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Condensations by Sodium. XXX. The Metalation of Olefins and the Preparation of β,γ-Unsaturated Acids

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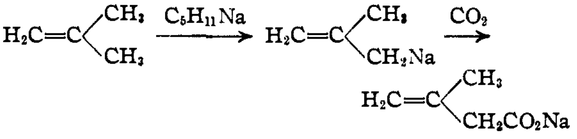
Olefins can be converted by amylsodium to alkenylsodium reagents. This reaction, just observed, is important in a preparative way because the products, when carbonated, yield β,γ-unsaturated acids which, in most cases, have not been prepared hitherto. The work furnishes also a basis for a comparison of the relative hydrocarbo acidities[1] of the olefins and of the relative acidities at various positions in an olefin, and shows that an alkyl group reduces this acidity even as it does in aromatic compounds. Finally, this acidity appears to be closely related to the general reactivity of the olefins in reactions where a labile hydrogen atom is involved, because the compounds primarily produced by polymerization of olefins in acid solution can be predicted from the data of relative acidities, as determined by the alkaline reagents.

Metalation of Olefins.—The formation of alkenylsodium compounds takes place so easily that its non-observance in our previous studies now appears surprising. Any interchange that did occur in the past has, however, been extremely slight, since the quantity of olefin present has been very low, the effectiveness of stirring has been much less than at present and the reaction time has been short. Attention was first directed to this new reaction by a preparation of amylpotassium, analogous to that of amylsodium. The product, after carbonation, contained a trace of unsaturated acids which boiled within the same range as caproic acid. The new products were derived from the reaction shown below between

$$C_5H_{11}K + C_5H_{10} \longrightarrow CH_2{=}CHCH(K)C_2H_5 \text{ and } KCH{=}CHC_3H_7$$

amylpotassium and 1-pentene, an olefin which happened to be present in the reaction mixture because of a disproportionation in the reaction of amyl chloride with amylpotassium which occurred during the preparation of the latter by addition of amyl chloride to metallic potassium. Amylsodium was then found to react with the olefin as did amylpotassium provided a sufficient quantity of the hydrocarbon was present and the reaction was given time for completion.

Isobutene is readily attacked by amylsodium. The product, after carbonation, is the hitherto unreported β-methylvinylacetic acid, as shown by analysis of the *p*-bromophenacyl ester derivative, and by isomerization of the acid under the influence of alkali to the known β,β-dimethylacrylic acid. Evidence that a dicarboxylic acid, β-methyleneglutaric acid, $H_2C{=}C(CH_2COOH)_2$, the result of dimetalation, is present in a higher boiling fraction, is given by ozone cleavage to formaldehyde and acetonedicarboxylic acid.



$$H_2C{=}C\begin{array}{l}CH_3\\CH_3\end{array} \xrightarrow{C_5H_{11}Na} H_2C{=}C\begin{array}{l}CH_3\\CH_2Na\end{array} \xrightarrow{CO_2} H_2C{=}C\begin{array}{l}CH_3\\CH_2CO_2Na\end{array}$$

By a similar series of reactions propene gives vinylacetic acid, though in smaller yield than the methylvinylacetic acid. This metalation occurs readily also but a comparison of the relative activities of propene and isobutene is difficult to make because propene is so volatile. Propene shows a smaller amount of interchange with benzylsodium than with amylsodium, and this fact accords with the view that the latter is a salt of a weaker acid and, therefore, is more reactive.

1-Pentene reacts with amylsodium slightly under conditions which are very suitable for the metalation of isobutene; but if 1-pentene is used as a solvent in the preparation of amylsodium, and the mixture is allowed to stand overnight, a nearly quantitative conversion to a mixture of 1-pentenyl-3-sodium, $CH_2{=}CHCH(Na)C_2H_5$, and 1-pentenyl-1-sodium, $NaCH{=}CHC_3H_7$ in the proportion of about four to one results. The two carboxylic acids derived therefrom boil at nearly the same temperature. Their separation is accomplished easily by a multiple fractional extraction process[2] similar to that reported for separating bases. The efficiency of such a separation depends on the relative strength of the acids; and this difference is sufficiently great to permit a good separation of the α,β- and β,γ-isomers in a relatively brief time.

2-Butene consumes more amylsodium than does 1-butene although both show much less interchange under the conditions employed than does propene or isobutene. Mono- and disubstitution products are present. Hydrogenation of the disubstituted acids derived from 2-butene gives principally adipic acid and some α-methylglutaric acid. Trimethylethylene and tetramethylethylene likewise have only moderate reactivity. The former is somewhat more reactive than the latter.

The experience with 1-pentene suggests that good yields of mixtures of acids can be obtained from all of these olefins when time–concentration–temperature tests are made. These aspects of the

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[1] Morton, *Chem. Rev.*, **35**, 1 (1944).

[2] Hunter and Nash, *Ind. Eng. Chem.*, **27**, 836 (1935); Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., N. Y., 1938, p. 199.

problem will, of course, be studied in the future, but the present results indicate qualitatively the relative activity of the various hydrogen atoms in the olefins.

Relative Acidities.—In a previous paper[1] the activity of the hydrogen atoms was interpreted as the behavior of hydrocarbo acids whose strength was of the order 10^{-40} to 10^{-30}. Metalation was regarded as an acid–salt interchange. The facility of this interchange and the proportions of products obtained in each reaction provides the rating of comparative acidities in propene, the butenes and the pentenes shown below. The type reactive hydrogen atoms are underscored. The extreme degrees of acidity in each series are well defined; the order of acidities of the olefins which react slowly is less certain but is probably the same as the order in which the compounds are written below.

TABLE I

Olefins	Highly reactive	React slowly	React very slowly, if at all
Propene	$H_2C{=}CHC\underline{H_3}$ >		$\underline{H_2}C{=}CHCH_3$[a]
Butenes	$H_2C{=}C(C\underline{H_3})_2$ >	$CH_3CH{=}CHC\underline{H_3}$ and $CH_2{=}CHC\underline{H_2}CH_3$ >	$\underline{H_2}C{=}CHC_2H_5$[a]
Pentenes	$H_2C{=}\underset{\underset{\displaystyle C_2H_5}{\vert}}{C}{-}C\underline{H_3}$[b] >	$CH_3CH{=}C(C\underline{H_3})_2$ and $CH_2{=}CHC\underline{H_2}C_2H_5$ >	$\underline{H_2}C{=}CHC_3H_7$

[a] The hydrogen underscored in this compound is so unreactive that no substitution occurs. [b] The position of this compound is predicted from the results with propene and the butenes.

A vinyl group markedly activates the hydrogen atom on an adjacent carbon atom. For example propene is very reactive. The reactivity is possibly increased when a second methyl group is introduced on the same side of the vinyl group, as in isobutene. These two most active olefins are the only hydrocarbo acids in which a change in the position of the double bond with a corresponding shift of hydrogen, does not produce a different species of olefin; and this condition, which is analogous to the structure which contributes by resonance to the strength of the ions of carboxylic, nitric, sulfuric and other acids, may be an important factor in the comparative strength shown by these hydrocarbo acids. The acidity of the hydrogen atom attached to methyl in isobutene or propene is so much greater than that attached to the methylene group, that no monosubstitution product, with sodium at the latter position, is found.

When methyl or alkyl groups are on both sides of the double bond, as in 2-butene, or when alkyl groups are attached to the methyl group which supports the acidic hydrogen, as in 1-butene or 1-pentene, the acidity at the methyl group is greatly reduced and that on the vinyl system is made evident. 1-Pentene shows 20% of its acidity on the terminal methylene group, and the dicarboxylic acid product from 2-butene shows some substitution at the vinyl group.

These results in alkylvinyl systems parallel, in general, the acidities in the alkylaryl compounds[3] in which the order is

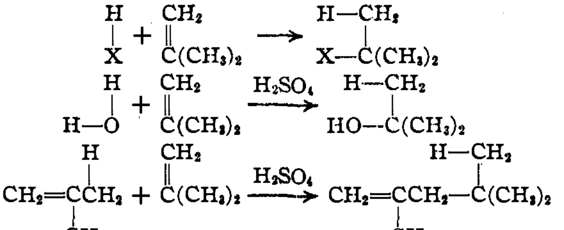
$C_6H_5C\underline{H_3} > CH_3C_6H_4C\underline{H_3}$ and

$C_6H_5C\underline{H_2}CH_3 > \underline{H}C_6H_4CH(CH_3)_2$

Toluene is outstandingly the most reactive member of this group, xylene and ethyl- or propylbenzene are less reactive; and cumene[4] has such decreased activity on the alkyl group that substitution occurs on the ring.

Relation to Polymerization.—If acidity should happen to be synonymous with hydrogen activity in olefins, it should be possible to predict the proportions of products produced in other reactions from the relative strengths as determined from this work, subject, of course, to some variations caused by the special conditions present. We shall apply this idea to the polymerization of olefins by acid: first, by showing that polymerization can be regarded as a reaction common to all acids, and, second, by showing that the proportions of the polymers produced accord with the relative order of acidities.

Polymerization can be regarded as one of the general class of reactions in which acids add to olefins. Strong acids, such as hydrochloric, sulfuric and trichloroacetic, add readily to olefins; the weaker hydroxo acid, water, requires the presence of a mineral acid as a catalyst; and the still weaker hydrocarbo acids, the olefins, require also the aid of a catalyst. The similarity of these reactions is shown by the equations below.



$$\begin{array}{c}H\\|\\X\end{array} + \begin{array}{c}CH_2\\\|\\C(CH_3)_2\end{array} \longrightarrow \begin{array}{l}H{-}CH_2\\\quad|\\X{-}C(CH_3)_2\end{array}$$

$$\begin{array}{r}H\\|\\H{-}O\end{array} + \begin{array}{c}CH_2\\\|\\C(CH_3)_2\end{array} \xrightarrow{H_2SO_4} \begin{array}{l}H{-}CH_2\\\qquad|\\HO{-}C(CH_3)_2\end{array}$$

$$CH_2{=}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2 + \overset{\overset{\displaystyle CH_2}{\|}}{C}(CH_3)_2 \xrightarrow{H_2SO_4} CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}CH_2{-}\overset{\overset{\displaystyle H{-}CH_2}{|}}{C}(CH_3)_2$$

Now in polymerization the reaction with the mineral acid is reversible; but that with the hydrocarbo acid is irreversible. Hence the latter goes to completion. Since the strong mineral acids react without a catalyst, the reasonable as-

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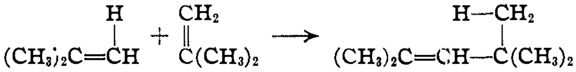
[3] Morton, Little and Strong, THIS JOURNAL, **65**, 1339 (1943); see also ref. 1.

[4] Morton, Massengale and Brown, *ibid.*, **67**, 1620 (1945).

sumption for the catalyzed reactions is that the stronger the acid, the easier the addition. In accordance with this view, the major product from the polymerization of isobutene should be 2,4,4-trimethyl-1-pentene as shown above. The minor product could only result from the acidity at the methylene group and would be 2,4,4-trimethyl-2-pentene, according to the equation below.

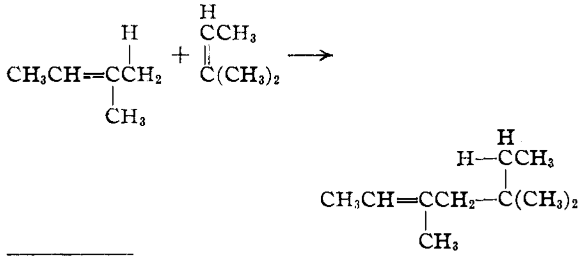


$$(CH_3)_2C{=}\overset{H}{\overset{|}{C}}H + \overset{CH_2}{\overset{\|}{C}}(CH_3)_2 \longrightarrow (CH_3)_2C{=}CH{-}\overset{H-CH_2}{\overset{|}{C}}(CH_3)_2$$

In reality both products are formed[5] in the proportion of four to one.

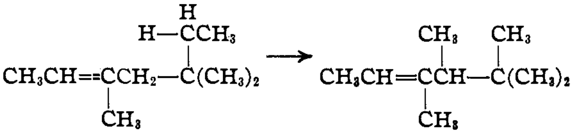
The detailed picture is, of course, more complicated. For example, the acidity of the hydrogen atoms in the olefins will be affected by solution in aqueous sulfuric acid because the act of solution must involve an attachment of some kind between the double bond and the acid; and this attachment must simultaneously alter the degree of acidity of the hydrogen atom which derives its activity from the adjacent double bond. Certainly isobutene, dissolved in acid, could not have precisely the same relative acidities as its methyl and methylene ends, as it would in the unattached state. It is not surprising, therefore, that both the methyl and the methylene group of isobutene show acidity and that two products, rather than one, are obtained in the polymerization of isobutene. This effect upon the active hydrogens has a bearing on the general problem of whether a catalyst activates one component or affects both in an addition process. In this instance at least it does not appear safe to disregard, as apparently can be done in some other addition reactions, such as the aldol condensation,[6] the influence which the catalytic reagent may exert on both components of the reaction, as contrasted with the primary influence on one component.

The polymerization products from other olefins can be predicted by similar reasoning but the initial reaction products are sometimes subject to a rearrangement in the sulfuric acid medium. The most active hydrogen atoms in trimethylethylene, for example, should be on the side of the vinyl group that has two methyl groups. The addition of the hydrocarbo acid to the olefin should, therefore, be as follows.



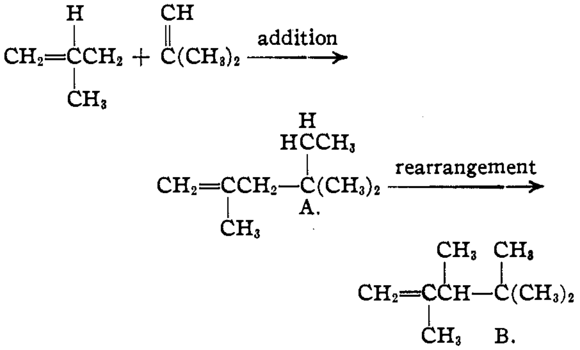
$$CH_3CH{=}\underset{\underset{CH_3}{|}}{\overset{H}{\overset{|}{C}}}CH_2 + \overset{\overset{H}{CCH_3}}{\overset{\|}{C}}(CH_3)_2 \longrightarrow CH_3CH{=}\underset{\underset{CH_3}{|}}{C}CH_2{-}\overset{\overset{H}{H-CCH_3}}{\overset{|}{C}}(CH_3)_2$$

This compound is, in fact, the principal product. A rearrangement, however, occurs which effects a transmigration of methyl and hydrogen to give some 3,4,5,5-tetramethyl-2-hexene.[7] The rearrangement is undoubtedly facilitated by the presence of two methyl groups at C_5, a situation[8] which would cause the two other carbon atoms joined to that carbon, to be brought nearer to each other.

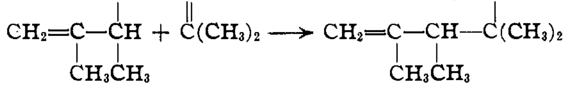


$$CH_3CH{=}\underset{\underset{CH_3}{|}}{C}CH_2{-}\overset{\overset{H}{H-CCH_3}}{\overset{|}{C}}(CH_3)_2 \longrightarrow CH_3CH{=}\underset{\underset{CH_3}{|}}{C}\overset{CH_3}{\overset{|}{C}}H{-}\overset{CH_3}{\overset{|}{C}}(CH_3)_2$$

More complicated problems, which arise from the reaction of isobutene and the amylenes (trimethylethylene in large proportion) obtained when mixtures of *t*-butyl alcohol and *t*-amyl alcohol are treated with sulfuric acid at 80°, can be predicted on a like basis. The most active hydrogen atoms are clearly those in isobutene. The addition of isobutene to trimethylethylene should give the nonene, 2,4,4-trimethyl-1-hexene, indicated by A in the equation below. This product has a structure identical with that of the above decene, which undergoes rearrangement, except for the lack of a methyl group on the left side; and rearrangement of A to 2,3,4,4-tetramethyl-1-pentene (B) occurs so readily that none of A is found, although 50% of all the nonene fraction is B.[9] The formation of B as a primary product would have to be from the reaction shown below, and the necessary pentene would neither be present in this amount nor have the required acidity relative to isobutene.



$$CH_2{=}\underset{\underset{CH_3}{|}}{\overset{H}{\overset{|}{C}}}CH_2 + \overset{CH}{\overset{\|}{C}}(CH_3)_2 \xrightarrow{\text{addition}} CH_2{=}\underset{\underset{CH_3}{|}}{C}CH_2{-}\overset{\overset{H}{HCCH_3}}{\overset{|}{C}}(CH_3)_2 \text{ A.} \xrightarrow{\text{rearrangement}} CH_2{=}\underset{\underset{CH_3}{|}}{C}\overset{CH_3}{\overset{|}{C}}H{-}\overset{CH_3}{\overset{|}{C}}(CH_3)_2 \text{ B.}$$



$$CH_2{=}\underset{\underset{CH_3}{|}}{\overset{H}{\overset{|}{C}}}{-}\underset{\underset{CH_3}{|}}{C}H + \overset{CH_2}{\overset{\|}{C}}(CH_3)_2 \longrightarrow CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}\underset{\underset{CH_3}{|}}{C}H{-}\overset{H-CH_2}{\overset{|}{C}}(CH_3)_2$$

The second major nonene product would be the result of the reverse addition of trimethylethylene to isobutene, and this reaction also takes place in the manner expected, to the extent of 23%.

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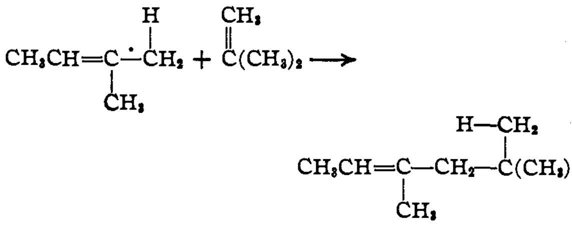
[5] Whitmore and co-workers, This Journal, **54**, 3706, 3710, 3714 (1932).

[6] Watson, *Trans. Faraday Soc.*, **37**, 707, 713 (1941); Ingold, *ibid.*, 720 (1941); Breslow and Hauser, This Journal, **62**, 2385 (1940)

[7] Drake, Kline and Roci, *Bur. Standards J. of Research*, **13**, 705 (1934).

[8] Bersley, Ingold and Thorpe, *J. Chem. Soc.*, **97**, 1080 (1915); Ingold and Thorpe, *ibid.*, **115**, 320 (1919); Baker and Thorpe, *ibid.*, **117**, 1579 (1920).

[9] Whitmore and Mixon, This Journal, **63**, 1460 (1941).



$$\mathrm{CH_3CH{=}\overset{H}{\underset{CH_3}{C}}\dot{-}CH_2 + \overset{CH_2}{\overset{\|}{C}}(CH_3)_2 \longrightarrow CH_3CH{=}\underset{CH_3}{C}{-}CH_2{-}\overset{H-CH_2}{C}(CH_3)_2}$$

The remaining products are the result of the activity of less active hydrogen atoms, coupled with methyl–hydrogen interchange and possible rearrangement of the double bond.

In all the above, the acid medium alters the degree, but not the position, of maximum acidity. The major and minor products in polymerization accord with those expected from the study of acid–salt interchange.

In the case of hydrocarbo acids which contain an aromatic nucleus, this condition is no longer true. The position of maximum acidity in toluene, for example, is at the methyl group if judged by acid–salt interchange, but is on the ring if judged by polymerization with an olefin in acid medium. Toluene and propene give isopropyltoluene and not isobutylbenzene.[10] This result indicates that sulfuric acid causes a complete, rather than a partial, alteration in the point of maximum acidity, and emphasizes again that the acid catalyst affects both the active hydrogen and the double bond.

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Experimental

Amylpotassium and the Metalation of 1-Pentene (by R. L.).—Amylpotassium was prepared by the addition over a one-hour period of 10 g. (0.094 mole) of amyl chloride, dissolved in 40 ml. of pentane, to 11 g. (0.28 g. atom) of finely divided potassium metal suspended in 200 ml. of pentane at -10 to -15°. The stirring was continued at this temperature for twenty minutes after which the mixture was allowed to warm to 0°, stirred at that temperature for twenty minutes more, and then carbonated. The caproic acid recovered after the customary processing was 3.6 g. or 35%. The caproic acid showed a small amount of unsaturation.

In general this preparation of amylpotassium parallels the process for the preparation of amylsodium. The high speed stirring apparatus used for amylsodium is employed. The potassium sand is made in hot octane but the yield of amylpotassium is much lower in octane than in pentane. Hence the octane is replaced by pentane before addition of amyl chloride.

1-Pentene (25 ml. or 0.23 mole) was added at -20° to the amylpotassium thus prepared. The temperature was then allowed to rise to 30° and maintained there for five hours. After carbonation and the usual processing, the combined acids amounted to 4.8 g., which boiled from 81–96° (4 mm.) and had refractive indices which varied from $n^{20}\mathrm{D}$ 1.4330 to 1.4355. A dibromo derivative of the acid did not crystallize but the methyl ester (from diazomethane) distilled at 95° (4 mm.) and contained 52.9 and 53.4% of bromine (theory is 55.5%). Ozonization of the acid in ethyl acetate at -30° and decomposition of the ozonide with hydrogen and palladium–calcium carbonate catalyst at 30 pounds pressure gave a mixture of aldehydes from which some pure formaldehydedimethon derivative (m. p. 190–191°, recorded[11] value 191°) was isolated. Permanganate oxidation at 0° with high speed stirring gave a solution from which a small amount of calcium oxalate was precipitated. From the same solution after concentration and extraction with ether, large crystals of ethylmalonic acid were obtained which melted at 110.5 to 111.5° (recorded[12] value 111.5°). The acids produced are therefore unsaturated. Their separation will be described in the experiment in which 1-pentene is metalated by amylsodium.

Metalation of Isobutene (by M. L. B.).—Amylsodium (0.19 mole) was prepared in the customary manner from amyl chloride and sodium sand in pentane. Isobutene (30 ml. or 0.34 mole) was then added dropwise over a half-hour period at 25°. Stirring was continued for five hours and the mixture then allowed to stand overnight before carbonation. After several hours water was added, the aqueous layer acidified and the acids extracted by petroleum ether and then by ethyl ether as is the practice in these studies. A pale yellow oil was obtained by evaporation of the petroleum ether extract. When cooled to 0°, the oil formed colorless needles which melted at approximately 20° and had a refractive index of $n^{20}\mathrm{D}$ 1.4240 and a neutralization equivalent of 101. This material proved to be β-methylvinylacetic acid, identical with that isolated in the next fraction.

The residue from the ether extraction yielded 3 g. of a product when distilled at 49° (3 mm.) and 3 g. of a higher boiling compound, 110–150° (3 mm.), which solidified as an oily wax. The low boiling product had a refractive index of $n^{20}\mathrm{D}$ 1.4328 and a neutralization equivalent of 100.1. It absorbed catalytic hydrogen over platinum black equivalent to 0.99 double bond per carboxyl group, and yielded the formaldehydedimethon derivative after being ozonized. The p-bromophenacyl ester melted at 42.0 to 42.3°. *Anal.* Calcd. for $\mathrm{C_{13}H_{13}O_3Br}$: C, 52.5; H, 4.38; Br, 26.9. Found: C, 52.3, 52.4; H, 4.35, 4.39; Br, 26.5, 26.8. Aqueous 25% potassium hydroxide at 100° for twenty-five minutes converted a sample of the acid to the known β,β-dimethylacrylic acid which melted at 68.9–69.3° (recorded[11] value 70°). These facts accord with the view that the low boiling acid is β-methylvinylacetic acid. This compound has not been reported previously in the literature.

The waxy solid from the higher boiling product (neutralization equivalent 76) was cleaved by the ozonization process to formaldehyde and acetone dicarboxylic acids. The former was identified by the dimethon derivative and the latter by a strong positive Denigès mercuric oxide test.[11] The methyl ester of the unsaturated acid was prepared by use of diazomethane. The ester was then hydrogenated, and the reduced product saponified. Crystals of β-methylglutaric acid which melted at 86–86.5 (recorded[11] value 87°) were thus obtained.

Metalation of Propene (by M. L. B.).—A suspension of amylsodium prepared as in the previous experiment was cooled to -50°. Propene (30 ml., 0.36 mole) was cooled to the same temperature and added dropwise over a thirty-minute period. During the next hour the mixture was allowed to warm to room temperature, and for the following two and half-hours was stirred at 25°. At least 20 ml. of propene, lost by evaporation during these operations, was recovered in a cold trap. The mixture was carbonated on the next day and the acids recovered by the customary petroleum ether and ether extractions. The petroleum ether layer contained 5.3 g. of caproic acid from unused amylsodium. The ether layer contained 4.5 g. of vinylacetic acid which boiled at 71–72 (12 mm.) and was identified by its refractive index, $n^{20}\mathrm{D}$ 1.4220, neutralization equivalent, 88, and by other properties as de-

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[10] Ipatieff, Corson and Pines, THIS JOURNAL, **58**, 919 (1936).

[11] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, N. Y., 1941.

[12] Conrad, *Ann.*, **204**, 136 (1880).

scribed by Mannich.[13] A residue (1.59 g.) which remained after the vinylacetic acid was distilled had a neutralization equivalent of 74, was unsaturated and lost carbon dioxide at about 200°. It is possibly a mixture of a disubstitution product of propylene with some butylmalonic acid.

Benzylsodium was prepared by the addition of 110.5 g. (1.2 mole) of sulfur-free toluene to about 0.14 mole of amylsodium prepared as described above. The temperature was maintained at −5 to −10° during the first twenty minutes and then, after warming, at 25–30° for three hours. The color, meanwhile, changed from blue to gray to green and eventually to yellow. The quantity of benzylsodium thus obtained was 0.14 mole. Propene (25 ml.) was then passed into the suspension of benzylsodium as described above. The vinylacetic acid, separated from this experiment, was 2.7 g.

Metalation of 1-Pentene by Amylsodium (by M. H.).—Amyl chloride, 30.6 ml. 0.25 mole, was added dropwise to a suspension of fine sodium sand (11.6 g., 0.5 g. atom) in 200 ml. of 1-pentene, Phillips Petroleum pure grade, which had been fractionated through a fifty-plate column just before use. The temperature was −10° during the hour necessary for addition of the chloride, and was 20–25° during the subsequent three-hour period of stirring. The next morning the mixture was carbonated and the acids extracted in the customary manner. The petroleum ether extract contained 19 g. of acid which boiled at 89–92° (5 mm.) and had one double bond as measured by the catalytic hydrogenation method for every carboxyl group. No caproic acid was, therefore, present. From five such experiments a total of 40 g. of acid was obtained, which, by previous tests with ozonization, was known to be a mixture, probably of α,β- and β,γ-unsaturated acids.

The mixture of hexenoic acids was subjected to a multiple-fractional extraction process. The acid was dissolved in enough pentane to make 500 ml. of solution, which was then divided into ten aliquot parts. Five portions of aqueous hydroxide, each equivalent to one of the aliquot parts of the hexenoic acid, were used. The acids and alkali solutions were then shaken with each other according to the plan necessary for the operation of this multiple fractional extraction method of separation. Once these solutions have been prepared, the operation of the fractional extraction requires only about an afternoon's work. The ten fractions of acids thus separated had refractive indices, $n^{20}\text{D}$, equal to 1.4385, 1.4367, 1.4350, 1.4340 for the first four and 1.4335 for the last six. It would appear that the original acid mixture was composed largely (probably about 85%) of an acid which had a refractive index of 1.4335 and a smaller amount of another acid which had a higher value, around 1.4385. The acid present in largest amount is the stronger acid corresponding to a β,γ-unsaturated acid and the one in smaller amount is the weaker one corresponding to an α,β-acid. A sample from fraction number 10 was converted to the *p*-bromophenacyl ester which melted at 41.5–42.0° after recrystallization from dilute ethanol.

Anal. Calcd.: C, 54.02; H, 4.8; Br, 25.7. Found: C, 54.1, 53.9; H, 4.55, 4.56; Br, 25.6, 25.6.

Ozone degradation of the acid and hydrogenation of the ozonide gave formaldehyde which was identified by the dimethon derivative.

A *p*-bromophenacyl ester derivative from fraction number one melted at 62.0 to 62.5°.

Anal. Calcd.: C, 54.02; H, 4.8; Br, 25.7. Found: C, 54.1, 53.9; H, 4.55, 4.56; Br, 25.6, 25.6.

Ozone degradation and hydrogenation gave a mixture of aldehydes whose dimethon derivatives did not crystallize readily into pure components. When the crystals were allowed to form slowly they were of sufficient size to be separated by hand into two portions which melted a 128–130° and 191–193°. Further crystallizations and mechanical separation was ineffective in raising the melting point of the lower product to 142°, the melting point of the butyraldehyde derivative. The other product, which was present in much larger amount, was purified until it melted at 208° corresponding with the derivative of the keto acid. Permanganate oxidation of the acid in the number 10 fraction gave oxalic acid, which was identified as the calcium salt, and butyric acid, which was identified by the melting point, 81.5–82°, of the phenylphenacyl ester.

Metalation of Other Olefins (by M. L. B. and E. M.).—The olefin was added to 0.19 mole of amylsodium prepared as described above. The olefin was added dropwise at 25°, the mixture was stirred for three or four hours, and then carbonated the next day. The acid products were recovered by the usual petroleum ether and ether extractions, followed by vacuum distillation. The results are of qualitative value as an indication of the relative ease of metalation of these compounds.

In this manner, 0.3 mole of 1-butene gave 15 g. of caproic acid from unused amylsodium and 1.7 g. of an oily residue from the ether extraction. From this oil about 0.5 g. of a crude solid, which gave a positive Baeyer test for unsaturation, was separated by cooling. From the products of the reaction with 0.3 mole of 2-butene, 11.5 g. of caproic acid was recovered together with 3.5 g. [b. p. 55–57 (3 mm.)] and 2 g. of a higher boiling waxy solid from the ether extract, both of which gave positive Baeyer tests for unsaturation. The low boiling unsaturated acid had a refractive index $n^{20}\text{D}$ 1.4308 and a neutralization equivalent equal to 103. Attempts to obtain a crystalline dibromide or amide derivative were unsuccessful. The higher boiling solid, when hydrogenated in acetic acid with a platinum oxide catalyst, gave a mixture of crystals which were separated by fractional crystallization from concentrated hydrochloric and nitric acids. One product melted at 78–80° corresponding with α-methylglutaric acid (recorded value 78–80°) and the other and larger portion melted at 151–151.5° and showed no depression when mixed with adipic acid.

From the reaction with 0.32 mole of trimethylethylene, 11.2 g. of caproic acid was recovered together with 3.1 g. of other acids which showed unsaturation but gave no solid derivative. The same reaction with tetramethylethylene yielded 15.1 g. of caproic acid and 2.6 g. of other acids, some of which after about three months had crystallized.

Summary

Olefins undergo an acid–salt interchange readily with amylpotassium or amylsodium. The former reagent is more powerful than the latter. The process is well suited for obtaining active organoalkali metal salts of the olefins. Carbonation gives β,γ-unsaturated acids which have so far not been available.

Isobutene reacts very readily with amylsodium and gives, after carbonation, β-methylvinylacetic acid and β-methyleneglutaric acid.

Propylene is converted by similar reactions to vinylacetic acid.

1-Pentene is metalated chiefly at C_3 and to a small extent at C_1. The carbonated products are readily separated by multiple fractional extraction.

The order of acidity of the various hydrogen atoms in the olefin is (a) on methyl groups on one side of the double bond, (b) on methyl groups on both sides of the double bond or on methylene groups flanked by a double bond and an alkyl group and (c) on the carbon atom which is part of the vinyl group.

A relationship between the comparative acidity as judged by acid–salt interchange and the activity of hydrogen atoms in sulfuric acid polymerization of olefin is discussed.

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[13] Mannich, *Arch. Pharm.*, **237**, 415 (1935).