

THE PROPARGYLIC REARRANGEMENT. VI.<sup>1</sup> THE ORIGIN AND  
STRUCTURE OF THE DIMERIC ACID FOUND IN THE CARBONA-  
TION PRODUCTS OF GRIGNARD REAGENTS FROM PRIMARY  
PROPARGYLIC BROMIDES

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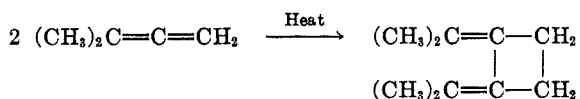
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The carbonation of Grignard reagents from primary propargylic bromides,  $\text{RC}\equiv\text{CCH}_2\text{Br}$  (I), where R was the normal propyl, butyl, or amyl group, yielded a mixture (A), consisting of a solid allenic acid,  $\text{RC}=\text{C}=\text{CH}_2$  (II), an isomeric



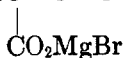
liquid acetylenic acid,  $\text{RC}\equiv\text{CCH}_2\text{CO}_2\text{H}$  (III), and an unidentified solid acid,  $\text{R}_2\text{C}_7\text{H}_5\text{O}_2\text{CO}_2\text{H}$  (IV) (1). The acid IV was called (1) dimeric because it had twice the molecular formula of II or III and contained only one *free* carboxy group as determined by neutral equivalants. Low pressure catalytic hydrogenation showed the presence of two double bonds (1). This paper deals with the origin and structure of the dimeric acid IV where R was the normal butyl group.

*The origin.* Since the dimeric acid IV had twice the molecular formulas of II and/or III, we thought it possible that it was formed by a condensation of two molecules of II or III or one molecule of II with III during the isolation or purification of products. Such reasoning would be in line with the claimed behavior of allenic hydrocarbons which dimerize to cyclobutanes (2).



Pure samples of II or III or equimolar mixtures of II and III were heated in the presence or absence of neutral solvents, basic or acidic catalysts; but no IV was isolated.

The clue to the origin of IV was found when it was realized that although different lots of the Grignard reagent yielded variable yields of total acid product on carbonation, the ratio of the acids present in the mixture also changed. More specifically, it was found that experiments which yielded relatively large quantities of the allenic acid II yielded small quantities of the dimeric acid IV and *vice versa*. This led to the belief that the acid II or its bromomagnesium salt,  $\text{RC}=\text{C}=\text{CH}_2$  (II MgBr), might somehow be the precursor in the formation of



IV. This theory was substantiated two different ways:

<sup>1</sup> The Propargylic Rearrangement. V., Sammuel, Hollingsworth, and Wotiz, *J. Am. Chem. Soc.*, **75**, 4856 (1953).

<sup>2</sup> Abstracted from a portion of the M.S. (1951) and Ph.D. (1954) dissertations of J. S. M., University of Pittsburgh. We would like to acknowledge the generous support of the National Institutes of Health in awarding Dr. Matthews a predoctoral Fellowship.

(a) Usually the carbonation of the Grignard reagent from I yielded the acids II and IV in a range of ratios from 28:1 to 5:1.<sup>3</sup> However, when a tenth-molar quantity of pure II was added to the Grignard reagent (prepared from a molar quantity of I) before carbonation and hydrolysis, the ratio of II to IV of 1:1 was decreased. If II or II MgBr was not a precursor in the formation, an increase in the ratio rather than a decrease was expected to be found.

To test the possibility that the addition of pure acid III, or its bromomagnesium salt,  $\text{RC}\equiv\text{CCH}_2\text{CO}_2\text{MgBr}$  (III MgBr), could also change the ratio of II to IV, the Grignard reagent prepared from a molar quantity of I was divided in half. The first half was carbonated by pouring on Dry Ice, and on hydrolysis it yielded a predominance of acid II over the acid IV. To the second half was added a half molar quantity of pure acetylenic acid III. Upon pouring on Dry Ice and hydrolysis no acid II or IV was found, and 93% of the acetylenic acid was recovered. What apparently happened was that the active hydrogen in the added acid III hydrolyzed the Grignard reagent yielding III MgBr and hydrocarbons. The pouring on Dry Ice did not cause carbonation as a Grignard reagent was no longer present. Thus no acid II or IV could be formed, and acid III was not likely a precursor in the formation of IV.

(b) Experiments in which the mode of carbonation was reversed, *i.e.* Dry Ice was added to it, also showed that II or II MgBr is the precursor in the formation of the dimeric acid IV. An ether solution of the Grignard reagent from I was again divided in half. One half was carbonated by pouring on Dry Ice and on hydrolysis yielded 32% of acidic material. The ratio of the allenic acid II to the dimeric acid IV in this particular case was 28 to 1. To the other half was added portions of Dry Ice. On hydrolysis it yielded 17% of IV and no II; the total yield of acidic material was 28%. These results were explained on the basis of competitive reactions that take place between the Grignard reagent and carbon dioxide and between the Grignard reagent and the formed bromomagnesium salt of the allenic acid, II MgBr. Fast carbonation (*i.e.* pouring on Dry Ice) keeps the carbon dioxide in excess and yields mainly acids II and III,<sup>4</sup> whereas in the slow addition of Dry Ice to the Grignard reagent we are keeping the Grignard reagent in excess, and it then reacts with the formed II MgBr, giving high yields of IV and low or no yields of II.

It should also be noted that the total yield of acids obtained by pouring the Grignard reagent on Dry Ice was higher than by placing Dry Ice into it. The second procedure apparently gives rise to large amounts of neutral compounds such as ketones and/or alcohols which is in line with previously reported observations (3).

Additional support of the view that the allenic acid II or its bromomagnesium

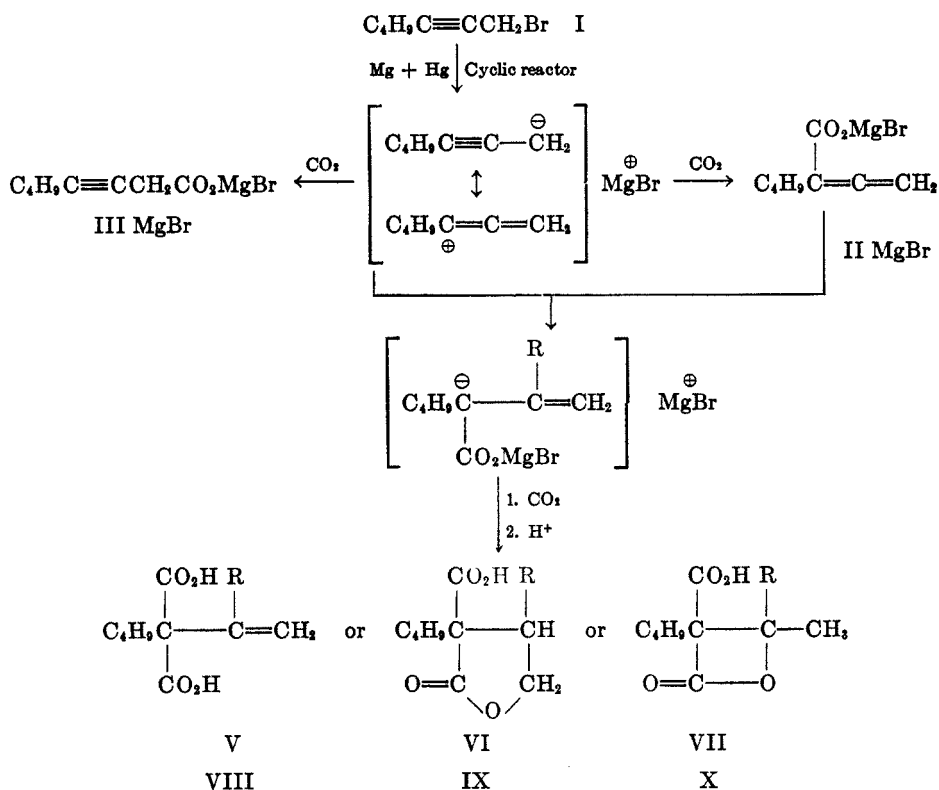
<sup>3</sup> The temperature of solvents in the separation and purification of the acids is an important factor because IV not only melts with decomposition but also slowly decomposes in hot solvents below its melting point. Acids II and III are stable under such conditions. Prolonged heating of solutions containing these three acids increases the ratio of II to IV.

<sup>4</sup> We found the best way to eliminate the formation of the dimeric acid IV is to carbonate by pouring the Grignard reagent on an ether-Dry Ice slurry rather than on solid Dry Ice.

salt, II MgBr, can react with Grignard reagents was found in the reaction of II with two moles of ethylmagnesium bromide. Upon hydrolysis 2-butyl-3-ethyl-

butenoic acid,  $\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{C}(\text{CO}_2\text{H})=\text{CH}_2$  was isolated in 85% yield (4).

These findings suggested that the dimeric acid could arise from the addition of the Grignard reagent from I to the II MgBr during carbonation, *i.e.* a reaction between the carbonated and uncarbonated Grignard reagent at the time of carbonation. The reaction and possible structures may be formulated as follows:



R =  $\text{C}_4\text{H}_9\text{C}\equiv\text{C}-\text{CH}_2$ — in compounds (V, VI, VII)

R =  $\text{C}_4\text{H}_9\text{C}=\text{C}=\text{CH}_2$  in compounds (VIII, IX, X)

*Determination of structure. Properties of the dimeric acid (IV).* The pure dimeric acid IV is a white crystalline compound melting at 99–100° with decomposition. It is extremely soluble in ether but insoluble in petroleum ether (b.p. 30–60°) and was crystallized from a mixture of these two solvents. It is stable at room temperature for long periods of time only if it is pure. If its melting

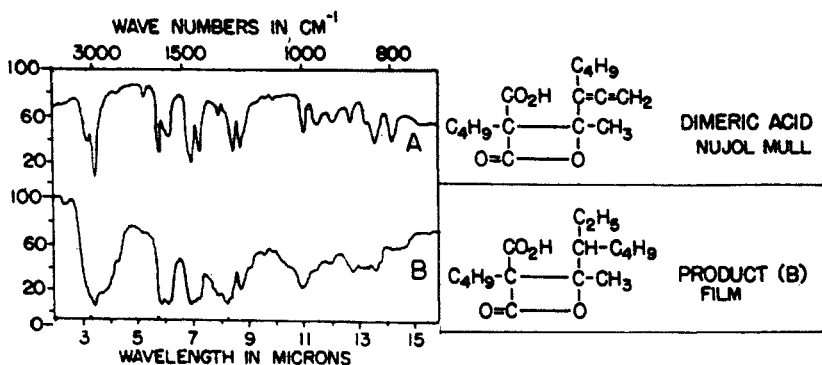


FIG. 1

point is only one degree below the maximum, it decomposes slowly even in the cold. Although it has only a slight odor when pure, it acquires a strong rancid odor when partly decomposed. It is difficult to recrystallize the dimeric acid when an appreciable amount of decomposition products are present. Such solutions upon crystallization sometimes separate an oil along with the dimeric acid. No attempt was made to study these oils or decomposition products.

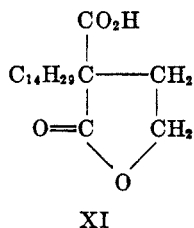
Its infrared spectrum<sup>5</sup> (Figure 1, Curve A) showed (among other bands discussed later on) the presence of single absorption band near  $1930\text{ cm}^{-1}$  characteristic of an allenic bond to which there is no electron withdrawing group attached (5). Upon catalytic hydrogenation (Product B) this band disappeared (Figure 1, Curve B). Thus, structures V, VI, and VII were eliminated as possibilities for the structure of the dimeric acid IV. The allene band most likely originates from the presence of the  $\text{C}_4\text{H}_9\text{C}=\text{C}=\text{CH}_2$  radical.

The infrared spectrum of IV showed also the presence of a "free" carboxy group by the carbonyl group absorption band near  $1740\text{ cm}^{-1}$  and the bonded hydroxyl band near  $3000\text{ cm}^{-1}$ . Since the dimeric acid behaved as a monobasic acid when titrated with cold dilute alkali, the other carboxy group was not "free." This was also substantiated by the reaction of IV with diazomethane in ether. The product was the monomethyl ester of IV. The fact that the second carboxy group was not "free" suggested the presence of a lactone. The acid VIII being  $\beta,\gamma$ -unsaturated could yield a  $\beta$ - or  $\gamma$ -lactone, in this case compound IX or X. The lactonization of  $\beta,\gamma$ -unsaturated acids is well known (6).

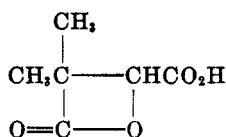
The behavior of  $\beta$ - and  $\gamma$ -lactono- $\alpha$ -carboxylic acid toward alkali was therefore investigated. Some of the  $\gamma$ -lactono acids were recently prepared to study their antibacterial activity (7), but no information on their neutralization equivalents was available. The properties<sup>6</sup> of XI were therefore compared. A neutralization equivalent showed it to behave as a monobasic acid, *e.g.* the lactone ring

<sup>5</sup> All infrared spectra were determined using a Baird double beam spectrometer and were interpreted by Dr. Foil A. Miller and co-workers at the Mellon Institute.

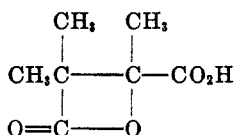
<sup>6</sup> We wish to thank Dr. C. J. Cavallito for the generous supply of this compound.



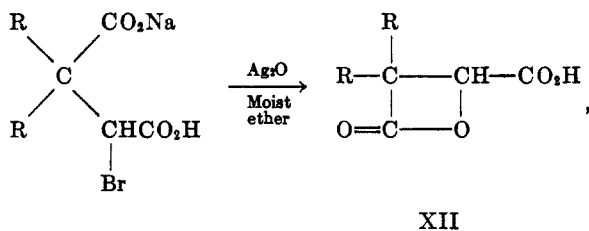
did not open on titration. A further literature search revealed that  $\beta$ -lactono- $\beta$ -carboxylic acids behave similarly. Thus Baeyer and Villiger (8) reported that the acid



titrated as a monobasic acid at room temperature and as a dibasic acid at elevated temperatures. Komppa (9) found that

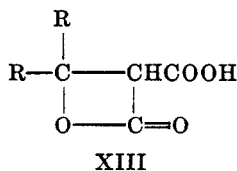


had to be boiled with an excess of potassium hydroxide before the lactone was opened. Kandiah (10) prepared  $\beta$ -lactono acids as indicated,



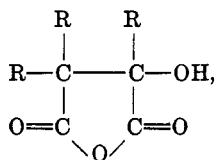
which also behaved as monobasic acids, and as dibasic acids only after prolonged treatment with alkali.<sup>7</sup>

<sup>7</sup> The products of reaction of malonic acid, a ketone, and acetic anhydride in sulfuric acid medium were reported by [Meldrum, *J. Chem. Soc.*, **93**, 598 (1908); also reference (10)] as having the structure



These compounds titrated as monobasic acids. However, more recently [Davidson and

The dimeric acid IV decomposed at its melting point with the evolution of carbon dioxide. This behavior suggested a carboxylic acid with an electron withdrawing group (*e.g.* carbonyl or carboxyl group) attached to the  $\alpha$ -carbon atom. This is present in compounds IX and X. Compounds of the type XII are reported to yield on distillation an anhydride,



rather than carbon dioxide (11).

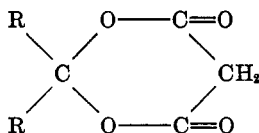
A controlled decarboxylation of the dimeric acid IV ( $\text{C}_{16}\text{H}_{24}\text{O}_4$ , Neutral equivalent 280) was achieved by refluxing a benzene solution with a drop of sulfuric acid. In this manner a quantitative evolution of carbon dioxide was observed. The product (C) from different runs had a neutral equivalent ranging from 294 to 424. If only decarboxylation took place, the product would have a neutralization equivalent of 236, calculated for  $\text{C}_{15}\text{H}_{24}\text{O}_2$ . The product was a mixture which contained some material in which neither a carboxyl group nor an easily opened lactone ring was present. The formation of such products was more extensive during the distillation of IV. The distillate (D) from two separate runs had neutralization equivalents of 468 and 611, respectively. Interestingly, when D of neutralization equivalent of 468 was hydrogenated, it absorbed four moles of hydrogen (97% of theory) based on a molecular weight of 472 ( $2 \times 236$ ).

The ozonization of IV yielded a complex mixture of products from which it was not possible to isolate individual compounds for identification purposes.

*Properties of the hydrogenated dimeric acid B.* Since IV absorbed 2 moles of hydrogen with a subsequent disappearance of the allene linkage to yield B, more attention was given to this product. Unfortunately B resisted all attempts of crystallization. The product of hydrogenation, freed of solvent at room temperature, had to be used in all of the subsequent work. The neutralization equivalents ( $pK_a$  3) were high, ranging from 310 to 318, the theory for  $\text{C}_{15}\text{H}_{27}\text{O}_2\text{CO}_2\text{H}$  being 284. However, the Rast molecular weight determinations showed values ranging from 266 to 282. That only one "free" carboxyl group was also present in B

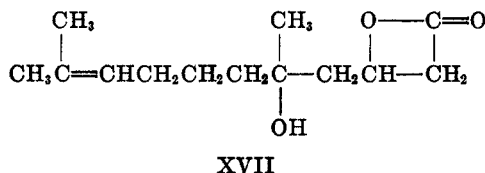
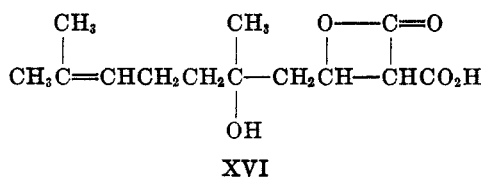
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Bernhard, *J. Am. Chem. Soc.*, **70**, 3426 (1948)] it was shown that these compounds have the structure

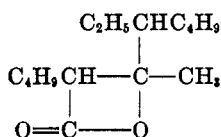


or its enol form. These findings were confirmed here by studying the infrared spectra of the compounds.

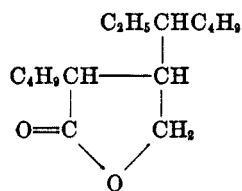




the  $\beta$ , $\delta$ -dilactone or citrylidine malonic acid (XV) was refluxed with ten normal sodium hydroxide and then acidified the products were XVI and XVII. Furthermore, it was also shown that the  $\beta$ -lactone of menthylideneacetic acid was recovered upon acidification of its sodium salt (15). These examples clearly illustrate that the  $\beta$ -lactone can be as stable as  $\gamma$ - or  $\delta$ -lactones. Therefore it was concluded that product *F* consisted mainly of compound XVIII or XIX.



XVIII



XIX

Attempts were made to prepare solid derivatives of *F* by reacting an alkaline solution of *F* with 3,5-dinitrobenzoyl chloride or with phenyl isocyanate. The failure could be better explained considering the presence of XVIII in *F*, which in basic medium contains a tertiary hydroxy group which is difficult to esterify or which dehydrates readily. Structure XIX would yield a primary hydroxy group on opening of the lactone. The preparation of a solid silver salt of the hydroxy acid which analyzed properly for the carbon and hydrogen content was successful.

The presence of a lactone in *F* was demonstrated in reducing it to a diol with lithium aluminum hydride. It was necessary to hydrolyze the reduction complex with sodium hydroxide (16) in order to prevent dehydration. The product (*G*) was freed of solvent and had to be used without distillation. A Zerewitinoff determination showed the presence of two hydroxyl groups by liberating 80% of the theory of two moles of methane (calculated for  $\text{C}_{18}\text{H}_{32}\text{O}_2$ ) from methylmagnesium bromide. However, *G* contained some unsaturated product as seen by the infrared absorption band near  $900 \text{ cm}^{-1}$ , elementary analyses, and by the absorption of 27% of theory of one mole of hydrogen. This unsaturated product in *G* could originate from the reduction of the  $\alpha$ , $\beta$ -unsaturated acid in *F* or by the dehydration of the diol in *G*. Dehydration of the diol was especially noticeable



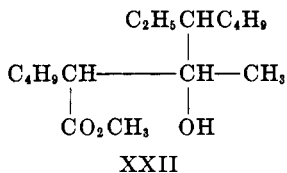
when the lithium aluminum hydride reduction complex was hydrolyzed with acid and distilled. Such a product (*H*) was a monohydric (Zerewitinoff determination, elementary and molecular weight determination) unsaturated (spectroscopic analysis and hydrogenation) alcohol. The apparent ease of dehydrogenation suggested the presence of a tertiary hydroxy group in the reduced product. The structure XVIII is favored over XIX on this count.

Another successful method for opening of the lactone in *F* was its reaction with diazomethane in an aqueous methanol solution. The product was the mixture *J*.

*The properties of J.* The infrared spectrum of *J* showed the presence of a carbonyl group of an ester by its absorption band near  $1700\text{ cm}^{-1}$ , a terminal double bond band near  $900\text{ cm}^{-1}$ , and a double bond conjugated with a carboxy group by its absorption near  $1610\text{ cm}^{-1}$ . When *J* was hydrogenated it absorbed 80% of theory of one mole of hydrogen (calculated for  $\text{C}_{16}\text{H}_{30}\text{O}_2$ ) to yield product *K*. Its infrared spectrum showed the presence of only an  $\alpha,\beta$ -unsaturated ester. Apparently *J* is a mixture of isomeric olefinic esters (elementary analysis) of which the conjugated double bond was not readily hydrogenated. The terminal double bond is likely  $\beta,\gamma$  with respect to the carboxy group as it was possible to rearrange it into conjugation by treatment with alkali. In the infrared spectrum of the alkali treated product the absorption band near  $900\text{ cm}^{-1}$  practically disappeared whereas the absorption near  $1610\text{ cm}^{-1}$  became stronger.

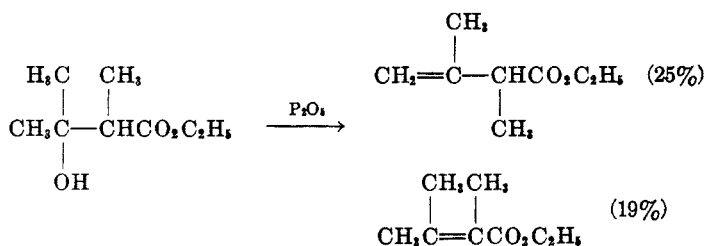


The two olefinic esters in *J* are likely compounds XX and XXI. The ozonization of *J* resulted in the isolation of methyl  $\alpha$ -ketoheptanoate (in form of its 2,4-dinitrophenylhydrazone) and formaldehyde (in form of the dimedone anhydride derivative). The isolation of other fragments was unsuccessful. The former compound may have originated from XX and the latter from XXI present in the mixture *J*. Compound XX could have originated from the  $\alpha,\beta$ -olefinic acid in *F* or by the dehydration of the tertiary alcohol XXII which was likely the primary product when XVIII reacted with diazomethane. Another

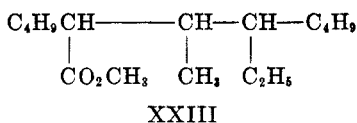


possible product in such a dehydration was XXI. The relatively large amount of XXI in *J* was not surprising since Holdsworth (17) on dehydrating ethyl  $\beta$ -methyl- $\beta$ -hydroxyvalerate found only the  $\beta,\gamma$ -olefinic ester,  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)-$

$\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ , and the dehydration of ethyl  $\alpha,\beta$ -dimethyl- $\beta$ -hydroxybutyrate yielded a mixture in which the  $\beta,\gamma$ -olefinic ester predominated (18).



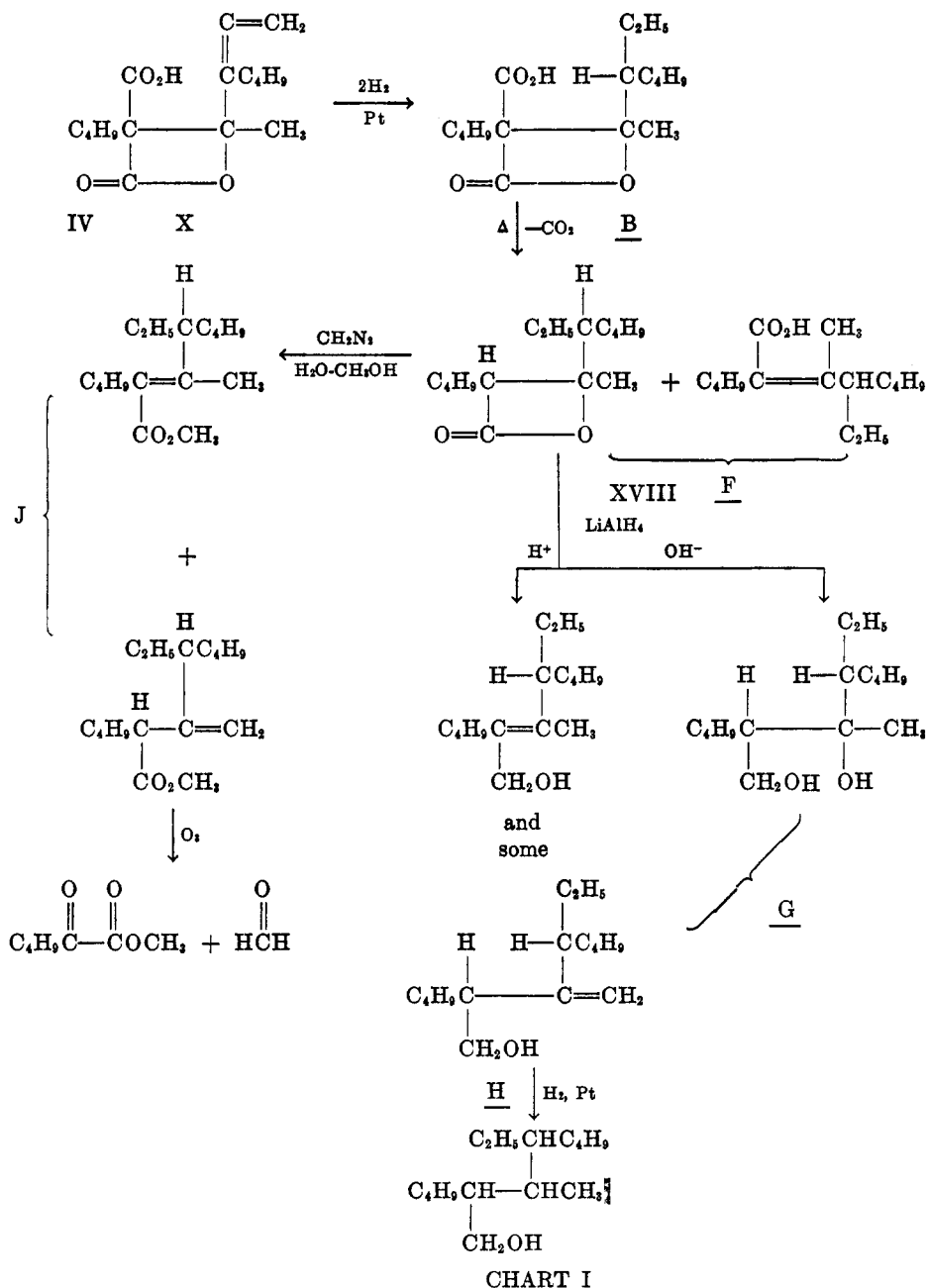
The presence of highly branched esters in *K*, mostly compound XXIII, was also demonstrated in the failure to saponify it by refluxing with 20% potassium hydroxide. Since hydrolysis of esters is the reverse of esterification, one can recall the findings that acids with alkyl groups in the  $\alpha$  and  $\beta$  positions, such as diisopropylacetic acid, esterify at a rate too slow to measure (19). Ester XXIII has substituents in the  $\alpha,\beta$ , and  $\gamma$ -positions. However, saponification was successful by adding *K* to a solution of sodium methoxide in methanol. A neutralization equivalent of 239 was obtained for the formed acid, the theory for  $\text{C}_{15}\text{H}_{30}\text{O}_2$  being 242.



*Infrared spectra.* This section is intended as a correlation of the spectroscopic evidence for the lactone in the dimeric acid IV. Its spectrum (Fig. 1, Curve A) showed (among others discussed previously) bands near 1640 and 1740  $\text{cm}^{-1}$ . These bands are also present in the product of hydrogenation *B* (Fig. 1, Curve B). However, upon decarboxylation of *B* by distillation, the band near 1640  $\text{cm}^{-1}$  virtually disappeared in the mixture *F*. It is therefore likely that this band was due to the "free" carboxyl group in IV and *B*, and that the 1740  $\text{cm}^{-1}$  band was due to the carbonyl group in the lactone. The infrared spectra of highly substituted  $\beta$ - or  $\gamma$ -lactones were not reported previously. Product *F* was then a mixture containing a preponderance of the lactone XVIII. The same conclusion can be arrived at by considering the hydroxyl group absorption band in the four micron region. Thus IV contained a band near 3150  $\text{cm}^{-1}$  due to the free hydroxyl group and a band near 2800  $\text{cm}^{-1}$  due to the bonded hydroxyl group. The former band is virtually absent in the mixture *F* which shows only the presence of strongly bonded hydroxyl group by the absorption near 2700  $\text{cm}^{-1}$ .

On the basis of all the presented evidence the structure of the dimeric acid IV is the  $\beta$ -lactonic acid X,  $\alpha,\gamma$ -dibutyl- $\alpha$ -carboxy- $\beta$ -methyl- $\beta$ -hydroxy- $\gamma,\delta$ -hexadienoic acid  $\beta$ -lactone. Several arguments could be raised against the  $\gamma$ -lactonic acid IX. One is the fact some of the  $\alpha,\beta$ -olefinic acid present in *F* indicates the  $\beta$ -lactone. Another, the ease with which the hydroxyl group is lost on opening

of the lactone suggested it to be a tertiary hydroxyl. The compound IX would have yielded a primary hydroxy group in such reactions. Furthermore, the literature contains reports (12) of ready polymerization of  $\beta$ -lactones, whereas  $\gamma$ -lactones fail to react under such conditions. Some of the reactions used in the identification are listed in Chart I.



## EXPERIMENTAL

1,2-Heptadiene-3-carboxylic acid (II) and 3-octynoic acid (III) were prepared from 1-bromo-2-heptyne (I) as previously described (1).

*Preparation of IV.* A one-liter flask containing 400 ml. of dry ether was attached to the cyclic reactor (1). The dropping-funnel contained a solution of 38.3 g. (0.22 mole) of 1-bromo-2-heptyne (I) in 150 ml. of dry ether. This was added at the rate of one drop per two seconds to a flowing stream of dry ether passing over the amalgamated magnesium turnings. After completion of addition the ether was refluxed for one half hour. The ethereal Grignard solution was cooled to room temperature and fitted with a "Y" tube topped by a condenser. Through the side arm of the "Y" tube was added small pieces of Dry Ice at a rate allowing the disappearance of the Dry Ice between additions. Approximately two moles of Dry Ice was added in this fashion. The carbonated Grignard reagent was allowed to come to room temperature. The solution was hydrolyzed with a saturated solution of ammonium chloride followed by a dilute solution of hydrochloric acid. The ethereal layer was drawn off and the water layer extracted with ether. The combined ether solutions were extracted several times with a saturated solution of sodium carbonate, and the combined aqueous extracts were acidified with cold dilute hydrochloric acid. The resulting organic acids were taken into ether, the ether solution washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The ether solution was filtered from the magnesium sulfate and the solvent of the filtrate evaporated under a vacuum (about 20 mm. pressure) at room temperature yielding 15.3 g. (49.7%) of acidic material. Recrystallization from petroleum ether (30–60°) yielded 13.1 g. (42.5%) of the dimeric acid IV, m.p. 99–100° and 2.2 g. (7.2%) of the crude acetylenic acid III. The infrared spectrum of IV is Curve A in Fig. 1.

*Anal.* Calc'd for  $C_{16}H_{24}O_4$ : C, 68.6; H, 8.2; N.E., 280; M.W., 280.

Found:<sup>8</sup> C, 68.6; H, 8.6; N. E., 280; M. W., 289.

The  $pK_a$  in 50% ethanol was 2.5.

The *methyl ester* of IV was prepared by dissolving 1.0514 g. (0.0038 mole) of IV in 30 ml. of dry ether to which a solution of diazomethane in dry ether was added until a yellow color persisted. The ether was removed under reduced pressure at room temperature leaving one gram of a liquid product ( $n_D^{25}$  1.4840) which would not crystallize from various solvents. The crude product was analyzed.

*Anal.* Calc'd for  $C_{17}H_{26}O_4$ : C, 69.4; H, 8.8.

Found: C, 68.3; H, 8.8.

*The addition of II to 1-bromomagnesium-2-heptyne.* A solution of 44 g. (0.25 mole) of I in 300 ml. of dry ether was converted into the Grignard reagent using the previously described high dilution technique (1). On cooling, a solution of 4 g. (0.028 mole) of previously prepared II in 50 ml. of ether was added. The reaction products were carbonated and isolated as previously described (1). The total yield of acidic compounds was 10.9 g. (31%), of which 3.7 g. (10.6%) was the dimeric acid IV, 3.9 g. (11.1%) was the allenic acid II, and the residue consisted mainly of the acetylenic acid III (3.2 g., 9.1%).

*The addition of III to the Grignard from I.* The Grignard reagent in 200 ml. of ether was prepared from 16.6 g. (0.093 mole) of I.<sup>9</sup> The solution was divided into two equal portions by forcing it under nitrogen into a graduated separatory-funnel. Part A was poured on Dry Ice. The total yield of acidic compounds was 0.9 g. (13.8%), of which 0.5 g. (7.7%) was acid II, 0.1 g. (1.5%) acid IV, and 0.2 g. (3.0%) crude acid III. Part B was mixed with an ethereal solution of 5.6 g. (0.04 mole) of an authentic sample of III.<sup>10</sup> The solution was then poured

<sup>8</sup> Microanalyses by the Microanalytical Laboratory of the University of Pittsburgh.

<sup>9</sup> Because of improper operation of the cyclic reactor the yield of Grignard reagent was low.

<sup>10</sup> Prepared by hydrolysis of  $C_4H_9C\equiv CCH_2CN$ . Newman and Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

on Dry Ice and worked up as usual. The total acidic portion was 5.2 g. (93% recovery) of acetylenic acid.

*Carbonation by the addition of Dry Ice to the Grignard reagent from I.* The Grignard reagent, prepared from 35.0 g. of bromide I, was divided into half as described above. Part A was poured on Dry Ice. On hydrolysis 4.4 g. (32%) of acids were found of which 3.9 g. (28%) was the allenic acid II, 0.1 g. (0.8%) dimeric acid IV, and 0.4 g. (3%) crude acetylenic acid III. To part B small pieces of Dry Ice were added at a rate to allow the disappearance of it between additions. Hydrolysis yielded 3.9 g. (28%) of acidic compounds, of which 2.4 g. (17%) was acid IV, and 1.5 g. (11%) was the crude acid III. No allenic acid II was found.

*The hydrogenation of IV (Formation of B).* The hydrogenation was performed in a semi-micro hydrogenation apparatus (20). Platinum oxide catalyst (0.0200 g.) was reduced and 0.6614 g. (0.00236 mole) of dimeric acid in glacial acetic acid was added. A pressure slightly above atmospheric was used throughout the hydrogenation. The volume of hydrogen absorbed was 106 ml. (100%) S. T. P. The solution was filtered and the acetic acid evaporated at room temperature under a vacuum. The residue was dissolved in ether, washed with water, dried over magnesium sulfate, filtered and the filtrate evaporated under a vacuum at room temperature to constant weight.

*Anal.* Calc'd for  $C_{16}H_{28}O_4$ : C, 67.6; H, 9.8.

Found: C, 67.4; H, 9.6.

Its infrared spectrum is Fig. 1, Curve B. N. E.: Theory, 284. The  $pK_a$  in 50% ethanol was 3. Found (avg.): 314.2. Molecular weight: Theory, 284; Found: 278 (avg.).

The *methyl ester* of B was prepared by dissolving it in ether to which an ether solution of diazomethane was added until the yellow color persisted. The residue after the evaporation of the solvent was analyzed.

*Anal.* Calc'd for  $C_{17}H_{30}O_4$ : C, 68.5; H, 10.1.

Found: C, 68.7; H, 9.7.

*Decarboxylation of IV. (a) Formation of C.* A 100-ml. flask was topped by a condenser connected to a carbon dioxide absorption tube and to a bubble counter. The flask contained 60 ml. of dry, thiophene-free benzene in which was dissolved 0.7067 g. (0.0025 mole) of IV, and a drop of concentrated sulfuric acid. While the solution was refluxed the evolved carbon dioxide was swept through the absorption tube by a slow stream of carbon dioxide-free nitrogen. The absorption tube was weighed periodically until no more absorption occurred. The weight of carbon dioxide absorbed was 0.110 g. (100%). The benzene solution was washed with water to remove the sulfuric acid, dried over magnesium sulfate, and filtered. The benzene was removed from the filtrate at 35°, leaving approximately 0.6 g. of a tarry, dark yellow residue.

*Anal.* Calc'd for  $C_{15}H_{24}O_2$ : C, 76.3; H, 10.2; N. E., 236; M. W., 236.

Found: C, 65.7; H, 8.5; N. E., 299; M. W., 229 (avg.).

(b) *Formation of D.* A sample of IV (unknown weight) was distilled leaving a dark viscous higher-boiling residue. The distillate, b.p. 150–153° at 3 mm.,  $n_D^{25}$  1.4855, had a neutral equivalent of 468. On hydrogenation using Adam's catalyst, 0.1133 g. of this distillate absorbed 20.0 ml. (S.T.P.) of hydrogen.

*The decarboxylation of B. (a) Formation of E.* A procedure similar to the one used in the formation of C was used. From 2.4741 g. (0.0067 mole) of B, 0.3694 g. (96.5% yield) of carbon dioxide was evolved.

*Anal.* Calc'd for  $C_{15}H_{28}O_2$  (E): C, 75.00; H, 11.66.

Found: C, 71.45; H, 10.3.

(b) *Formation of F.* The distillation of the crude B (prepared by the hydrogenation of 0.66 g. of IV) gave F (83% over-all yield), b.p. 136–137° at 1.5 mm.,  $n_D^{25}$  1.4655.

*Anal.* Calc'd for  $C_{15}H_{28}O_2$ : C, 75.0; H, 11.7; N. E., 240; M. W., 240.

Found: C, 75.3; H, 11.5; N. E., 247; M. W., 230 (avg.).

The  $pK_a$  in 50% ethanol was 6.

The *silver salt* of F was prepared by dissolving 1 g. (0.0042 mole) of F in dilute alcohol, raising the pH of the solution to 8.3, using sodium hydroxide, and adding silver nitrate. The

product was set in the dark overnight, filtered, and the semisolid washed with acetone. The solid residue was dried under a vacuum and analyzed.

*Anal.* Calc'd for  $C_{13}H_{29}AgO_3$ : C, 49.3; H, 7.9.

Found: C, 48.6; H, 7.1.

*The reaction of F with lithium aluminum hydride (LAH).* (a) *The formation of G.* A solution of 2.2 g. (0.0092 mole) of *F* in 50 ml. of dry ether was added to a suspension of 2 g. LAH in 120 ml. of dry ether. The reaction was cooled in ice and hydrolyzed (16) by adding in succession two ml. of water, three ml. of 15% sodium hydroxide, and then six ml. of water. The ether layer was decanted from the solids which were then extracted with three 75-ml. portions of ether. The combined ether solution was dried over magnesium sulfate and filtered. The ether was evaporated at room temperature under a vacuum. The residue (2.0 g.,  $n_D^{25}$  1.4657) was analyzed.

*Anal.* Calc'd for  $C_{15}H_{32}O_2$ : C, 73.8; H, 13.1.

Found: C, 77.7; H, 11.8.

In a Zerewitinoff determination 10.5 ml. (avg., STP) of methane was liberated. The theory for 2 OH groups was 14.4 ml.

(b) *The formation of H.* A 3-g. (0.0125 mole) sample of *F* was reduced with LAH as described above. The product was hydrolyzed by adding to the reaction product cooled in ice, 10 ml. of water followed by a 10% solution of sulfuric acid until all the formed solids disappeared. The ether layer was washed with 20 ml. of 5% sodium bicarbonate and dried over magnesium sulfate and filtered. The filtrate was freed from solvent by evaporation under vacuum at room temperature. The residue (3 g.) was distilled, collecting the fraction (71% yield) boiling at 109 to 110° at 1.1 mm.,  $n_D^{25}$  1.4680.

*Anal.*, Calc'd for  $C_{15}H_{30}O$ : C, 79.7; H, 13.3; M. W., 226.

Found: C, 79.9; H, 10.9; M. W., 222 (avg.).

Zerewitinoff determination: Calc'd for an OH: 9.9 ml. Found: 9.9 ml. (STP).

*The reaction of F with diazomethane. The formation of J.* Acid *F* (4 g., 0.0167 mole) was dissolved in a mixture of 75 ml. of methanol and 25 ml. of water. A solution of diazomethane in ether was added until a faint yellow color persisted. The solvent then was removed under reduced pressure at room temperature until the solution turned cloudy. The cloudy solution was extracted several times with ether. The ether extracts were combined and dried over magnesium sulfate. The ether solution was filtered and the solvent removed under a vacuum at room temperature leaving a yellow liquid weighing 4.2 g. (100% yield). The liquid was distilled yielding 3.4 g. (81%),  $n_D^{25}$  1.4560, b.p. 122–123° at 1.6 mm. of product *J* and a residue which weighed 0.5 g.

*Anal.* Calc'd for  $C_{16}H_{30}O_2$ : C, 75.6; H, 11.8.

Found: C, 75.4; H, 11.4.

*The hydrogenation of J, formation of K.* Using platinum oxide catalyst, 0.9947 g. (0.0039 mole) of *J* absorbed 70.8 ml. (S.T.P.) of hydrogen (80.5% for one double bond in  $C_{16}H_{30}O_2$ ). The solvent was removed under reduced pressure leaving a clear yellow oil,  $n_D^{25}$  1.4518. It was distilled, yielding a single fraction (*K*), (80% yield) b.p. 127° at 9 mm.,  $n_D^{25}$  1.4505.

*Anal.* Calc'd for  $C_{16}H_{32}O_2$ : C, 75.0; H, 12.5.

Found: 75.3; H, 11.5.

*The rearrangement of the double bond in J.* To 20 ml. of 10% potassium hydroxide in a 100-ml. flask was added 0.3 g. of *J*, and the solution was refluxed for 15 hours. The solution was extracted continuously with ether for 18 hours. The ether solution was dried over magnesium sulfate, filtered and the ether removed under reduced pressure. The residue weighed 0.3 g.

*The ozonolysis of J.* A mixture of oxygen-ozone of unknown concentration was slowly bubbled for 15 hours at room temperature through a solution of 0.6 g. (0.0024 moles) of *J* dissolved in 15 ml. of acetic acid. The solution was poured into 15 ml. of water containing 5 ml. of 3% hydrogen peroxide and refluxed for 20 minutes. The volume of the solution was reduced under reduced pressure. A solution of 2,4-dinitrophenylhydrazine was added to

the oily residue yielding a yellow precipitate. Repeated recrystallization from dilute alcohol yielded a compound, m.p. 144.5–146°.

*Anal.* Calc'd for  $C_{11}H_{13}N_4O_6$ : C, 48.2; H, 4.9; N, 17.3.

Found: C, 48.3; H, 5.4; N, 17.5.

A mixture melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of methyl  $\alpha$ -ketoheptanoate (1) showed no depression.

In a separate experiment a solution of 2.3 g. (0.0096 mole) of *J* in 40 ml. of acetic acid was ozonized for 21.5 hours. The resulting solution was added dropwise to a stirred mixture of 100 ml. of a 50% solution of acetic acid and granulated zinc. From the other neck of the three-necked, 100-ml. flask a tube led to three eight-inch test tube traps in series containing a dimedone solution. While the ozonide solution was added dropwise, a slow stream of nitrogen was passed through the apparatus to sweep into the dimedone any formed formaldehyde. The solution was stirred for one hour without and one-half hour with heating (50°). On standing, crystals deposited in the dimedone tubes. These were filtered and recrystallization from dilute alcohol raised the melting point to 170–172°. Literature: m.p. 171°.

*Anal.* Calc'd for the anhydride of formaldehyde-dimedone  $C_{17}H_{21}O_3$ : C, 74.7; H, 7.7.

Found: C, 74.6; H, 7.9.

*Hydrolysis of K.* (a) *Unsuccessful.* To a 100-ml. flask containing 25 ml. of 20% potassium hydroxide was added 0.3 g. (0.0012 mole) of *K* and the mixture was refluxed for 22 hours. The alkaline solution was continuously extracted with ether for four hours, the ether solution dried over magnesium sulfate, filtered, and the solvent evaporated under reduced pressure. The residue weighed 0.3 g.,  $n_D^{25}$  1.4525.

(b) *Successful.* To a cooled solution of 0.5 g. (0.0125 mole) of sodium in 10 ml. of dry methanol was added 0.2 g. (0.0008 mole) of *K*. A precipitate occurred almost immediately. This was filtered and the solid acidified with dilute hydrochloric acid and extracted with ether. The ether solution was dried over magnesium sulfate, filtered, and the ether removed under reduced pressure at room temperature, leaving 0.2 g. of a pale yellow liquid. A neutralization equivalent was taken. N. E. Calc'd for  $C_{16}H_{20}O_2$ : 242. Found: 239.

#### SUMMARY

1. The "dimeric" acid IV found in the carbonation product of the Grignard reagent from 1-bromo-2-heptyne (I) was formed in the reaction of this Grignard reagent with the bromomagnesium salt of the also formed allenic acid II at the time of carbonation.

2. The acid IV was identified as  $\alpha, \gamma$ -dibutyl- $\alpha$ -carboxy- $\beta$ -methyl- $\beta$ -hydroxy- $\gamma, \delta$ -hexadienoic acid  $\beta$ -lactone (X). Some of the reactions used in the identification are listed in Chart I.

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