potassium dodecanoate indicate that the transition occurs with the C_8 alcohol, but additional evidence, now being obtained, will be necessary before more definite ideas as to the extent of penetration of these long chain alcohols into the soap micelle can be advanced.

Summary

Additional evidence as to the presence of two loci of solubilization in soap micelles is obtained from solubilization data of hydrocarbon and polar compounds in soap solutions containing added electrolyte. The addition of potassium chloride to a 0.32 N potassium tetradecanoate (KC_{14}) solution results in an enhancement of solubility of n-heptane and a decrease of n-octanol. With 0.05 N KC_{14}–KCl solutions, the solubilities of both polar and non-polar compounds increase. However, after the initial increase up to about 0.50 N potassium chloride, the solubility of the alcohol again decreases. Even though the critical micelle concentration of a soap depends only on the equivalent concentration of the ion opposite in charge to that of the colloidal electrolyte, the nature of both anion and cation affect solubilization. Thus in the solubilization of n-heptane for equivalent concentrations of additive, KCl > K_2SO_4 > $K_4Fe(CN)_6 \cdot 3H_2O$ whereas the reverse order holds when n-octanol is solubilized. However, these latter data present additional proof as to the two loci of solubilization, one in the hydrocarbon center of the micelle, the other in the palisade layer in the region occupied by the soap molecules. As the chain length of the solubilized alcohol is increased, there is a gradual transition from polar type to non-polar type solubilization most strikingly indicated when comparing C_8 and C_{10} alcohols. Qualitative measurements of viscosity indicate that the addition of very small amounts of long chain alcohols to soap–salt systems result in the formation of very viscous, almost gel-like, systems. The maximum viscosities always occur at concentrations of alcohol below the limit of solubilization (as indicated by turbidity).

St. Paul, Minn.   Received November 11, 1949

Polymerization. XII. The Metalation of Olefins and Dienes and their Use in Alfin Polymerization of Butadiene[1]

By Avery A. Morton, Frank D. Marsh, Robert D. Coombs, Anne L. Lyons, Siegfried E. Penner, Hugh E. Ramsden, Vernon B. Baker, Ernest L. Little and Robert L. Letsinger

Since early in the study of polymerization in this Laboratory, the metalation of olefins[2] and dienes[3] has been prominent because some products help induce catalytic polymerization and most undergo double bond shifts such as might occur in the polymer. This paper describes the metalation of ethylene, several straight chain and branched olefins, diallyl and some conjugated dienes. Many products can serve as organometallic intermediates in reactions. Vinylsodium and most of the branched chain alkylsodium compounds are free from or unaffected by allylic shifts, hence each gives one monosubstituted product. Others give mixtures. New β,γ-unsaturated carboxylic acids have been isolated. Isobutene disodium has interesting possibilities in Wurtz reactions. All metalated compounds, except for diallyl and 2-methyl-1,3-pentadiene, are relatively ineffective as catalysts with butadiene.

Metalation of Olefins.—Amylsodium converted ethylene to vinylsodium in good yield provided sodium isopropoxide was present.

Vinylsodium, in turn, metalated benzene, hexene-1, toluene and fluorene with progressive ease (see Table I). Like phenylsodium, it did not add to 1,1-diphenylethylene. In eighteen hours there was no addition where amylsodium reacted[4] completely in four to six hours.

TABLE I
METALATION OF HYDROCARBONS BY VINYLSODIUM–SODIUM ISOPROPOXIDE

Compound	Moles[a] Hy/VS	Reaction time, days	Acrylic acid recovered, %	Carboxylic acid from metalation, %
Benzene	2.0	12	56	11
Hexene-1	2.0	12	19	42
Toluene	1.5	8	10	53
Fluorene	1.2	7	0	88

[a] Hy/VS. is hydrocarbon to vinylsodium.

The same reagent with possibly a trace of pentoxide metalated 1-alkenes (Table II), mostly by replacement of an allylic hydrogen so that on carbonation the ratio of straight chain and branched chain acids was 2:3. However, the proportions of allylic isomers varied with the reagent since the reaction of methyl iodide with octenylsodium gave about 2:1 straight to branched chain products. Some metalation at C-1 without allylic shift occurred but this fell

(1) This work was in large part carried out under the auspices of the Office of Rubber Reserve, Reconstruction Finance Corporation, and in small part, with the aid of a grant from The Research Corporation, New York.

(2) Morton, *Chem. Reviews*, **35**, 16 (1944); Morton, Brown, Holden, Letsinger and Magat, THIS JOURNAL, **67**, 2224 (1945).

(3) Morton and Brown, *ibid.*, **69**, 160 (1947).

(4) Morton and Wohlers, *ibid.*, **69**, 167 (1947).

with excess olefin, more with long reaction time. The results by carbonation confirm previous experience[5] except for the straight chain allylic isomer from pentene-1 in the absence of isopropoxide. The difference may be due to a trace of pentoxide, the greatly improved stirring,[6] or a change in temperature. The results of Lüttringhaus[7] from metalation of dodecene-1 by isoamylsodium (prepared as is n-amylsodium) are similar, though without differentiation between metalations at C-1.

TABLE II

METALATION OF PENTENE-1, HEXENE-1 AND OCTENE-1 BY AMYLSODIUM

Olefin	Ex.[a]	Time hr.	Cap.	B.	S.	Con.	Di.	Tot.
Pentene-1	292	24	6.1	48.1	32.0	5.0	15.7	106.9
	20	264	0	34.6	19.2	2.3	14.9	71.0
Hexene-1	25	24	69	8.8	5.5	4.3	11.9	99.5
	40	24	22.4	16.2	14.7	11.8	12.1	77.2
	125	24	0	51.3	31.8	5.7	11.8	100.6
	40	264	11.9	43.7	23.4	1.8	17.5	98.3
Octene-1	33	24		48.1	30.0	1.6		

[a] Excess over the amount theoretically needed for consumption by a monosubstitution reaction. [b] The order is that in which the acids or their esters usually appeared when fractionated. The symbols refer respectively to caproic acid, branched chain acid of the allylic system, straight chain acid of the allylic system, conjugated (α,β-unsaturated) acid, diacid and total acids.

No condition that permitted exclusively mono- or di-metalation[8] of isobutene was found (Table III). Excess olefin favored the mono- but the di-product was large, especially at the start. Use of gaseous isobutene or just enough for di-substitution did not exclude the mono-. Heat decreased the mono- without benefit by disproportionation to the di-. Triethylamine—a coördinating agent for cations—favored the mono- and the joint effect of excess olefin and amine gave the highest, 49%, yield of mono product.

The carboxylic acids from isobutene were characterized fully, and the Wurtz reactions with ethyl bromide, ethylene bromide and trimethylene bromide gave the hydrocarbons expected from its two sodium compounds. Among the interesting products are the dimer of the anion obtained with ethylene bromide (which seems as satisfactory for coupling anions—tested also with benzylsodium— as the tetramethylethylene bromide of Ziegler)[9] and the cyclic product obtained with trimethylene bromide.

Metalation of alkene-1 systems with branching at C-2 was slow (required more than a day) and occurred (Table IV) at C-3 if that atom had two or three hydrogens, at C-1 if no hydrogen was at C-3, and at a C₄ methyl group with two shifts of the double bond if only one hydrogen was at

(5) Morton and Holden, ibid., 69, 1675 (1947).

(6) Morton and Redman, Ind. Eng. Chem., 40, 1190 (1948).

(7) Lüttringhaus, Wagner-V. Sääf, Sucker and Borth, Ann., 557, 66 (1945).

(8) Morton, Brown, Holden, Letsinger and Magat, THIS JOURNAL, 67, 2224 (1945).

(9) Ziegler and Snell, Ann., 437, 227 (1924).

TABLE III

EFFECT OF VARIABLES[a] ON THE PROPORTIONS OF THE TWO SODIUM COMPOUNDS OBTAINED FROM THE METALATION OF ISOBUTENE BY AMYLSODIUM

Amt.[b]	N(C₂H₅)₃ equiv. per RNa	React. time, hr.	Acids from C₄H₇Na, %	C₄H₈Na₂ %
T		2	10	6
T		3	23	16
T		[4	15	17][c]
T		6	17	26
T		24	16	52
T		1536	24	45
E		1	8	9
E		7.5	16	61
E		1536	41	27
E		24	24	58
E		[24	11	32][d]
E		[24	7	24][d]
T	0	24	16	52
T	0.5	24	26	52
T	1.0	24	19	56
T	1.5	24	20	54
T	3	24	11	33
T	5	24	26	41
E	0	24	23	55
E	0.4	24	34	47
E	.8		37	54
E	1.0	24	39	41
E	1.5		42	35
E	3.0	24	49	29

[a] Variables not listed as a column in the Table are marked in brackets with footnotes. [b] "T" refers to the theoretical amount of isobutene calculated on the basis of amylsodium effecting di-substitution in isobutene. "E" refers to an excess of isobutene, in these cases 3.2 moles of isobutene to 1 of amylsodium. [c] Same as the preceding experiment except that the isobutene was passed as a gas over the surface of the reaction mixture. [d] The conditions in these two experiments were the same as the one preceding, except that the temperatures were 95 and 145° respectively instead of 25°.

C-3. Even this last might have come from attack at C-3, followed by allylic shifts and intramolecular metalations to give a salt of a hydrocarbon acid of higher acidity. By such steps 3-methyl-1-butene, $CH_3CH(CH=CH_2)CH_3$, acted as should 2-methyl-1-butene, $CH_2=CH(C_2H_5)CH_3$. All β,γ-unsaturated acids mentioned in this paper are new except (1) those from isobutene and pentene-1 which were obtained[5,8] by this same

TABLE IV

BRANCHED CHAIN OLEFINS THAT WERE METALATED AND HYDROGEN ATOM (UNDERSCORED) WHICH IS REPLACED BY SODIUM

Olefin	Structure	Acid.[b] %
3-Methylbutene-1	$CH_2=CHCH(C\underline{H_3})CH_3$[a]	22
3,3-Dimethylbutene-1	$C\underline{H_2}=CHC(CH_3)_3$	61
2,3-Dimethylbutene-1	$CH_2=C(C\underline{H_3})CH(CH_3)_2$	59
2,3,3-Trimethylbutene-1	$CH_2=C(C\underline{H_3})C(CH_3)_3$	57
2-Ethylbutene-1	$CH_2=C(C\underline{H_2}CH_3)C_2H_5$	28

[a] This compound acts as if it were $CH_3CH_2C(C\underline{H_3})=CH_2$. [b] Acid derived by carbonation.

reaction but are characterized more extensively in this paper, (2) acrylic acid which is obtained from vinylsodium and (3) one of the acids from octene-1. The process is, therefore, important for obtaining these little known compounds.

Metalation of Diallyl and Piperylene.—Diallyl was readily metalated and, after carbonation, yielded three monocarboxylic acids with properties consistent for CH_2=$CHCH(CO_2H)CH_2CH$=CH_2, CH_2=$CHCH_2CH_2CH$=$CHCO_2H$, and CH_3-CH=$CHCH_2CH$=$CHCO_2H$. The double bond shift found was surprisingly, at the far end from the carboxyl group. A dicarboxylic acid with properties consistent for HO_2CCH=$CHCH_2CH$=$CHCH_2CO_2H$, showed that two sodium ions were as far apart as possible, as for butene.[5] Other dicarboxylic acids and some polymer were present, the latter consistent with cross-linking when rubber is metalated.[10]

In contrast to butadiene and isoprene,[11] piperylene is metalated. The carbonation products are complex. One appears to be CH_2=$CHCH$=$CHCH_2Na$, since the corresponding acid was found. The same compound forms when 1,4-pentadiene reacts with phenylsodium, as reported in a paper[12] published since completion of our work.

Polymerization.—Two tests were used. The first was a direct one with the metalated olefin and sodium isopropoxide. Only slight activity was found from the mono-olefins and the polymers had low viscosities. The former failures[13] with two catalysts—sodium isopropoxide/butenylsodium and sodium 1-phenyl ethoxide/allylsodium—which were inactive until correctly proportioned,[14] necessitated a range of alkoxide concentration. Catalytic activity was thereby found for sodium isopropoxide with two metalated hydrocarbons, isobutene and diallyl, where previous[13] tests failed. These results, and those with benzylsodium,[15] are characteristic of some Alfin reagents.

The second method of testing[15] was by addition of hydrocarbon to the active catalyst, sodium isopropoxide/allylsodium. This test is positive if replacement of the allyl component occurs, although the hydrocarbon might also alter polymerization, as by paralleling the modifier[16] action in emulsion processes. That branched chain olefins had no effect in such tests was not surprising, since allylsodium should not metalate them. Piperylene caused a marked lowering of gel. The action was definite when piperylene was added one-half hour before a test; hence metalation might occur.

Mechanism of the Metalations.—A common idea for explaining the action of alkali metal

(10) Morton and Ramsden, THIS JOURNAL, **70**, 3132 (1948).

(11) Morton, Brown and Magat, ibid., **69**, 161 (1947).

(12) Paul and Tchelitcheff, Bull. soc. chim., 108 (1948).

(13) Morton, Magat and Letsinger, THIS JOURNAL, **69**, 950 (1947).

(14) Morton, Welcher, Collins, Penner and Coombs, ibid., **71**, 481 (1949).

(15) Morton and Little, ibid., **71**, 487 (1949).

(16) Smith, ibid., **68**, 2059 (1946).

salts is that the anion is responsible for all activity. Such a simple concept is inconsistent with the physical and chemical behavior of these reagents. For example, they are insoluble aggregates of ions. Polar bonds must, therefore, break before or as new anions form. An anion should not independently break these bonds, and emerge from the aggregate to remove a proton from a hydrocarbon and form a new ion. An alternative concept of an ion pair[17] considers the anion inactive until the attraction of the cation is lessened.[18] Coördination[19] within the aggregate (the sodium ion in sodium chloride has a coördination number of six) plays a part. Half of the aggregate is sodium chloride, where the coördination number is six; that in amylsodium must be four or six. At the surface the full value is unsatisfied. There reaction begins by adsorption whereupon a pair of electrons from the olefin forms a coördination bond with the sodium ion. "A," in Fig. 1, shows a section with the olefin polarized and protons correspondingly activated. A shift of the electrons—see arrows in "B"—gives one product; another shift, "C," gives another, which exists in two allylic forms. Activation by adsorption on one ion, but with salt formation at a second sodium (not shown) accounts also for the third product.
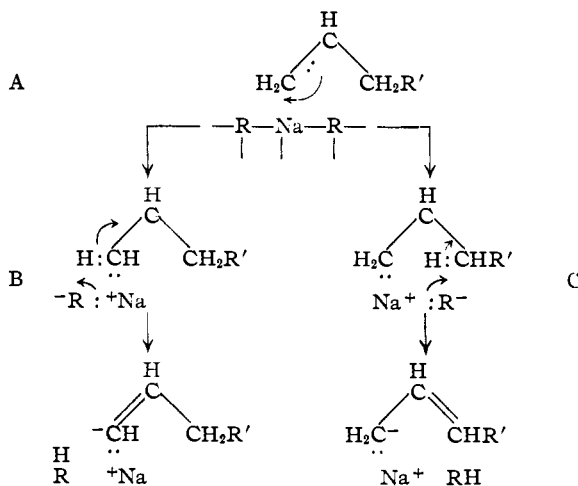

Fig. 1.—Diagram that shows one way by which an olefin is activated by adsorption at the sodium ion of an ionic aggregate and then changed to an ion by reaction with either of two adjacent anions.

This picture accounts for (1) the effects by alkoxides since the composition of the aggregate must affect spacing and coördination and (2)

(17) Morton, Chem. Reviews, **35**, 1 (1944); THIS JOURNAL, **69**, 969 (1947).

(18) The steps were described at a symposium on organometallic compounds during the Spring Meeting of the American Chemical Society, Chicago, 1948.

(19) That organic compounds form coördination complexes with alkali metal ions has been demonstrated by Sidgwick and Plant, J. Chem. Soc., **127**, 209 (1925); Sidgwick and Brewer, ibid., 2379; Brady and Baker, ibid., 952 (1932).

the increased metalation at the terminal methylene group in hexene-1 at the beginning since the initial attachment occurs there. The proposal also provides for (a) a gradual shift of the attractive force of cation from the old to a new anion; (b) sufficient activation for an olefin to undergo a reasonably rapid acid-salt interchange; (c) the directive influence in the metalation of aromatic systems and (d) differences in types of polymerization caused by seemingly unrelated ions in the vicinity.

Acknowledgments.—The authors are greatly indebted ·to Christiana Clapp and Jeanne Kilduff, for valuable assistance in preparation, purification and identification of many compounds and for measurements of the properties of the polymers. They are also indebted to S. M. Nagy, Philip H. Towle and Louise W. Spencer for elemental analyses.

Experimental

Experiments on ethylene, two straight chain olefins and toluene are by F. D. M., octene by R. D. C., isobutene by A. A. L., branched chain olefins by S. E. P., diallyl by H. E. R. and V. B. B., and piperylene and the other dienes by E. L. L. and R. L.\L.

General Methods.—Sodium sand was made by stirring the metal in olefin-free decane at 110–130° for one minute at 10,000 r. p. m.[5] under nitrogen. After the liquid was cooled and siphoned off with nitrogen pressure, the sand was washed several times by dry pentane.

Amyl chloride was made from technical n-pentanol and thionyl chloride. The product was distilled, stirred twice with 5% of its volume of concentrated sulfuric acid, washed, dried and fractionated. Subsequently small amounts of alcohol were found in this chloride so that the amylsodium therefrom contained pentoxide.

Amylsodium was prepared by dropwise addition at −10° of 0.5 mole of amyl chloride on 1 g. atom of the sodium in pentane in the 1-l. flask with high-speed stirring. More than this "standard" quantity was made in the same proportion. The yield of amylsodium, around 80%, was used as the basis for subsequent calculations.

Any alkoxide was made by addition of an alcohol to the amylsodium about an hour after all amyl chloride was added. Usually 0.20 mole of alcohol per gram atom of sodium was used.

The olefin was then added as specified or in sufficient excess, usually 20% if a liquid, to more than consume the amylsodium. The fraction was completed in a few hours for all but the branched chain olefins but the common practice was to let the mixture stand until the next day before carbonation. For longer times, the mixture was transferred to a nitrogen-filled bottle by siphon under nitrogen pressure. The bottle was then sealed with a cork covered with glyptal resin cement. Reaction mixtures were thus kept for months without noticeable loss, except for amylsodium which slowly decomposed (blue to brown color) as expected from the study[20] of its pyrolysis.

For carbonations the suspensions and the pentane rinses were forced onto about 20-fold excess of solid carbon dioxide. The mixture then stood overnight. Alcohol was later used to consume small particles of sodium and water was added to dissolve the salts.

The aqueous layer was shaken with petroleum ether or ether to remove neutral material. It was then acidified, usually with sulfuric acid, and extracted two or three times with petroleum ether to remove monocarboxylic acids. The aqueous layer was next saturated with salt and extracted with ethyl ether to remove dicarboxylic acids. Rarely did this method fail to make a good separation.

The ether fraction usually contained some high-boiling or viscous material, which was probably a polymerization product, judged by the comparatively high neutralization equivalent. The monocarboxylic acids could be separated when necessary by a preliminary stripping from the polymer acids at reduced pressure.

The monocarboxylic acids were isolated by fractionation or by multiple fractional extraction. For the former, a column of 50 plates with jacket temperature control in three sections were used. Often the ester was made from the silver salt and methyl iodide, and fractionated in order to test for allylic isomerism during fractionation, but the results were unchanged. For the second method of separation, two variations were examined. One, described by Hunter and Nash,[21] uses the differences in the acidity of the acids, and was preferred over the buffered extraction described by Craig,[22] because it was adaptable to large quantities and needed no adjustment of pH.

Identification of the Acids.—The carboxyl group was always located by hydrogenation to a saturated acid and comparison of suitable derivatives. The position of the double bond was judged to be β, γ- if no molecular exaltation of refractivity was found and if the iodine absorption was appreciable.[23] α,β-Acids (0.1 g.) consume less than 5% iodine during one hour at 25° in a saturated bicarbonate solution with the theoretical amount of 0.1 N iodine–potassium iodide. β,γ-Acids consume varying amounts in forming β-iodolactones. If very fast, the addition of 5–10 ml. of carbon tetrachloride to dissolve the β-iodolactone is helpful.

As a rule branched β,γ-unsaturated acids reacted slower than the straight chain one, the difference being large enough to provide differentiation between two types by a reaction-time curve. For instance, 2-propyl-3-butenoic acid showed 62% absorption in one hour and 92% in six hours. A straight chain compound, 3-hexenoic, showed about 82% in one hour, 94% in two hours.

Also the β,γ-unsaturated acids were treated with strong alkali in order to rearrange them to the α,β-acids which in turn were similarly characterized by amide or anilide derivatives and were hydrogenated to known acid identical with those from the original β,γ-products. 2-Ethyl-3-butenoic acid was exceptional, however, in that it formed another β,γ-unsaturated acid rather than the α,β-one.

Ozonization also located the double bond. Usually this reaction was in ethyl acetate at −30°, and the ozonide was hydrogenated at 30 lb. pressure over palladium on calcium carbonate. The aldehyde was isolated as the methone derivative or its anhydride. The methone or 2,4-dinitrophenylhydrazone was used for the ketones. Mixed melting points with authentic derivatives were made in nearly every case. Only minor differences from recorded values were usually found but the dimethone and dimethone anhydride from butyraldehyde melted 134.9–135.8° and 136.2–137°, respectively, where the recorded[24a] values are 133.8 to 142° and 141°. Also the dimethone of acetaldehyde melted at 141.4–142.4° (recorded,[24b] 139°) and the corresponding anhydride was 171.5–172.7° (recorded 173–174°). The hitherto unknown dimethone anhydride of valeraldehyde melted 117.3–118.3° and the corresponding compound from the methyl ester of glyoxylic acid melted 202.5–203.5°. *Anal.* Calcd. for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.59; H, 7.32.

Neutralization equivalents or saponification equivalents were always made and accorded with those expected. Absorption of hydrogen over Adams platinum catalyst was in all cases in essential agreement with that expected.

Infrared absorptions were also made of the esters of the β,γ-products from the straight chain alkenes and the bands for the olefin system found in the normal position, that is, free from conjugation with the carboxyl group. These values are not recorded.

(20) Morton and Newey, THIS JOURNAL, **64**, 2247 (1942).

(21) Hunter and Nash, *Ind. Eng. Chem.*, **27**, 837 (1935).

(22) Craig and co-workers, *J. Biol. Chem.*, **161**, 321 (1935).

(23) Linstead and May, *J. Chem. Soc.*, 2565 (1927).

(24) (a) Kao, *Science Repts. Natl. Tsing Hua Uni.*, Ser. A-1, 187 (1932); Klein and Linser, *Mikrochemie, Pregl. Festschrift*, 226 (1929);

(b) Vorländer, *Z. anal. Chem.*, **77**, 241 (1929).

Anilides, p-toluidides, naphthalides and similar derivatives were made (a) by addition of excess amino to the acid chloride dissolved in ether or benzene or (b) (always for β,γ-unsaturated compounds) by use of a Grignard reagent.[25] For the latter, the amine was added to standard ethylmagnesium bromide solution after which an ether solution of the ester was added. After ten minutes of reflux, dilute hydrochloric acid was added and the organic layer evaporated at reduced pressure. The crude amide was then crystallized from hexane, cyclohexane, alcohol or mixtures of these solvents.

Hydrocarbon Reagents.—The hydrocarbons were usually purified commercial materials or were synthesized. Characteristic colors were obtained when each was metalated. Ethylene (98% pure, Matheson Chemical Company) was passed through a 4 foot by 1 inch column of beads countercurrent to concentrated sulfuric acid, and then through an equal volume of solid potassium hydroxide, before being passed into the mixture of amylsodium-sodium isopropoxide (each 0.6 mole). The color of the suspension became black.

Pentene-1 (Phillips Petroleum Company, technical grade), after fractionation in a 50-plate column, boiled at 29.6–30.0° and had n^{25}D 1.3685 (see ref. 26). Metalated pentene-1 is a yellow suspension. The hexene-1 was Phillips Petroleum Company research grade, guaranteed 99.2 to 99.10 pure, or its equivalent prepared from hexanol-1 with careful fractionation through a 50-plate column (b. p. 63.6°, n^{20}D 1.3879, and $d^{20}{}_4$ 0.6737). The metalated suspension has a metallic gray color.

Octene-1 was obtained from the Connecticut Hard Rubber Company (now the Humphrey–Wilkinson Company, Inc., New Haven) and was carefully fractionated. The isobutene was Phillips Petroleum Company technical grade, and was added either as the condensed liquid or as a gas. It yielded a purple-colored suspension.

3-Methyl-1-butene was prepared[27] from 3-methyl-1-butanol and yielded a brown-colored suspension. 2,3-Dimethyl-1-butene was prepared[28] from pinacolyl alcohol[29] over hot aluminum phosphate on pumice instead of alumina.[28] When metalated the color was purple. 3,3-Dimethyl-1-butene also came from the pinacolyl alcohol and gave a black-colored suspension. 2,3,3-Trimethyl-1-butene was prepared from 2,3,3-trimethyl-2-butanol by dehydration[30] over iodine or, better over alumina, at 300–310°. 3-Ethyl-1-butene—Connecticut Hard Rubber Company—was dried over calcium chloride and fractionated.[31] The color was brown. Diallyl was prepared from allyl chloride and magnesium.[32] The color of the suspension was brick red. Commercial piperylene (Phillips Petroleum Company) was refluxed with iodine and fractionated. The product (n^{20}D 1.4309) is 85–90% trans.[33]

Carboxylic Acid from Monoölefins.—The structures of the hitherto unknown acids listed below have been proven by the methods described but by request of the Editor, the constants of known compounds used for identifying the products and references to such information are in general omitted. All acids are named, as far as possible, as derivatives of the longest chain that contains an unsaturated system with a carboxyl group at one end of the chain.

The β,γ-**Unsaturated Acids.**—2-Ethyl-3-butenoic acid from 1-pentene had b. p. 67° (3 mm.), $d^{25}{}_4$ 0.9437; n^{25}D

(25) Hardy. *J. Chem. Soc.*, 398 (1936).

(26) Tables of Physical and Thermodynamic Properties of Hydrocarbons issued by American Petroleum Institute Research Project 44, U. S. Bureau of Standards (1945).

(27) Norris and Reuter, THIS JOURNAL, **49**, 2629 (1927).

(28) Brooks, Howard and Crefton, *J. Research U. S. Bur. of Standards*, **24**, 33 (1940).

(29) Adkins, "Reactions of Hydrogen." University of Wisconsin Press, Madison, Wis., 1937, p. 50.

(30) Edgar and Calingaert, THIS JOURNAL, **51**, 1486 (1929).

(31) Huntress and Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons. New York. N. Y., 1941.

(32) Cortese. THIS JOURNAL, **51**, 2266 (1929).

(33) Frank, Emmich and Johnson. *ibid.*, **69**, 2313 (1947).

1.4265; M_d 31.02; calcd., 30.98. Its methyl ester had b. p. 50–51° (34 mm.) ; $d^{25}{}_4$ 0.8957, n^{25}D 1.4132; M_d obs., 35.66; calcd., 35.71. Formaldehyde was obtained by ozonization. The p-toluide melted at 86.7–87.5°. *Anal.* Calcd. for $C_{13}H_{17}ON$: C, 76.80; H, 8.43; N, 6.99. Found: C, 76.51; H, 8.31; N, 1.17. The anilide melted at 93.5–94.3°. *Anal.* Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99; N, 7.40. Found: C, 75.89; H, 7.99; N, 7.10. The p-bromanilide melted at 113.7–115.2°. *Anal.* Calcd. for $C_{12}H_{14}ONBr$: C, 53.75; H, 5.26; N, 5.22. Found: C, 53.65; H, 5.19; N, 5.35.

3-Hexenoic acid from 1-pentene melted at -21 to $-20°$, a value nearer to $-18°$[34] than the other value 4–5°,[35] recorded in the literature. The methyl ester boiled 67–68° (34 mm.); $d^{25}{}_4$ 0.9132; n^{25}D 1.4240; M_d 35.71; calcd., 35.82; b. p. 74° (3 mm.); $d^{25}{}_4$ 0.9650; n^{25}D 1.4375; M_d 31.01; calcd., 30.98. Ozonization gave acetaldehyde probably by decomposition of an aldehydo acid. The p-toluide melted 53.4–54.4° again lower than a recorded value 95–96°, an understandable fact since several of the compounds in this series seem to exist in two forms. *Anal.* Calcd. for $C_{13}H_{17}ON$: C, 76.80; H, 8.43; N, 6.89. Found: C, 76.76; H, 8.47; N, 6.62. The β-naphthalide melted 87.4–88.1°. *Anal.* Calcd. for $C_{16}H_{17}ON$: C, 80.30; H, 7.16; N, 5.85. Found: C, 79.97; H, 7.11; N, 5.78. The p-bromoanilide had an initial melting point at 90–92°. Repeated crystallizations caused a wider range, probably from the seeming existence of two forms, so that the final value was from 90–96°. *Anal.* Calcd. for $C_{12}H_{14}NOBr$: C, 53.75; H, 5.26; N, 5.22. Found: C, 53.82; H, 5.18; N, 5.26.

2-Propyl-3-butenoic acid from 1-hexene had b. p. 62.5° (1 mm.); $d^{25}{}_4$ 0.9297; n^{25}D 1.4292; M_d 35.55; calcd. 35.60. Ozonolysis gave formaldehyde. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.45. Found: C, 65.86; H, 9.70. The methyl ester boiled 60–61° (25 mm.); $d^{25}{}_4$ 0.8904; n^{25}D 1.4181; M_d, 40.25; calcd., 40.33. The anilide melted 67.8–68.8°. *Anal.* Calcd. for $C_{13}H_{17}ON$: C, 76.80; H, 8.43; N, 6.89. Found: C, 76.61; H, 8.56; N, 6.87. The p-toluide melted 96.2–97.2°. *Anal.* Calcd. for $C_{14}H_{19}ON$: C, 77.37; H, 8.82; N, 6.45. Found: C, 77.26; H, 8.93; N, 6.43. The p-bromophenacyl ester melted 29.2–29.7°. *Anal.* Calcd. for $C_{15}H_{17}O_3Br$: C, 55.38; H, 5.27; Br, 24.58. Found: C, 55.19; H, 5.29; Br, 24.60.

3-Heptenoic acid from 1-hexene boiled at 69.9° (1 mm.); $d^{25}{}_4$ 0.9471; n^{25}D 1.4402; M_d 35.66; calcd., 35.60. *Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.43. Found: C, 65.67; H, 9.49. The methyl ester boiled 78–79° (25 mm.); $d^{25}{}_4$ 0.9047; n^{25}D 1.4285; M_d 40.48; calcd., 40.33. Ozonization gave butyraldehyde. The usual derivatives are difficult to prepare in the case of straight chain β,γ-unsaturated acids. The anilide, p-toluide, morpholide and benzylamide derivatives were oils and the p-bromoanilide melted over a range after repeated crystallizations. The β-naphthalide melted 77.5–78.5°. *Anal.* Calcd. for $C_{17}H_{19}ON$: C, 80.65; H, 7.56; N, 5.53. Found: C, 80.62; H, 7.62; N, 5.59. The p-bromophenacyl ester melted 70–71°. *Anal.* Calcd. for $C_{15}H_{17}O_3Br$: C, 55.38; H, 5.27; Br, 24.58. Found: C, 55.25; H, 5.24; Br, 24.74.

2-Amyl-3-butenoic acid from 1-octene boiled at 90° (1 mm.); $d^{20}{}_4$ 0.9183; n^{25}D 1.4387; M_d 44.92; calcd., 44.83. Ozonization gave heptaldehyde (from decomposition of an aldehydo acid) and formaldehyde. *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.2: H, 10.3. Found: C, 69.3; H, 10.47. M. p. of β-naphthalide 84.8–85.6°. *Anal.* Calcd. for $C_{19}H_{23}ON$: C, 81.1; H, 8.2; N, 5.0. Found: C, 81.2; H, 8.2; N, 5.2. M. p. of p-bromophenacyl ester 44.3–45.1°. *Anal.* Calcd. for $C_{17}H_{21}O_3Br$: C, 57.8; H, 6.0; Br, 22.6. Found: C, 58.0; H, 6.0; Br, 22.7.

3-Nonenoic acid[36] from 1-octene boiled at 106° (1 mm.); $d^{20}{}_4$ 0.9254; n^{25}D 1.4454; M_d 45.18; calcd., 44.83.

(34) Fittig and Delisle, *Ann.*, **255**, 61 (1889).

(35) Ecott and Linstead, *J. Chem. Soc.*, 2153 (1929).

(36) Zaar, *Ber. Schimel.* 297 (1929); *Chem. Centr.*, **101**, I, 363 (1930).

Ozonization gave acetaldehyde and caproaldehyde. The β-naphthalide melted 70.3–71.3°. *Anal.* Calcd. for C_{19}-$H_{22}ON$: C, 81.1; H, 8.2; N, 5.0. Found: C, 81.2; H, 8.2; N, 5.2. The *p*-bromophenacyl ester melted 68.2–69.3°. *Anal.* Calcd. for $C_{17}H_{21}O_3Br$: C, 57.8; H, 6.0; Br, 22.6. Found: C, 57.7; H, 6.0; Br, 22.6.

3-Methyl-3-butenoic acid from isobutene boiled at 95.5–96.6° (30 mm.) and melted at 17.5–19.5°; d^{20}_4 0.9873; n^{20}D 1.4328; M_d 26.23; calcd. 26.36. The *p*-bromophenacyl ester melted 44–44.5° (previous[3] value 42.0–42.3°).

3-Methylenepentandioic-1,5 acid from isobutene becomes contaminated with the anhydride of 3-methylglutaconic acid when melted or distilled. The anhydride is conveniently precipitated by addition of petroleum ether to an ether solution of the mixture (obtained after distillation). The mother liquor is then evaporated and the waxy residue crystallized from carbon tetrachloride or precipitated from benzene solution by addition of petroleum ether. The pure diacid thus obtained contrasts with the anhydride in that it gives no purple color with ferric chloride, is not substituted by bromine and yields formaldehyde when ozonized. It melted at 50–60°. *Anal.* Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.59. Found: C, 49.43; H, 5.57. The bis-bromophenacyl ester melted 129.2–130.1°. *Anal.* Calcd. for $C_{22}H_{18}O_6Br_2$: C, 49.09; H, 3.37; Br, 29.50. Found: C, 49.10; H, 3.48; Br, 29.80.

3-Ethyl-3-butenoic acid from 3-methyl-1-butene boiled at 63° (2 mm.); m. p. −5 to −3°; d^{25}_4 0.9643; n^{26}D 1.4361; M_d 30.94; calcd., 30.98. Ozonization gave formaldehyde. *Anal.* Calcd. for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.99; H, 9.06. The *p*-toluide melted at 83.0–84.0°. *Anal.* Calcd. for $C_{13}H_{17}ON$: N, 6.89. Found: N, 6.91.

3-Methyl-3-pentenoic acid was derived by rearrangement from 3-ethyl-3-butenoic acid under the influence of 25% sodium hydroxide for thirty-nine hours. It was the only failure to obtain an α,β-unsaturated acid by such treatment. The rearrangement was incomplete and the second β,γ-acid was recovered by fractionation; b. p. 71° (3 mm.), n^{25}D 1.4520; iodine absorption, 60.5% in one hour.

3-Isopropyl-3-butenoic acid from 2,3-dimethyl-1-butene boiled at 80° (2 mm.); d^{25}_4 0.9480; n^{25}D 1.4380; M_d 35.49; calcd., 35.60. Ozonization gave formaldehyde. A 1-g. sample in a test-tube crystallized with an audible click when cooled in liquid nitrogen, then melted when placed in an acetone-bath at −72°. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.36; H, 9.92. The anilide melted at 63.5–64.5°. *Anal.* Calcd. for $C_{13}H_{17}ON$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.65; H, 8.61; N, 6.89. The *p*-bromophenacyl ester melted at 32.0–32.6°. *Anal.* Calcd. for $C_{15}H_{17}O_3$-Br: C, 55.38; H, 5.27; Br, 24.58. Found: C, 55.30; H, 5.29; Br. 24.66.

Hydrogenation of this acid yielded 3,4-dimethylpentanoic acid; b. p. 75° (2 mm.); d^{25}_4 0.9239; n^{25}D 1.4235; M_d 35.92; calcd. 36.06. In the absence of unquestioned characterization in the literature, this product was shown to be identical with one prepared by an independent synthesis. Hydrogen bromide was passed at 0° for one hour into 24 g. (0.286 mole) of 2,3-dimethyl-1-butene with di-*t*-butyldiperphthalate contained in a pressure bottle. The bottle was capped, shaken ten hours, saturated again at 0° and again shaken one and one-half hours. After being filtered, the yellow liquid was distilled (130–170°) to give 36 g. of a mixture of bromides, of which 62% was tertiary, as shown by hydrolysis.[37] The primary bromide (6 g.) boiled at 142–146° (764 mm.). This product, by Grignard carbonation, yielded 2.4 g. of acid, b. p. 75° (2 mm.) and $n^{24.3}$D 1.4242. The anilide melted at 110.3–111.2° and was identical (mixed melting points) with the anilides derived from the hydrogenated β,γ- and α,β-unsaturated acids.

3-*t*-Butyl-3-butenoic acid from 2,3,3-trimethyl-1-bu-

tene boiled at 70° (1 mm.); m. p. 26.5–27.5°; d^{25}_4 0.9412; n^{25}D 1.4440; M_d 40.16; calcd., 40.21. Ozonization gave formaldehyde. *Anal.* Calcd. for $C_8H_{14}O_2$: C, 65.57; H, 9.92. Found: C, 67.46; H, 9.93. The anilide melted at 88.6–89.6°. *Anal.* Calcd. for $C_{14}H_{19}ON$: N, 6.45. Found: N, 6.47. A twenty-five minute reflux of the acid with 55% sulfuric acid gave, after dilution with ice, extraction with ether and evaporation of the washed and dried extract, 75% of crude lactone, which was crystallized twice from hexane as hard colorless cubes, m. p. 100–100.7° (recorded[38] for *t*-butylbutyrolactone, 99–100°).

2-Methyl-3-ethyl-3-butenoic acid from 2-ethyl-1-butene boiled at 75° (3 mm.); d^{25}_4 0.9437; n^{25}D 1.4372; M_d 35.61; calcd. 35.60. *Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 64.92; H, 9.32. Ozonalysis gave formaldehyde.

α,β-**Unsaturated Acids from Monoölefins.**—Two acids, previously known, but obtained from the mixtures produced by carbonations, were characterized by derivatives which provided adequate differentiation from the other products.

2-Propyl-2-butenoic acid, which was obtained by alkaline rearrangement from 2-propyl-3-butenoic acid, melted at 52–53°. Ozonolysis gave acetaldehyde. *Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.45. Found: C, 65.64; H, 9.44. It yielded an anilide—m. p. 63.5–64.1°. *Anal.* Calcd. for $C_{13}H_{17}ON$: C, 76.80; H, 8.43; N, 6.89. Found: C, 76.64; H, 8.37; N, 6.90. The *p*-toluide melted 83.5–84.4°. *Anal.* Calcd. for $C_{14}H_{19}ON$: C, 77.37; H, 8.82; N, 6.45. Found: C, 77.32; H, 8.77; N, 6.46. The *p*-bromophenacyl ester melted at 68.4–69.3°. *Anal.* Calcd. for $C_{15}H_{17}O_3Br$: C, 55.38; H, 5.27; Br, 24.58. Found: C, 55.09; H, 5.26; Br, 24.73.

2-Heptenoic acid, obtained either by alkaline rearrangement from 3-heptenoic acid or directly from carbonation of metalated 1-hexene, melted at −12 to −11°. Its *p*-toluidide, prepared either from the ester or acid, melted first at 74.5–75.5° and then from 80.0 to 88.5°. *Anal.* Calcd. for $C_{14}H_{17}ON$: C, 77.37; H, 8.82; N, 6.45. Found: C, 77.23; H, 8.82; N, 6.21. The anilide melted 74.3–75.3°. *Anal.* Calcd. for $C_{13}H_{17}ON$: C, 76.80; H, 8.43; N, 6.89. Found: C, 76.82; H, 8.45; N, 6.85. The *p*-bromanilide melted 128.7–129.3°. *Anal.* Calcd. for $C_{13}H_{16}ONBr$: C, 55.33; H, 5.72; N, 4.97; Br, 28.32. Found: C, 54.94; H, 5.74; N, 5.13; Br, 28.4. The methyl ester boiled at 85–86° (25 mm.); d^{25}_4 0.9367; n^{25}D 1.4360; M_d 39.69; calcd., 40.33. Ozonization gave valeraldehyde and the methyl ester of glyoxylic acid.

Carboxylic Acids from Diolefins.—The products from diallyl were isolated by both methods. The lowest boiling acid was the third acid obtained by fractional extraction, the second one by distillation was the first one by extraction and therefore was the strongest acid. Some black and white solid polymer acids were also obtained when the alkaline layer of the diallyl products was acidified.

2-Vinyl-4-pentenoic acid (b. p. 64–69° (3 mm.); n^{24}D 1.4689) was obtained from diallyl. After eight months it was only slightly yellowish (n^{22}D 1.4590), a fact indicative of a β,γ-unsaturated acid. Ozonization yielded formaldehyde. Hydrogenation gave 2-ethylpentanoic acid.

Hepta-2,6-dienoic acid (b. p. 76–81 (2 mm.); n^{22}D 1.4720) from diallyl polymerized after standing a few days, as expected of an α,β-unsaturated acid. Ozonization yielded formaldehyde. Hydrogenation yielded *n*-heptylic acid.

Hepta-2,5-dienoic acid (b. p. 90° (1 mm.); n^{24}D 1.4721) from diallyl became a viscous yellow liquid and eventually solid. Ozonization yielded acetaldehyde. Hydrogenation gave *n*-heptylic acid.

Octa-2,5-dien-1,8-dioic acid from diallyl melted at 190.2–194.2°. Permanganate gave oxalic acid. No maleic anhydride adduct formed. Strong alkali treatment gave another acid (m. p. 219.7–224.7). Hydrogenation yielded suberic acid.

(37) Michael and Weiner, *J. Org. Chem.*, **4**, 541 (1939).

(38) Newman and Rosher, *ibid.*, **9**, 221 (1944).

TABLE V

PRODUCTS OBTAINED BY REACTIONS OF ORGANIC BROMIDES OR IODIDE WITH METALATED HYDROCARBONS

Metalated hydrocarb.	Halide (B)	Moles	Product hydrocarbon	G.	%	B. p. or m. p., °C.	$n^{20}D$	d^{20}_4	H.
Isobut.	C_2H_5Br	1.6	2-Methylpentene-1	5.9	4	61.5–63	1.3926		0.94
			2-Propylpentene-1[b]	32.5	35	161.5–118	1.4137	0.7299	0.94
Isobut.	$C_2H_4Br_2$	0.8	2,5-Dimethylhexadiene-1,5[c]	9.7	11	113–115.5	1.4310	.7518	1.99
Isobut.	$(CH_2)_3Br_2$	1.6	Methylenecyclohexane[d]	19.2	12	101.5–103.5	1.4478	.8043	.98
			2,8-Dimethylnonadiene-1,8[e,f]	18.6	7	76–76.5(18 mm.)	1.4429	.7763	1.99
Tol.[a]	$C_2H_4Br_2$	0.67	Dibenzyl[g]	135.6		51.4–52.1			
Et. benz.[a]	$C_2H_4Br_2$	0.67	Diphenylbutane[h]	65					
Oct.-1	CH_3I		3-Methyloctene-1	25		135	1.4131		
			Nonene-2	55		144	1.4202	.7342	1.04
			Hexadecadiene[i]	20		62 (1 mm.)	1.4412		1.94

[a] Toluene and ethylbenzene were metalated with twice the theoretical amount of amylsodium.[39] [b,c,d,e] The products from ozonization are respectively di-n-propyl ketone, acetonylacetone, cyclohexanone and nonadione-2,8. [f] Observed M_d 51.99; calcd., 52.05. Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.74; H. 13.21. A fraction (10.1 g.) that boiled higher [139–142° (4 mm.)] than this diene was also obtained. [g] Crude dibenzyl (160.2 g.) was collected at 130–170° (13 mm.). The evolved ethylene was recovered as the ethylene dibromide (121.6 g.), nearly equal to the theoretical (125 g.). [h] The crude mixture boiled 70–140° (3 mm.). The recovered ethylene dibromide accounted for 71.5% of the amylsodium originally used. [i] Position of double bonds not determined. [j] For comparisons with recorded values, see references 31, 40 and 41.

Hexa-3,5-dienoic acid from piperylene boiled 83–90° (10 mm.), $n^{20}D$ 1.4650. Ozonization gave formaldehyde. The p-bromophenacyl ester melted at 94–95°. Anal. Calcd. for $C_{14}H_{15}O_3Br$: C, 54.1; H, 4.5; Br, 25.8. Found: C, 54.0; H, 4.40; Br, 25.85. The maleic anhydride adduct melted at 146–148° (uncor.); neut. equiv., 71. Anal. Calcd. for $C_{10}H_{10}O_5$: C, 57.3; H, 4.81. Found: C, 57.6; H, 4.84.

The acid slowly resinified. Alkali yielded sorbic acid; hydrogenation gave caproic acid.

Reactions of Organosodium Compounds with Alkyl Halides.—The halides were added dropwise to the organosodium reagent. Significant results are recorded in Table V.

Reaction of Vinylsodium.—A stock suspension of vinylsodium was prepared, containing approximately 1.2 moles each of vinylsodium and sodium isopropoxide, and free from amylsodium. Hexene-1, benzene, toluene and fluorene were stirred, each with 0.11 mole of vinylsodium per 20% mole excess hydrocarbon in 100 ml. of pentane. After carbonation (see Table I) the acids were determined by fractionation, neutralization equivalents and/or crystallization.

Unsymmetrical diphenylethylene[42] (40 g.) was added dropwise over one hour to 0.23 mole of the vinylsodium suspension. After six hours of stirring and eighteen hours of standing, carbonation yielded 5.5 g. of acrylic acid and 5 g. of the usual viscous residue obtained from vinylsodium alone. Thirty-seven grams (92.5%) of the diphenylethylene was recovered.

Polymerization by Metalated Olefins.—The metalated olefins prepared for the carbonation studies were tested frequently for polymerization activity, as described before, on 20 ml. of butadiene in 180 ml. of pentane. Typical results are given in Table VII.

Polymerization by Metalated Dienes.—Amylsodium with one equivalent of sodium isopropoxide reacted with 10% excess cis-piperylene (maleic anhydride purification), trans (85–90%) piperylene, isoprene,[43] diallyl and 2-methyl-1,3-pentadiene. Each (20 ml.) was then tested on 30 ml. of butadiene in 190 ml. of pentane for one hour. Typical conversions are respectively 13, 10, 4, 100 and 77%. The corresponding intrinsic viscosities were 5.6, 6.0, 1.1, 12.7 and 5, and the gels were 17, 47, 17, 60 to

(39) Morton, Little and Strong, THIS JOURNAL, 65, 1339 (1943).

(40) Egloff, "Physical Constants of Hydrocarbons." Reinhold Publishing Co., New York, N. Y.

(41) Tuot and Delépine, Compt. rend., 211, 56 (1940).

(42) Allen and Converse, "Organic Syntheses," Coll. Vol. I, 226 (1941).

(43) Morton, Brown and Magat, THIS JOURNAL, 69, 161 (1947).

TABLE VI

COMPARATIVE POLYMERIZATION ACTIVITY OF ALKENYL-SODIUM COMPOUNDS

Olefin	Subst.[a] at $CH_2=CH-CH_3$ 1 2 3	Reag.[b] moles × 10^4	Conv.[c] %	Comp. act.[d]	Intr. vis.	Gel %
Propene	None	10	57[e]	114	12.8	40
1-But.[f]	3-Me.			40	6	
Isobut.	2-Me.	18	14	0.8	1.8	28
		54	55	1.1	1.1	19
3-Me.-1-but.	2-Et.	28	9	.3	2.2	21
		83	32	.4	1.4	13
2,3-Dimet.-1-but.	2-Isopro.	28	5	.2	1.6	71
		83	15	.2	1.3	57
2,3,3-Trime.-1-but.	2-t-But.	28	2	.1	1.4	38
		83	10	.1	1.0	39
2-Et.-1-but.	2-Et.-3-Me.	25	1	.04	1.9	41
		75	5	.07	2.7	55
3,3-Dime.-1-but.	3-Trime.	31	2	.06	2.2	56
		93	8	.09	1.5	61
Ethylene	......[g]	41	2	.05	.6	7
		82	2	.03	.5	17
		124	5	.04	.4	6

[a] Alkyl groups attached to the propylene system. [b] Calculated on an assumed 80% yield of amylsodium and 100% use in the olefin metalation process. This figure is probably high. [c] Conversion of 30 ml. of butadiene during one hour, except for propylene. [d] Approximation of comparative activity. Conv./moles of reag. [e] One-half hour polymerization time. [f] Data from experiments by Welcher.[21] [g] No carbon, C-3, is present. The activity on styrene[44] ((30 g.) was a little greater; 4.1 milliequivalents caused 13.4% conversion to a polymer with viscosity, 0.68.

36, 19 to 3. The fluctuation in gel came as the catalyst aged.

Influence of Unsaturated Hydrocarbons on Alfin Polymerization.—The olefins were pentene-1, 2,3-dimethylbutene-1, 3,3-dimethylbutene-1, 3-methylbutene-1, and 2-ethylhexene-1 in a little more than equivalent amount necessary to react with the allylsodium of the catalyst. The olefin was allowed to stand with the catalyst for at least twelve days and often as much as forty-eight days. No change whatever in polymerization could be observed,

(44) The authors are greatly indebted to E. Grovenstein for this polymerization.

although in some cases the color of the catalyst suspension changed.

The effect of piperylene (80–85% *trans*) on 20 ml. of active catalyst per 30 ml. of butadiene is shown in Table VII for a 2-pentoxide/allylsodium and an isopropoxide/allylsodium catalyst. The polymerization time was 30 minutes and the alkoxide to allylsodium ratio was 1 to 1.

Table VIII records similar results for several dienes.

TABLE VII

INFLUENCE OF PIPERYLENE ON THE POLYMERIZATION OF BUTADIENE BY ALFIN CATALYSTS

Catalyst	Piperylene, ml.	Contact[a] time, min.	Conversion, %	Gel %	Intrin. visc.
P₂P	0		52	65	6.6
	1	2	48	47	7.6
	5	2	41	0	6.3
	10	2	36	0	6.9
	10	5	69	0	6.9
	20	5	60	0	6.7
PP	1.3	90	91	11	14.0
	5	60	36	0	13.5

[a] Contact time of piperylene with catalyst before addition of butadiene.

TABLE VIII

EFFECT OF DIENES ON POLYMERIZATION

Catalyst[a]	Dienes[b]	Moles of diene	React. time, min.	Poly. time, min.	Conversion, %	Intrin. viscosity	Gel, %
PP No. 1	0	0	0	90	100	16.9	96
PP No. 1	Pip.	0.02	30	90	96	14.2	18
PP No. 1	Iso.	0.12	30	90	100	11.5	13
PP No. 2	0	0	0	60	100	15.4	44
PP No. 2	Pip.	0.02	0	60	100	20.4	28
PP No. 2	Pip.	.01	30	60	100	11.5	0
PP No. 2	Pip.	.02	30	60	100	8.5	0
PP No. 2	Iso.	.12	0	60	100	11.4	4.9
PP No. 2	Mep.	.05	30	60	100	17	20
Benz.	0	0	0	60	63	3.9	38
Benz.	Pip.	.02	30	60	63	7.5	0

[a] PP no. 1 and PP no. 2 are different catalysts, one of which caused the formation of much gel. Benz. catalyst means sodium isopropoxide benzylsodium. [b] Pip. refers to piperylene (80–85% *trans*), iso to isoprene, and Mep. to methyl-1,3-pentadiene, a mixture of 85% 2-methyl and 15% 4-methyl.

Summary

Ethylene and straight and branched chain 1-alkenes are metalated on the methylene or methyl group next to a double bond, if present, otherwise on a vinyl carbon. If only one hydrogen is on the adjacent carbon, rearrangement or other changes occur. Allyl isomerism of metalated straight chain olefins occurs and three carbonated products form, but branched chain olefins usually form only one. Isobutene forms two. Carbonated and Wurtz products are possible.

Diallyl and piperylene are metalated. Carbonation yields at least four acids from diallyl and one from piperylene.

The metalated olefins and piperylene make poor Alfin catalysts, but metalated diallyl is fair. Olefins do not affect a good Alfin catalyst but dienes may possibly do so by reacting with the catalyst.

## Antispasmodics. VI.[1] Additional Substituted Beta Amino Ketones

BY J. J. DENTON, H. P. SCHEDL, W. B. NEIER AND MARY BROOKFIELD

In paper I[2] of this series we attempted to correlate the structures of various β-aminoethyl aromatic ketones with their antispasmodic activities. Because of the activity of some of these ketones, we became interested in extending our series, studying principally (a) more complex amino groups, and (b) more complex aromatic nuclei.

The majority of the ketones reported in this paper were prepared by the Mannich reaction, which, in most of the cases, was carried out by the method of Winstein.[3] By this method acetophenone, paraformaldehyde, and *dl*-iso-1,2-diphenyl-2-aminoethanol hydrochloride in the molar ratio of 1:1.5:1 interacted to give a good yield of β-[*dl*-iso-(1,2-diphenyl-2-hydroxyethylamino)] - propiophenone hydrochloride (II). Under the same conditions, the same starting materials in the molar ra-

tio of 1:3:2 gave β-[3-(4,5-diphenyloxazolidyl)]-propiophenone hydrochloride (III).

Compound III, less soluble than II, crystallized directly from the reaction mixture. Neutralization of an aqueous solution of III gave a base with one less carbon atom and identical with the base from II. That the carbon atom was lost as formaldehyde was shown by the formation of a suitable derivative.

$$C_6H_5COCH_2CH_2NHCH(C_6H_5)CHOH(C_6H_5) \cdot HCl$$
II
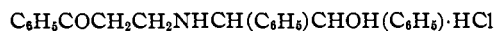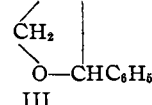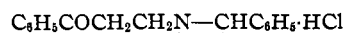
$$C_6H_5COCH_2CH_2N\text{—}CHC_6H_5 \cdot HCl$$
$$CH_2$$
$$O\text{—}CHC_6H_5$$
III

Oxazolidine formation by the ring closure of a 2-amino alcohol with an aldehyde has recently been reported by Heinzelman.[4] Their products,

(1) For paper V of this series see THIS JOURNAL, 72, 3279 (1950).

(2) Denton, Turner, Neier, Lawson and Schedl, *ibid.*, 71, 2048 (1949).

(3) Winstein, Jacobs, Seymour and Linden, *J. Org. Chem.*, 11, 215 (1946).

(4) Heinzelman, Kolloff and Hunter, THIS JOURNAL, 70, 1386 (1948).