# Carbanion Chemistry. II. Allylic Ethylations and Related Reactions

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Metalation of olefins at the allylic position occurs readily in the presence of alkali metal; this metalation is generally rapid if a primary–secondary or a primary–tertiary resonating structure is formed, and slow if an internal or secondary–secondary structure of the anion results; moreover, metalation at a tertiary carbon, even to form a primary–tertiary carbanion, is very slow. Alkylation of an olefin occurs *via* a chain reaction when the carbanion resulting from metalation adds to another olefin molecule. For primary–primary or primary–secondary carbanions, the rate of addition to ethylene does not seem to be dependent on molecular weight; conversely, a given carbanion adds fastest to ethylene, slower to propylene, and very slowly to butenes. Steric factors and the relative nucleophilicity of primary, secondary, and tertiary carbanions also affect rates of addition. Aliphatic carbanions containing an isolated double bond can undergo an intramolecular addition, resulting in ring formation.

Polymerizations of olefins in the presence of alkali metals or organoalkali compounds are well known. Early reports of the results of the effect of sodium on olefins are due to Walker,[1] Egloff and Parrish,[2] and Jungers and Taylor.[3]

Nearly 20 years later Mark and Pines[4] subjected several simple olefins and olefin pairs to reaction in the presence of organosodium initiators; from their results emerged the first definitive statements concerning the relative stabilities and reactivities of carbanions as functions of their structures. Patents directed to the polymerization of monoolefins in the presence of sodium dispersions have been issued to Freed,[5] and the codimerization of ethylene with various olefins containing allylic hydrogens has also been reported in patents.[6,7] A method for the production of relatively low molecular weight polymer from olefins having at least three carbon atoms, using as catalysts alkali metals supported on porous, absorbent carbon, has been disclosed,[8] and an interstitial compound of potassium and graphite, $C_8K$, was employed by Podall, Foster, and Giraitis[9] for the polymerization of ethylene.

Clusius and Mollet[10] found that supported cesium was capable of polymerizing ethylene and other olefins to yield both gaseous and liquid products. When this work was repeated by another group of investigators,[11] considerable selectivity to produce certain liquid products was observed. Recently it has been shown[12] that, through proper choice of alkali metal catalyst and reaction conditions, 4-methyl-1-pentene or 4-methyl-2-pentene can be selectively formed by dimerization of propylene.

Consideration of the known behavior of carbanionic intermediates, together with the results of our experiments as presented below, indicates that the alkali metal catalyzed condensations of olefins are quite selective; in this paper we attempt to systematize our observations concerning this selectivity.

**Simple Allylic Ethylations. A. Propylene.**—The results of several typical allylic ethylations are summarized in Table I and described below. The prototype allylic ethylation is that of propylene, which probably proceeds *via* addition of the allyl carbanion to ethylene, resulting in the formation of the 1-penten-5-ide carbanion, a quasi-aliphatic carbanion which abstracts a proton from another molecule of propylene, thus regenerating an allyl carbanion which can continue the chain reaction.

Chain-ending reactions may involve either the irreversible destruction of an active carbanion species, usually as the result of the presence of impurities in the reactants, or the formation of heavy polymers which inactivate the catalyst either by physical means (coating the catalyst) or by chemical means (acting as proton donors to the carbanion–metal ion pair). Evidence suggestive that each of these chain-ending reactions may occur follows: (a) we have observed that, unless the hydrocarbon feeds are thoroughly dried, alkylation occurs but slowly if at all; (b) catalyst recovered after removal of light hydrocarbon product could be reused once, but then became inactive; washing with boiling *n*-heptane restored nearly all of the original activity, but even this regeneration could be repeated only a few times and thereafter was ineffective; and (c) the polymeric residue recovered after several experiments was observed to be hydrogen deficient (0.1–0.5 H atom/C atom). The alkylation chain reaction can also be stopped when desired by addition of water, alcohols, carbon dioxide, or hydrogen. In the absence of chain-stopping agents, the chain-carrying reactions should alternate until one of the reagents is exhausted, and resume on replenishing that reagent.[13] In our experiments, the chain reaction was stopped by rapidly cooling the autoclave and removing the reactants.

The major side reactions, for convenience in discussion, can be divided into two types: isomerization and multiple addition, both of which are illustrated in Table

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[1] H. W. Walker, *J. Phys. Chem.*, **31**, 961 (1927).

[2] G. Egloff and C. I. Parrish, *Chem. Ind.* (London), 321 (1937).

[3] J. C. Jungers and H. S. Taylor, *J. Chem. Phys.*, **4**, 94 (1936).

[4] V. Mark and H. Pines, *J. Am. Chem. Soc.*, **78**, 5946 (1956).

[5] W. V. Freed (to E. I. du Pont de Nemours and Co.), U. S. Patents 2,466,694 (April 12, 1949), 2,492,693 (Dec. 27, 1949).

[6] R. D. Closson, A. J. Kolka, and W. B. Ligett (to Ethyl Corp.), U. S. Patent 2,751,426 (June 19, 1956).

[7] Ethyl Corp., British Patent 732,796 (June 29, 1955).

[8] D. L. Esmay, P. Fotis, Jr., and W. A. Wilson (to Standard Oil Co., Indiana), U. S. Patent 2,881,234 (April 7, 1959).

[9] H. Podall, W. E. Foster, and A. P. Giraitis, *J. Org. Chem.*, **23**, 82 (1958).

[10] K. Clusius and H. Mollet, *Helv. Chim. Acta*, **39**, 363 (1956).

[11] G. Lemetre, V. Martello, and G. Nobile-Orazio, *Chim. Ind.* (Milan), **40**, 470 (1958).

[12] (a) R. M. Schramm (to California Research Corp.), U. S. Patent 2,986,588 (May 30, 1961); California Research Corp., British Patent 824,917 (Dec. 9, 1959); (b) British Petroleum Co. Ltd., Belgian Patents 601,719, 601,720 (March 23, 1961), 619,715 (Oct. 31, 1962); (c) Ethyl Corp., French Patent 1,303,743 (Sept. 14, 1962).

[13] (a) M. Szwarc, M. Levy, and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956); *cf.* also R. Waack, A. Rembaum, J. D. Coombes, and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 2026 (1957); H. Brody, M. Ladacki, R. Milkovitch, and M. Szwarc, *J. Polymer Sci.*, **25**, 221 (1957); M. Szwarc, *Nature*, **178**, 1168 (1956); D. J. Worsfold and S. Bywater, *J. Polymer Sci.*, **26**, 299 (1957); (b) H. Pines and V. Mark, *J. Am. Chem. Soc.*, **78**, 4316 (1956).

TABLE I

ETHYLATION OF SOME SIMPLE 1- AND 2-OLEFINS[a]

| | Olefin ethylated | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Propyl- lene | Iso- butene | 1-Butene | 2-Butene | 1- Pentene | 2- Pentene | 1- Hexene | 2- Hexene | 1- Heptene |
| Conditions | | | | | | | | | |
| Olefin/ethylene, mole ratio | 0.6 | 1.0 | 0.9 | 0.9 | 1.0 | 1.0 | 1.0 | 0.7 | 0.6 |
| Temp., °C. | 200 | 200 | 175 | 200 | 200 | 200 | 200 | 200 | 200 |
| Maximum pressure, p.s.i.g. | 2200 | 2180 | 2000 | 2100 | 1950 | 2000 | 2020 | 860 | 1190 |
| Time to $P_{max}/2$, hr. | 0.3 | 0.3 | 0.6 | 0.3 | 0.3 | 0.2 | 0.1 | 0.3 | 1.1 |
| Total time at run temp., hr. | 0.4 | 0.7 | 0.6 | 0.4 | 0.3 | 0.2 | 0.3 | 0.3 | 1.1 |
| Conversion of olefin, %[b] | 89 | 71 | 52 | 59 | 44 | 48 | 34 | 23 | 51 |
| Conversion of ethylene, % | 55 | 89 | 67 | 64 | 64 | 65 | 59 | 44 | 83 |
| Selectivity, wt. % of converted olefin | | | | | | | | | |
| To 3-ethylated 1-olefin | 42 | 48 | 46 | 58 | 43 | 37 | 46 | 38 | ... |
| To monoethylated internal *n*-olefin ("*n*-4-olefin") | | | 25 | 17 | 29 | 33 | 47 | 52 | ... |
| To isomerized monoethylated products | 30 | 19 | 13 | 10 | Trace | Trace | Trace | 7 | ... |
| To total monoethylated product | 72 | 67 | 84 | 85 | 81[c] | 83[d] | 93 | 97 | 93 |
| To total diethylated product | 14 | 29 | 11 | 8 | 8 | 8 | 5 | Trace | 7 |
| To hydrogenated olefin | 1 | Trace | Trace | 1 | ... | ... | ... | ... | ... |
| To olefin dimers | 5 | ... | ... | ... | ... | ... | ... | ... | ... |
| To higher boiling liquid and residue | 8 | 4 | 5 | 6 | 11 | 9 | 2 | 3 | ... |

[a] Over 1 wt. % of 1:1 (molar ratio) Li–K catalyst. [b] Exclusive of double-bond position isomerization of starting olefin. [c] Includes 9% 4-methyl-2-hexene from internal metalation of 2-pentene. [d] Includes 13% 4-methyl-2-hexene from internal metalation of 2-pentene.

I. Both types of side reactions can be explained best by a remetalation of the initial reaction product.

Double-bond position isomerization[14] is illustrated by the large amounts of 2-pentene (30–60%, depending on reaction conditions) found in the reaction products of propylene ethylation. We do not, however, observe any aliphatic skeletal rearrangement *via* carbanions, although rearrangements of aromatic carbanions *via* phenyl migration have been observed by others.[15] At 200°, thermodynamic data[16] indicate that among *n*-pentenes only 6% should be 1-pentene, with the equilibrium proportion of 1-pentene becoming even less at lower temperatures. Other data obtained in a number of different systems indicate that double-bond position isomerization of olefins over liquid alkali metals is a moderately slow process and that any desired approach to equilibrium may be reached by the use of sufficiently long contact time.[17] *cis–trans* isomerization in the pentenes is practically complete in our experiments (65–75% *trans* in the *cis–trans* mixture—API Project 44 data indicate about 55% *trans*, but this figure may be low[17]). It is of interest that isomerization with the liquid alkali metals is less specific than the isomerization observed over supported sodium metal on alumina catalysts where selective isomerization of 1-pentene to *cis*-2-pentene occurs.[17]

Multiple addition is illustrated by the 3-ethyl-1-pentene and 3-heptene, as well as small amounts of higher olefins, found in the reaction products. These heptenes probably arise from addition of the resonating allylic pentenide carbanion to ethylene at either the 3-position or the 1-position, respectively.

A third side reaction, chiefly of interest in the ethylation of propylene or propylation of olefins or aromatics, is the homopolymerization of propylene resulting from addition of the allyl carbanion to propylene. The product, 4-methyl-1-pentene, can itself undergo isomerization and multiple alkylation.

A fourth type of side reaction which can occur in the propylene–ethylene system is the internal allylic metalation of 2-pentene, resulting in the formation of 4-methyl-2-hexene on addition of ethylene.

**B. Butenes.**—Isobutene, in the presence of ethylene and alkali metals, behaves in a manner similar to propylene. The $C_3$ and $C_4$ compounds each undergo the same types of reactions comparable rates, with the exception that isobutene does not readily homodimerize (see Tables I and IV).

*n*-Butenes each give rise to an end-methylated allyl carbanion which adds readily to ethylene. As a first approximation, both 1- and 2-butene give the same resonating allylic carbanion, and, because of its asymmetry, the anion gives rise to two initial $C_6$ compounds on addition to ethylene: 3-methyl-1-pentene from the secondary anion and 2-hexene from the primary anion.

The ethylation products each undergo the same further reactions described above for propylene ethylation, *viz.*, isomerization and multiple addition, both dependent on remetalation of the initial products. 3-Ethyl-1-hexene and internal *n*-octenes, as well as *n*-hexene isomers, are the reaction products of 2-hexene ethylation and isomerization, respectively.

Remetalation, hence also isomerization and multiple addition, do not occur so rapidly with 3-methyl-1-pentene as with 2-hexene. These results, together with the well-known difficulty of isomerizing 4-methyl-1- and -2-pentene to 2-methyl-1- and -2-pentenes over certain alkali metals,[4,18] probably have their common basis in the difficulty of removing a proton from a ter-

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[14] H. Pines and H. Eschinazi, *J. Am. Chem. Soc.*, **77**, 6314 (1955); **78**, 1178 (1956); H. Pines, J. A. Vesely, and V. N. Ipatieff, *ibid.*, **77**, 347 (1955); H. Pines and V. N. Ipatieff (to Universal Oil Products Co.), U. S. Patent 2,804,489 (Aug. 27, 1957); H. L. Wilson and R. Drogin (to Esso Research and Engineering Co.), U. S. Patent 2,740,820 (April 3, 1956); L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958); I. V. Gostunskaya, N. I. Tyunkina, and B. A. Kazansky, *Proc. Acad. Sci. USSR, Chem. Sect.*, **108**, 273 (1956); *cf.* also A. Lüttringhaus and W. Rief, *Ann.*, **618**, 221 (1958).

[15] E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957); H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).

[16] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

[17] T. M. O'Grady, R. M. Alm, and M. C. Hoff, American Chemical Society, Division of Petroleum Chemistry, Preprints, Vol. 4, No. 4, 1959, p. B65.

[18] R. D. Closson, W. B. Ligett, and A. J. Kolka, French Patent 1,303,743 (Sept. 14, 1962).

tiary carbon atom; this effect is also described in our companion paper.[19]

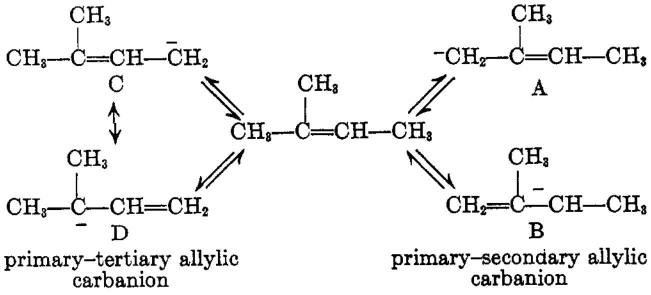
In addition to the expected compounds, traces of methylcyclopentane have been found among the reaction products of *n*-butenes and ethylene over alkali metals. Methylcyclopentane probably occurs as the result of an intramolecular nucleophilic addition,[20] described below.

**C. *n*-Pentenes.**—The product distributions in ethylation of 1- and 2-pentenes are almost identical, at least as a first approximation, showing that the allylic carbanion formed initially from either 1- or 2-pentene is the same anion.

A new type of allylic carbanion was formed, first observable in the ethylation of *n*-pentenes because of the size and asymmetry of the *n*-pentene molecule. While 1-pentene can be metalated only in the 3-position to give an allylic carbanion, 2-pentene can be metalated either at the 1-position, giving the same anion as derived from 1-pentene, or the metalation can occur at the 4-position, giving a symmetrical, internal allylic carbanion, which on ethylation gives 4-methyl-2-hexene. Internal allylic carbanions of this type seem to be difficult to produce by the direct action of alkali metal on an internal olefin (*cf.* 3-heptene, below).

**D. Higher 1- and 2-Olefins.**—We have carried out ethylations similar to those described above on 1-hexene,[6] 2-hexene, and 1-heptene. Qualitatively, our results show that any $\alpha$- or $\beta$-olefin can be monoethylated and even diethylated under mild conditions in the presence of ethylene and alkali metal. The structure of the primary ethylation products can best be described as a 3-ethylated 1-olefin and a *n*-4-olefin. There does not seem to be any definite dependence of the rate of reaction upon the size of the 1- or 2-olefin used. Conversion and selectivity values seem to be roughly independent of molecular weight; moreover, selectivity to the 3-ethylated $\alpha$-olefin is generally 1.0–1.5 times the selectivity to the *n*-4-olefin, again, independent of molecular weight.

**Metalation and Ethylation of 2-Methyl-2-butene.**—Four allylic carbanionic structures are produced from 2-methyl-2-pentene, in two resonating pairs, as shown below. Each of these two anions adds to ethylene in two different ways, giving four $C_7$ olefins with distinctive, identifiable structures.



The $C_7$ products obtained show that all four anionic structures A–D were formed and ethylated; the distribution of nonalkylated $C_5$ isomers recovered represents an approach toward the thermodynamic equilibrium ratio among the isoamylene isomers. The conversion of 2-methyl-2-butene is similar to the conversion of 2-butene in 2-butene–ethylene copolymerization. The distribution of $C_7$ isomers (including that material which has undergone re-ethylation and double-bond position isomerization) can be used to determine, approximately, the stability ratio or ease of formation of the primary–secondary and primary–tertiary anions, and the relative reactivities of the primary, secondary, and tertiary sites through two alkylation experiments: one in which an excess and one in which a deficiency of ethylene is used. These ratios are listed in Table II.

TABLE II

ETHYLATION OF 2-METHYL-2-BUTENE[a]

| | $C_2/C_5$ mole ratio 1 | $C_2/C_5$ mole ratio 4 |
|---|---|---|
| Conditions | | |
| Maximum pressure, p.s.i.g. | 1300 | 2500 |
| Reaction time, hr. | 0.3 | 0.6 |
| Addition product ratios | | |
| Total primary–secondary/total primary–tertiary[b] | 2.3 | 1.7 |
| Secondary of primary–secondary/primary of primary–secondary | 2.1 | 1.9 |
| Tertiary of primary–tertiary/primary of primary–tertiary | 0.5 | 1.4 |

[a] At 200°, over 1 wt. % Li–K. [b] Statistically corrected.

The data presented in Table II show the following. (1) The primary–secondary allylic carbanion can be formed over alkali metals about twice as fast as the primary–tertiary carbanion.[21] This behavior may account for the observed much slower isomerization of 3-methyl-1-pentene to the 2-olefin relative to the isomerization of 4-methyl-1-pentene to its corresponding 2-olefin.[19] (2) The secondary site of the primary–secondary carbanion and, to a lesser extent, the tertiary site of the primary–tertiary carbanion are, as expected, more reactive toward an excess of ethylene than are the corresponding primary sites. The secondary is about twice as nucleophilic as the primary site, regardless of the ethylene concentration. (3) The data show the tertiary site to be less reactive than the secondary site, relative to the corresponding primary site. However, the reactivity of the tertiary position seems to be highly dependent on ethylene concentration.

**Formation of Secondary–Secondary Carbanions.**—The results discussed above show that, in propylene, isobutene, 2-butene, and 2-methyl-2-butene, the hydrogen atoms on a primary carbon atom allylic to a double bond are easily removed with alkali metal. Moreover, some secondary hydrogens such as are found allylic to the double bond of *n*-1-olefins are apparently as easily removed as are primary allylic hydrogens, provided that the resulting carbanion has a primary–secondary resonating structure.

An allylic carbanion in which the negative charge resides only on secondary or tertiary carbon atoms should be harder to form than a primary–secondary carbanion, because of the loss of stabilizing influence imparted by the primary carbanion. Examples of olefins which can form secondary–secondary carbanions are cyclohexene, cyclopentene, 3-heptene, and 2-pentene; the first three can form only secondary–secondary carbanions on initial metalation, while 2-pentene can be converted into either a primary–secondary or a secondary–secondary carbanion. Our ethylation experiments show that secondary–secondary allylic carbanions are

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[19] Paper I: C. W. Bittner, W. V. Bush, G. Holzman, and A. W. Shaw, *J. Org. Chem.*, **30**, 3286 (1965).

[20] M. Kolobielski and H. Pines, *J. Am. Chem. Soc.*, **79**, 5820 (1957).

[21] *Cf.* G. Wittig and H. Schloeder, *Ann.*, **592**, 38 (1955).

Table III

Ethylation of Some Secondary–Secondary Carbanions[a]

| | Olefin ethylated | | |
|---|---|---|---|
| | Cyclohexene | Cyclopentene | 3-Heptene |
| Conditions | | | |
| Ethylene/olefin, mole ratio | 1.0 | 1.2 | 1.0 |
| Maximum pressure, p.s.i.g. | 1260 | 1510 | 2700 |
| Reaction time, hr. | 0.2 | 14 | >7.1 |
| Conversion of olefin, % | 44 | 33 | 4 |
| Products, wt. % of converted olefin | | | |
| Hydrogenated olefin | 3 | Trace | ... |
| Allylic monoethylated | 77 | 61 | 80[b] |
| Vinylic monoethylated | 2 | ... | |
| Allylic diethylated | 16 | 4 | ... |
| Unidentified and residue | 2 | 35 | 20 |

[a] At 200°, over 1 wt. % Li–K. [b] Unidentified $C_9$.

indeed difficult to form, with the notable exception of the cyclohexenide ion (see Table III).

**A. Cyclohexene.**—Probably because of steric factors,[22] the cyclohexene ring is easily metalated over the alkali metal catalyst. In the presence of ethylene, the cyclohexenide anion forms mono- and diethylcyclohexenes, with conversion of cyclohexene and ethylene comparable with those observed in 2-butene ethylation. Moreover, there is a very high selectivity for the allylic-substituted 3-ethylcyclohexene and a high selectivity for a single diethylated cyclohexene; together, these two compounds account for 91 mole % of the ethyl-substituted cyclohexene products.

There is also found a small amount of the vinylic 1-ethylcyclohexene.[23] Direct vinyl substitution would be expected to be very slow because of the lower acidity (greater p$K_a$) of the vinyl hydrogen compared with the allyl hydrogen, but 1-ethylcyclohexene could have arisen from the ethylcyclohexene through a cyclic complex such as that described earlier by Pines[25] (and which we believe, on the basis of the high *cis* content of the product, to be responsible for the isomerization of 3-methyl-1-pentene to 3-methyl-2-pentene).

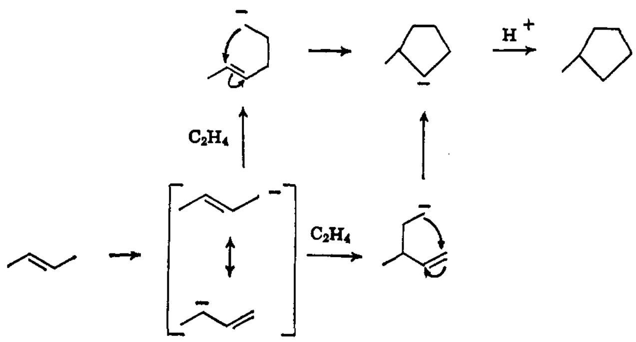
**B. Cyclopentene.**—In contrast to the behavior of cyclohexene,[22] there was only a very slow reaction between cyclopentene and ethylene. Moreover, we find that, in the presence of alkali metals, the ethylated cyclopentene is mostly allylic, in contrast to Morton and Finnegan's results using a different catalyst system at room temperature.[24]

**C. 3-Heptene.**—At 200° in *n*-decane, conversion of 3-heptene is an order of magnitude less than the conversion of cyclohexene under similar conditions, and the selectivity of converted 3-heptene is entirely for monoethylated products.

**D. 2-Pentene.**—The reaction products from ethylation of 2-pentene, when compared with those from ethylation of 1-pentene, indicate that 2-pentene can be, slowly, internally metalated. The secondary–secondary carbanion from 2-pentene adds to ethylene to give 4-methyl-2-hexene; that more 4-methyl-2-hexene is obtained from 2-pentene than from 1-pentene indicates that it is probably derived directly from 2-pentene and only indirectly from 1-pentene *via* double-bond position isomerization.

**Intramolecular Alkylations.**—One of the classical examples of the anionic cyclization of hydrocarbons (*i.e.*, intramolecular alkylations), is Pines' study of the cyclodimerization of α-methylstyrene to 1-methyl-1,3-diphenylcyclopentane,[20] in which each of the anionic intermediates is resonance stabilized, either by allylic or by benzylic resonance. The nucleophilicity of the intermediates is thus reduced, and therefore the tendency to form high polymers or to abstract protons before completion of the cyclization reaction is diminished.

Occurrence of the intramolecular addition reaction in the aliphatic series is illustrated by the methylcyclopentane found among the $C_6$ products of *n*-butene ethylation. Methylcyclopentane occurs to the extent of 0.7% or less of the total liquid products (solvent-free) of butene–ethylene copolymerization. The formation of methylcyclopentane is evidence of the occurrence of an anionic cyclization reaction similar to that of Pines, but in which only the initial intermediate anion is resonance stabilized.



We have also observed small amounts of methylcyclopentane among the products of alkali metal catalyzed propylene polymerization[19]; we believe that this report describes for the first time a carbanionic ring closure in a nonaromatic system.

**Allylic Propylations and Butylations.**—The prototype allylic propylation is the dimerization of propylene.[4,8,12,18,19,26] The salient features of the reaction are that the allyl carbanion adds principally to the central carbon atom of propylene[4] and that, as we have found, the rate of addition of allyl carbanion to propylene is only about one-tenth as fast as the rate of addition to ethylene.

In Table IV are summarized the results of some alkali metal catalyzed propylations and butylations. It can be seen from the data therein that allylic butylations are even slower than propylations, by a factor of 1–2 powers of 10; these butylations, moreover, give very complex product mixtures. The rate of the metalation step seems to be roughly independent of the size of the olefin metalated (for a given class of olefins, say, *n*-1-olefins), but the addition reaction is strongly rate controlled by the molecular weight of the olefin to which a given allylic carbanion is being added. The isobutenide anion, for example, adds rapidly to ethylene, moderately fast to propylene, and very slowly to butenes. The

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[22] A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3164 (1962).

[23] See ref. 4; *cf.* also Morton's findings[24] in the cyclopentene system, and the results of C. D. Broaddus, T. J. Logan, and T. J. Flautt [*J. Org. Chem.*, **28**, 1174 (1963)] using alkali alkyls.

[24] A. A. Morton and R. A. Finnegan, *J. Polymer Sci.*, **38**, 19 (1959).

[25] H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958); *cf.* V. A. Kropachev, B. A. Dolgoplosk, and K. V. Danilovich, *Proc. Acad. Sci. USSR, Chem. Sect.*, **111**, 763 (1956); *cf.* also ref. 24.

[26] A. W. Shaw and G. Holzman (to Shell Oil Co.), U. S. Patent 2,994,725 (Aug. 1, 1961); A. W. Shaw, G. Holzman, and W. V. Bush (to Shell Oil Co.), U. S. Patent 3,006,976 (Oct. 31, 1961).

TABLE IV

SOME TYPICAL ALLYLIC PROPYLATIONS AND BUTYLATIONS[a]

| | Feed | | | | | |
|---|---|---|---|---|---|---|
| | Propylene + isobutene | Propylene + 2-butene | Propylene + 1-butene | 2-Butene | isobutene + 1-butene | isobutene |
| Conditions | | | | | | |
| $C_3/C_4$ (mole ratio) | 1.0 | 1.0 | 1.0 | ... | 1.1[b] | .. |
| Maximum pressure, p.s.i.g. | 1900 | 2040 | 2560 | 2300 | 1800 | 540 |
| Reaction time, hr. | 4.9 | 3.8 | 7.2 | 24 | 7.0 | 3.0 |
| Conversion, % | | | | | | |
| $C_3$ | 67[c] | 38 | 35 | ... | ... | ... |
| $n$-$C_4$ | ... | 11[d] | 12[e] | 7[d] | 13[e] | ... |
| $i$-$C_4$ | 25 | ... | ... | ... | 14 | <1 |
| Products, mole % of converted $C_4$ | | | | | | |
| Hydrogenated $C_4$ | ... | 9 | 15 | *Ca.* 10 | 18 | .. |
| Propylated $C_4$ | 89[f] | 45 | 35 | ... | ... | .. |
| Butylated $C_4$ | 10 | Trace | 27 | 56 | 56 | 100 |
| Higher boiling liquid and residue | 1 | 46 | 23 | 34 | 26 | ... |

[a] At 200°, over 1 wt. % Li–K. [b] 1-Butene/isobutene. [c] Products, wt. % of converted $C_3$: propane, 12; propylene dimer, 35; propylated $C_4$, 41; solid residue, calculated as $(C_3H_6)_n$, 12. [d] To other than 1-butene. [e] To other than 2-butene. [f] 94% of $C_7$ is 2,4-dimethyl-1-pentene.

reasons for the rate differences are not entirely clear, and probably involve both steric and electronic factors.

**Summary Discussion.**—The experimental results presented in this report have been organized in such a way as to illustrate present knowledge concerning some of the capabilities of alkali metal catalyzed reactions. It must be emphasized, however, that many questions concerning these reactions are still unanswered or inconclusively answered by the results reported. Among the factors which affect the course of allylic alkylations to an unknown extent are pressure, temperature, solvent, and the nature of the catalyst.[19] Further refinement of existing conclusions and hypotheses would require detailed additional study of the kinetics of the several reactions occurring.

The reactions so far studied have led to the following conclusions. (1) Metalation occurs readily over alkali metal catalysts at a carbon atom allylic to a double bond. When the double bond is terminal, the metalation reaction is fast if the allylic carbon is primary or secondary (*i.e.*, has three or two "$\alpha$ hydrogens") and very slow if the allylic carbon is tertiary. When the double bond is not terminal, metalation is rapid only at a primary allylic position, with the notable exception of cyclohexene. (2) Alkylation of an olefin occurs *via* addition of its corresponding allylic carbanion to another olefin molecule. Addition to ethylene is fastest, to propylene, slower for a given carbanion, and addition to butenes and higher olefins is extremely slow. (3) In contrast, there does not seem to be a marked correlation between addition rate and the size of an allylic anion adding to a given olefin (*e.g.*, to ethylene), when the anion is derived from a normal 1- or 2-olefin. (4) Addition rates may vary among anions of the same size, however, depending on whether the resonating structures of the allylic carbanion place the negative charge on a primary, secondary, or tertiary carbon. Steric factors would also be expected to influence metalation and addition rates to some degree. (5) Allylic or benzylic carbanions can undergo intramolecular addition reactions, resulting in formation of a new ring. Only those cyclization reactions in which the intermediates are resonance stabilized appear to give good yields.

## Experimental Section

The discussion above is based on batch autoclave experiments; it is not based on a physical–chemical mechanism study in the classical sense. However, we feel that through the measures described below we have minimized any extraneous effects due to "preconditioning" the feed or resulting from the "thermal inertia" of the autoclave. The intermediates and reaction sequences proposed have been deduced principally from the structures of the observed products of our reactions, together with pertinent data from similar studies reported in the literature.

The reactor used in our experiments was a 250-ml., 316 stainless steel Magne Dash[27] autoclave, equipped with recording temperature and pressure indicators. Heat was supplied by a specially designed 220-v. furnace capable of raising the temperature of the autoclave from 20 to 200° in about 5–10 min.; this heating rate was sufficiently rapid that a semiquantitative measure of the rate of the reaction could be obtained by using the time necessary for the pressure to drop from its maximum value at 200° to one-half of that maximum value. The furnace was also equipped with cooling coils, through which water could be passed, making it possible to "freeze" (at least approximately) the composition of the reaction mixture by lowering the temperature from 200 to 30° in less than 5 min.

The hydrocarbons used were mostly Phillips Pure Grade[28] (99+ mole %), dried over sodium wire in the case of paraffin "solvents" or over Linde 4A Molecular Sieves[29] in the case of olefins. Cetane was Humphrey-Wilkinson ASTM grade,[30] purified over sodium wire. The only olefin used which was not of high purity was Phillips 95 mole % 3-heptene, containing, according to the manufacturer's literature, other isomeric heptenes. G.c. analysis indicated that *ca.* 4% of the sample was 2-heptene. It is possible that the entire (very small) amount of $C_9$ reaction products from ethylation of 3-heptene may have been derived from this impurity.

The alkali metals were reagent grade, cut from the center of a lump to remove scale, and washed free of kerosene with $n$-hexane or $n$-heptane. We have found that the Li–K combination used increases the rate of olefin condensation without noticeably affecting the rate of product double-bond position isomerization relative to that observed under similar reaction conditions with potassium alone.[19,26]

In a typical experiment, the autoclave was charged first with "solvent" and then with the metal catalyst (both weighed on a torsion balance to 0.1 g.) inside a dry nitrogen filled inert-atmosphere glove box. Oxygen, water, and carbon dioxide partial pressures were not precisely known, but a freshly cut piece of potassium would remain bright for several hours in the box.

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(27) Autoclave Engineers, Inc., Erie, Pa.

(28) Phillips Petroleum Co., Special Products Division, Bartlesville, Okla.

(29) Linde Co., Division of Union Carbide Corp., Tonawanda, N. Y.

(30) Humphrey-Wilkinson, Inc., North Haven, Conn.

The reactants were then admitted to the autoclave, the most volatile component last. Normally liquid reactants (*e.g.*, pentenes) were placed in the autoclave while still in the drybox. After all normally liquid hydrocarbons were placed in the autoclave, the vessel was sealed and removed from the drybox. Butenes were fed into the reactor as liquids under argon pressure, and propylene and ethylene, as gases under available cylinder pressure. The amounts of these volatile components charged were obtained by difference of the weights of the autoclave plus contents on a Metrogram[31] capacitance balance, to within 0.1 g.

The autoclave was then heated to the desired run temperature within 0.5 hr.; the experiment was considered to be completed when the pressure inside the autoclave had dropped to one-half of the initial maximum. The autoclave was cooled to room temperature and then depressured, while reheating slowly to 200°, into an evacuated ($\leq$10 mm.) series of three liquid nitrogen cooled traps. The first of these traps was also the kettle of a still, being connected to the other two through a 30 × 1 cm. Vigreux column. After warming and stabilizing the cold trap condensate to room temperature, with the gas being collected in a water-displacement gas holder, the gas and liquid were sampled for analysis.

The gas samples were analyzed by gas chromatography (g.c.) on a 50 ft. × 0.25 in. column of dimethylsulfolane on firebrick, operated at 40° using 40 cc./min. of helium carrier gas and thermal conductivity detector cells. Prior calibration with authentic samples showed that this column was capable of separating and identifying individual hydrocarbons through $C_6$ and estimating amounts to 0.1% of the 2-ml. gas sample used. Gas samples were also routinely analyzed by mass spectrography (m.s.); m.s. and g.c. gave results in agreement to within 1–2%. Liquid samples were kept refrigerated at $-20°$ until analyzed by g.c. on two different columns. Samples of 5-$\mu$l. volume were chromatographed on dimethylsulfolane (as above) to identify and estimate hydrocarbons through $C_6$; a 50 ft. × 0.25 in. column of SF-96 silicone oil[32] on firebrick operated at 125° with 50 cc./min. of helium carrier and thermal conductivity detector cells was used to identify, by boiling point, hydrocarbons through $C_{16}$ and estimate relative amounts to 0.1% of the 10-$\mu$l. sample charged. Within the range of overlap (*i.e.*, through $C_6$), agreement between the two chromatograms was within 1–2%.

Other methods used for more positive characterization of the principal products were infrared spectroscopy to determine olefin type; m.s. of compounds purified by g.c. to determine carbon skeleton by fragmentation pattern; n.m.r. to verify the 3-heptene structure (from *n*-pentene + ethylene) relative to 2-heptene. Compounds higher than $C_9$ remain unidentified.

Several preparative-scale experiments were made in a 1-gal. autoclave, and the products from these experiments were subjected to precision fractional distillation in a 20-plate Oldershaw column at 10:1 reflux ratio. 3-Methyl-1-pentene had b.p. 53.1°, lit.[33] b.p. 53.6°; 3-ethyl-1-pentene had b.p. 83.9–84.2°, lit.[33] b.p. 85.0°. Several of the fractions from these distillations were subjected to quantitative hydrogenation over Raney nickel to confirm olefinicity (or lack thereof, in the case of methylcyclopentane), and m.s. and g.c. of the resultant paraffins provided additional confirmation of the carbon skeleton.

In each experiment (whether 250-ml. scale or 1-gal. scale), the sum of the weights of liquid product and residue and weight of gas calculated from its volume and average molecular weight was 97–102% of the total weight of the materials charged. The total product weight was normalized to equal the charge weight before calculating product distribution.

The cooled, evacuated autoclave was opened in the drybox. The residue in nearly every case was observed to be hard, shiny, black granules which reacted briskly with isopropyl alcohol (IPA). Toluene–IPA "solutions" of the residues from a number of experiments were chromatographed to determine the boiling range of (at least part of) the organic polymer present; the failure of any component of the solution other than toluene and IPA to emerge from the g.c. column indicated that the polymer had an initial boiling point well above 300–350°. After the first several experiments, the residue was deactivated with IPA and then water, and discarded, without other than visual observation.

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(31) H. A. Hadley Associates, Inc., Burlington, Vt.

(32) Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

(33) M. P. Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Co., New York, N. Y., 1943.

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# Reactions of 1,4-Dichloro-1-butenes with Magnesium. A New Cyclobutene Synthesis[1]

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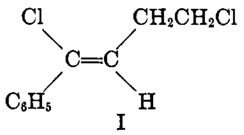
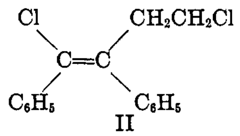
The reactions of *trans*-1,4-dichloro-1-phenyl-1-butene (I) and *cis*-1,4-dichloro-1,2-diphenyl-1-butene (II) with magnesium in ether afford 1-phenylcyclobutene (III) and 1,2-diphenylcyclobutene (VIII) in 5–46 and 90% yields, respectively. A study of the reaction products from I indicates that the reaction of I to form the vinyl Grignard reagent is more rapid than that to form primary Grignard reagent. Evidence that vinyl Grignard reagents do not maintain stereochemical identity is presented.

In the course of other work[3] quantities of *trans*-1,4-dichloro-1-phenyl-1-butene (I) and of *cis*-1,4-dichloro-1,2-diphenyl-1-butene (II) became available.[4] With the thought that interesting primary mono-Grignard reagents might be formed, ethereal solutions of I and II were allowed to react with magnesium. Treatment of the resulting solutions with water produced unexpected products. Study of these reactions revealed two facts of interest: (a) a new cyclobutene synthesis was at hand; and (b) the rate of reaction of the vinylic chloride of I (and presumably of II) with magnesium was greater than the rate of reaction of the primary chloride.


I


II

When ethereal solutions of I were allowed to react with excess sublimed magnesium[5] for periods of from 1.5 to 41 hr., reaction mixtures were obtained which on hydrolysis afforded four or five products. The results were not strictly reproducible, but examination

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(1) The material in this paper was taken from the Ph.D. thesis presented by G. Kaugars to The Ohio State University, 1964. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-569-64.

(2) Upjohn Fellow, 1960–1961; Lubrizol Fellow, 1962–1963.

(3) M. S. Newman and G. Kaugars, *J. Org. Chem.*, in press.

(4) For proof of the stereochemistry of I and II, see ref. 3 above.

(5) We thank the Dow Chemical Co., Midland, Mich., for generous donations of pure sublimed magnesium. In our experience Grignard reagents prepared with this magnesium are much lighter in color than those prepared with commercial magnesium turnings.