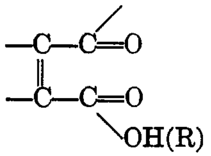
[Contribution from the Cobb Chemical Laboratory, University of Virginia]

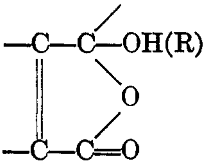
THE REDUCTION OF *CIS* AND *TRANS* 2,3-DIMETHYL-3-*p*-XENOYLACRYLIC[1] ACIDS AND THEIR ESTERS

ROBERT E. LUTZ and MONROE COUPER[2]

Received August 31, 1940

In the open-chain forms of the *cis* unsaturated 1,4-ketonic acids and their esters (I) and also in the corresponding *trans* compounds, there is present the conjugated unsaturated 1,4-dicarbonyl system, O═C—C═C—C═O, reduction of which undoubtedly involves primary addition of hydrogen or its equivalent at the terminal oxygen atoms. In the cyclic forms of the *cis* acids and their esters (II) there is present the analogous system, O═C—C═C—C—O, in which a C—O link is in place of one of the carbonyl groups; this system also may function in some degree as a unit, as it does in the reduction of the cyclic *cis*-3-bromobenzoyl-3-methylacrylic ester (1). The 2,3-dimethyl-3-xenoylacrylic derivatives have been studied further in this connection because they show a particularly marked tendency to function in the cyclic forms.


I


II

Reduction of the open-chain compounds. The reduction of *trans*-2,3-dimethyl-3-xenoylacrylic acid (III) with zinc and acetic acid proceeds directly to the less stable of the two stereoisomeric saturated 1,4-ketonic acids (IVB). Reduction by zinc and aqueous sodium carbonate produces a mixture of the two stereoisomers, IVA and IVB (these two acids will be described below in a separate section). The methyl ester of the *trans* acid (V) and also the *cis* open-chain ester (VII) are likewise reduced by

$$\begin{array}{c} CH_3-C-COC_{12}H_9 \\ \| \\ HOCO-C-CH_3 \end{array} \xrightarrow[AcOH]{Zn} \begin{array}{c} CH_3-CH-COC_{12}H_9 \\ | \\ CH_3-CH-COOH \end{array}$$

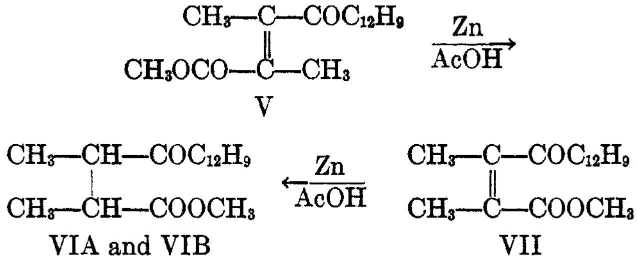
III IVB

---

[1] Named in terms of acrylic rather than tiglic acid in order to minimize the use of special names in this field and to simplify the naming of compounds with various substituents on the ethylene linkage.

[2] Holder of a Philip Francis duPont Research Fellowship, 1937–1938; at present Instructor in Chemistry, University of Virginia.

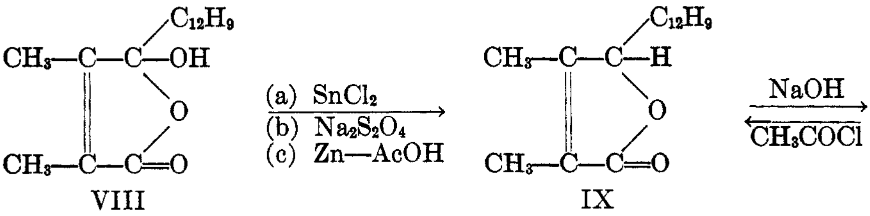
zinc and acetic acid but to mixtures of the two stereoisomeric 2,3-dimethyl-3-xenoylpropionic esters.

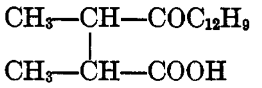


It is evident from the ease of reduction of these compounds and from the formation of the same products from both *cis* and *trans* esters, that the conjugated system is involved through 1,6-reduction. The formation chiefly of the unstable acid (IVB) in the zinc-acetic acid reduction of the unsaturated *trans* acid (III) was surprising, and it would be of interest to know what the open-chain form of the *cis* acid would give under the same conditions. This point, it now appears, cannot be determined, since the *cis* acid seems to function largely if not exclusively in the cyclic form.

Reduction of the cyclic ester. The cyclic or pseudo ester of *cis*-2,3-dimethyl-3-xenoylacrylic acid (VIII) is not acted upon by zinc and boiling conc'd acetic acid. This was disappointing, but perhaps not surprising in view of the absence of the complete unsaturated 1,4-dicarbonyl system; however, it is to be contrasted with the facile reduction of the analogous cyclic *cis*-3-bromobenzoyl-3-methylacrylic pseudo ester (1) by the same reagent.

Reductions of the cis *acid* (VIII) with stannous chloride, sodium hydrosulfite, or zinc and acetic acid, give the α,β-unsaturated lactone (IX) described below in a separate section. The saturated 1,4-ketonic acid (IV) is not formed to any significant extent in these reductions, although it can be made from the unsaturated lactone (IX) by hydrolysis with sodium hydroxide. The course of these reductions is to be contrasted with that of the open-chain *cis* ester, which takes place in a normal fashion to give directly the ester of the saturated ketonic acid.





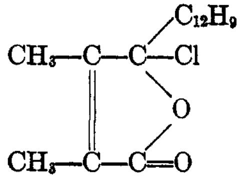
$$\begin{array}{l} CH_3\text{—}CH\text{—}COC_{12}H_9 \\ \qquad\;\; | \\ CH_3\text{—}CH\text{—}COOH \end{array}$$

IV

In connection with the mechanism of these reductions of the *cis* acid, several points should be considered. The stereoisomeric saturated acids (IVA and IVB) once formed are stable under the various reducing conditions and can be converted into the unsaturated lactone (IX or XIV) only upon dehydration, using acetyl chloride or acetic anhydride and sulfuric acid; neither of the saturated acids, therefore, can have been involved as an intermediate in the reductions. The unsaturated lactone (IX) therefore must have been formed either through direct reduction of the acid in its lactonol[3] form (VIII) or through cyclization of an intermediate enolate produced by 1,6-reduction of either form, VIII or I. The *trans* acid (III), necessarily open-chain, is reduced normally and presumably 1,6 to give intermediate enolates which ketonize to the saturated ketonic acid (IV); in this case, no evidence of cyclization was observed. The entirely different course of reduction of the *cis* acid, then, indicates that 1,6-reduction of the open-chain form is not involved, although one might assume the formation of a stereoisomeric intermediate enolate which would cyclize rather than ketonize during the reaction, just as one highly hindered γ-diketone monoenolate stereoisomer is known to furanize consistently rather than to ketonize (2). Reduction of the *cis* acid, then, probably involves exclusively the direct (or possibly 1,4) reductive elimination of hydroxyl from the lactonol form, VIII.

The reduction of the *cis* acid (VIII) by stannous chloride in hydrochloric and acetic acids may be regarded as a special case, and very probably involves conversion into the pseudo acid chloride (X) (a type of reaction which occurs easily in this series), followed by direct reductive elimination of the halogen to give as the chief product the stable α,β-unsaturated lactone (IX). The unstable enol lactone (XIV) could not have been involved here to any considerable extent, because under these conditions it is converted only partly into the stable α,β-unsaturated lactone (IX) and undergoes hydrolysis instead largely to the saturated ketonic acid (IV), as was shown in separate experiment. The mechanism suggested would explain why the reduction goes with such extraordinary ease as compared with the relatively slow reduction when the more powerful reducing combination, zinc and acetic acid, is used. Analogous reductions of mucobromyl bromide (3) and the pseudo acid bromide of β-phenyl-β-benzoylacrylic acid (4) may be cited.

[3] The term lactol is commonly used for this type of compound but we have expanded this to lactonol to express better the relationships involved.



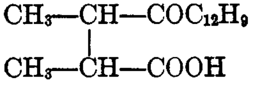
X

Reduction of the *cis* acid (or rather perhaps its sodium salt) with zinc and aqueous sodium carbonate, gives directly the saturated 1,4-ketonic acid (IV). The α,β-unsaturated lactone (IX) under these conditions is stable, and therefore could not have been an intermediate. It would therefore appear that the sodium salt is involved, and functions in the open-chain form or possibly a resonance hybrid between the open-chain and cyclic forms. However, in view of the relatively few reactions of the acid which might reasonably be attributed to the open-chain form, namely, this reduction with zinc and sodium carbonate, and methylation with diazomethane, it seems worth while to suggest the possibility that the acid and even the sodium salt may function exclusively in the cyclic form, but may react at times through a conjugated system in such a way as to produce open-chain products [*cf.* the discussion of alcoholysis of the *cis* acid halides in the preceding paper (5)]. Analogy for this is to be seen in the reduction of the *cis*-3-bromobenzoyl-3-methylacrylic pseudo ester to the open-chain enol ether of the saturated 1,4-ketonic acid (1). Such a possibility has been suggested in the methylation of 4-benzoyloxy-2,5-diphenyl-2-hydroxyfuranone[4]-3 with diazomethane (6) and may be applied also to the methylation of the silver salt. In fact, methylation by methyl iodide of the colorless silver salt of *ortho*-benzilcarboxylic acid, which is believed to be in the lactonol form, produces directly the open-chain ester (7).

*The stereoisomeric 3-*p*-xenoyl-2,3-dimethylpropionic acids* (IV). The product obtained on hydrolysis of the unsaturated lactone (IX) was a mixture of two stereoisomeric saturated ketonic acids with the higher-melting form-A predominating. The isomer-B was not easily isolated from this mixture and was separated best as the methyl ester after diazomethane esterification of the residual mixtures from fractional crystallizations. A way was found to prepare in good yield the low-melting isomeric acid (IVB) and from it the methyl ester (VIB). The action of alkali on

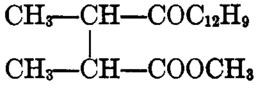
[4] The term furanone is obviously a misnomer. More properly it should be dihydrofuranone and numbered to indicate the positions involved. However, since a true furanone is impossible and since the abbreviated term has been used extensively (9), it will be retained here, but the expanded and proper term dihydrofuranone will be used when it is necessary to indicate the carbons involved.

either acid-A or -B produced an equilibrium-mixture of the two acids with the less soluble form-A predominating. However, the sodium salt of the isomer-B proved to be difficultly soluble in 10% sodium hydroxide in contrast with the isomer-A sodium salt which is very soluble, and it crystallized from solution in good yield under properly controlled conditions. The free acid-B could then be liberated by treatment with acids, and was purified, characterized, and converted with diazomethane into the low-melting ester (VIB). Alkaline hydrolysis of both of the esters (VIA and VIB) produced chiefly the acid (IVA).



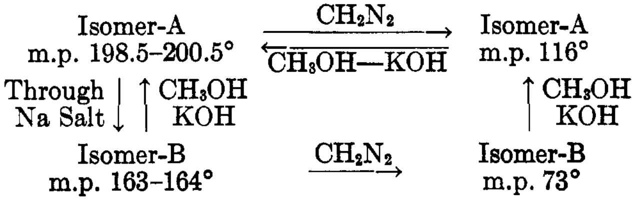
$$\begin{array}{l} CH_3—CH—COC_{12}H_9 \\ \qquad\;| \\ CH_3—CH—COOH \end{array}$$

IV



$$\begin{array}{l} CH_3—CH—COC_{12}H_9 \\ \qquad\;| \\ CH_3—CH—COOCH_3 \end{array}$$

VI

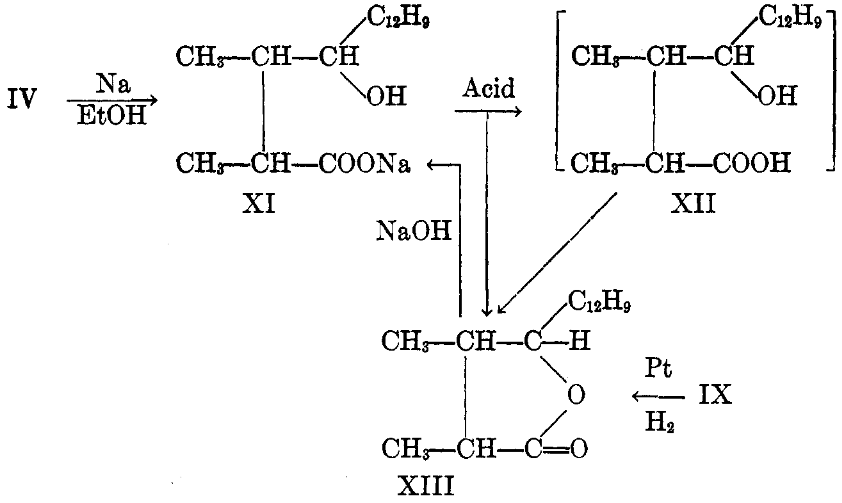


The less soluble and higher-melting isomeric acid-A and its ester are the more stable isomers as shown by the predominance of the acid-A at equilibrium in alkaline solution, and by the conversion of the ester-B into the ester-A by means of alcoholic alkali, a reaction which precedes the eventual hydrolysis.

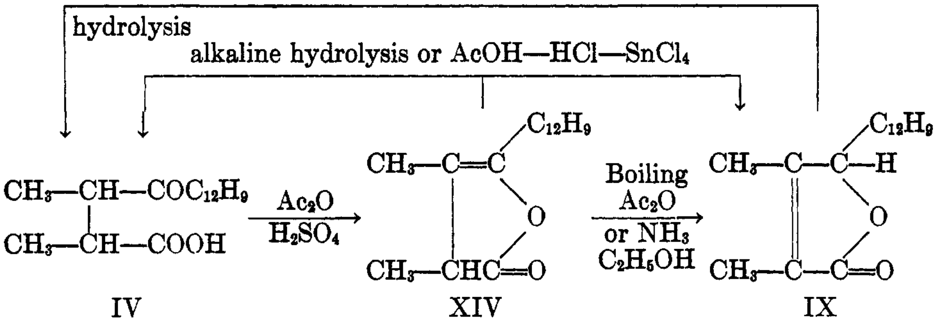
Both the 3-xenoyl-2,3-dimethylpropionic acids-A and B are converted by acetic anhydride and sulfuric acid into the same unsaturated lactone (IX) in which the possibility of stereoisomerism has disappeared.

*Reduction of 2,3-dimethyl-3-*p*-xenoylpropionic acid-A* (IV). The combination sodium and alcohol attacked the carbonyl group of this acid; on acidification of the product, the hydroxy acid lactonized, and was obtained as a mixture, presumably of stereoisomers, from which one compound (XIII) was isolated by painstaking fractional crystallization. Catalytic hydrogenation of the unsaturated lactone (IX) also gave this same butyrolactone (XIII). In one isolated experiment the free hydroxy acid (XII) was obtained on acidification of the sodium salt (XI), but this was not duplicated in several attempts. The sample of hydroxy acid (XII) lost water on melting, giving the lactone (XIII).

The isomeric unsaturated lactones. The unsaturated lactone obtained in reduction of the *cis* acid undoubtedly has the structure (IX) with the double bond α,β to the carbonyl group. Interest in the mechanism of

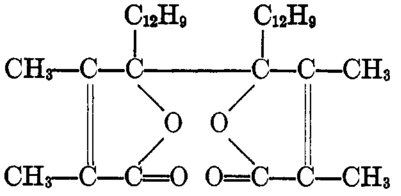


reduction here led us to a further study of the lactone and to the isolation of an unstable isomer. Similar stable and unstable unsaturated butyrolactones have already been reported by Thiele (4), who showed that γ-ketonic acids tend to enolize under the influence of acetic anhydride and sulfuric acid to give first a true enol lactone, which is unstable and is readily rearranged under the influence of acids or bases, with migration of the double bond into conjugation with the carbonyl group. In the case in hand the results are exactly parallel. The saturated γ-ketonic acid (IVA or IVB) when treated at room temperature with acetic anhydride containing a trace of sulfuric acid gives the unstable enol lactone (XIV), and this in turn is readily rearranged into the stable isomer (IX) when treated in alcohol with a little ammonium hydroxide, or when subjected to the action of boiling acetic anhydride.



Alkaline hydrolysis of the unstable enol lactone (XIV) gives the saturated acid (IV) along with some of the stable lactone (IX), which is some-what less easily hydrolyzed under these conditions, but which in the end also can be converted into the acid. Acid hydrolysis, using a mixture of conc'd acetic and hydrochloric acids (containing stannic and stannous chlorides in order to simulate more exactly the conditions employed in reduction of the *cis* acid), also brought about rearrangement to the stable unsaturated lactone (IX) in 40% yield, this product being shown in separate experiments to be stable under these and even more drastic conditions. Along with the stable unsaturated lactone, there was obtained also a 57% yield of the saturated acid (IV), a product of hydrolysis independent of the rearrangement.

Both unsaturated lactones (XIV and IX) react with Tollen's reagent to give a deposit of silver and a crystalline dimolecular oxidation-product which is identical with the product of coupling two molecules of the *cis* pseudo acid chloride (X) by means of copper bronze. The structure XV is therefore assigned to the dimolecular compound and is analogous to that of the dimolecular compounds obtained from the 3-hydroxyfurans by air oxidation or by the action of copper bronze on the 2-bromo-3-furanones (9).

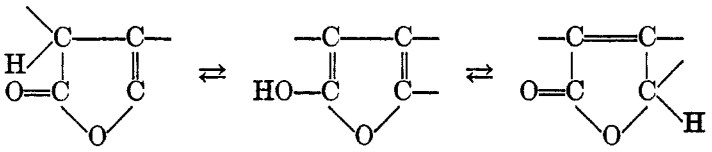


XV

It is worthy of note that the enol lactone (XIV) is oxidized to the dimolecular product (XV) by sulfuric acid in acetic anhydride, and in this respect is unlike the more stable α,β-unsaturated lactone (IX). Apparently, this oxidation, which proceeds even in the presence of zinc dust, is due to sulfuric acid since the reaction takes place equally well when air is excluded but not when phosphoric acid is substituted for sulfuric. Small amounts of the dimolecular product also are obtained in the reduction of the *cis* unsaturated acid (VIII) with zinc, acetic anhydride, and conc'd sulfuric acid; possibly dimolecular reduction is involved here; however, this is not certain, because the dimolecular product is formed also upon application of these conditions directly to the unstable enol lactone (XIV) which might conceivably have been formed as an intermediate in amounts sufficient to account for the result.

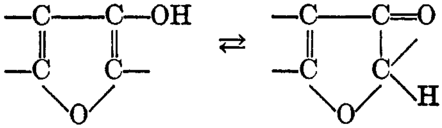
Both unsaturated lactones (IX and XIV) on treatment with alkali give the yellow color which is characteristic of the type, as noted by Thiele

(8), and which was attributed by him to the enolic or α-hydroxyfuran form (XVII).



XVI XVII XVIII

There is obviously a close analogy between this group of compounds and the β-hydroxyfurans (XIX) and β-furanones (XX). The β-hydroxyfurans are obtained best as acylates or halogenomagnesium derivatives; they are unstable in the free state, ketonize rapidly, and are easily oxidized to peroxides or to α,α-dimolecular compounds (9). In the ketonic form as β-furanones they are straightforward analogs of the unstable enol lactones of the type XIV, and are also, though to a lesser degree, analogs of the stable unsaturated lactones of type (IX). Evidently the relative stability of the unsaturated lactones of the latter type is connected with the conjugation of the α,β-unsaturated carbonyl system which is present. The β-hydroxyfuran (XIX) has the adjacent α-position as the reactive one, and in the hypothetical α-hydroxyfuran (XVII) the opposite α-position is the active position, as would be expected.



XIX XX

Incidentally, attention should be called to the close analogy between the dimolecular oxidation in both the α- and β-oxyfuran series and the first steps in the dimolecular oxidation of indoxyl to indigo.

EXPERIMENTAL

*3,4-Dimethyl-5-*p*-xenyl-2,5-dihydrofuranone-2* (2,3-dimethyl-4-xenylbutenoic acid γ-lactone) (IX). A mixture of 10 g. of *cis*-dimethylxenoylacrylic acid, 15 cc. of conc'd hydrochloric acid, 45 cc. of conc'd acetic acid, and 20 g. of stannous chloride was refluxed for 30 minutes. The hot solution was filtered directly into several volumes of water. After coagulation, the product was crystallized from ethanol, giving 8 g. (85%), and on repeated crystallization from methanol, it melted at 133.5°.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1.

Found: C, 81.6, 82.2; H, 6.3, 6.3.

A similar result was obtained using conditions similar to those above but involving long standing at room temperature, with production largely of the same product

(IX) together with unchanged material and a very small amount of the higher-melting form of the saturated acid (IVA).

Ammoniacal silver nitrate solution reacted with IX to give an immediate deposition of silver (an intermediate and fleeting yellow coloration was noted).

Ozonolysis did not give significant results. No evidence of bromination was observed in chloroform (on standing). Sulfuric acid in acetic anhydride was without action. The compound is stable toward the prolonged action of stannous chloride-hydrochloric-acetic acid mixtures, and toward refluxing methanolic sulfuric acid.

*5,5′-Bis-(3,4-dimethyl-5-*p*-xenylfuranone-2)* (XV). In a typical experiment, 2.5 g. of silver nitrate in 12 cc. of water and 12 cc. of conc'd ammonium hydroxide was mixed with 25 cc. of 10% sodium hydroxide, and poured into 50 cc. of ethanol containing 1 g. of either the above unsaturated lactone (IX) or the labile enol lactone (XIV). Rapid precipitation of silver and the dimolecular oxidation-product occurred. After standing for 2 hours, the precipitate was filtered off and the product leached from the silver residue with chloroform. In an alternative scheme, the silver was removed by washing the residue with dilute nitric acid (yield 0.91 g. or 91%).

*2,3-Dimethyl-3-*p*-xenoylpropionic acid-A* (IVA). A mixture of 6.6 g. of the α,β-unsaturated lactone (IX), 2.1 g. of potassium hydroxide, and 40 cc. of methanol was shaken occasionally over a period of a few hours until the solution became clear. After standing, a total of 20 hours, the solution was diluted with water (it showed no turbidity) and was acidified with 5 cc. of conc'd acetic acid. The precipitate after coagulation was digested with 70 cc. of hot methanol and on cooling a 62% yield of nearly pure acid was obtained (in other runs, the yields ranged from 60–75%). From the residues the lower-melting isomer-B could be isolated as the methyl ester after treatment with diazomethane. Hydrolysis at refluxing temperatures (30 minutes) was more rapid but the yields were lowered to 50%.

The acid-A was purified by repeated crystallization from methanol and from other solvents, conc'd acetic acid, acetone, ethanol, chloroform, and benzene-ethyl acetate mixtures. It was obtained as colorless needles melting at 198.5–200.5°.

Anal. Calc'd for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4.
Found: C, 76.3; H, 6.5.

The acid-A was converted in good yield into the α,β-unsaturated lactone on treatment for one hour at refluxing temperature with acetyl chloride. It is stable toward the various reducing combinations; namely, stannous chloride-conc'd acetic and hydrochloric acid mixtures at room temperature (it was dehydrated to the α,β-unsaturated lactone by this reagent at refluxing temperature), sodium hydrosulfite in boiling sodium carbonate solution, and zinc dust and boiling conc'd acetic acid (heating for 1 hour).

The methyl ester (VIA) was prepared from the acid in the usual way with ethereal diazomethane (yield 91%), or by the action of methanol and sulfuric acid (refluxing for one hour). On crystallization from methanol, it melted at 116°.

Anal. Calc'd for $C_{19}H_{20}O_3$: C, 77.0; H, 6.8.
Found: C, 77.0; H, 6.6.

Hydrolysis in methanolic potassium hydroxide (12 hours at room temperature) gave a crude acid mixture from which a yield of 61% of the isomer-A was isolated.

*2,3-Dimethyl-3-*p*-xenoylpropionic acid-B* (IVB). A solution of 0.5 g. of the isomer-A in 5 cc. of 10% sodium hydroxide was prepared by warming the mixture to 50–60°. After 20 hours at room temperature, crystals began to deposit. After 3 days, 0.35 g. (65%) of the sodium salt of the isomer-B had separated. It was recrystallized from water, and melted at 118–120° (it evidently held solvent of crystallization).

Upon dissolving in hot conc'd acetic acid and diluting with water and cooling, 1.8 g. of the free acid-B was obtained. Crystallization from benzene brought the melting point to 164–165°. It gave a sharp mixture melting point depression with the isomer-A.

Anal. Calc'd for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4.
Found: C, 76.4; H, 6.6.

In connection with reduction studies, it was shown that this acid (IVB) was stable toward aqueous sodium carbonate and sodium hydrosulfite (refluxing for 1.5 hours).

The methyl ester (VIB) was obtained from the acid in the usual way with diazomethane or with acid and methanol, and it was isolated also upon methylation of the low-melting residues obtained from hydrolysis of the α,β-unsaturated lactone (IX) (separated from the high-melting isomeric ester by fractional crystallization from 75% ethanol). The melting point was 73°.

Anal. Calc'd for $C_{19}H_{20}O_3$: C, 77.0; H, 6.8.
Found: C, 77.0; H, 6.5.

Hydrolysis. The action of methanolic potassium hydroxide (15 minutes at room temperature) on this ester gave the higher-melting ester (VIA) which crystallized directly from the solution. These crystals were filtered off and identified. Upon standing for 4 hours, the filtrate was acidified and a sample of the high-melting acid (isomer-A) was obtained.

*3,4-Dimethyl-5-*p*-xenyl-2,3-dihydrofuranone-2* (XIV) (2,3-dimethyl-3-xenoylpropionic acid enol lactone). One drop of conc'd sulfuric acid was added to a suspension of 2.2 g. of either acid IVA or IVB in 10 cc. of acetic anhydride, and after shaking for 5 minutes, the solution became clear and bright yellow. Upon successive additions of a few drops of water, cautiously, and on standing, a crystalline precipitate appeared (1.8 g. or 87%). This product required careful handling since excessive heating in solvents caused rearrangement. It was crystallized best from methanol by saturating at room temperature and then cooling to −25°. The colorless product, dried in a vacuum desiccator, melted at 93.5–95°.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1.
Found: C, 81.9; H, 6.5.

This compound showed an immediate reaction with Tollen's reagent and gave the dimolecular oxidation-product XV. It reacted with bromine in carbon tetrachloride to give a non-crystalline product. Rearrangement to the stable isomer (IX) was brought about by the action of refluxing acetic anhydride (15 minutes), by adding a few drops of conc'd ammonium hydroxide to a hot alcohol solution (a fleeting yellow coloration was noted); and it was also brought about by the typical reducing combination, 70% alcohol and sodium hydrosulfite (refluxing for 2 hours).

Oxidation resulted when a solution of 0.1 g. of the enol lactone (XIV) in 2.5 cc. of acetic anhydride was treated with 3 drops of sulfuric acid, the dimolecular product XV precipitating upon standing for 10 minutes. After standing for a total of one hour, 0.03 g. was obtained (m.p. 230–232°). A second crop brought the yield to 50%. Small amounts of this product were often obtained during the preparation of the enol lactone (XIV). Exclusion of air through use of an atmosphere of nitrogen did not change the result, nor did the presence of zinc dust. When 85% phosphoric acid was used in place of sulfuric acid, and air bubbled through the solution, no dimolecular product was found.

Alkali hydrolysis with methanolic potassium hydroxide involved a yellow coloration which disappeared within 6 hours. After standing for a total of 12 hours, the saturated acid IVA was isolated in 64% yield.

Acid hydrolysis took place under certain of the reducing conditions employed in this research, and, therefore, this labile enol lactone XIV could not have been the chief intermediate product in the reactions concerned. Since in the reduction the unstable enol lactone, if formed, would have been produced slowly and in the presence of ever-increasing amounts of stannic chloride, the following test was carried out. Two grams of the enol lactone (XIV) and 2.67 g. of stannic chloride ($SnCl_4 \cdot 5\ H_2O$) were weighed in separate containers and added in ten portions each to a stirred mixture of 4 g. of conc'd hydrochloric acid, 42.5 cc. of conc'd acetic acid, and 4 g. of stannous chloride ($SnCl_2 \cdot 2\ H_2O$). After 15 hours at room temperature, the reaction-mixture was diluted with water and the precipitate leached with sodium carbonate, which removed 1.21 g. (57%) of impure dimethylxenoylpropionic acid-A (recovered by acidification of the extract and identified). There remained 0.8 g. (40%) of material insoluble in sodium carbonate, which was identified as the stable α,β-unsaturated lactone (IX). Each of these products was shown to be stable under these reaction conditions.

Reduction of cis-*2,3-dimethyl-3-*p-*xenoylacrylic acid* (VIII). The reductions with stannous chloride are described under the preparation of the α,β-unsaturated lactone (IX).

Reduction with sodium hydrosulfite was without effect on the *cis* acid in 70% methanol (refluxing for 2 hours), but when small or large amounts of sodium carbonate were added to the mixture, reduction proceeded; in a typical case, after refluxing the mixture for one hour, the α,β-unsaturated lactone (IX) was obtained in 86% yield.

Zinc dust and conc'd acetic acid reduction in the usual way (refluxing for 2 hours) gave a poor yield of the same α,β-unsaturated lactone (IX), and reductions with shorter heating time gave considerable amounts of unchanged material.

The action of 1 g. of zinc dust on a mixture of 0.5 g. of the *cis* acid and 5 cc. of saturated aqueous sodium carbonate (stirring for 0.5 hours at 80–90°) gave 0.38 g. of the saturated acid IVA (contaminated evidently by some of the stereoisomer). None of the α,β-unsaturated lactone (IX) was detected, and this compound (IX) was subsequently subjected to identical conditions and was recovered unchanged.

Reduction of 0.5 g. in 10 cc. of acetic anhydride containing 2 drops of conc'd sulfuric acid (one hour at room temperature) gave largely unchanged material together with 0.05 g. of the dimolecular compound (XV) which was obtained as a residue when the product was dissolved in methanol. Without the zinc dust, no reaction occurred.

Reduction of the cis *ester* (*open-chain*) (VII) with zinc dust and conc'd acetic acid (refluxing for 2 hours) gave a mixture of the saturated esters VIA and VIB. The pseudo ester was partly unchanged when treated under the same conditions, but some non-crystalline by-products were produced.

Reduction of trans-*2,3-dimethyl-3-xenoylacrylic acid* (III) with zinc dust and conc'd acetic acid (room temperature for one hour) gave a product (92%) which consisted largely of the saturated acid-B. It was purified and identified. No definite reduction-products were obtained when sodium hydrosulfite was used under various conditions. The combination zinc dust and aqueous sodium carbonate (boiling for 0.5 hours) produced an 85% yield of a mixture of the saturated acids IVA and IVB from which the higher-melting isomer was isolated and identified specifically.

Reduction of the methyl ester (V) did not take place under the same conditions, but when the reaction-mixture was refluxed for one hour, a mixture (87%) of the two saturated esters was obtained. The action of stannous chloride, conc'd acetic and hydrochloric acids (refluxing for 30 minutes) produced the stable α,β-unsaturated lactone (IX).

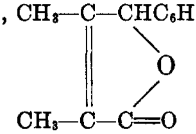
*2,3-Dimethyl-4-*p*-xenylbutyrolactone* (XIII). Catalytic reduction of the stable α,β-unsaturated lactone (IX) in ethanol proceeded slowly. The absorption of hydrogen continued beyond five molecules without any break, indicating an attack upon the aromatic nucleus. Even after absorption of two molecules of hydrogen some unchanged material remained. The best method for obtaining small but optimum yields of the dihydro compound was to stop the reaction after absorption of 1.5 to 2 molecules of hydrogen; absolute ethanol was used as solvent with the platinum oxide catalyst. Slow, quiet crystallization gave the dihydro compound, which was purified by crystallizing from methanol; melting point 151°.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.2; H, 6.8.
Found: C, 81.5; H, 7.1.

A small amount of this same product was isolated in a similar catalytic reduction of the labile enol lactone (XIV) but in this case, surprisingly, the chief product was the stable α,β-unsaturated lactone (IX) formed by rearrangement. It was demonstrated that the solvent alone did not bring about this rearrangement and the phenomenon may possibly be attributed to traces of alkali in the catalyst.

Sodium and alcohol reduction of the higher-melting dimethylxenoylpropionic acid (IVA) required drastic conditions, and a large excess of sodium was used. The product, on fractional crystallization from ethyl acetate and from methanol, gave a 5% yield of the dihydro compound (XIII).

Hydrolysis in one experiment (not repeated) on a very small scale with 10% sodium hydroxide to which was added a few drops of ethanol, gave a new acid which melted at 90–108° and which could be dissolved in alkali and reprecipitated by acid. Upon crystallization from benzene it melted at 110–113.5° with effervescence, resolidified at once, remelted at 142–149°, and was then identified as the lactone (XIII). The acid changed to the lactone spontaneously on standing for several days at room temperature.

3,4-Dimethyl-5-phenyl-3,4-furanone-2 (2,3-dimethyl-4-phenyl-2,3-butenoic acid γ-lactone),  $\begin{array}{l} CH_3{-}C{-}CHC_6H_5 \\ \quad\;\; \| \quad\;\; \diagdown \\ \quad\;\; \| \qquad\; O \\ \quad\;\; \| \quad\;\; \diagup \\ CH_3{-}C{-}C{=}O \end{array}$. The yield of *cis*-3-benzoyl-2,3-dimethylacrylic acid (10) was greatly improved by crystallization of the product from a 9:1 mixture of ligroin and ethyl acetate. A suspension of 4.6 g. of this acid in 25 cc. of water was treated with saturated sodium carbonate solution until it dissolved; 25 cc. of a saturated solution of sodium hydrosulfite was then added and the mixture refluxed for 10 minutes. The amber colored oil which appeared (3.7 g. or 87%) was distilled under reduced pressure; b.p. 141° at 21 mm. pressure; n_D^{25} 1.5442; dispersion ($n_F - n_C$) 0.0162.

Anal. Calc'd for $C_{12}H_{12}O_2$: C, 76.6; H. 6.4.
Found: C, 76.2; H, 6.4.

Similar results were obtained using stannous chloride in a conc'd acetic and hydrochloric acid mixture (refluxing for 30 minutes).

The product with Tollen's reagent gave an immediate yellow coloration followed by formation of the characteristic black precipitate.

3-Benzoyl-2,3-dimethylpropionic acid, $C_6H_5COCH(CH_3)CH(CH_3)COOH$, was prepared by hydrolysis of the above described furanone by allowing a solution of 40 g.

in 125 cc. of methanol and 15 g. of potassium hydroxide to stand at room temperature for 10 days. The product was crystallized from ethyl acetate; yield 31.9 g. (73%). When a larger excess of alkali was used or the reaction carried out at a higher temperature, the yield was greatly diminished, and propiophenone was isolated from the residual oils as the semicarbazone (identified). Careful search failed to reveal a stereoisomeric acid. This acid has been mentioned already in the literature (11) (m.p. 140–145°) but no analysis was given. Our product was crystallized twice from ethyl acetate and eight times from 75% ethanol and melted at 150–152°.

Anal. Calc'd for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8.
Found: C, 69.5, 69.5; H, 6.9, 6.9.

The methyl ester, $C_6H_5COCH(CH_3)CH(CH_3)COOCH_3$, was made in good yield by the action of diazomethane on the acid in the usual way. The reaction was immediate and vigorous. The product distilled at 137-139° at 2-3 mm. pressure; n_D^{25} 1.511; dispersion $(n_F - n_C)$ 0.0144.

Anal. Calc'd for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3.
Found: C, 70.7; H, 6.9.

The ester was prepared also by the action of refluxing methanol and sulfuric acid. Hydrolysis with alcoholic potassium hydroxide (standing 17 hours at room temperature) of samples prepared by either method gave the parent acid. Attempts to make a crystalline semicarbazone failed.

SUMMARY

Reduction of *trans*-2,3-dimethyl-3-*p*-xenoylacrylic acid and methyl ester and of the open-chain *cis* ester gives the saturated compounds, presumably through 1,6-reactions. The *cis* pseudo ester is not easily reduced.

The *cis* acid in reduction appears to function as the α,β-unsaturated lactonol or 5-hydroxyfuranone. Stannous chloride reduction probably involves the 5-chlorofuranone as an intermediate. The product of these reductions is the α,β-unsaturated lactone. Reduction in alkaline medium gives the saturated acid and appears to involve the open-chain form.

The stereoisomeric 2,3-dimethyl-3-xenoylpropionic acids and their esters have been prepared. Further reduction by sodium and alcohol gives the corresponding γ-lactone which is obtainable also by catalytic reduction of the α,β-unsaturated lactone.

The dimethylxenoylpropionic acids are dehydrated to an unstable enol lactone which readily undergoes rearrangement into the more stable α,β-unsaturated lactone (by shift of the double bond). Hydrolysis of these unsaturated lactones regenerates the saturated ketonic acids and oxidation gives an 5,5′-dimolecular product.

The analogy between the unsaturated lactones (as α-furanones) and the β-hydroxyfurans and β-furanones is discussed.

CHARLOTTESVILLE, VA.

REFERENCES

(1) LUTZ, *J. Am. Chem. Soc.*, **56**, 1378 (1934).
(2) LUTZ AND KIBLER, *J. Am. Chem. Soc.*, **62**, 360 (1940).

(3) Hill and Cornelison, *Am. Chem. J.*, **16,** 188, 277 (1894).
(4) Thiele and Straus, *Ann.*, **319,** 174 (1901).
(5) Lutz and Couper, *J. Org. Chem.*, **6,** 77 (1941).
(6) Lutz and Smith, results to be published shortly.
(7) Hantzsch and Schwiete, *Ber.*, **49,** 213 (1916).
(8) Thiele, *Ann.*, **319,** 144 (1901).
(9) Kohler, Westheimer, and Tishler, *J. Am. Chem. Soc.*, **58,** 264 (1936); **58,** 1885 (1936); **59,** 2314, 2316, 2322 (1937).
(10) Lutz and Taylor, *J. Am. Chem. Soc.*, **55,** 1593 (1933).
(11) Schroeter, Lichtenstadt, and Irineu, *Ber.*, **51,** 1591 (1918).