mechanism, with complete detachment of the migrating alkyl group as a trimethylcarbonium ion, would be expected to show much slower reaction rates.

The absence of *ortho* isomer from the equilibrium mixture and the high speed of isomerization of *o*-di-*t*-butylbenzene is obviously influenced by steric factors. No *t*-butylation *ortho* to an alkyl group, and in particular *ortho* to a *t*-butyl group, is possible. The substantial steric stress involved in *o*-di-*t*-butylbenzene is relieved during migration of the *t*-butyl group to the *para* and *meta* position, thus contributing to the ease of migration.

Experimental

Starting Materials.—*p*- and *m*-Di-*t*-butylbenzene were obtained by preparative-scale vapor phase chromatographic separation of a reaction mixture obtained through aluminum chloride catalyzed *t*-butylation of *t*-butylbenzene with isobutylene. The purity of these isomers was better than 99%.

Samples of *o*-di-*t*-butylbenzene were graciously provided by Professors E. M. Arnett and L. R. C. Barclay. The purity of *o*-di-*t*-butylbenzene used, based on gas chromatographic and infrared analyses, was about 95%.

General Process of Isomerization.—Reactions were carried out in stoppered vessels with magnetic stirring. In the case of the isomerization of *p*- and *m*-di-*t*-butylbenzene, 0.02 mole of aluminum chloride was used per 0.1 mole of aromatic, and 2 drops of water was added as promoter; the reactions were carried out in 100 ml. of purified carbon disulfide. In the case of the isomerization of *o*-di-*t*-butylbenzene, 0.001 mole of the aromatic was dissolved in 10 ml. of carbon disulfide and 0.0001 mole of aluminum chloride was added, without any measured amount of water. Owing to the high dilution of the system and the difficulty in handling the small amount of catalyst under absolutely anhydrous conditions, it was assumed that a sufficient amount of moisture as cocatalyst was present in the system. Samples were drawn periodically, the reaction was stopped with water, and the organic material was extracted with ether. Dried ether extracts were analyzed by gas-liquid chromatography.

In the tables, the amounts of *o*-, *m*-, and *p*-di-*t*-butylbenzenes are given as normalized per cent. Per cent given for the products of disproportionation represent mole per cent of total aromatic present.

Gas-Liquid Chromatographic Analysis.—The analyses were carried out on a Perkin-Elmer Model 154-D vapor fractometer equipped with Golay-type capillary column and hydrogen flame ionization detector. Peak areas were calculated using a Perkin-Elmer Model 194 printing integrator. The capillary column used was 150 ft., coated with polypropylene glycol operated at 104° with a He carrier-gas pressure of 20 p.s.i. Characteristic retention times of *t*-butylbenzene, di-*t*-butylbenzenes and 1,3,5-tri-*t*-butylbenzene observed are summarized in Table IV.

TABLE IV

RETENTION TIMES OF *t*-BUTYLBENZENE, DI-*t*-BUTYLBENZENES AND 1,3,5-TRI-*t*-BUTYLBENZENE

Compound	Time, min.
t-Butylbenzene	7
p-Di-*t*-butylbenzene	26
m-Di-*t*-butylbenzene	16
o-Di-*t*-butylbenzene	44
1,3,5-Tri-*t*-butylbenzene	33

Acknowledgment.—We are extremely grateful to Professors E. M. Arnett and L. R. C. Barclay for gifts of *o*-di-*t*-butylbenzene.

A Comparison of Alkylpotassium and Alkylsodium Reagents in Metalation of α-Olefins

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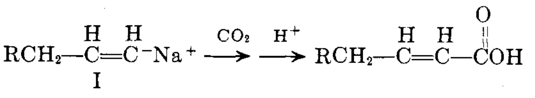
Metalation of 1-dodecene with *n*-butylpotassium differs from metalation with *n*-butylsodium in three respects. The variation in ratio of α,β- to β,γ-unsaturated carbonation products with time is much less marked in the potassium system. At short reaction time the β,γ-products arising from an allyl intermediate predominate, whereas α,β-unsaturated acid was the major product with *n*-butylsodium under these conditions. Olefin recovered from the potassium system is unchanged, while extensive isomerization was noted in the sodium case. Preparation of 1-potassio-1-dodecene from 1-bromo-1-dodecene shows that this precursor to the α,β-unsaturated acid undergoes rearrangement to the allyl intermediate. These results are explained on the basis of competitive metalation at the vinyl and allyl positions.

Recent studies[1,2] of the metalation of alkylbenzenes, using alkylsodium and alkylpotassium reagents, apparently clarify earlier discrepancies[3-6] as to the position of metalation in these systems. Benkeser, *et al.*, suggest that in both cases there is a kinetically favored reaction at a ring position followed by equilibration to the thermodynamically favored α-position and they account for differences in product distribution with the two reagents by more rapid equilibration reactions in the potassium case.

We have reported[7] earlier that when 1-dodecene is metalated with *n*-pentylsodium[8] a large proportion of α,β-unsaturated acid is isolated if the reaction mixture is carbonated after short reaction time. This product is thought to arise from a vinylsodium intermediate (reaction 1). At longer reaction times the expected[9,10]



$$\underset{\text{I}}{RCH_2—\overset{H}{C}=\overset{H}{C}{}^-Na^+} \xrightarrow{CO_2} \xrightarrow{H^+} RCH_2—\overset{H}{C}=\overset{H}{C}—\overset{O}{\overset{\|}{C}}OH \quad (1)$$

β,γ-products from carbonation of an allyl intermediate predominate (reaction 2). This variation in compo-

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(1) R. A. Benkeser and T. V. Liston, *J. Am. Chem. Soc.*, **82**, 3221 (1960).

(2) R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *ibid.*, **84**, 4971 (1962).

(3) A. A. Morton, C. E. Chaff, Jr., and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955).

(4) A. A. Morton and E. J. Lanpher, *ibid.*, **23**, 1636 (1958).

(5) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

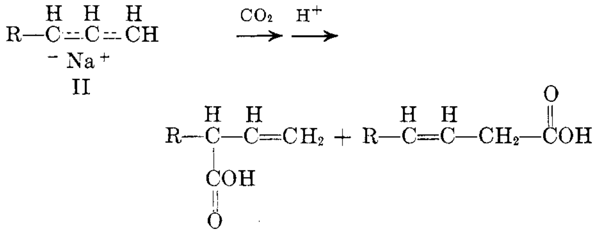
(6) D. Bryce-Smith, V. Gold, and D. P. N. Satchell, *ibid.*, 2743 (1954).

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

(8) *n*-Butylsodium, prepared from *n*-butyl chloride and sodium dispersion, has been shown to give similar results.

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

(10) 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.*, **72**, 3785 (1950).



$$\underset{\text{II}}{\mathrm{R{-}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}\overset{H}{C}H\ \ {}^{-}Na^{+}}}\ \xrightarrow{CO_2}\ \xrightarrow{H^+}\ \mathrm{R{-}\overset{H}{\underset{\underset{\underset{O}{\|}}{COH}}{C}}{-}\overset{H}{C}{=}CH_2 + R{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_2{-}\overset{\overset{O}{\|}}{C}OH} \quad (2)$$

sition of the acidic product with time is reminiscent of Benkeser's[1] results and might be similarly interpreted. Thus, a kinetically favored proton abstraction at the nonresonance-stabilized vinyl position followed by equilibration to the thermodynamically favored allyl position would explain the observed results. However, the vinylsodium precursor of the conjugated product was stable under the metalation conditions for the time intervals involved. For this reason, it was concluded that the accompanying isomerization of excess 1-dodecene to 2-dodecene followed by competitive metalation was the preferred explanation.

Since quite rapid equilibration is required in the alkylbenene system for metalation with alkylpotassium compounds, we have compared alkylsodium with alkylpotassium in metalations of α-olefins. We now wish to report the results of that study.

In Table I are typical data from the reaction of a 4:1 mole ratio of 1-dodecene to *n*-butylpotassium.[11]

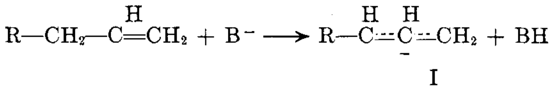
TABLE I

REACTION OF 1-DODECENE WITH *n*-BUTYLPOTASSIUM[a]

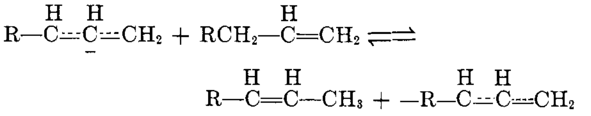
Time, min.	Composition of acid product, % α,β-Unsaturated[b]	β,γ-Unsaturated[c]	Composition of recovered olefin, % 1-Dodecene	2-Dodecene
5	18	82	~100	0
20	20	79	~100	0
35	21	78	~100	0
50	17	83	~100	0
140	14	86	~100	0
1260	8	92	~100	0

[a] See the Experimental section for a material balance on this reaction system. [b] Principally *trans*-2-tridecenoic acid. [c] A mixture of approximately two parts α-vinylundecanoic to one part 3-tridecenoic acid.

Perhaps the most striking contrast with pentylsodium metalation is the lack of isomerization of the excess olefin. With *n*-pentylsodium, migration of the double bond to the 2-position is essentially complete within 2 hr.[12] Although Lanpher[13] reported that alkylpotassium reagents are poorer catalysts for olefin isomerization than alkylsodium compounds, the reason for this difference is obscure. The most probable mechanism for isomerization in systems of this type



$$\mathrm{R{-}CH_2{-}\overset{H}{C}{=}CH_2 + B^- \longrightarrow \underset{\text{I}}{R{-}\overset{H}{C}{\cdots}\underset{-}{\overset{H}{C}}{\cdots}CH_2} + BH} \quad (3)$$

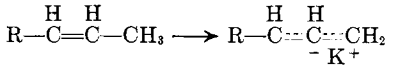


$$\mathrm{R{-}\overset{H}{C}{\cdots}\underset{-}{\overset{H}{C}}{\cdots}CH_2 + RCH_2{-}\overset{H}{C}{=}CH_2 \rightleftharpoons R{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_3 + {-}R{-}\overset{H}{C}{\cdots}\underset{-}{\overset{H}{C}}{\cdots}CH_2} \quad (4)$$

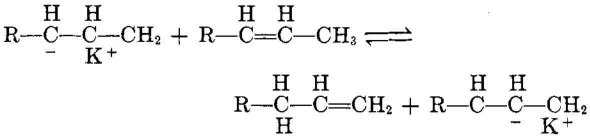
is that discussed by Pines.[14-16] There are at least three ways to rationalize this difference between alkylsodium and alkylpotassium reagents by this mechanism. First, reaction 3 may proceed slowly with alkylpotassium compounds limiting isomerization by a lack of the necessary allylic intermediate I. Second, I may be formed in a rapid reaction, but it may undergo protonation predominantly at the internal position to regenerate 1-olefin.[17] Finally, reaction 4 may be a slow process with allylpotassium compounds compared with allylsodium reagents.

Although we have no quantitative data on the comparative yields of allylic intermediates[18] using alkylsodium and alkylpotassium reagents, it can be seen from Table I that, after 5 min., carbonation produces the acidic products expected from the allylpotassium compound (reaction 2). Thus, the allyl intermediate is present in the reaction mixture and the lack of isomerization probably depends on some factor other than the first alternative suggested above.

If the allyl intermediate is preferentially protonated at the internal position, as in the second alternative, metalation experiments with excess 2-olefin should demonstrate this process. Since metalation of 1- and 2-olefins produces the same allylic system,[7,9] preferential protonation at the internal position should cause migration of the double bond from the 2- to the 1-position. Both 2-hexene and a mixture of 1- and 2-hexene were metalated with *n*-butylpotassium for periods of 2–18 hr. The isomeric content of the olefins did not vary during these reaction periods; thus the second alternative is eliminated.



$$\mathrm{R{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_3 \longrightarrow R{-}\overset{H}{C}{\cdots}\overset{H}{C}{\cdots}CH_2\ \ {}^{-}K^{+}} \quad (5)$$



$$\mathrm{R{-}\overset{H}{C}{-}\underset{-\ K^+}{\overset{H}{C}}{-}CH_2 + R{-}\overset{H}{C}{=}\overset{H}{C}{-}CH_3 \rightleftharpoons R{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{C}{=}CH_2 + R{-}\overset{H}{C}{-}\overset{H}{C}{-}\underset{-\ K^+}{CH_2}} \quad (6)$$

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(11) The mole ratio is based on the amount of *n*-butyl chloride added to a potassium dispersion. Both Benkeser[1] and Finnegan [R. A. Finnegan, *Tetrahedron Letters*, 1303 (1962)] have reported the occurrence of side reactions in this preparation. It is assumed throughout this paper that metalation of the olefin is due to *n*-butylpotassium. Support for this assumption comes from an experiment in which carbonation was effected immediately after completion of *n*-butyl chloride addition; at least 90% of the product was pentanoic acid. The yield was not determined in this particular run; however, separate runs gave yields of alkylpotassium in the 40–50% range, based on weight of acidic product obtained on carbonation. See also the material balance reported in the Experimental section.

(12) A future paper will discuss our observations at long reaction times.

(13) E. J. Lanpher, Symposia Preprints, Division of Petroleum Chemistry, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1959, Vol. 4, No. 4, p. B-5.

(14) H. Pines and L. A. Schaap, "Advances in Catalysis and Related Subjects," Vol. 12, Academic Press, New York, N. Y., 1960.

(15) See also A. Lüttringhaus, C. Wagner-v. Sääf, E. Sucker, and G. Borth, *Ann.*, **557**, 52 (1947).

(16) Recently intramolecular olefin isomerizations using potassium *t*-butoxide in *t*-butyl alcohol-*d* [D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962)] and potassium *t*-butoxide in dimethyl sulfoxide [S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *ibid.*, **85**, 2115 (1963)] have been reported. The mechanisms offered for these reactions depend upon rapid protonation of the anionic intermediate by the conjugate acid (*t*-butyl alcohol) produced in proton removal. Since it is doubtful that the conjugate acids produced in metalation reactions (alkanes) protonate the anionic intermediate at all, a mechanism of this type is not favored in the present system.

(17) This would, of course, be a contrathermodynamic process for which Ingold's Rule (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 565) could be applicable.

(18) H. Gilman and J. W. Morton, Jr. [*Org. Reactions*, **8**, 283 (1954)], report that in comparative metalations of dibenzofuran using ethyllithium, ethylsodium, and ethylpotassium, the extent of metalation increases by factors of 1, 46, and 139 in the order given when the reactions are interrupted after 2.5 hr.

Thus, of the three alternatives suggested, a relatively slow proton abstraction by the allylpotassium reagent seems most reasonable.[19] The preferential operation of an "α-effect"[7,20] in the sodium system could explain such a result; however, at the present time there is no way to validate such a proposal. Regardless of the reasons involved, the absence of a competing isomerization process simplifies the considerations involved in metalation of α-olefins.

Table I shows that the composition of the acid product is virtually constant during the first 50 min. and that only small variations occur over the entire reaction time. This observation supports our earlier conclusion[7] that the large variation observed with alkylsodium reagents was best accounted for by the accompanying isomerization of excess olefin.

That a decrease in the relative amount of acidic product arising from vinyl proton abstraction does occur, however, is evident. Since no isomerization of the excess olefin was detected, the data suggested that the vinylpotassium intermediate was unstable under the reaction conditions. To test this hypothesis, the preparation of this intermediate by an alternate route was undertaken. Table II contains the data obtained from the reaction of 1-bromo-1-dodecene with potassium metal, and shows comparative data for the sodium case.

TABLE II

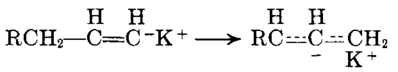
Reaction of 1-Bromo-1-dodecene with Potassium[a]

Time, hr.	α,β-Unsaturated,[b] %	β,γ-Unsaturated,[c] %	Tridecanoic %	2-Tridecynoic, %
0.25	68.2	~0	15.5	16.2
1	59.6	8.0	12.1	20.1
4	44.4	29	~0	27
29	13.4	62.5	2.1	24.5
Reaction of 1-Bromo-1-dodecene with Sodium[d]				
0.5	92.1	0	3.4	4.3
2	92.0	~0	~0	7.7
24	82.0	6.6	3.9	7.7

[a] In a separate experiment which was carbonated after 1 hr., a 47% yield of C_{13} acids was obtained. [b] A mixture of *cis*- and *trans*-2-tridecenoic acids. The relative amounts of these isomers remain fairly constant over the reaction period, indicating geometrical stability of the vinylsodium and vinylpotassium compounds (see ref. 23). A more detailed examination of this point is planned. [c] A mixture of α-vinylundecenoic and 3-tridecenoic acids. [d] In a separate experiment which was carbonated after 1 hr., a 62% yield of C_{13} acids was obtained.

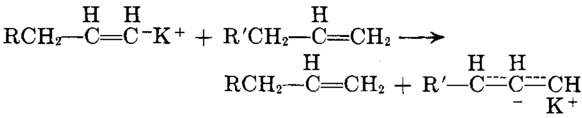
From Table II it is immediately evident that the relative amount of β,γ-products arising from an allyl intermediate increases at the expense of α,β-unsaturated product. This data provides strong evidence for the conversion of vinylpotassium intermediates to allylpotassium compounds. Moreover, the reaction proceeds with sufficient rapidity to account for the decrease in α,β-unsaturated acid noted in Table I.

Since the data shown in Table II were obtained in the absence of any added olefin, the possibility existed that the presence of excess olefin could result in a rapid conversion of vinylpotassium to allylpotassium compounds. This would then have prevented a simple interpretation of the variation in acidic products as recorded in Table I. Accordingly, experiments were conducted in which excess 1-octene was added to the vinylpotassium compound. In this run reaction of 1-bromo-1-dodecene with potassium metal provided the vinyl intermediate as shown by carbonation after 30-min. reaction time. A tenfold excess of 1-octene was then added and stirring was continued for 3.5 hr. Carbonation gave an acidic product which was composed of C_{13} α,β-unsaturated acids (relative yield 48%), C_{13} β,γ-unsaturated acids (relative yield 13%), and C_9 β,γ-unsaturated acids (relative yield 38%), as well as 2-tridecynoic and tridecanoic acids. Of immediate interest to the data in Table I is the presence of a relatively large amount of acidic product attributable to the vinyl intermediate (48%). This observation suggests that any vinyl potassium compound formed during metalation of α-olefins undergoes a relatively slow conversion to the resonance-stabilized allyl intermediate. Since C_{13} β,γ-unsaturated acids were obtained in the presence of excess 1-octene, it appears that an intramolecular process (reaction 7)



$$\mathrm{RCH_2{-}\overset{H}{C}{=}\overset{H}{C}^{-}K^{+} \longrightarrow R\overset{H}{C}{\cdots}\underset{-\ \ K^{+}}{\overset{H}{C}}{\cdots}CH_2} \qquad (7)$$

may be operative in this reaction as well as in that recorded in Table II. The occurrence of C_9 β,γ-unsaturated products is best accounted for by a *trans*-metalation process (reaction 8) which must also be

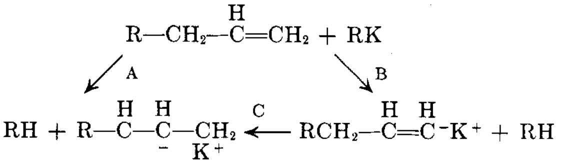


$$\mathrm{RCH_2{-}\overset{H}{C}{=}\overset{H}{C}^{-}K^{+} + R'CH_2{-}\overset{H}{C}{=}CH_2 \longrightarrow RCH_2{-}\overset{H}{C}{=}CH_2 + R'{-}\overset{H}{C}{\cdots}\underset{-\ \ K^{+}}{\overset{H}{C}}{\cdots}CH_2} \qquad (8)$$

operative during metalation of α-olefins by organopotassium compounds.

From the foregoing data it is possible to deduce the major course of the metalation of α-olefins by alkylpotassium reagents. During the initial metalation reaction there is a competition for proton removal from both the vinyl and allyl positions; *i.e.*, reaction paths A and B of Scheme I are both rapid compared with C. Furthermore, as a plot of the ratio of α,β- to β,γ-acids against time will show that at zero time[21] approximately 20% of the acid product is attributable to the vinyl intermediate, it appears that reaction A proceeds approximately four times as fast as does B. This ratio contrasts with our alkylsodium results[7] wherein the predominant product at short reaction time was the α,β-unsaturated acid and suggests that resonance stabilization is a more important factor in the potassium system. This can be explained by the fact that the carbon–potassium bond is more ionic than the carbon–sodium bond and thus behavior more nearly like a true anionic reaction is obtained.

SCHEME I



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[19] It has been reported [H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **63**, 2479 (1941)] that benzylpotassium fails to metalate dibenzofuran under conditions wherein benzylsodium is effective.

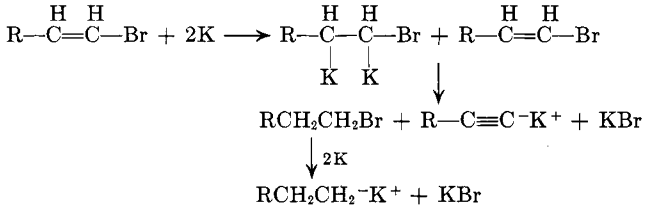
[20] J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

[21] W. O. Haag and H. Pines, *ibid.*, **82**, 387 (1960).

Our results (see Table II) support the contention[1,2] that intermediate potassium compounds rearrange more rapidly than analogous sodium derivatives, although in the present system it appears that the major course of the reaction is determined by competitive metalation rather than kinetic *vs.* thermodynamic processes.

The relative amounts and types of side products formed in the reactions of 1-bromo-1-dodecene were also of interest. As shown in the first entry of Table II (15 min.) nearly equal amounts of tridecanoic and 2-tridecynoic acids were isolated after a short reaction time.[22] One can speculate that a process similar to alkali metal–amine reduction,[23,24] accounts for these results (Scheme II). Although some inconsistencies in the saturated to acetylenic products are observed, dehydrohalogenation of starting material by the saturated alkylpotassium compound would be expected[25] and would explain the over-all result of increasing the acetylenic to saturated ratio. Other pathways can be visualized to explain these results and further work will be necessary to establish or discredit this proposal.

SCHEME II



Summary.—In comparing metalations of 1-olefins with alkylsodium and alkylpotassium reagents, it appears that the following generalizations can be made. Alkylsodium compounds are much more effective in causing isomerization of excess olefin than are alkylpotassium reagents.[13] As discussed in the text, this difference may be due to relatively slow proton abstractions by allylpotassium intermediates. In considering the initial positions of metalation, both reagents apparently give competitive reactions at terminal vinyl and allyl positions. These reagents differ, however, in that alkylpotassium compounds give preferential metalation at the allyl position, with respect to the vinyl position, while the reverse is true with alkylsodium reagents. A rationalization for this difference can be developed assuming that resonance stabilization plays a more important role in the more ionic organopotassium system. Finally, this work suggests that vinylsodium and vinylpotassium compounds are unstable with respect to their allyl isomers and that rearrangement to the more stable form is more rapid in the potassium case.

Experimental

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

Metalating Agent.—*n*-Butylpotassium was prepared by the addition of *n*-butyl chloride to a previously prepared dispersion of potassium in *n*-octane at 0°.[10] Several runs of this preparation gave yields varying from 40–50% as measured by the acidic product formed upon carbonation. Esterification and gas–liquid chromatographic (g.l.c.) analysis of a run, which was carbonated immediately after addition of *n*-butyl chloride was complete, showed the product to be at least 90% pentanoic acid.

Material Balance for the Reaction of 1-Dodecene with *n*-Butylpotassium.—Potassium metal (15.6 g., 0.4 g.-atom) was placed in a Morton flask under 200 ml. of octane. The system was kept under a blanket of dry nitrogen throughout the reaction. The mixture was heated above the melting point of potassium and stirred vigorously with a high-speed stirring apparatus[7] for approximately 3 min. The resulting potassium sand was allowed to cool slowly to room temperature. At this time a few drops of a solution of *n*-butyl chloride in octane (18.4 g., 0.2 mole in 25 ml. of octane) was added to the mixture. A dark color immediately developed in the reaction flask, whereupon the temperature was lowered to −10° and maintained at −10–0° during the addition of the remaining *n*-butyl chloride solution. This addition required 40 min. Upon completion, 1-dodecene (67.2 g., 0.4 mole) was added to the reaction vessel rapidly and the resulting mixture allowed to warm to room temperature. Stirring was continued at a moderate rate for 4 hr. and then the reaction mixture was allowed to stand overnight under nitrogen. Carbonation was effected by pouring over excess solid carbon dioxide. The total time elapsed before carbonation was 22 hr. and 10 min. After the carbon dioxide had dissipated a small amount of ethanol, approximately 25 ml., was added to destroy any unreacted potassium metal. Water, approximately 200 ml., was added and the organic and aqueous layers were separated after thorough stirring. The organic layer was extracted with an additional 50 ml. of water and the water layers were combined. Acidification with 20% hydrochloric acid was followed by ether extraction. The ether layers were dried over anhydrous $MgSO_4$ and filtered; the ether layer was evaporated on a Rinco evaporator to yield 22.0 g. (52% based on *n*-butyl chloride) of an acidic product. A 5-g. portion of this product was esterified by refluxing with 50 ml. of methanol and several drops of sulfuric acid for 4 hr. The usual work-up provided 4.9 g. of ester product which analyzed by g.l.c. for at least 93% β,γ-unsaturated C_{13} methyl esters.[7] The infrared spectrum of this material showed strong bands at 6.1, 10.1, 10.3, and 10.9 μ.[7]

The organic layer containing excess dodecene was dried over anhydrous $MgSO_4$. Octane was removed by distillation through a Vigreux column (124° at 1 atm.) and the dodecene layer (46 g.) was collected at 93–95° (15 mm.). The infrared spectrum of this material shows very intense bands at 6.1, 10.1, and 11.0 μ indicating 1-dodecene. This accounts for 94% of the 1-dodecene used.

A similar material balance for the reaction between 1-dodecene and *n*-amylsodium accounted for 96% of the 1-dodecene used. The recovered dodecene in this case was, however, devoid of infrared bands at 6.1, 10.1, and 11.0 μ indicating essentially complete isomerization.

Analyses.—Gas–liquid chromatographic analyses were performed on an Aerograph Model A-90-S using 10-ft., 0.25-in. columns. A polyester (succinic acid–triethylene glycol) liquid phase (*ca.* 15%) supported on acid-washed Chromosorb-W was used. Compositions of the products were determined from the relative areas obtained by multiplying the peak height by the width at half-height.

Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer.

Nuclear magnetic resonance (n.m.r.) spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as an internal reference and adopting the τ-scale.[26]

Characterization of Acidic Products.—These products were characterized by infrared and g.l.c. comparison with the acidic products isolated and characterized in the previous paper.[7] An additional product, tridecanoic acid (Table II), is reported in this paper. This product was identified by g.l.c. comparison of its methyl ester to an authentic sample, accompanied by n.m.r. and infrared spectral studies. The n.m.r. spectrum showed only absorptions at τ 6.3 ($-OCH_3$), 7.75 (activated methylene), 8.73 (nonactivated methylene), and 9.12 ($C-CH_3$). The infrared

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[22] In some experiments smaller amounts of tridecanoic acid were realized at short times; however, in all cases the ratio of tridecanoic to 2-tridecynoic acids was less than 1.

[23] A. J. Birch and H. Smith, *Quart. Rev.*, **12**, 17 (1958).

[24] For simplicity the intermediate is shown as the covalent addition product.

[25] D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958).

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

spectrum was entirely consistent with a long-chain saturated ester.

Characterization of Recovered Olefins. Dodecene-1.—After carbonation of the metalation mixtures at the time intervals shown in Table I, the acidic and neutral fractions were separated in the usual manner. Distillation of the organic layer provided a dodecene fraction with an infrared spectrum showing intense bands at 10.1 and 11.0 μ with no absorption at 10.3 (*trans*) or 14.2 μ (*cis*).[27] This spectrum is identical with that of the starting material and it was therefore concluded that no isomerization had occurred.

During the course of this work several reactions had been run for periods of approximately 20 hr. In some cases slight amounts of isomerization were indicated by a very weak infrared band at 10.3 μ (*trans*). In all cases very intense bands indicative of the terminal double bond were obtained. One experiment which was conducted for 48 hr. showed approximately 20% isomerization by infrared, while another run in which the metalation mixture was allowed to stand for 450 hr. showed approximately 40% isomerization as estimated from the infrared spectrum. In all these runs β,γ-unsaturated C_{13} acid products were obtained upon carbonation as described above. While the amounts of isomerization do not appear to be entirely reproducible in these heterogeneous reactions, these results justify the conclusion that isomerization is a relatively slow process in alkylpotassum systems.[7,13]

Hexene-1, *trans*-Hexene-2, and Mixtures Thereof.—Hexene-1, 2-hexene, and a 1:1 mixture of these two olefins were metalated as described above and carbonated after 2 and 18 hr. There was obtained an acid product with an infrared spectrum indicative of α-vinylbutyric acid (10.1 and 10.9 μ) and *trans*-3-heptenoic acid (10.3 μ). G.l.c. analyses of the corresponding esters showed two products with appropriate retention times. The infrared spectra of the recovered organic phases show that the relative intensities of the 10.1-, 10.3-, and 11.0-μ absorption were unchanged from those of the starting materials. It was therefore concluded that relatively little, if any, isomerization had occurred.

Preparation of 1-Bromo-1-dodecene.—This preparation was described previously.[7]

Reaction of 1-Bromo-1-dodecene with Potassium Dispersion.—A dispersion of potassium (3.9 g., 0.1 g.-atom) in 200 ml. of octane[10] was prepared and 1-bromo-1-dodecene (10 g., 0.04 mole) was added dropwise at room temperature. Stirring was continued and 40-ml. portions of the reaction mixture were removed after 15 min., 1 hr., and 4 hr. These were carbonated by pouring over excess solid carbon dioxide. The remaining reaction mixture was allowed to stir an additional 25 hr. and then carbonated. All operations were conducted under an atmosphere of dry nitrogen. The usual work-up, esterification, and analyses gave the results recorded in Table II. In a separate experiment, using the same amounts of materials, in which the entire reaction mixture was carbonated after stirring for 1 hr., 4.1 g. (47%) of C_{13} acids was obtained. In an analogous experiment using sodium metal 5.4 g. (62%) of C_{13} acids was obtained.

Addition of 1-Octene to 1-Potassio-1-dodecene.—A preparation of 1-potassio-1-dodecene using 7.8 g. (0.2 g.-atom) of potassium dispersed in octane and 10.0 g. (0.04 mole) of 1-bromo-1-dodecene was carried out as described above. This reaction mixture was stirred 0.5 hr. and a portion carbonated. The acid product was esterified and analyzed by g.l.c. It contained C_{13} α,β-unsaturated acids and no detectable amount of C_{13} β,γ-unsaturated acids. To the remaining reaction mixture was added 1-octene (46 g., 0.4 mole) and stirring was continued for an additional 3.5 hr. The entire reaction mixture was then poured over excess dry ice. Esterification with methyl alcohol and a catalytic amount of sulfuric acid, followed by g.l.c. analysis, showed the presence of C_9 β,γ-unsaturated acids (28%), by comparison with the acidic product obtained from carbonation of the metalation of 1-octene with butylsodium for 24 hr., C_{13} β,γ-unsaturated acids (10%), C_{13} α,β-unsaturated acids (34%), tridecanoic acid (12%), and 2-tridecynoic acid (15%).

A separate run was made in which 1-potassio-1-dodecene was generated from 1-bromo-1-dodecene (4.0 g., 0.016 mole) and potassium metal (1.5 g., 0.04 g.-atom) as described above. Octene-1 (17.9 g., 0.16 mole) was added immediately after completion of addition of the alkenyl bromide and the mixture stirred for 1.5 hr. Carbonation provided 1.1 g. (33%) of crude acid product. Esterification with methanol and a catalytic amount of sulfuric acid provided an ester product whose gas chromatogram showed the same peaks as those cited above.

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[27] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 45-51.

Coordination in Solutions. II. Acid Dissociation Constants in Water and Structural Reassignments of the Isomeric Chlorosalicylaldehydes[1,2]

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When the Reimer–Tiemann reaction with *m*-chlorophenol was repeated, using the procedure of Hodgson and Jenkinson, all three of the theoretically possible products were isolated and identified. The isomer, designated as "4-chlorosalicylaldehyde" by Hodgson and Jenkinson, is shown to be 6-chlorosalicylaldehyde. The p*K* values for acid dissociation, in molar concentration units, of 3-, 4-, 5-, and 6-chlorosalicylaldehyde and that of 2-chloro-4-hydroxybenzaldehyde are 6.61, 7.18, 7.41, 8.26, and 6.60, respectively, in aqueous soution at 25.0° and μ of 0.100 maintained with sodium perchlorate. The change in acidity caused by a chloro substituent in each ring position can be correlated with that observed in the corresponding phenol, anion stabilities, and intramolecular hydrogen bond strengths. Changes in the latter were also measured by n.m.r. spectroscopy and ultraviolet spectral shifts upon methylation. The unusually low acidity of 6-chlorosalicylaldehyde can be explained by the proximity of the *o*-chloro substituent to the carbonyl group.

A study of the four chloro derivatives of salicylaldehyde[4] was undertaken to determine the dependence of the chelating ability of the ligand upon the ring position of the substituent and, by comparison with the nitro derivatives,[2] upon the π-electron acceptor (nitro) or donor (chloro) characteristics of the substituent.[5,6] The acid dissociation constants in aqueous solution are presented in this paper as measures of the

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[2] Part I of this series: L. B. Magnusson, C. Postmus, Jr., and C. A. Craig, *J. Am. Chem. Soc.*, **85**, 1711 (1963).

[3] (a) Argonne National Laboratory; (b) Brooklyn College; (c) National Science Foundation Undergraduate Research Participant, Brooklyn College, 1961-1962.

[4] The salicylaldehydes are numbered with the carbonyl group in the 1-position and the hydroxyl group in the 2-position.

[5] J. G. Jones, J. B. Poole, J. C. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

[6] K. Clarke, R. A. Cowen, G. W. Gray, and E. H. Osborne, *ibid.*, 245 (1963).