolysis upon work-up to produce the observed products[14] (reactions 4-7). Al-



$$\underset{1}{ROCH_2{-}\overset{H}{C}{=}CH_2} + n\text{-BuLi} \longrightarrow \xrightarrow{H_2O} \underset{2}{ROH} + \underset{3}{BuCH_2\overset{H}{C}{=}CH_2} \quad (3)$$



$$ROCH_2{-}\overset{H}{C}{=}CH_2 + n\text{-BuLi} \longrightarrow \underset{4}{ROC{=\!=}\underset{\bar{Li}^+}{\overset{H}{C}}{=\!=}CH_2} + BuH \quad (4)$$



$$4 \longrightarrow RO^{\ominus} + \underset{5}{:\underset{H}{C}{-}\overset{H}{C}{=}CH_2} \quad (5)$$

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[7] C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.* **73**, 1437 (1951).

[8] (a) T. J. Prosser, *ibid.*, **83**, 1701 (1961); (b) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

[9] C. D. Broaddus, *ibid.*, **87**, 3706 (1965).

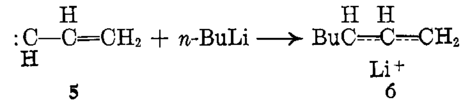
[10] R. Paul and S. Tchelitcheff, *Compt. rend.*, **235**, 1226 (1952).

[11] It should be noted that, while allylic hydrogens are available to produce a resonance-stabilized isomer, $RO\overset{H}{C}{=\!=}\underset{-}{\overset{H}{C}}{=\!=}CH{-}CH_3\,Na^+$, no carbonation products from this intermediate are observed. This system, in which the α-vinyl hydrogen is apparently activated by oxygen, represents a case in which competitive metalation at the allylic position is not observed. For discussions of competitive metalation in olefins, see C. D. Broaddus, *J. Org. Chem.*, **29**, 2689 (1964); R. A. Finnegan and R. S. McNees, *ibid.*, **29**, 3241 (1964).

[12] H. Pines and L. A. Schaap, *Advan. Catalysis*, **12**, 117 (1960).

[13] Some dibutyl ketone was also obtained; however, there was no evidence for unsaturation in the ketonic product as required by reaction of allylic or vinylic intermediates.

[14] For a similar reaction of benzyl phenyl ether, see ref. 4.

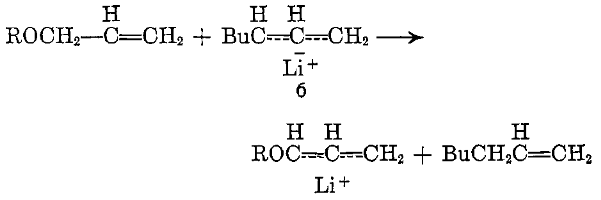


$$\underset{\mathbf{5}}{:\underset{H}{C}-\overset{H}{C}=CH_2} + n\text{-BuLi} \longrightarrow \underset{\mathbf{6}}{Bu\overset{H}{C}\overset{-}{\cdots}\underset{Li^+}{\overset{H}{C}}\overset{-}{\cdots}CH_2} \qquad (6)$$

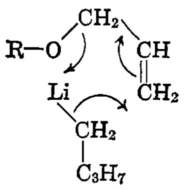
$$\mathbf{6} + H_2O \longrightarrow BuCH_2\overset{H}{C}=CH_2 \qquad (7)$$

though this scheme offers an intriguing possibility, several observations weigh against its validity. First, the olefin obtained has been shown to be very predominantly the terminal isomer. For the outlined mechanism to be operative, this observation would require that the intermediate alkylallyllithium compound **6** undergo protonation (reaction 7) exclusively at the alkyl-substituted position, while the favored position of protonation should be the terminal or unsubstituted position to produce 2-heptene.[15] Furthermore, this pathway would require the consumption of 2 moles of *n*-butyllithium/mole of alkyl allyl ether while complete rapid reactions were obtained using *ca.* 1:1 mole ratios of reactants. Additionally, quenching the reaction mixture with deuterium oxide should provide deuterated olefin,[4] while in fact both mass spectral and n.m.r. analyses indicate that the heptene-1 obtained contains essentially no deuterium. Finally, attempts to trap any intermediate carbene or "carbenoid"[16] species with cyclohexene were unsuccessful.[17]

Many of the above objections would be invalidated if reactions 5 and 6 were rapid compared to 4 and were followed by an equally rapid metalation of alkyl allyl ether by heptenyllithium, *i.e.*, reaction 8. However, the isolation of only heptene-1 would still require that proton abstraction occur only at the alkyl-substituted position of **6**, making this proposal unlikely. It appears much more reasonable from these considerations to account for the major products, heptene-1 and *n*-alkyl alcohol, by a nucleophilic displacement process. While this data allows no distinction between possible displacement paths, it is interesting to note that initial coordination of the lithium atom with oxygen[18] could provide a six-membered cyclic transition state **7** for an S_N2' process.



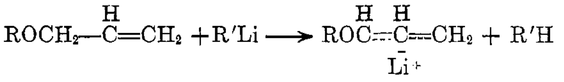
$$ROCH_2-\overset{H}{C}=CH_2 + \underset{\mathbf{6}}{Bu\overset{H}{C}\overset{-}{\cdots}\underset{Li^+}{\overset{H}{C}}\overset{-}{\cdots}CH_2} \longrightarrow RO\overset{H}{C}\overset{-}{\cdots}\underset{Li^+}{\overset{H}{C}}\overset{-}{\cdots}CH_2 + BuCH_2\overset{H}{C}=CH_2 \qquad (8)$$



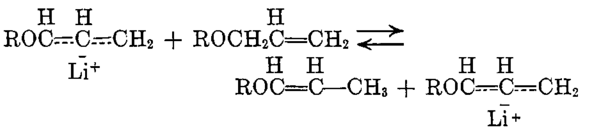
7

As recorded in the Results section, maintaining the reaction temperature at 30-40° resulted in the formation of alkyl *cis*-propenyl ether (23%) as well as high yields of octanol (77%) and presumably heptene-1. That lower temperatures favor isomerization of alkyl allyl ethers to the corresponding alkyl *cis*-propenyl ethers with respect to cleavage (reaction 3) was demonstrated more dramatically at −33°. In a liquid ammonia bath the very predominant product from the reaction of alkyl allyl ethers and *n*-butyllithium was alkyl *cis*-propenyl ether. These results made the consideration of isomerization (see later discussion) prior to cleavage necessary. That isomerization does not occur before cleavage is shown by the stability of alkyl *cis*-propenyl ethers to the cleavage reaction conditions. Refluxing octyl *cis*-propenyl ether with an equimolar amount of *n*-butyllithium in hexane for 2 hr. before hydrolysis returned a high yield of unchanged starting material.[19]

It then appears that competitive isomerization and cleavage reactions are involved in this system, with low temperature favoring isomerization. The most commonly accepted mechanism for double-bond isomerization with organoalkali compounds is that described by Pines and Schaap[12] and Lüttringhaus, *et al.*,[20] which can be shown in this case as



$$ROCH_2-\overset{H}{C}=CH_2 + R'Li \longrightarrow RO\overset{H}{C}\overset{-}{\cdots}\underset{Li^+}{\overset{H}{C}}\overset{-}{\cdots}CH_2 + R'H \qquad (9)$$



$$RO\overset{H}{C}\overset{-}{\cdots}\underset{Li^+}{\overset{H}{C}}\overset{-}{\cdots}CH_2 + ROCH_2\overset{H}{C}=CH_2 \rightleftarrows RO\overset{H}{C}=\overset{H}{C}-CH_3 + RO\overset{H}{C}\overset{-}{\cdots}\underset{Li^+}{\overset{H}{C}}\overset{-}{\cdots}CH_2 \qquad (10)$$

Several points about the data obtained from these low temperature isomerization reactions merit discussion. First, the propenyl ethers obtained appear to be entirely the *cis* isomers by n.m.r. and infrared spectral analysis (see Experimental Section). This same stereoselective isomerization was observed by earlier workers using potassium *t*-butoxide and can be explained[8] by an electrostatic interaction[21] between the alkali metal atom and the *cis*-allyl anionic intermediate.

Secondly, quenching reaction mixtures by carbonation as well as by addition of deuterium oxide shows that there is no significant accumulation of the alkoxyallyl anionic intermediate **4**. Thus, the acid obtained from carbonation is identical with pentanoic acid by infrared spectral comparison and arises from *n*-butyllithium. Analysis of the product by n.m.r. after addition of deuterium oxide gives no evidence for the incorporation of deuterium in the alkyl *cis*-propenyl ether. For the anionic mechanism outlined in reactions 9 and 10 to be

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[15] (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 418; (b) N. Bouman and G. J. Hoijtink, *Rec. trav. chim.*, **76**, 841 (1957); (c) V. A. Kropachev, B. A. Dolgoplosk, and K. V. Danilovich, *Proc. Acad. Sci. USSR, Sect. Chem.*, **111**, 763 (1956).

[16] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

[17] Cyclopropane derivatives have been identified in similar reaction systems using ether solvents.[2,4]

[18] Coordination of the cation is very commonly proposed in metalation of compounds containing heteroatoms. For example, see W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 2467 (1963).

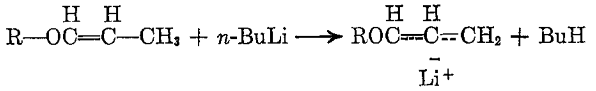
[19] Lesser reactivity by the propenyl isomer is consistent with either displacement processes at a vinyl carbon as compared to allyl (J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 176) or with a proton abstraction sequence[8,9]; however, the dramatic change from an exothermic process to no reaction appears more in keeping with the differences expected from nucleophilic displacements.

[20] A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker, and G. Borth, *Ann.*, **557**, 46 (1947).

[21] A similar kind of interaction was used to account for the preferential formation of *cis* isomers during olefin isomerization [W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960)]. For a recent discussion of stereoselective isomerizations based on olefin conformation in several systems, see C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 69 (1962).

compatible with these observations, the allyl anionic intermediate **4** must undergo reaction with alkyl allyl ether more rapidly than does *n*-butyllithium. Similar tentative conclusions were derived from data obtained from metalation of α-olefins with *n*-butylsodium[22]; however, in that case the obvious heterogeneity of the reaction mixture offered other possible explanations based on surface coating. In the present system, varying degrees of association of the organolithium species involved might be invoked to explain the data; however, recent kinetic studies[23a] indicate that inordinately rapid metalation reactions by resonance-stabilized lithium species can be expected.[23b]

Since both allyl and propenyl ethers could undergo metalation to produce **4** by an irreversible process, the absence of this species in these isomerization reactions indicated that the *cis*-propenyl isomer was reacting slowly, if at all. That reaction 11 is comparatively



$$\mathrm{R{-}O}\overset{\mathrm{H}}{\mathrm{C}}{=}\overset{\mathrm{H}}{\mathrm{C}}{-}\mathrm{CH_3} + n\text{-BuLi} \longrightarrow \mathrm{RO}\overset{\mathrm{H}}{\mathrm{C}}{=\!=}\underset{\overset{-}{\mathrm{Li^+}}}{\overset{\mathrm{H}}{\mathrm{C}}}{=\!=}\mathrm{CH_2} + \mathrm{BuH} \qquad (11)$$

9 **4**

slow was shown independently by the addition of *n*-butyllithium to a sample of octyl *cis*-propenyl ether followed by stirring for 2 hr. and quenching with deuterium oxide. The ether recovered from this reaction mixture (95%) showed no deuterium incorporation by n.m.r. analysis. This difference in rates of reaction of the isomeric ethers with *n*-butyllithium is most readily accounted for by their known[8] difference in ground state stabilities; *i.e.*, the more stable isomer **9** reacts slower.[24]

In summary then, isomerization of alkyl allyl ethers by *n*-butyllithium at low temperatures appears consistent with an anionic mechanism[12,22] in which proton abstraction from the alkyl allyl ether (reaction 9) is slow relative to isomerization steps involving allylic intermediates[23a] (reaction 10) to produce alkyl *cis*-propenyl ethers which are stable to the reaction conditions,[8,23b] *i.e.*, do not undergo proton loss. At higher temperatures alkyl allyl ethers undergo cleavage to the corresponding alcohol and 1-olefin most probably by a displacement process.

It should be emphasized that these studies pertain only to hydrocarbon solvents.[25] In fact, preliminary investigations indicate that in ethereal solutions the predominant course of reaction for alkyl allyl ethers with *n*-butyllithium is Wittig rearrangement, while alkyl *cis*-propenyl ethers are again comparatively unreactive.

Experimental Section

Preparation of Allyl Ethers.—During the course of this work, dodecyl, octyl, and hexyl allyl ethers were allowed to react with *n*-butyllithium. No significant differences in reactions were noted with the variation in the chain length of the alkyl group. The preparation of dodecyl allyl ether is given as an example. Allyl alcohol (1 l.) was dried by distillation from sodium metal (10 g.). To the distilled alcohol was added sodium metal (34.5 g., 1.5 g.-atoms) in approximately 1-g. pieces. The system was kept under an atmosphere of nitrogen and the temperature was maintained between 45 and 55°. Upon disappearance of the sodium metal, dodecyl bromide (350 g., 1.4 moles) was added to the reaction mixture which was stirred at 50° for 48 hr. After this period the mixture was poured into 1.5 l. of water and extracted with ether, the extract was dried with anhydrous $\mathrm{MgSO_4}$, and the solvents were removed on a rotary evaporator to yield 322.0 g. of crude material. Distillation (b.p. 86–87° at 0.1 mm.) gave 307 g. (98.5%) of pure material by gas chromatographic analysis.

Octyl allyl ether was prepared in a similar manner and hexyl allyl ether was purchased from Peninsular Chemical Co., Gainesville, Fla.

Preparation of *cis*-Propenyl Ethers.—These compounds were prepared by a slight modification of the method developed by Prosser.[8] The corresponding allyl ethers were heated to 150° for 24 hr. in the presence of 10 wt. % of potassium *t*-butoxide. Water was then added to the reaction mixture and the product was extracted with ether; the ether extract was dried with anhydrous magnesium sulfate and distilled to give material having the spectral characteristics recorded in the following discussion.

Spectral Analyses.—Infrared spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer and n.m.r. spectra were obtained using a Varian A-60 n.m.r. spectrometer. Chemical shifts are reported on the τ scale.[26]

N.m.r. Spectra of Alkyl Allyl Ethers.—The n.m.r. spectra of alkyl allyl ethers show complex multiplets in the vinyl proton region centered at τ 4.2 and 4.8, two triplets centered at τ 6.1 (J = 5 c.p.s.), a triplet centered at τ 6.68, intense absorption at τ 8.72, and a triplet at τ 9.1. In the case of octyl allyl ether the relative areas in the order given are very close to the theoretical (1:2:2:2:12:3) and the assignments are, therefore, the single vinyl hydrogen, the two terminal vinyl hydrogens, the two hydrogens allylic to the double bond and adjacent to the oxygen atom, the methylene group adjacent to oxygen, the chain methylene hydrogens, and the terminal methyl group, respectively.

N.m.r. Spectra of Alkyl *cis*-Propenyl Ethers.—The n.m.r. spectra of alkyl *cis*-propenyl ethers, obtained by the method of Prosser,[8a] show a doublet (J = 6 c.p.s.) which is further split into two quartets ($J \sim 2$ c.p.s.) centered at τ 4.2, a quintuplet centered at τ 5.78 (J = 6 c.p.s.), a triplet centered at τ 6.35, a doublet (J = 6 c.p.s.) which is further split into two doublets ($J \sim 2$ c.p.s.) centered at τ 8.5, intense absorptions at τ 8.72, and a triplet at τ 9.1. In the case of dodecyl *cis*-propenyl ethers, the relative areas (the integration curve did not separate the absorptions at τ 8.5 and 8.72) in the order given are very close to the theoretical 1:1:2:23:3. The assignments are, therefore, the vinyl hydrogen adjacent to oxygen, the vinyl hydrogen adjacent to methyl, the methylene hydrogens adjacent to oxygen, the allylic methyl group, the chain methylene hydrogens, and the terminal methyl group, respectively.

Reaction of Hexyl Allyl Ether with *n*-Butyllithium in Refluxing Hexane.—Hexyl allyl ether (14.1 g., 0.1 mole) was dissolved in 50 ml. of hexane and placed in a three-necked flask under a blanket of dry $\mathrm{N_2}$. To this solution was added 63 ml. of *n*-butyllithium in hexane (*ca.* 1.6 *N*, 0.1 mole) dropwise from a syringe. An immediate temperature rise accompanied the addition. The temperature was maintained at reflux for the remainder of the addition which required approximately 30 min. Stirring was continued for 1 hr. after completion of the addition, at which time the temperature had dropped to 30°. Deuterium oxide (2 ml., 99.5%) was added and the mixture was stirred for 30 min. The mixture was dried with anhydrous magnesium sulfate, filtered, and distilled twice through a 24-in. spinning-band column to yield a material (6.5 g., 62%, b.p. 88–91°) whose infrared spectrum is identical with that of a terminal olefin, *i.e.*, strong bands at 6.1, 10.1, and 11.0 μ. No absorptions for *cis* or *trans* (10.3 μ) double bonds were present.[27]

The n.m.r. spectrum of this material was entirely consistent with heptene-1 both in absorption characteristics and in relative

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(22) C. D. Broaddus, T. J. Logan, and T. J. Flautt, *J. Org. Chem.*, **28**, 1174 (1963).

(23) (a) R. Waack and P. West [*J. Am. Chem. Soc.*, **86**, 4494 (1964)] gave the order for the rate of metalation of triphenylmethane with organolithium reagents as benzyl- > allyl- > *n*-butyl- > phenyl- > vinyl- > methyllithium. (b) The enhanced reactivity of resonance-stabilized organolithium compounds, *i.e.*, as predicted from basicities, can be accounted for by greater polarizability[23] or by the operation of an α effect,[22] both of which have been discussed by J. O. Edwards and R. G. Pearson [*ibid.*, **84**, 16 (1962)].

(24) Deuterium exchange studies using potassium *t*-butoxide in *t*-butyl alcohol-*d* indicate the same order of reactivity.[9]

(25) It has been previously reported[20] that allyl ethers undergo cleavage in ethereal Grignard systems.

(26) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(27) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 45–51.

areas of hydrogens. In a separate run the peak corresponding to heptene-1 on g.l.p.c. was trapped and its mass spectrum was recorded. The parent peak appeared at m/e 98, consistent with nondeuterated heptene-1.[28]

After distillation of the low-boiling material, a pot residue was obtained (10.8 g.) whose infrared spectrum is consistent with a primary alcohol[28] and starting material.[8] G.l.p.c. comparison[29] of this mixture to authentic samples of hexyl allyl ether and *n*-hexyl alcohol[30] showed the mixture to consist of 87% *n*-hexyl alcohol and 13% starting material.[31]

In a separate run using dodecyl allyl ether (5.6 g., 0.025 mole) in 12 ml. of hexane, one-half the required amount of *n*-butyllithium (1.6 *N*, 8 ml., 0.012 mole) was added and the mixture was refluxed for 2 hr. The addition of 1 ml. of D_2O, after allowing the mixture to stand overnight, provided a high-boiling product (5.0 g.) which was 52% starting material and 48% dodecyl alcohol, by g.l.p.c. analysis. The n.m.r. spectrum showed no evidence for deuterium incorporation nor isomerization to dodecyl *cis*-propenyl ether, and the vinyl proton region was identical with that of the starting material.

Reaction of Octyl Allyl Ether with *n*-Butyllithium in Hexane at 30–40°.—Octyl allyl ether (1.0 g., 0.006 mole) was dissolved in 25 ml. of hexane and placed in a three-necked reaction flask which was surrounded with a water bath. Dropwise addition of 10 ml. of *n*-butyllithium in hexane (1.6 *N*) resulted in a 10° temperature rise (from 25 to 35°). After the addition was complete, the mixture was stirred for 1.25 hr. and then hydrolyzed by the addition of excess water. The organic layer was collected, dried with anhydrous magnesium sulfate, and filtered, and the low-boiling material was removed at aspirator pressure to give 0.8 g. of product whose infrared spectrum was consistent with a mixture of octyl *cis*-propenyl ether[8] and a primary alcohol.[27] G.l.p.c. comparison to authentic samples showed the mixture to consist of 77% *n*-octyl alcohol and 23% octyl *cis*-propenyl ether.

Reaction of Alkyl Allyl Ethers with *n*-Butyllithium at $-33°$.—Dodecyl allyl ether (5.0 g., 0.022 mole) was dissolved in 25 ml. of hexane, placed in a one-neck reaction flask, and cooled to $-33°$ in a liquid ammonia bath. To this solution was added 5 ml. of *n*-butyllithium (1.6 *N*) in hexane. The resulting solution was allowed to stand for 6 hr. before the addition of 2 ml. of deuterium oxide. The mixture was dried with anhydrous magnesium sulfate and filtered, and the low-boiling material was removed to give a material (4.4 g.) which was predominantly octyl *cis*-propenyl ether by infrared and n.m.r. analysis.

Reaction of Alkyl Allyl Ether with *n*-Butyllithium in Excess Cyclohexene.—Dodecyl allyl ether (10 g., 0.044 mole) was dissolved in 50 ml. of cyclohexene and 38 ml. of *n*-butyllithium (1.6 *N*) was added dropwise. The reaction mixture was stirred overnight, hydrolyzed, and worked up as before. Distillation through a spinning-band column provided only heptene-1 as a new olefinic species. The n.m.r. spectrum of this material was entirely consistent with heptene-1 as was the mass spectrum,[28] indicating that norcarane derivatives could only have been formed in very low yield, if at all.

Attempted Reaction of Alkyl *cis*-Propenyl Ethers with *n*-Butyllithium.—Hexyl *cis*-propenyl ether (2.0 g., 0.014 mole) was dissolved in 50 ml. of hexane and 20 ml. of *n*-butyllithium (1.6 *N*) was added dropwise to the solution. The reaction mixture was allowed to stir overnight and then carbonated by pouring over excess Dry Ice through a syringe. The usual work-up of an acidic fraction provided an acid product (1.3 g., 38%) having an infrared spectrum identical with that of pentanoic acid. The neutral layer from this reaction (2.35 g.) had an infrared spectrum consistent with octyl *cis*-propenyl ether admixed with ketone. G.l.p.c. comparison to an authentic sample of dibutyl ketone indicated that carbonation provided ketones as well as acidic product. No evidence for the carbonation of an alkoxyallyl anionic species was obtained.

In a similar manner octyl *cis*-propenyl ether (1 g., 0.006 mole) was mixed with 10 ml. of *n*-butyllithium (1.6 *N*) and stirred for 1.25 hr. before addition of 2 ml. of deuterium oxide. The usual work-up provided a material (0.95 g.) having an n.m.r. spectrum identical with that of the starting compound. Thus, no significant incorporation of deuterium had occurred.

Additionally, to dodecyl *cis*-propenyl ether (5.6 g., 0.025 mole) in 12 ml. of hexane was added *n*-butyllithium (1.6 *N*, 16 ml.) and the resulting solution was refluxed for 2 hr. The addition of 1 ml. of D_2O and work-up provided a quantitative recovery of starting material which did *not* contain deuterium by n.m.r. analysis.

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[28] This data was obtained from a Bendix time-of-flight mass spectrometer to which was attached an Aerograph Model A-90P gas chromatograph. The author is indebted to Drs. J. C. Wootton and W. L. Courchene, of these laboratories, for this data.

[29] Using an Aerograph Model A-90P equipped with a 10-ft., 0.25-in. polyester column at an approximate flow rate of 60 cc./min.

[30] Obtained from Matheson Coleman and Bell.

[31] Percentages are taken directly from areas (peak height times width at half-height) and are not corrected for differences in thermal conductivity.

Mono- and Dialkylation of Phenylacetonitrile by Means of Sodamide and Sodium Hydride. Alkylation of Diphenylacetonitrile[1a]

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Monoalkylations of phenylacetonitrile with alkyl halides by means of sodamide in liquid ammonia or toluene were generally accompanied by dialkylation even though molecular equivalents of the reactants were employed. Toluene is preferable to liquid ammonia for certain monoalkylations, but the latter solvent is better for certain others. Also monoalkylation of phenylacetonitrile with *n*-butyl bromide by sodium hydride in 1,2-dimethoxyethane was accompanied by dialkylation. Further alkylation of the monobutyl derivative of phenylacetonitrile with benzyl chloride was effected by sodamide in liquid ammonia. Di-*n*-butylation of phenylacetonitrile was accomplished in excellent yield in a single operation with 4 molecular equiv. of *n*-butyl bromide and sodamide or sodium hydride. β-Phenylethylation of diphenylacetonitrile was realized in good yield by both reagents.

Many monoalkylations of phenylacetonitrile with alkyl halides have been reported.[2] Most of them were effected by sodamide in an inert solvent, but a few were done with this base in liquid ammonia.[3] Monomethylation and monobenzylation in the latter medium were shown[3] to be accompanied by considerable dialkylation even though phenylacetonitrile (I) was first converted to its sodio salt I′ by 1 molecular equiv. of sodamide, and the halide then added. Evidently equilibration between I′ and the monoalkyl derivative II occurred to regenerate I and form sodio salt II′ which underwent further alkylation to give dialkyl derivative III (Scheme I).

We have found, as would be expected,[3] that various monoalkylations by sodamide in liquid ammonia or even toluene are accompanied by some dialkylation. The results are summarized in Table I in which are

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[1] (a) Supported in part by the National Science Foundation. (b) Union Carbide and Carbon Chemicals Co. Fellow, 1962.

[2] A. C. Cope, H. L. Holmes and H. O. House, *Org. Reactions*, **9**, 107 (1957).

[3] C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 494 (1956).