

Anal. Calcd. for $C_4H_9NO_2Br$: N, 7.70. Found: N, 7.68.

α -Benzamido- γ -hydroxybutyric Acid.—In a typical run 59.5 g. (0.5 mole) of α -amino- γ -hydroxybutyric acid was dissolved in 500 ml. of *M* sodium hydroxide. The solution was cooled in an ice-bath and 58 ml. of benzoyl chloride and 250 ml. of 2 *M* sodium hydroxide were added simultaneously at such a rate that the temperature remained below 10° and the solution alkaline. The addition required about one hour. After stirring for two hours more, the solution was acidified with 60 ml. of concentrated hydrochloric acid and thoroughly extracted with ether to remove benzoic acid and the small amount of α -benzamido- γ -benzoxybutyric acid which forms. The aqueous solution upon cooling overnight in the refrigerator yielded 95 g. of α -benzamido- γ -hydroxybutyric acid which melted at 126–127°. This product contained 5.92% N. Recrystallization by dissolving in sodium hydroxide and addition of acid raised the nitrogen content but the melting point remained unchanged.

Anal. Calcd. for $C_{11}H_{13}NO_4$: N, 6.28. Found: N, 6.18%.

Similar yields were obtained by benzoylating the lactone hydrobromide, provided the calculated amount of 2 *M* sodium hydroxide to neutralize the hydrobromide was added in addition to that used for benzoylation.

α -Benzamido- γ -benzoxybutyric Acid.—The ether extracts from the previous reaction were combined and evaporated nearly to dryness on the steam-bath. The crystalline mass was filtered off and washed with a little ether to remove any benzoic acid. The product (3 g.) was dissolved in the minimum amount of hot 95% ethanol and crystallized by addition of an equal volume of water and cooling the solution. The compound crystallizes as thin plates melting at 198°. These crystals were dissolved in dilute sodium hydroxide, heated for fifteen minutes, then the solution was cooled and acidified. Benzoic acid separated out and was extracted with ether. The aqueous layer was cooled in the refrigerator overnight and crystals melting at 125° separated. A mixed melting point with a known sample of α -benzamido- γ -hydroxybutyric acid melted at 125–126°.

Anal. Calcd. for $C_{18}H_{17}NO_5$: N, 4.28. Found: N, 4.27.

***dl*-Benzamido-aspartic Acid.**—Forty grams of crude α -benzamido- γ -hydroxybutyric acid was dissolved in 300 ml. of water containing 10 g. of sodium hydroxide. The solution was cooled in an ice-bath and 40 g. of potassium permanganate added at such a rate that the temperature never exceeded 10°. When all the permanganate dis-

solved, the solution was allowed to reach room temperature and the manganese dioxide filtered off. After the excess permanganate was reduced with methanol, decolorizing carbon was added and the suspension filtered. The filtrate was acidified with excess hydrochloric acid and allowed to set in the refrigerator overnight. The crystalline product of *dl*-benzamido-aspartic acid weighed 34 g. This is the monohydrate as reported by Karrer and Schneider¹¹ and by Cocker⁷ and does not give a sharp melting point.

Anal. Calcd. for $C_{11}H_{11}NO_5 \cdot H_2O$: N, 5.48. Found: N, 5.36.

A sample which was dried in a vacuum for four hours at 110° melted at 176–177° (reported¹¹ 175°).

Anal. Calcd. for $C_{11}H_{11}NO_5$: N, 5.90. Found: N, 5.87.

***dl*-Aspartic Acid.**—Twenty-six grams of benzamido-aspartic acid monohydrate were refluxed for six hours in 200 ml. of water containing 15 ml. of 12 *M* hydrochloric acid. The benzoic acid which crystallized upon cooling was filtered off and the rest extracted from the filtrate with ether. The solution was evaporated to dryness (vacuum pump) and the residue was dissolved in 150 ml. of 95% ethanol. Crystallization took place immediately upon the addition of 15 ml. of pyridine. After setting overnight in the refrigerator the product was filtered out, washed with cold water, alcohol and ether. The recovery of aspartic acid from the benzamido derivative was 95%. The product decomposed above 280°.

Anal. Calcd. for $C_4H_7NO_4$: N, 10.53. Found: N, 10.42.

Acknowledgment.—The γ -butyrolactone was generously supplied by the Cliffs Dow Chemical Company.

Summary

A convenient synthesis of *dl*-aspartic acid is described. α -Amino- γ -hydroxybutyric acid (or the lactone hydrobromide) prepared from γ -butyrolactone was benzoylated to give α -benzamido- γ -hydroxybutyric acid. This compound was oxidized by alkaline potassium permanganate to benzamido-aspartic acid, from which *dl*-aspartic acid was obtained by hydrolysis.

(11) Karrer and Schneider, *Helv. Chim. Acta*, **18**, 1286 (1930).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. VII. The Structure of the Alfin Catalyst¹

BY AVERY A. MORTON AND MURIEL E. T. HOLDEN^{1a}

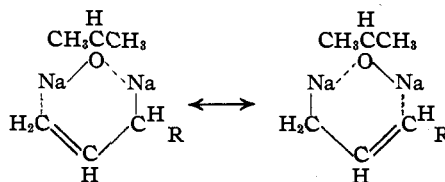
In the previous paper² the combination of sodium isopropoxide with the metalation product of propylene or certain other olefins was shown to have the unique property of inducing the catalytic polymerization of dienes. This behavior is distinct from that shown by alkenylsodium compounds alone, which merely add to dienes to form a series of adducts. The combination was called an Alfin catalyst. As a structure for the complex,

(1) This study was carried out under the auspices of the Rubber Reserve Company.

(1a) Present address: E. I. du Pont de Nemours Company, Photo Products Department, Parlin, New Jersey.

(2) Morton, Magat and Letsinger, *This Journal*, **69**, 950 (1947).

the cyclic doubly coordinated formula shown below in two forms was suggested. One criterion of such a structure is that the alkenyl-sodium compound could exist in two possible forms that would be regarded as allylic isomers or as structures that might contribute to resonance. A second cri-



terion would be reduced chemical reactivity on the part of the organosodium component. The purpose of this paper is to test the conformity of some alkenylsodium compounds to the suggested behavior.

The Tautomerism of Alkenylsodium Compounds with and without the Presence of Isopropoxide.—Propene, butene-1, butene-2 and pentene-1 have been metalated by amylsodium in order to discover the positions at which metalation occurs, the proportion of products that are allylic isomers, and the effect that sodium isopropoxide may have on this proportion. The specific influence of this alkoxide is contrasted with the lack of special effect exerted by the *n*-propoxide or by triethylamine.

Metalation of propylene yields almost exclusively allylsodium, judged by the amount of vinylacetic acid obtained after carbonation. A low yield for this reaction was reported in a previous paper.³ In the present work repeated additions of liquid propylene eventually produced a high yield and complete utilization of the amylsodium (see Table I). The isomeric sodium compounds that,

traces of crotonic acid had been formed, no certainty that 1-propenyl-1-sodium was the source would exist because crotonic acid always forms by allyl rearrangement of vinylacetic acid after the latter has stood for a time. The dicarboxylic acid, present in varying amounts, was converted by hydrogenation to glutaric acid and through ozonolysis to glyoxylic acid. No methylsuccinic acid was found among the products of hydrogenation. Hence the parent disodium compound was $\text{NaCH}=\text{CHCH}_2\text{Na}$.

The results of metalation of 1-butene and 2-butene by amylsodium are presented in Table II. The total percentage of allylic isomers is approximately constant, irrespective of the butene used or of the presence of isopropoxide. So also is the distribution of the two pertinent structures constant within the error of measurement. The dominating anion structure is the one that has the vinyl group with no substituent on one end, and this result agrees with the discussion already presented¹ on the relative strength of similar hydrocarbon acids and of the effect of methyl groups on acidity. The isolation of about 20% of α,β -pentenoic acid might seem to show the presence of 1-pentenyl-1-sodium, $\text{NaCH}=\text{CHCH}_2\text{CH}_2$, formed by direct metalation of 1-butene. This evidence can, however, be questioned on the ground that the acid is obtained from 2-butene as well as from 1-butene. An alternative source of this pentenoic acid is by an allylic shift in the corresponding β,γ -acid. This change does occur when the β,γ -acid is allowed to stand for several months, but does not take place during distillation since the pure acid could be refluxed under vacuum for several hours without change in the refractive index. Several other steps exist in the process of isolation of the acids where a change might occur. The problem of the formation of this small amount of material was incidental to the major problem of the hexenoic acids, where the alkoxide played a definite and singular role.

by carbonation, would produce crotonic acid and methacrylic acid were not present in large enough amount to be detected by this method. Even if

The dicarboxylic acid portion yielded adipic acid when hydrogenated. α -Methylglutaric acid was not detected. The tendency of the two so-

TABLE I
METALATION OF PROPYLENE BY AMYLSODIUM

Amount of propylene	Total acids, ^a g.	Proportions of acids, %		
		Caproic	Vinyl-acetic	Di-acid
Two 60-ml. portions ^b	11.5	23	59	15
Three 60-ml. portions ^c	12.6	16	60	24
Four 60-ml. portions ^c	12.1	0	93	7
Gaseous propylene ^d	11.0	25	54	21

^a Maximum yield possible is 16.3 g. based on 0.19 mole of amylsodium. ^b The propylene was added at -50° , the mixture allowed to warm to 20° during ninety minutes and the contents then stirred for an hour longer, after which the flask was cooled to -50° and the second lot of propylene added. The mixture was stirred for a while and then allowed to stand overnight. ^c The successive additions of propylene were made as described under (a) except for the larger number of times. ^d Propylene was bubbled through the reaction mixture at 20° .

TABLE II

METALATION OF 1-BUTENE AND 2-BUTENE BY AMYLSODIUM

Sodium compound ^a	Distribution of carboxylic acids derived from				1-Butene, %	
	1-Butene, % Without iso-propoxide	2-Butene, % With iso-propoxide	1-Butene, % Without iso-propoxide	2-Butene, % With iso-propoxide	With NEt ₃	With NEt ₃ and iso-propoxide
Total percentage of allylic isomers	60	66	63	63	58	72
$\text{CH}_2\text{CHCH}=\text{CH}_2$	40	43	40	39	39	48
\updownarrow						
$\text{CH}_2\text{CH}=\text{CHCH}_2$	20	23	23	24	19	24
$\text{CH}_2\text{CH}_2\text{CH}=\text{CHNa}$	5	6	5	8.6	0	8
$\text{C}_4\text{H}_8\text{Na}_2$	23	18	21	18	25	20
$\text{C}_5\text{H}_{11}\text{Na}$	3	0	3	0.5	0	0

^a The position of the sodium ion in the compounds listed in this column corresponds to the position of the carboxyl group in the carboxylic acid.

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

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

TABLE III
DISTRIBUTION OF PRODUCTS OF METALATION OF 1-PENTENE BY AMYLSODIUM

Sodium product ^a	Percentage of carbonated product									
	Without alkoxide	With n -C ₃ H ₇ -ONa ^b 0.08 mole	0.02	With i -C ₃ H ₇ ONa ^b mole				With 2-C ₄ H ₉ ONa ^b 0.08 mole	With NEt ₃ ^c	With i -C ₃ H ₇ -ONa ^b and NEt ₃ ^c
Total percentage of allylic isomers	65, 72	67	67	64	67	72	69	62	67	72
C ₂ H ₅ CHCH=CH ₂	65, 72	67	67	59	55	43	41	57	67	48
C ₂ H ₅ CH=CHCH ₂										
C ₂ H ₅ CH=CHCH ₂ } Na	0	0	0	5	12	29	28	5	0	24
C ₂ H ₅ CH=CHNa	20	20	20	20	18	20	22	21	20	20
C ₅ H ₈ Na ₂	8	8	7	8	10	8	9	7.2	6.7	8

^a The position of the sodium ion in the compounds listed in this column corresponds to the positions of the carboxyl groups in the carboxylic acids isolated. ^b The amounts of alkoxide are the amounts of alcohol added to 0.19 mole of amylsodium. 0.08 mole is, therefore, very nearly one equivalent of alkoxide to one alkenylsodium. ^c The amount of amine is two mole equivalents based on the amylsodium.

dium ions to take positions as far apart from each other as possible is worthy of mention, particularly when the dicarboxylic acid derived from propylene indicated that there was no bar to the presence of sodium at C₁ and C₃.

Two metalations were carried out in the presence of triethylamine because this compound would be expected to coördinate with the metal ion. The results were substantially the same as without the amine as far as the ratio of allylic isomers is concerned. Only in the case of 1-butenyl-1-sodium did any difference seem to exist and this result is not regarded as very important because of the small quantities involved and the magnitude of the possible error. The products obtained in the presence of both triethylamine and isopropoxide are essentially the same as with isopropoxide alone. The proportions of the two significant structures seem clearly to be determined by the nature of this anion and to be unaffected by the presence of other substances.

The products of metalation of 1-pentene are shown in Table III. The percentage of allylic isomers is surprisingly constant. The proportion of the two structures involved, however, varies widely. Without alkoxide or with n -propoxide, one structure only is present, and that one corresponds to the compound with the double bond at the end of the chain and sodium at C₃. Even in the presence of a very small amount of isopropoxide, none of the isomeric acid is present. As the quantity of alkoxide is gradually increased to 0.08 mole, where one isopropoxide is present for each amylsodium, the proportions of the two acids gradually shift. Beyond that quantity no further change occurs. In the case of 2-pentoxide the amount of the isomeric acid is considerably less, 0.08 mole of the 2-pentoxide being equivalent to 0.04 mole of the isopropoxide. Triethylamine has no effect on the proportions of acids.

The quantity of acid that corresponds to metalation of 1-pentene on the end methylene group is constant. This acid is probably the result of primary metalation rather than the product of an allylic shift of Δ^3 -hexenoic acid because this α,β -iso-

mer is present in the first three and the ninth experiments even though the β,γ -acid, from which it should be derived, is absent (see Table III). Such consistency would be expected only from a primary metalation of the terminal methylene group. The high proportion of this product as compared with the lower proportion of the corresponding product from the metalation of propene and of 1-butene accords with that expected from the added length of the alkyl chain. The result has a parallel in the alkylbenzene compounds. Metalation of toluene, for example, occurs in the side methyl group. As the alkyl chain is lengthened and branched, metalation in the side chain becomes more difficult. In the case of isopropylbenzene, metalation by amylsodium occurs in the aromatic ring and as far from the alkyl group as possible.⁵

The specific relation of the above facts to the cyclic double coördination formula for the Alfin catalyst will now be summarized in reverse order. The results with 1-pentenylsodium show that the alkenyl anion, in the absence of isopropoxide, does not have the isomeric structure that corresponds to an allylic shift in the anion. The second state is attained, however, by the presence of this particular alkoxide, to a degree dependent on the amount of alkoxide up to a certain limit, as if definite compound formation were involved. The cation of the alkoxide can apparently do what the cation of the alkenylsodium compound alone cannot do, namely, create an alternative center of anion activity in pentenylsodium. The results with the butenylsodium compounds show that the alkoxide is not needed to create allylic isomerism in the butenyl anion and does not alter the isomerism that already exists. A similar isomerism undoubtedly exists in propenylsodium because the propenyl anion is more symmetrical than the butenyl anion. Such isomerism alone, however, is not sufficient to cause Alfin catalysis with propenylsodium or with butenylsodium; the presence of a specific alkoxide is necessary. These requirements for a unique but definite combination

(5) Morton, Massengale and Brown, THIS JOURNAL, 67, 1620 (1945).

that will also be unusually favorable for the occurrence of allylic isomerism are nicely fulfilled in the proposed double coordination ring formula shown at the beginning of this paper. Such equivalent structures in a ring might also be regarded as contributing to a state of resonance.

Comparative Reactivity of Alkenylsodium Compounds with and without Alkoxide.—The reactivity of allylsodium, within and without catalyst combination, was measured in two substitutions, one addition and one cleavage reactions (see Table IV). The combination of allylsodium with sodium isopropoxide is clearly less reactive in the metalation of either isobutene or benzene than is allylsodium itself. A similar difference exists in the addition to 1,1-diphenylethylene. The cleavage of diisopropyl ether, however, is about the same, irrespective of whether the allylsodium is within or without the catalyst complex.⁶

TABLE IV

COMPARATIVE REACTIVITY OF ALLYLSODIUM AND PP AND P₂P CATALYSTS TOWARD ACID-SALT INTERCHANGE, ADDITION TO A DOUBLE BOND, AND CLEAVAGE OF AN ETHER

Sodium reagent	Acid-salt interchange		Addition to 1,1-diphenylethylene, %	Cleavage of diisopropyl ether, %
	with isobutene, %	with benzene, %		
Allylsodium	38	31	32	44
Allylsodium with sodium isopropoxide	19	9	9	40
with sodium 2-pentoxide	46	35	18	43

The results with the allylsodium 2-pentoxide catalyst show an enhanced tendency toward metalation; and this result accords with the evidence that the 2-pentoxide does not enter into catalyst combination as readily as does the isopropoxide, judged by the effect on the resonance in the pentenyl anion, as already described in Table II. For reasons discussed below, the 2-pentoxide that is outside of the catalyst combination should accelerate the metalation.

The normal role of an alkoxide is to increase the reactivity of organosodium reagents, as is evidenced by (a) the repeated additions of propylene needed to use all of the amylsodium (see Table I), as contrasted with the usual requirement⁷ of only one or two additions needed for metalation of propylene by amylsodium in the presence of isopropoxide; (b) the smaller amounts of amylsodium found after metalation of the butenes in the presence of alkoxide as contrasted with the results in the absence of alkoxide (see Table II) and (c) the comparison tests in which 2 g. of carboxylic acid was obtained by the metalation of 1-butene with 0.19 mole of amylsodium, whereas 5.7 g. of acids

(6) Actually the test with diisopropyl ether was scarcely fair because one product of cleavage would be sodium isopropoxide, which would then combine with the allylsodium to form the complex.

(7) Unpublished research.

was obtained from only 0.11 mole of amylsodium in the presence of isopropoxide. Indeed, so marked had been the acceleration of metalation by alkoxide that the preparation of the Alfin catalysts have for some time always been carried out by addition of the olefin to amylsodium after the alcohol has been added so that the alkoxide will be present to assist in the metalation of the olefin.

As a working hypothesis the accelerating influence that a non-metalating agent, the alkoxide, has on the metalating activity of a very active organoalkali metal reagent, can be explained by the assumption that a complex anion, $[C_6H_{11}Na:OR]^- Na^+$, is present. Such a view would be consistent with the assumption of the double coordination complex and with the observation that phenylsodium, a reagent that is practically unable to add⁸ to a diene or to 1,1-diphenylethylene, is, nevertheless, in the presence of certain salts, such as sodium chloride, sodium hydroxide and sodium methoxide, to induce butadiene to polymerize catalytically,⁹ although far less effectively than most of the Alfin catalysts. Further studies that show the likelihood of the existence of the simpler complex salts are in progress.

Experimental

Metalation of the Alkenes.—All reactions were carried out under conditions as nearly identical as possible. Amylsodium was prepared by the addition of *n*-amyl chloride to two equivalents of sodium sand in pentane, unless otherwise specified, over a one-hour period at -10° in a 500 ml. two-creased flask. Agitation was with the high-speed stirrer regularly used in this work. A piece of paper was wrapped around the lower part of the stirring apparatus or the top of the flask to make a collar, in which solid carbon dioxide could be kept, to act as a condenser. This device was very necessary with the volatile olefins added later. After addition was completed, the stirring was continued for thirty minutes longer at -10° , after which the mixture was ready for addition of alcohol or olefin. The yield of amylsodium was usually around 0.19 mole, that is, 75%. Multiples of this amount were made as desired in larger flasks. The maximum size was a 3-liter creased flask, but after one such reaction was slow in getting started and became uncontrollable from the presence of too much amyl chloride at one time, the size of the batch was reduced, for safety reasons, to a 1-liter flask.

The olefin was added to the amylsodium in considerable excess. In the case of propylene (Phillips Petroleum Company pure grade), the volatility was so great as to require additions of very large amounts (see Table I).

The butenes (Phillips pure grade) were added at -10° in 3.5 mole excess (60 mm. with 0.68 mole per 0.19 mole of amylsodium), the mixture was allowed to warm to 20° , near which temperature it was stirred for an hour. The contents were again cooled to -10° and once more treated with 60 ml. of the butene, as before. The mixture was finally allowed to stand overnight before carbonation. The addition of isopropyl alcohol was made after the first addition of the butene. The triethylamine (Eastman Kodak Co. pure grade, refractionated) was added to the alkenylsodium and stirred three hours before carbonation.

In the case of 1-pentene (Phillips technical grade, which was claimed to have 95% minimal purity, was refractionated through a 35-plate column) the first experiment listed in Table III, that is, the one in which no alkoxide or amine was present, was made with 1-pentene as the solvent in place of pentane during the preparation of amylsodium.

(8) Morton and Wohlers, *THIS JOURNAL*, **69**, 167 (1947).

(9) Morton and Letsinger, *ibid.*, **69**, 172 (1947).

In all others, the pentene was used in four-fold excess over the amylosodium, together with enough pentane to form the solvent during the preparation of the organosodium reagent. The conditions otherwise were the same as for other preparations of amylosodium. After the mixture had warmed to room temperature and had been stirred for three hours, it was allowed to stand overnight before carbonation in order to give every opportunity for the pentene to consume all the amylosodium. The isopropyl alcohol, or *n*-propyl alcohol, when used to make the alkoxide, was added after the first half-hour at -10° . Unless otherwise specified the amount of alcohol was 0.08 mole per 0.19 mole of amylosodium. The triethylamine was added as described for butenylsodium.

In order to carbonate them, the contents were forced, by pressure of nitrogen, onto powdered solid carbon dioxide in a 3-liter flask. The mixture was allowed to stand until the excess solid carbon dioxide had evaporated. Water (500 ml.) was added to dissolve the sodium salts. Two layers separated. The organic layer was discarded, and the aqueous layer was extracted with 100 ml. of petroleum ether to remove traces of decane or other hydrocarbon. Concentrated hydrochloric acid was then added to the solution of the sodium salts. The least soluble acids were extracted with petroleum ether, and the more soluble acids were then extracted with ethyl ether after the aqueous layer had been saturated with sodium chloride. The organic extracts were dried over anhydrous magnesium sulfate. Subsequently the extracts were filtered, and evaporated in order to recover the free acids.

The acids from the petroleum ether extract were fractionated at reduced pressure through a 35-plate column; those from the ether extract were first distilled from an ordinary Claisen flask in order to separate the volatile monobasic acids from the dibasic acids, after which the volatile acids were either fractionated separately or, more usually, added to those from the petroleum ether extract and then fractionated. In all cases a sufficient quantity of acid was used to permit the collection of fractions at points where the curve for temperature *vs.* quantity was level. The smallest amount thus fractionated was 35 ml. and the largest was 100 ml. In order to obtain such quantities several metalations were made simultaneously.

One sample of acids from 1-pentene was also fractionated by a multiple-fractional extraction process.¹⁰ The α -ethylvinylacetic acid was thereby concentrated in the strong acid fractions and the Δ^2 -hexenoic acid was obtained in the weak acid fractions. The efficient fractionating column made further use of this method unnecessary.

By the above fractional distillation, vinylacetic acid (b. p. 65–72 (2 mm.), n_D^{20} 1.4220) was the only product obtained from the monocarboxylic acid fraction derived from propylene. The butenes yielded three fractions: α -methylvinylacetic acid, $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CO}_2\text{H}$, b. p. 42–46° (2 mm.), n_D^{20} 1.4250; Δ^3 -pentenoic acid, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CO}_2\text{H}$, b. p. 55–59° (2 mm.), n_D^{20} 1.4388, and Δ^2 -pentenoic acid, $\text{C}_2\text{H}_5\text{CH}=\text{CHCO}_2\text{H}$, b. p. 85–102° (2 mm.), n_D^{20} 1.4550–1.4570. This last acid was contaminated with caproic acid if the utilization of amylosodium was incomplete. 1-Pentene similarly yielded at most three fractions: α -ethylvinylacetic acid, $\text{CH}_2=\text{CHCH}(\text{C}_2\text{H}_5)\text{CO}_2\text{H}$, b. p. 80–86° (2 mm.), n_D^{20} 1.4293; Δ^3 -hexenoic acid, $\text{C}_2\text{H}_5\text{CH}=\text{CHCH}_2\text{CO}_2\text{H}$, b. p. 91–94° (n_D^{20} 1.4350, and impure Δ^2 -hexenoic acid, b. p. 100–102° (2 mm.), n_D^{20} 1.4495. The pure acid was a solid.

Each of the above fractions was shown to have the correct neutralization equivalent and correct unsaturation as determined by catalytic hydrogenation over platinum oxide. Where the possibility of contamination with caproic acid (from unused amylosodium) existed these methods were important for analysis; and in preliminary tests the ratio of unsaturation per number of carboxyl groups was applied to the mixture of monobasic acids in order to discover conditions where consumption of amylosodium was complete.

(10) Hunter and Nash, *Ind. Eng. Chem.*, **27**, 837 (1935); see also ref. (4).

The identity of vinylacetic acid prepared in these reactions has already been established.⁸ In addition, the vinylacetic acid was characterized by the anilide derivatives, m. p. 57–58°; recorded¹¹ value 58°.

The identity of the three acids derived from the butenes was indicated by the fact that they had the structures expected from the corresponding fractions in the series from the next higher homolog, 1-pentene, which had been examined even more carefully because those acids supplied the more pertinent evidence that the isopropoxide was necessary for an allylic change. A 5-g. sample of the lowest boiling acid from the butene, namely, α -methylvinylacetic acid, was ozonized and the ozonide then hydrogenated. Formaldehyde was isolated as the dimethone, m. p. 188–189° (recorded¹² value 189°). A similar treatment of a sample from the second fraction. Δ^3 -pentenoic acid, yielded acetaldehydedimethone, m. p. 139° (recorded¹³ value 139–141°). These tests were conducted on the respective products obtained from 1-butene and also from 2-butene. Moreover, a similar test on a mixture of the two isomeric acids showed that the two methones could be isolated and separated by crystallization from 80% alcohol, this test being regarded as evidence that the fractions from the fractionations were relatively pure, since only one of the methones could be obtained from each fraction. The original butenes were also ozonized in order to insure that 1-butene gave the formaldehyde with no acetaldehyde and 2-butene gave acetaldehyde but no formaldehyde, with results in full agreement with the view that the two alkenes contained no impurity that would lead to error from ozonolysis. A sample of Δ^3 -pentenoic acid under the influence of alkali also underwent a change in refractive index from 1.4380 to 1.4550, the last value in the neighborhood of that for the third fraction. Such a rearrangement is characteristic of β,γ -unsaturated acids. When the highest boiling acid, Δ^2 -pentenoic acid, was ozonized, glyoxylic acid was eventually separated and characterized as the dimethone, m. p. 207.9–208.5° (cor.), recorded¹³ value 208°.

The identity of the three monobasic acids derived from 1-pentene was established by ozonization, permanganate oxidation, and hydrogenation. Ozonization of the lowest boiling acid, α -ethylvinylacetic acid, yielded formaldehyde, characterized as described above by the dimethone derivative. The *p*-bromophenacyl ester of the acid melted at 41.5 to 42.0°, after recrystallization from 50% alcohol.

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.

The isomeric second acid from 1-pentene, namely, Δ^3 -hexenoic acid, gave dimethone derivatives after ozonization that proved difficult to separate. Alkaline permanganate oxidation of 3.7 g. of the acid with 400 ml. of basic permanganate solution for one day at room temperature, followed successively by filtration, concentration to 100 ml., acidification with hydrochloric acid and steam distillation until no more acid volatilized, yielded a distillate from which (after it had been made alkaline, concentrated to 50 ml., neutralized by hydrochloric acid, and treated with *p*-bromophenacyl bromide), white crystals, m. p. 62–63°, were isolated. The melting point of *p*-bromophenacyl *n*-propionate is recorded¹² as 63.0, 63.4°. A mixed melting point with an authentic sample showed no depression. A mixed melting point with an authentic sample of the corresponding ester of *n*-butyric acid (m. p. 44–46°) did show a depression. Another sample (1 g.) of the Δ^3 -hexenoic acid was dissolved in hexane and reduced with hydrogen over a platinum oxide catalyst. The *p*-phenylphenacyl ester of this product melted at 64–65°. The recorded¹² value for *p*-phenylphenacyl caproate is 65°.

The third acid from 1-pentene, namely, Δ^2 -hexenoic acid, was a solid, m. p. 36–37°, but was often obtained as a

(11) Autenrieth and Pretzell, *Ber.*, **38**, 2547 (1905).

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

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liquid which crystallized in a very short time. The *p*-bromophenacyl ester melted at 62.0–62.5°.

Anal. C, 53.1, 52.8; H, 4.50, 4.45; Br, 25.7, 25.8.

Ozonization of some of the slightly impure Δ^2 -acid yielded a mixture of dimethone derivatives. The crystals were allowed to form for two weeks in 80% alcohol solution in a beaker covered by another inverted beaker so that the solution was kept free from dust while it slowly evaporated. By this method crystals that were large enough to be separated by hand were obtained. Further recrystallizations of the two fractions thus obtained yielded the dimethone of glyoxylic acid, m. p. 207–208°, identical with that from the corresponding acid from 1-butene. The other group of dimethone crystals yielded, however, no pure product. Alkaline permanganate (1.28 g. of potassium permanganate in 100 ml. of water with 1.5 ml. of 50% aqueous potassium hydroxide solution) oxidation at 50–70° for three hours of 0.35 g. of the acid, followed successively by filtration, concentration of the filtrate to 50 ml., acidification with acetic acid until the solution was just acid, and addition of calcium chloride yielded 0.19 g. of calcium oxalate, a 50% yield. The filtrate from this calcium oxalate precipitation was made just neutral with sodium carbonate and then refluxed with 0.69 g. of *p*-phenylphenacyl bromide. When cooled, white crystals, m. p. 81–82°, were obtained only a little below the melting point, 89°, recorded¹² for *p*-phenylphenacyl butyrate.

Samples of the dicarboxylic acids, left as residues from the evaporation of the ether extract, were hydrogenated over a platinum oxide catalyst in acetic acid. From 5 g. of the propylene product, a yellow oil was thus obtained that crystallized from benzene. The crystals melted at 96–97°. The melting point of glutaric acid is 97–98°. Hydrogenation of 15 g. of the semisolid wax from the corresponding fraction from 1-butene gave a liquid product that was first heated to 150° to decompose any butylmalonic acid present and then was steam distilled to remove traces of volatile acid. The resulting yellow solid was recrystallized from water and from ethyl acetate. The crude tan-colored powder then formed white crystals, m. p. 150–151°, when recrystallized from concentrated nitric acid. A mixed melting point with adipic acid showed no depression. The mother liquor from the nitric acid solution was allowed to evaporate and the residue then crystallized from concentrated hydrochloric acids. More adipic acid was thus obtained.

The dicarboxylic acid product from propylene was also ozonized. A few crystals of the dimethone of glyoxylic acid were isolated from the ozonide.

Comparative Reactivity.—The allylsodium was prepared from 0.19 mole of amyilsodium under conditions necessary to give complete conversion (see Table I). Liquid isobutene (60 ml.) was added at –10°. The reaction mixture was allowed to warm to room temperature, stirred at 20–25° for five hours, and then allowed to stand overnight before carbonation. The carboxylic acids were recovered in the usual manner by successive petroleum ether and ethyl ether extractions. Each extract was distilled and the refractive index of each fraction compared with values of the known products. The total weight of acids was 14.0 g. of which 5.3 g. was from metalation of isobutene. A similar run with the isopropoxide-allylsodium (PP) catalyst, derived from 0.38 mole of amyilsodium but with stirring for five hours at 20–25° instead of three hours (the overnight period was the same) yielded 21.5 g. of acid of which 4.4 g. was from isobutene. A similar run with a 2-pentoxide allylsodium (P₂P) catalyst yielded 17.1 g. of acid of which 8.0 g. was from isobutene.

The experiments with one mole of benzene were similar, except that the period of stirring at room temperature was five hours. The proportion of products was determined by calculation from the neutralization equivalent of the mixture of monoacid products. The respective neutralization equivalents for the products from reaction with allylsodium, PP catalyst and P₂P catalyst, were 97.0, 89.5 and 98.9. These values corresponded to 31, 9 and 35% benzoic acid, respectively.

For reaction with 1,1-diphenylethylene, the reagents were prepared in the same manner as described before and allowed to stand overnight. The freshly distilled ethylene compound (0.19 mole) was then added and the mixture stirred at 20–25° for two hours. Each mixture was then carbonated, treated with water, acidified and extracted with ethyl ether. In the case of the products from reaction with allylsodium and the P₂P catalyst, a white precipitate formed when water was added to the carbonated mixture, a behavior characteristic of the tertiary acids from the addition process.⁸ The volatile acid, vinylacetic acid, was recovered by distillation. The results are summarized in Table V.

TABLE V
REACTION OF ORGANOSODIUM REAGENTS WITH 1,1-DIPHENYLETHYLENE

Reagent	Acid pptd. by addition of water, g.	Vinylacetic acid distilled, g.	Non-volatile residue, g.	Addn. to (C ₆ H ₅) ₂ C=CH ₂ , %
Allylsodium	3.4	8.2	5.5	32
PP Catalyst	0	11.0	3.8	9
P ₂ P Catalyst	3.0	9.9	3.8	18

For the reaction with diisopropyl ether, the sodium reagents were prepared as for the diphenylethylene and then treated with 56 ml. (0.4 mole) of peroxide-free diisopropyl ether. Each mixture was then stirred for five hours and allowed to stand overnight before carbonation. The vinylacetic acid recovered (6.8, 6.9 and 7.3 g., respectively, from allylsodium, PP catalyst and P₂P catalyst) were compared to a 12.1-g. yield in the absence of the ether.

Summary

The metalation of propylene by amyilsodium gives allylsodium as the sole product of monometalation. The allyl anion can be assumed to undergo an allylic shift.

The metalation of 1-butene or 2-butene gives at least two monosodium products, judged by the study of the carbonation products. These products are the same irrespective of the butene used or of the presence of isopropoxide or of triethylamine. The result indicates that the butenyl anion undergoes an allylic shift.

The metalation of 1-pentene gives only two mono products in the absence of isopropoxide or in the presence of *n*-propoxide or triethylamine. One of these products represents metalation at C₃ and the other at C₁. In the presence of isopropoxide, a third product appears that corresponds to metalation at C₁, with an allylic shift. This product is formed at the expense of the C₃ sodium product. The amount is dependent on the amount of isopropoxide present up to the limit of one equivalent. The results indicate that the isopropoxide is essential to create an allylic shift in the pentenyl anion.

2-Pentoxide is less effective than the isopropoxide in causing an allylic shift to occur in the pentenyl anion.

The dicarboxylic acids isolated from the metalation of propylene and 1-butene indicate that the two metal atoms were located at the extreme ends of the alkyl chain.

Allylsodium is considerably more reactive toward isobutene, benzene and 1,1-diphenylethylene than is the complex of allylsodium with so-

dium isopropoxide but is only slightly more reactive than is the complex with sodium 2-pentoxide. No differentiation in reactivity with diisopropyl ether was noted.

These results are nicely explained by the assumption of the doubly coordinated cyclic ring formula for the Alfin catalyst.

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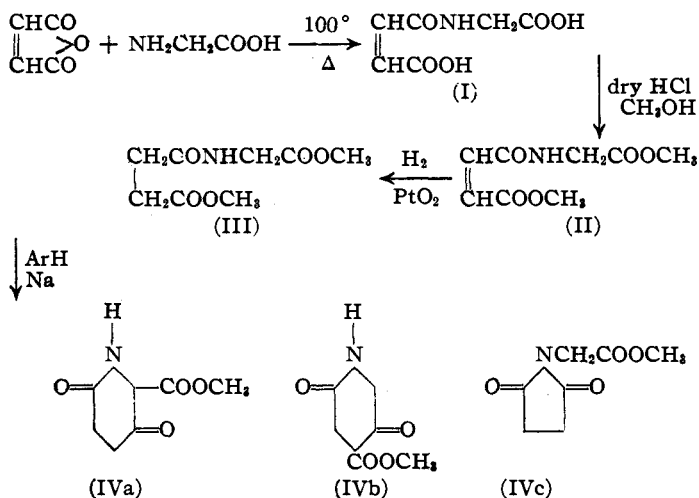
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Cyclization of N-Succinylglycine Dimethyl Ester

BY HAROLD WERBIN AND PAUL E. SPOERRI

This paper describes the synthesis of N-succinylglycine dimethyl ester (III), which appears to be unreported in the literature, and its cyclization to 2,5-diketo-1-pyrrolidineacetic acid methyl ester (IVc). Although a Dieckmann cyclization of (III) might have resulted in the formation of 6-carbomethoxy-2,5-diketopiperidine (IVa) or 4-carbomethoxy-2,5-diketopiperidine (IVb), neither of these products was isolated.

The synthesis and cyclization of N-succinylglycine dimethyl ester (III) was brought about through the sequence of reactions



Although the condensations of phthalic anhydride¹ and of succinic anhydride² on glycine have been reported in the literature, there seems to be no report of the action of maleic anhydride on glycine. It has been found that under mild reaction conditions amines, such as aniline³ and benzalhydrazine,⁴ add on to rather than condense with maleic anhydride. This has been found to hold true for the reaction of glycine and maleic anhydride. When heated together at 100°, the addition product, N-maleylglycine (I), resulted. The structure of (I) was shown to be HOOCCH=CHCONHCH₂COOH as follows: a nitrogen analysis proved that addition rather than con-

densation had taken place. If the addition had taken place across the double bond, the resulting compound on heating with water should give rise to a tribasic acid. If, on the other hand, the addition resulted in N-maleylglycine (I), this compound on heating with water might either remain unaffected structurally, or if it is sufficiently soluble in hot water to raise the latter's acidity, the amide linkage might be hydrolyzed, giving rise to glycine and maleic acid. Titration of a sample of the addition product which had been dissolved in boiling water required two equivalents of alkali, thus eliminating the structure resulting from addition across the double bond. The addition across the oxygen bridge was confirmed when maleic acid and glycine were isolated from a solution of the addition product in boiling water.

The fact that (I) was converted to N-maleylglycine dimethyl ester (II) by passing dry hydrogen chloride gas through a refluxing suspension of (I) in absolute methanol was further proof for the structure of (I) cited above. The unsaturated diester (II) was obtained in 35% yields. The use of cold rather than refluxing methanol decreased the yields to 15%. The low yields of (II) appeared to be due to hydrolysis as evidenced by the isolation of the hydrochloride of glycine methyl ester from the reaction mixture. N-Maleylglycine dimethyl ester (II) melting at 137° was converted to a diamide, m. p. 272°.

The reduction of (II) to N-succinylglycine dimethyl ester (III) with Raney nickel or platinum oxide as catalysts at 50 pounds pressure was quantitative.

The saturated dimethyl ester (III) was cyclized using the conditions usually employed in a Dieckmann condensation, *i.e.*, sodium or sodium methoxide and an aromatic hydrocarbon such as toluene or benzene. Table I shows the various conditions that were employed and the yields of 2,5-diketo-1-pyrrolidineacetic acid methyl ester (IVc) that were obtained. The latter was the only product that was isolated from every condensation reaction.

At first it was thought that the product result-

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