Vinyl Proton Abstraction during Metalation of α-Olefins

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Received November 13, 1962

The acidic products obtained from metalation and subsequent carbonation of 1-dodecene are shown to vary with time. At short reaction times 2-tridecenoic acid, arising from metalation at the terminal vinylic position, predominates. At longer reaction times the major products are β,γ-unsaturated acids, due to metalation at the allylic position. The precursor of 2-tridecenoic acid, 1-sodio-1-dodecene, was shown to be stable to the metalation conditions. The variation of products with time is accounted for by competing metalation of 2-dodecene formed in an accompanying isomerization of starting material. No metalation is observed at the secondary vinylic position although 2-sodio-1-dodecene was found to be stable under the reaction conditions. These observations are discussed in terms of relative rates of proton removal at the terminal vinylic, the allylic, and the secondary vinylic positions.

Metalation of α-olefins generally has been considered to proceed through preferential reaction at the resonance stabilized allylic position.[1] Thus the acidic products obtained by stoichiometric metalation and carbonation,[2,3] as well as the base-catalyzed isomerization of olefins,[4] have been accounted for by reaction at this position. Benkeser's[5] recent work on the metalation of cumene and ethylbenzene discloses a kinetically favored proton abstraction at a ring position followed by equilibration to the thermodynamically favored α-isomer. That the benzenoid positions are not subject to appreciable resonance stabilization has been established previously.[6] In olefinic systems containing no allylic protons, such as 3,3-dimethyl-1-butene, and those in which allylic resonance stabilization is hindered, metalation with an alkylsodium compound removes vinylic protons.[7,8] However, by isolation of some straight chain α,β-unsaturated acid, following metalation and carbonation of α-olefins, Morton[2] has shown that proton abstraction at the terminal vinylic position does occur.

Since α-olefins contain both primary and secondary vinylic positions, neither of which would be expected to exhibit much resonance stabilization, as well as a potentially resonance stabilized allylic reaction site, a re-examination of this system under non-equilibrium conditions seemed worthwhile.

Metalating agents were prepared from the corresponding alkyl chlorides and metal dispersions using typical high speed stirring techniques.[2] Reactions were conducted at room temperature, with portions of the heterogeneous reaction mixture being removed at the time intervals reported in Table I. Carbonation was effected by pouring the reaction mixtures over excess solid carbon dioxide. Characterization of products was accomplished by a combination of infrared, nuclear magnetic resonance, and gas–liquid chromatographic (g.l.c.) studies. Details are given in the Experimental section. Table I gives typical data obtained from the reaction of a four molar excess of 1-dodecene with pentylsodium.

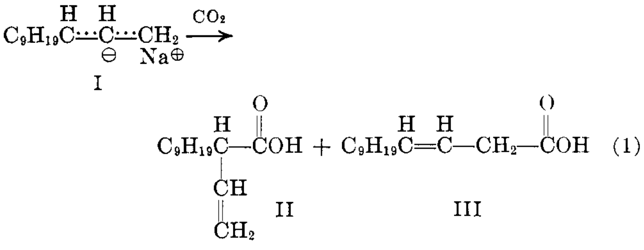
TABLE I

REACTION OF 1-DODECENE WITH PENTYLSODIUM[a]

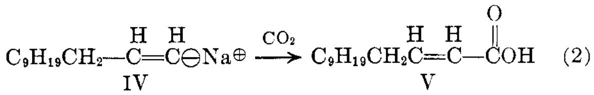
Time	Hexanoic acid, %	Acids from 1-dodecene, %	α-Vinylundecanoic, %	3-Tridecenoic, %[b]	2-Tridecenoic, %[b]	Recovered olefin composition, %	
						1-dodecene	2-dodecene[c]
5 min.	75	25	26	9	65	82	17
15 min.	50	50	31	12	52	57	42
20 min.	52	48	38	17	44	37	63
2 hr.	40	60	53	32	15	0	99

[a] The variations with time have been shown to be consistent in repeated runs, although the absolute values vary somewhat. [b] These are predominantly the *trans* isomers. [c] Approximately equal amounts of *cis* and *trans* isomers are present.

It is evident that the C_{13} acid products can be accounted for by allyl carbanionic I and terminal vinyl carbanionic IV intermediates.[9]



$$\underset{\text{I}}{C_9H_{19}\overset{H}{\underset{\ominus}{C}}\cdots\overset{H}{\underset{Na^{\oplus}}{C}}\cdots CH_2} \xrightarrow{CO_2} \underset{\text{II}}{C_9H_{19}\overset{H}{\underset{\underset{\displaystyle CH_2}{\displaystyle \|}}{\underset{\displaystyle CH}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}OH} + \underset{\text{III}}{C_9H_{19}\overset{H}{C}=\overset{H}{C}-CH_2-\overset{O}{\overset{\|}{C}}OH} \quad (1)$$



$$\underset{\text{IV}}{C_9H_{19}CH_2-\overset{H}{C}=\overset{H}{C}{\ominus}Na^{\oplus}} \xrightarrow{CO_2} \underset{\text{V}}{C_9H_{19}CH_2\overset{H}{C}=\overset{H}{C}-\overset{O}{\overset{\|}{C}}OH} \quad (2)$$

The g.l.c. data (see Experimental) show that little if any 2-carboxy-1-dodecene (VII), arising from proton abstraction at the secondary vinylic position, is realized. This can be rationalized on the familiar grounds that secondary positions yield higher energy anionic species than primary positions and that the higher energy requirement causes slower reaction. However, there is another possible explanation for the absence of this product. The secondary intermediate VI could be

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(1) R. A. Benkeser, D. J. Foster, D. M. Sauve, and J. T. Nobis, *Chem. Rev.*, **57**, 867 (1957).

(2) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Am. Chem. Soc.*, **7** 3785 (1950).

(3) A. Lüttringhaus, G. Wagner, V. Sääf, E. Sweker, and G. Borth, *Ann.*, **557**, 66 (1945).

(4) W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960).

(5) (a) R. A. Benkeser and T. V. Liston, *ibid.*, **82**, 3221 (1960); (b) R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *ibid.*, **84**, 4971 (1962).

(6) G. E. Hall, R. Piccolini, and J. D. Roberts, *ibid.*, **77**, 4540 (1955).

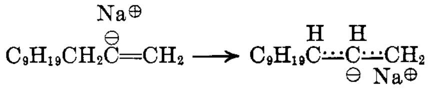
(7) A. A. Morton and R. A. Finnegan, *J. Polymer Sci.*, **38**, 19 (1959).

(8) R. A. Finnegan and R. S. McNees, *Chem. Ind.* (London), **36**, 1450 (1961).

(9) The possibility that the α,β-unsaturated product arises from isomerization of III seems unlikely for several reasons. (1) More pronounced isomerization would be required at short times. While it is true, as a referee suggests, that more pentylsodium is present during carbonation at these times, consumption of pentylsodium produces another strong base (I) which could also cause isomerization during carbonation. (2) Since carbonation occurs preferentially at the internal position one might expect to observe isomerization of II. We have found no evidence for this process. (3) As reported later in the text, metalation of *trans*-2-dodecene to produce I followed by carbonation gives no detectable amount of α,β-unsaturated product under the same conditions used for 1-dodecene.

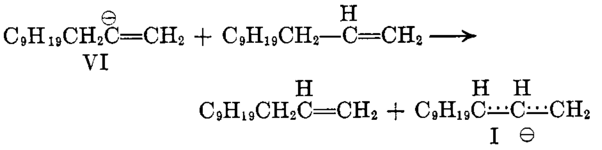
formed, but then undergo rapid conversion to the allyl isomer I and never be carbonated at the position of initial proton abstraction. We, therefore, generated 2-sodio-1-dodecene by another route and tested its stability to the metalation reaction conditions.

Two reaction paths can be visualized for the conversion of a secondary vinylorganosodium compound to a resonance stabilized allyl isomer. Either an intra- (reaction 3) or an intermolecular (reaction 4) process could give the postulated conversion. To determine



$$\mathrm{C_9H_{19}CH_2\overset{Na^{\oplus}}{\overset{\ominus}{C}}{=}CH_2 \longrightarrow C_9H_{19}\overset{H}{C}\cdots\underset{\ominus}{\overset{H}{C}}\cdots CH_2\ Na^{\oplus}} \qquad (3)$$

VI I



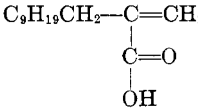
$$\mathrm{C_9H_{19}CH_2\overset{\ominus}{C}{=}CH_2 + C_9H_{19}CH_2{-}\overset{H}{C}{=}CH_2 \longrightarrow}$$

VI

$$\mathrm{C_9H_{19}CH_2\overset{H}{C}{=}CH_2 + C_9H_{19}\overset{H}{C}\cdots\underset{\ominus}{\overset{H}{C}}\cdots CH_2} \qquad (4)$$

I

if the intramolecular process was important, 2-sodio-1-dodecene was formed (see Experimental) in octane and allowed to stir for four hours at room temperature. The reaction mixture was then carbonated and the acidic product shown to be exclusively 2-carboxy-1-dodecene (VII). Thus intramolecular proton transfer in this compound does not appear to be facile.



$$\mathrm{C_9H_{19}CH_2{-}\underset{\underset{OH}{|}}{\underset{C=O}{\underset{|}{C}}}{=}CH_2}$$

VII

The possibility that intermediate VI was formed during olefin metalation, but underwent intermolecular reaction with excess olefin was tested similarly. The formation of 2-sodio-1-dodecene was repeated and a ten molar excess of 1-dodecene was added to the reaction mixture. After a two-hour stirring period the mixture was carbonated. The resulting C_{13} acid product consisted of at least 50% VII. It thus appears that, if an organosodium intermediate were formed at the secondary vinylic position during metalation, it would possess sufficient stability to give rise to carbonation products at this position at short reaction times.

One is then left with the reasonable postulate that metalation at a secondary vinylic position is slow compared to reaction at either a terminal vinylic or at an allylic position. Support for this explanation is found in the potassium amide-catalyzed deuterium exchange of 1-propene in ND_3,[10] wherein the rate of exchange of the first five protons has been found to be quite rapid compared to the exchange of the sixth.

From Table I it is apparent that considerable variation in the composition of C_{13} acid product occurs over the two-hour interval. The most striking observation is that the proportion of products attributable to an allyl intermediate, α-vinylundecanoic acid and 3-tridecenoic acid, increases at the expense of the proportion of product due to a vinyl intermediate, 2-tridecenoic acid. This leads to the conclusion that proton abstraction from the terminal vinylic position is more rapid than from the allylic position in this reaction.

The demonstration that 2-sodio-1-dodecene is stable to the reaction conditions and that no 2-carboxyl-1-dodecene is realized on metalation and carbonation of 1-dodecene, coupled with the decrease in the ratio of α,β to β,γ-unsaturated acids, suggests that the relative rates of proton removal from different positions of α-olefins by alkylsodium metalating agents decrease in the order terminal vinylic > allylic > secondary vinylic.

To rationalize this order, one can speculate that the ground state energies of the bonds in question are an important factor. The allylic system would undoubtedly afford stabilization at any point along the reaction coördinate where C–H bond breaking had occurred to a significant extent. In other systems[11–13] studies on isotope effects indicate that the transition state for proton removal from carbon does involve considerable bond breaking. Nevertheless, the respective ground state hybridization of the terminal vinyl and allyl positions, sp^2 *vs.* sp^3, could account for a somewhat faster reaction at the nonresonance stabilized sp^2 position in our system.[14,15] That the state of hybridization is not an overriding factor is evident from the lack of reaction at the internal sp^2 position.

The increase with time in the amount of allyl-derived products as compared to the vinyl-derived acid, noted in Table I, suggests an explanation similar to that offered for alkylbenzene metalation,[5] *i.e.*, that there is a kinetically favored formation of the nonresonance stabilized vinyl intermediate IV followed by conversion to the thermodynamically favored allyl isomer I. Since this would require a rather rapid disappearance of IV, we undertook an alternate synthesis of this intermediate to study its stability under metalation conditions.

Free radical addition of hydrogen bromide to 1-dodecyne[16] provided 1-bromo-1-dodecene. The product was found to be a mixture of *cis* and *trans* isomers in which *cis* predominates in a ratio of approximately 2:1.[17] Treatment of this mixture with *n*-butylsodium, under conditions essentially identical to the analogous reaction with 2-bromo-1-dodecene, gave not only the *cis*- and *trans*-α,β-unsaturated acids upon carbonation, but also a significant amount (44%) of 2-tridecynoic acid.[18] Reaction of the 1-bromo-1-dodecene mixture with sodium metal dispersed in octane provided the vinylorganosodium compounds[19] with only traces of

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[10] A. I. Shatenshtein, L. N. Vasil'eva, N. M. Dykhno, and E. A. Izrailevich, *Dokl. Akad. Nauk, SSSR*, **85**, 381 (1952); *Chem. Abstr.*, **46**, 9954 (1952).

[11] (a) A. Streitseiser, Jr., W. C. Langworthy, and D. E. Van Sickle, *J. Am. Chem. Soc.*, **84**, 251 (1962); (b) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 254 (1962).

[12] D. Bryce-Smith, V. Gold, and D. P. N. Satchell, *J. Chem. Soc.*, 2743 (1954).

[13] (a) F. S. Yakushin, A. I. Shatenshtein, E. A. Yakolera, and Yu. G. Dubinski, *Zh. Fiz. Khim.*, **33**, 2820 (1959); *Kinetika i Kataliz*, **1**, 489 (1960); (b) for a discussion of ref. 13a, see A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962).

[14] S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

[15] J. Hinze and H. Jaffe, *ibid.*, **84**, 540 (1962).

[16] C. A. Young, R. R. Vogt, and J. A. Nieuwland, *ibid.*, **58**, 1806 (1936).

[17] P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

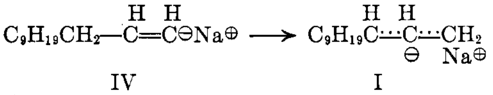
[18] The reaction of 1-bromo-1-propene mixtures with butyllithium has been reported to give exclusively acetylenic derivatives [D. V. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958)]. The fact that 2-bromo-1-dodecene gives only metal interchange with *n*-butylsodium, while elimination competes with metal interchange in the case of 1-bromo-1-dodecene, supports the suggestion [S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955)] that α-elimination is the preferred dehydrobromination reaction path.

[19] The question of geometric stability of these compounds is receiving further attention.

acetylenic by-product, as determined by examination of the carbonation products obtained.

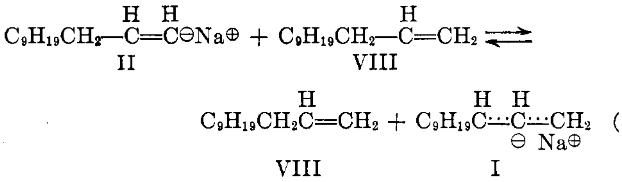
As in the case of 2-sodio-1-dodecene, two reaction paths can be visualized for the conversion of a terminal vinylorganosodium compound to an allyl intermediate. Thus, either an intra- (reaction 4) or an intermolecular (reaction 5) proton transfer could account for the observed decrease in the ratio of vinyl derived to allyl derived products with time.

Intramolecular



$$\underset{\text{IV}}{C_9H_{19}CH_2{-}\overset{H}{C}{=}\overset{H}{C}{}^{\ominus}Na^{\oplus}} \longrightarrow \underset{\text{I}}{C_9H_{19}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2} \quad \begin{matrix}\ \\ \ominus\ Na^{\oplus}\end{matrix} \qquad (4)$$

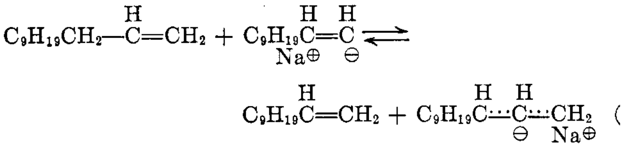
Intermolecular



$$\underset{\text{II}}{C_9H_{19}CH_2{-}\overset{H}{C}{=}\overset{H}{C}{}^{\ominus}Na^{\oplus}} + \underset{\text{VIII}}{C_9H_{19}CH_2{-}\overset{H}{C}{=}CH_2} \rightleftharpoons$$
$$\underset{\text{VIII}}{C_9H_{19}CH_2\overset{H}{C}{=}CH_2} + \underset{\text{I}}{C_9H_{19}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2} \quad \begin{matrix}\ \\ \ominus\ Na^{\oplus}\end{matrix} \qquad (5)$$

The feasibility of reaction path 4 was tested by preparing the vinylorganosodium mixture and stirring it at room temperature for four hours prior to carbonation. Even after this time interval there was no detectable amount of products arising from an allyl intermediate. It thus appears that this reaction path is not a contributing factor in the variation of acid isomers shown in Table I.

Similarly the possibility of intermolecular conversion was tested by the synthesis of 1-bromo-1-undecene and its conversion to the sodio derivative, followed by addition of a ten molar excess of 1-dodecene. If reaction path 5 is operative in the metalation sequence, one would expect a mixture of 1-sodio-1-undecene and 1-dodecene to give C_{13} acid products upon carbonation, *i.e.*



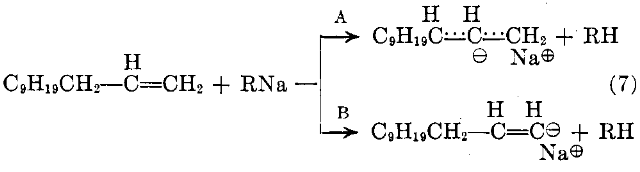
$$C_9H_{19}CH_2{-}\overset{H}{C}{=}CH_2 + C_9H_{19}\overset{H}{\underset{Na^{\oplus}}{C}}{=}\overset{H}{\underset{\ominus}{C}} \rightleftharpoons$$
$$C_9H_{19}\overset{H}{C}{=}CH_2 + C_9H_{19}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2 \quad \begin{matrix}\ \\ \ominus\ Na^{\oplus}\end{matrix} \qquad (6)$$

Repeated experiments, as described above, showed the presence of no detectable amounts of C_{13} acid products upon carbonation of the reaction mixture after four hours of agitation.

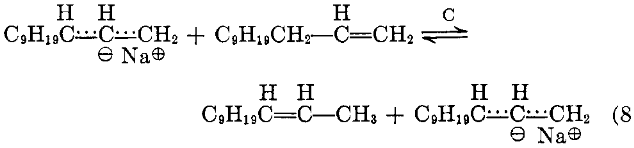
These studies strongly indicate that vinylorganosodium intermediates are stable to the reaction conditions employed in metalation of α-olefins. Therefore, kinetic *vs.* thermodynamic control is not an adequate explanation of the observed variation in acidic products.

The data included in Table I, however, suggest another explanation. It will be noted that as the reaction progresses the ratio of C_{13} to C_6 acid in the product increases, indicating that proton abstraction from olefin by the saturated metalating agent continues. It will also be noted that the composition of the recovered olefin is undergoing a marked change. Thus the starting four molar excess of 1-dodecene has been converted essentially quantitatively to internal olefin during the two-hour interval. One can then reason that the increase in proportion of allylic products is due to competing proton abstraction from the 2-olefin in which there are no terminal vinylic protons to be abstracted.

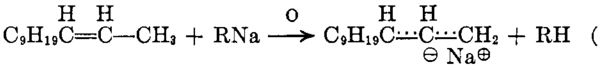
Our metalation results may then be rationalized by the following scheme.



$$C_9H_{19}CH_2{-}\overset{H}{C}{=}CH_2 + RNa \begin{cases} \xrightarrow{A} C_9H_{19}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2 + RH \quad (\ominus\ Na^{\oplus}) \\ \xrightarrow{B} C_9H_{19}CH_2{-}\overset{H}{C}{=}\overset{H}{C}{}^{\ominus} + RH \quad (Na^{\oplus}) \end{cases} \qquad (7)$$



$$C_9H_{19}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2 \ (\ominus\ Na^{\oplus}) + C_9H_{19}CH_2{-}\overset{H}{C}{=}CH_2 \overset{C}{\rightleftharpoons}$$
$$C_9H_{19}\overset{H}{C}{=}\overset{H}{C}{-}CH_3 + C_9H_{19}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2 \ (\ominus\ Na^{\oplus}) \qquad (8)$$



$$C_9H_{19}\overset{H}{C}{=}\overset{H}{C}{-}CH_3 + RNa \xrightarrow{D} C_9H_{19}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2 \ (\ominus\ Na^{\oplus}) + RH \qquad (9)$$

The reactions involving saturated metalating agent (A, B, and D) are essentially irreversible. This is shown by the fact that although the reactions were conducted in a large excess of octane, no detectable amount of nonanoic acid was observed. There is no reason to believe that alkenylsodium compounds react with pentane, as required for the reverse reaction, and not with octane.

The isomerization of 1-dodecene is shown as occurring through proton abstraction by the saturated metalating agent to give an allyl intermediate (reaction A). A chain process involving this intermediate and starting olefin accounts for the production of 2-dodecene.[20]

The increase in proportion of product formed by carbonation of an allyl, as opposed to a vinyl, intermediate is thought to be due to a competition for reaction with saturated metalating agent between 1-dodecene and 2-dodecene, *i.e.*, reaction D begins to compete with reactions A and B. To demonstrate the feasibility of this proposal *trans*-2-dodecene was synthesized and subjected to metalation conditions identical to those used for 1-dodecene. The products obtained, at five minutes, half an hour, one hour, and two hours, were exclusively attributable to the allyl intermediate I, with no evidence of α,β-unsaturated product. Furthermore Shatenshtein's[21] studies on the rates of deuterium exchange of 1- and 2-pentenes indicate that these compounds undergo base-catalyzed reactions at similar rates.

It readily can be seen from Table I that at least a four molar excess of 1-dodecene has undergone isomerization during a time interval in which proton abstraction by the saturated metalating agent, pentylsodium, is still occurring. Surface coating of the heterogeneous pentylsodium by deposition of insoluble allyl and vinyl organosodium compounds most probably causes a decreased reactivity of the saturated compound. However, an equally important factor in the apparent rapid isomerization of 1-dodecene, as compared to formation C_{13} organosodium compounds, could well be a more rapid rate of proton removal by the allyl intermediate.

This order of reactivity would be rather surprising since pentylsodium is undoubtedly more basic than the

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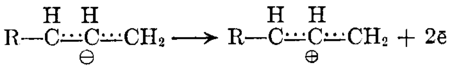
[20] H. Pines, "Advances in Catalysis and Related Subjects," Vol. 12, Academic Press, New York, N. Y., 1960.

[21] A. I. Shatenshtein, L. N. Vasil'eva, and N. M. Dykhno, *Zh. Fiz. Khim.*, **28**, 193 (1954).

allyl intermediate[22] and even in cases of equal basicity resonance stabilized anions usually[23] undergo nucleophilic attack on hydrogen at a slower rate than their saturated counterparts.[24] However, Morton's[25] observations on the effectiveness of alkyl- *vs.* alkenylsodium compounds as catalysts for olefin isomerization are pertinent. These workers have reported that pentenyl- and octenylsodium are more effective catalysts than pentylsodium based on elapsed time for noticeable exothermic reaction and completeness of isomerization during a given interval.[26] One can conjecture that the degree of covalent bonding[27] in a carbon–sodium bond causes some localization of the negative charge in the resonance stabilized compounds, with concomitant increase in basicity. This argument, however, could only account for a basicity approaching that of a saturated anion. Unless some other factor is operative, an allyl intermediate, in which the negative charge is contained in a system possessing π character, would be expected to abstract protons from a common substrate at a slower rate than the saturated analog. This additional factor could be the "alpha effect" proposed recently by Edwards and Pearson.[28] These authors explain the inordinately rapid proton abstractions by anions containing an alpha hetero atom as a stabilizing effect which the adjacent electron pair exerts on the transition state. This explanation is clarified by considering proton abstraction in the limiting case. Thus the negative species is pictured as donating two electrons to a distant substrate, thereby developing positive charge during the transition state. One then can rationalize the apparent high reactivity of the allyl anionic system by this concept since a stabilizing effect[29] would be present in the transition state of the allyl anion (10) which would not be present in the saturated system (11).



$$R{-}\underset{}{\overset{H}{C}}{\cdots}\underset{\ominus}{\overset{H}{C}}{\cdots}CH_2 \longrightarrow R{-}\overset{H}{C}{\cdots}\underset{\oplus}{\overset{H}{C}}{\cdots}CH_2 + 2\bar{e} \qquad (10)$$

$$RCH_2^{\ominus} \longrightarrow RCH_2^{\oplus} + 2e \qquad (11)$$

Although this effect may be a contributing factor, it certainly does not explain all the reported results.[26] Much more work is needed in this area before any definite conclusions can be drawn.

Experimental

Dodecene-1.—This olefin was purchased from Matheson Coleman and Bell and was distilled from sodium metal prior to use.

Metalating Agents.—The alkylsodium metalating agents were prepared by the addition of the corresponding alkyl chloride to a previously prepared dispersion of sodium in *n*-octane at 0°.[2] The high speed stirring apparatus used has been described.[30] Several runs of this preparation gave yields varying from 60 to 70% as measured by the acidic product formed upon carbonation.

Metalation Reactions.—Metalation was accomplished at room temperature by the addition of olefin to the alkylsodium–octane mixture with rapid stirring. Portions of the reaction mixture were removed at varying time intervals and poured over excess solid carbon dioxide. All operations were conducted under an atmosphere of dry nitrogen. The acidic and neutral fractions of the products were separated as usual.[2] Table I (see text) gives typical data obtained from repeated reactions of a four molar excess of 1-dodecene with *n*-pentylsodium.

Runs in which the total reaction mixture was carbonated after 18 hr. gave 40–50% yields. Distillation (b.p. 140–145° at 0.6 mm.) through an 8-in. Vigreux column failed to separate the C_{13} acid isomers.

Characterization of Acid Products.—The skeletal arrangement of the acid products was established by esterification, hydrogenation, and g.l.c. comparison of the resultant saturated esters to alternately synthesized standards. Esterification was accomplished either by addition of diazomethane in ether[31] or by refluxing the acid in excess methanol with a catalytic amount of sulfuric acid. Hydrogenation was carried out in a Parr hydrogenerator using 10% palladium on charcoal at 50 p.s.i. The g.l.c. standards were obtained as follows.

Methyl Tridecanoate (IX).—Tridecanoic acid was purchased from Matheson, Coleman and Bell and esterified using diazomethane in ether. Distillation through an 18-in. spinning band column gave the ester (b.p. 82–83° at 0.2 mm., n^{28}D 1.4320, lit.,[32] b.p. 71° at 0.1 mm. and b.p. 90.3° at 0.4 mm.) which was shown to be 99% pure by g.l.c.

Methyl α-Methyldodecanoate (X).—This ester was prepared by carbonation of the Grignard reagent obtained from 2-bromododecane followed by acidification and esterification. Distillation as above gave the ester (b.p. 65–66° at 0.1 mm., n^{28}D 1.4298) which was 99% pure by g.l.c. analysis.

Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.7; H, 12.3. Found: C, 74.2; H, 12.5.

Methyl α-Ethylundecanoate.—This ester was prepared by malonic ester condensations.[33] Distillation through an 18-in. spinning band gave the ester (b.p. 64–65° at 0.1 mm., n^{28}D 1.4295) which was 99% pure by g.l.c. analysis.

Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.7; H, 12.3. Found: C, 74.2; H, 12.5.

Methyl α-Propyldecanoate (XII).—This ester was also prepared by malonic ester condensations.[33] Distillation through the 18-in. spinning band column (b.p. 62–63° at 0.1 mm., n^{28}D 1.4288) gave the ester which was 98% pure by g.l.c. analysis.

Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.7; H, 12.3. Found: C, 73.5; H, 12.3.

Gas chromatographic analyses were performed on an Aerograph Model A-90-S using 10-ft., 1/4-in. columns. A polyester (succinic acid–triethylene glycol) liquid phase supported on acid washed Chromosorb-W was used. During the course of this work the percentage of liquid phase varied from 15 to 25%. Each column was shown to separate the four standards before use in analysis. Their order of emergence was XII, XI, X, and IX.

Gas–liquid chromatography of the hydrogenated esters obtained from metalation and carbonation of 1-dodecene shows that at least 98% of the C_{13} product is made up of methyl tridecanoate (IX) and methyl α-ethylundecanoate (XI). Comparison of the above chromatogram to that of methyl nonanoate shows that there is no detectable amount of this C_9 ester in the product. Apparently no metalation of the *n*-octane medium occurs.

The position of unsaturation and geometrical configuration of each unsaturated ester was established by g.l.c. collection of pure samples followed by a combination of hydrogenation, infrared, and nuclear magnetic resonance (n.m.r.) studies. Table II summarizes the hydrogenation and infrared data. Table III records the pertinent aspects of the n.m.r. spectra.

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[22] The Brönsted relation (R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chap. X) would predict a faster rate for the stronger base.

[23] R. P. Bell, "Acid-Base Catalysis," Clarendon Press, Oxford, 1941, p. 92.

[24] R. P. Bell, *J. Phys. Chem.*, **55**, 885 (1951).

[25] A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955).

[26] A referee reports that a later presentation of catalytic effectiveness (E. J. Lanpher, Symposia Preprints, Vol. 4, No. 4, p. B-5, Division of Petroleum Chemistry, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959) gives the order of sodium compounds as pentenyl > octenyl > pentyl = phenyl > butenyl > allyl > benzyl ≈ triphenylmethyl ≈ fluorenyl.

[27] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 18.

[28] J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

[29] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 148.

[30] "Sodium Dispersions," U. S. Industrial Chemicals Company, New York 16, N. Y., p. 18.

[31] F. G. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 165.

[32] K. S. Markley, "Fatty Acids," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 523.

[33] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p. 467.

TABLE II

INFRARED AND HYDROGENATION STUDIES ON THE UNSATURATED METHYL ESTERS OBTAINED FROM METALATION OF 1-DODECENE

	After hydrogenation g.l.c. shows identity with	Infrared absorptions, μ[a]	
		C=C	C—H
Methyl α-vinylundecanoate	XI	6.1	10.1 and 10.9
2-Carbomethoxy-1-dodecene	X	6.15	10.65
Methyl *cis*-2-tridecenoate	IX	6.1	12.25
Methyl *trans*-3-tridecenoate	IX	6–6.1	(sh) 10.3
Methyl *trans*-2-tridecenoate	IX	6.05	10.2

[a] See ref. 34.

The ratio of C_6 to C_{13} acids at the varying time intervals was determined by esterification and comparison of peak areas by g.l.c. Areas were obtained by multiplying the peak height by the band width at half height.

Characterization of Recovered Olefin.—The composition of recovered olefins was determined similarly. However, since resolution of peaks was not complete, the ratio of 1-dodecene:2-dodecene was estimated from peak heights. This was shown to be in reasonable agreement with an alternate method in which periodate–permanganate oxidation of the double bond is followed by esterification and g.l.c. analysis of the resultant ester mixture. For example, a sample of the olefin recovered after 5 min. (see Table I) was found to be 80% 1-dodecene and 19% 2-dodecene by this method.[35]

2-Bromo-1-dodecene.—1,2-Dibromodecane (50 g., 0.15 mole) was added dropwise to sodamide (7.8 g., 0.2 mole) in 500 ml. of ammonia and stirred for 30 min. The ammonia was allowed to evaporate (overnight) and the residue was treated with a solution of 25 ml. of ethanol in 300 ml. of diethyl ether followed by 100 ml. of water. The organic layer was separated, dried with magnesium sulfate, and distilled through a 6-in. Vigreux column to yield 20 g. (53%) of a mixture of 1-bromo-1-dodecene and 2-bromo-1-dodecene. These compounds were separable on the g.l.c. columns described previously. The mixture was distilled through an 18-in. spinning band column to give 3.6 g. of chromatographically pure 2-bromo-1-dodecene. The product showed a strong infrared absorption at 11.2 μ and no absorption at 10.7 μ, indicating isomeric purity.[34]

Anal. Calcd. for $C_{12}H_{23}Br$: C, 58.4; H, 9.13; Br, 32.2. Found: C, 58.6; H, 9.4; Br, 32.8.

Reaction of 2-Bromo-1-dodecene with Butylsodium.—A dispersion of sodium metal (4.6 g., 0.2 g.-atom) in 200 ml. of octane was prepared and *n*-butyl chloride (9.2 g., 0.1 mole) added dropwise at 0° with rapid stirring. The reaction mixture was allowed to stir for 30 min. after addition was complete. Then 2-bromo-1-dodecene (3.0 g., 0.012 mole) was added over a 5-min. interval. The mixture warmed to room temperature during the 4-hr. stirring period following addition. Carbonation was effected by pouring it over excess solid carbon dioxide. The acid products were isolated as described[2] and esterified by refluxing with a solution of 2 g. of sulfuric acid in 50 ml. of methanol for 1 hr. The esterification mixture was poured into 400 ml. of water and the organic layer extracted with ether. After drying with magnesium sulfate, the ether solvent was removed on a rotating evaporator yielding 2.1 g. (71%) of product. Gas–liquid chromatography showed the product to contain only one C_{13} ester which was shown to be 2-carbomethoxy-1-dodecene (see Tables II and III).

Reaction of 2-Sodio-1-dodecene with 1-Dodecene.—The reaction of 2-bromo-1-dodecene with butylsodium was repeated to give 2-sodio-1-dodecene (0.013 mole), whereupon 1-dodecene (16.8 g., 0.1 mole) was added to the reaction mixture. Stirring was continued for 4 hr. before carbonation was effected by pouring the reaction mixture over excess solid carbon dioxide. Work-up and esterification of the acid product gave a mixture of C_{13} isomers of which 51% was 2-carbomethoxy-1-dodecene by g.l.c. analysis.

Preparation of 1-Bromo-1-dodecene.—The procedure of Young[16] was used with modifications. Dodecyne-1 (50 g., 0.3 mole) obtained from Farchan Chemical Co. was used as purchased. To the neat acetylene was added benzoyl peroxide (1 g.) and then dry hydrogen bromide was passed into the mixture at 0° until the original weight had increased by 23.8 g. The reaction mixture was washed successively with water and 10% sodium hydroxide solution, dried with magnesium sulfate, and distilled to yield 52.8 g. (71%) of a mixture of *cis*- and *trans*-1-bromo-1-dodecene. The product was characterized by g.l.c. and subsequent conversion to the sodium compounds followed by carbonation and esterification (see Tables II and III).

Anal. Calcd. for $C_{12}H_{23}Br$: C, 58.4; H, 9.13; Br, 32.2. Found: C, 58.9; H, 9.5; Br, 31.7. Infrared absorption at 10.7 μ and none at 11.2 μ indicated the 1-bromo product.

Preparation of 1-Bromo-1-undecene.—The same procedure as described for 1-bromododecene-1 was used to give a 76% yield of product.

Anal. Calcd. for $C_{11}H_{21}Br$: C, 56.7; H, 9.0; Br, 34.2. Found: C, 56.2; H, 8.9; Br, 35.1.

Reaction of 1-Bromo-1-dodecene with Butylsodium.—Butylsodium was prepared as previously described[2] from sodium metal (4.6 g., 0.2 g.-atom) and *n*-butyl chloride (9.2 g., 0.1 mole) in 200 ml. of octane. To this mixture was added 1-bromo-1-dodecene (5.0 g., 0.020 mole) dropwise with stirring. The resulting product was allowed to stand overnight prior to carbonation by pouring over excess solid carbon dioxide. The usual work-up provided 2.6 g. (61%) of acidic product. Esterification and g.l.c. separation of the resulting ester mixture shows that 44% of the acid product is methyl-2-tridecynoate. Infrared absorption at 4.5 μ, hydrogenation to methyl tridecanoate, and an n.m.r. spectrum showing no vinylic protons established the identity of this product. The remaining 56% of acid product is accounted for by methyl *cis*- and *trans*-2-tridecenoate (see Tables II and III).

Reaction of 1-Bromo-1-dodecene with Sodium Dispersion.—A dispersion of sodium (6.9 g., 0.3 g.-atom) in 200 ml. of octane was prepared[2] and 1-bromo-1-dodecene (10.0 g., 0.04 mole) added dropwise at room temperature. Stirring was continued and a 50-ml. portion of the reaction mixture removed after 4 hr. This portion was poured over excess solid carbon dioxide to effect carbonation. The usual work-up and g.l.c. analysis showed three peaks in the approximate ratio of 2:1:0.1. Collection of pure samples by g.l.c. gave the data recorded in Table II and showed the mixture to consist of 2 parts methyl *cis*-2-tridecenoate, to 1 part methyl *trans*-2-tridecenoate, to 0.1 part methyl 2-tridecynoate. The remaining reaction mixture was allowed to stand for 24 hr. prior to carbonation. The acid mixture obtained was somewhat more complex in that peaks accounting for approximately 10% of the total C_{13} ester mixture were observed at retention times corresponding to the allylic products, methyl α-vinylundecanoate and methyl-2-tridecenoate; however, 90% of the product is still accounted for by vinyl intermediates.

Reaction of 1-Bromo-1-undecene with Sodium Dispersion.—This reaction was run in an identical fashion to that of 1-bromo-1-dodecene and again an acidic product consisting of three compounds in a ratio of *ca.* 2:1:0.1 was realized. The infrared spectrum of this mixture (2.7 g., 32%) was identical to the previous mixture.

Reaction of 1-Sodio-1-undecene with 1-Dodecene.—1-Sodio-1-undecene (0.021 mole, maximum) was generated as in the foregoing examples and 1-dodecene (33.6 g., 0.2 mole) added to the reaction mixture. Stirring was continued for 4 hr. prior to carbonation with excess solid carbon dioxide. The acid mixture obtained was composed of the same isomers, by g.l.c. analysis, as found in the absence of added 1-dodecene. No evidence of metalation of the added 1-dodecene was obtained.

Preparation of *trans*-2-Dodecene.—The method of Hennion[36] was used. Undecyne-1 (62.0 g., 0.407 mole) was converted to the Grignard reagent by reaction with ethyl Grignard (0.407 mole) in tetrahydrofuran. Methyliodide (57.8 g., 0.407 mole) was added and the reaction mixture refluxed 8 hr. at which time

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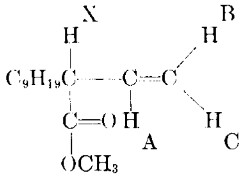
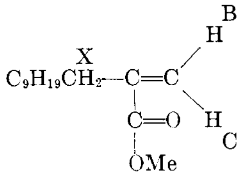
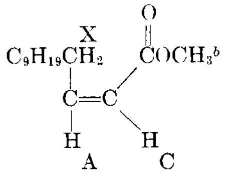
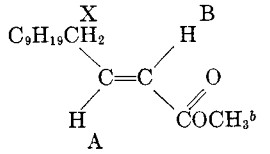
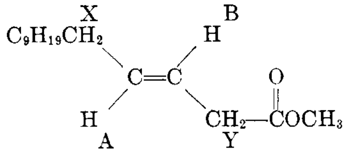
(34) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 45–51.

(35) We thank Dr. D. F. Kuemmel of these laboratories for performing the oxidative analyses.

(36) G. F. Hennion and T. F. Banigan, Jr., *J. Am. Chem. Soc.*, **68**, 1202 (1946).

TABLE III
N.M.R. CONSTANTS OF UNSATURATED METHYL ESTERS[a]

		τ_y	τ_x	τ_a	τ_b	τ_c	$\|J_{AB}\|$	$\|J_{AC}\|$	$\|J_{BC}\|$	$\|J_{AX}\|$	$\|J_{BX}\|$	$\|J_{CX}\|$	$\|J_{BY}\|$
(1)		..	7.09	4.2	4.9	4.9	17.0	9.0	2.0	8.0	~0	~0	..
(2)		..	7.75	..	4.54	3.95	..	..	1.8	...	1.5	0	..
(3)		..	7.38	3.89	..	4.33	..	11.0	...	7.0	...	1.5	..
(4)		..	7.85	3.18	4.32	..	16.0	..	...	7.0	1.5	...	..
(5)		7.06	8.00	3.52	3.52	..	[d]	..	...	~5[c]	[d]	...	~5[c]

[a] Samples were dissolved in carbon tetrachloride solution using tetramethylsilane as an internal reference and adopting the τ scale [G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)]. The spectra were obtained on a Varian A-60 spectrometer. First-order analysis was used for all compounds except 1. In this case an ABXY approximation [H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, **35**, 66 (1957)] was applied (H_B = A, H_C = B, H_A = Y, H_X = X). Consequently the signs of the spin coupling constants were not determined. [b] The values for these compounds are consistent with those reported [R. R. Fraser and D. E. McGreer, *Can. J. Chem.*, **39**, 505 (1961)] for methyl *cis*- and *trans*-crotonate. [c] These values are $^1/_2\,|J_{AX} + J_{BY}|$. [d] These values cannot be determined from the spectrum.

it was practically colorless. Dilute (*ca.* 5%) hydrochloric acid was added until all precipitated salts dissolved. The organic layer was washed several times with water, dried with magnesium sulfate, and distilled to give 59.3 g. (88%) b.p. 68–74° (0.2 mm.) of 2-dodecyne. The product shows no C—H stretch at 3.0 μ and a C≡C stretch at 4.7 μ; g.l.c. analysis shows the material to be 98% pure.

Reduction with sodium in liquid ammonia was used to produce *trans*-2-dodecene. Sodium (19.55 g., 0.85 g.-atom) was placed in 800 ml. of liquid ammonia in a three-necked flask equipped with stirrer and Dry Ice condenser. Dodecyne-2 (30.0 g., 0.18 mole) was added and the mixture was stirred overnight. The ammonia was allowed to evaporate and the residue hydrolyzed by the addition of 50 ml. of ethyl alcohol in 100 ml. of ether, followed by enough water to dissolve all salts. The organic layer was separated, dried with magnesium sulfate, and distilled at aspirator vacuum (102–106°) to give 18.7 g. (62%) of pure olefin, as shown by g.l.c. analysis.

Metalation of *trans*-2-Dodecene.—Metalation and carbonation was carried out in the manner described previously. Portions of the reaction mixture were removed at 5 min., 0.5 hr., 1 hr., and 2 hr. Characterization of the acid products, by g.l.c. of the methyl esters, shows that at least 95% of the C_{13} product is made up of α-vinylundecanoic acid and 3-tridecenoic acid in all cases and that no detectable amount of 2-tridecenoic acid is present in the product. Yields of the acidic product were not determined. The ratio of α-vinylundecanoic to 3-tridecenoic acid varied between 1.8 and 2.5.