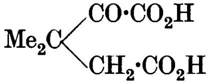
XXVIII.—*Studies in Keto-lactol Tautomerism. Part I. Ring-chain Tautomerism in α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid and a Synthesis of γ-Acetyl-ββ-dimethylbutyric Acid.*

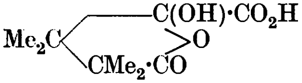
By MUHAMMAD QUDRAT-I-KHUDA.

RING-CHAIN tautomerism has been divided by Kon, Stevenson, and Thorpe (J., 1922, **121**, 651) into two types, namely, keto-cyclol tautomerism, which has been exhaustively investigated by Thorpe and his collaborators (Deshapande and Thorpe, J., 1922, **121**, 1432; Singh and Thorpe, J., 1923, **123**, 114; Bains and Thorpe, *ibid.*, p. 1207; Lanfear and Thorpe, *ibid.*, pp. 1685, 2868), and keto-lactol tautomerism, as an example of which γ-keto-αββ-trimethylglutaric acid (Balbiano's acid) may be cited : this reacts in both the keto-form (II) and the hydroxy-ring form (III) (Kon, Stevenson, and Thorpe, *loc. cit.*) ; its lower homologue exists in the keto-form (I) (Perkin and Thorpe, J., 1901, **79**, 757), and the next higher homologue only in the hydroxy-ring form (IV) (Rothstein and Shoppee, J., 1927, 532).

(I.)



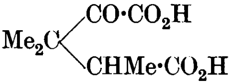
$\mathrm{Me_2C}\Big\langle\begin{matrix}\mathrm{CO{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CO_2H}\end{matrix}$



$\mathrm{Me_2C}\Big\langle\begin{matrix}\text{——}\mathrm{C(OH){\cdot}CO_2H}\\ \quad\mathrm{>O}\\ \mathrm{CMe_2{\cdot}CO}\end{matrix}$

(IV.)

(II.)



$\mathrm{Me_2C}\Big\langle\begin{matrix}\mathrm{CO{\cdot}CO_2H}\\ \mathrm{CHMe{\cdot}CO_2H}\end{matrix}$

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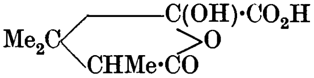


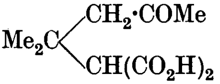
$\mathrm{Me_2C}\Big\langle\begin{matrix}\text{——}\mathrm{C(OH){\cdot}CO_2H}\\ \quad\mathrm{>O}\\ \mathrm{CHMe{\cdot}CO}\end{matrix}$

(III.)

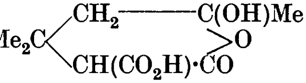
In the present series of papers, evidence will be brought forward of the existence of the latter type of tautomerism in some δ-ketonic acids. The effect of alteration of the carbon tetrahedral angle, due to the presence of different substituents, on the tautomeric character of the various acids will also be examined.

α-Carboxy-γ-acetyl-ββ-dimethylbutyric acid has been prepared by the alkaline hydrolysis of the condensation product of cyanoacetamide and mesityl oxide (compare Vorländer and Gärtner, *Annalen*, 1898, **304**, 17). Its reactions cannot be fully explained by the keto-formula (V) and it is necessary to assume that under certain conditions the acid exists in its lactol modification (VI).

(V.)



$\mathrm{Me_2C}\Big\langle\begin{matrix}\mathrm{CH_2{\cdot}COMe}\\ \mathrm{CH(CO_2H)_2}\end{matrix}$

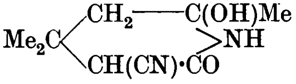


$\mathrm{Me_2C}\Big\langle\begin{matrix}\mathrm{CH_2}\text{——}\mathrm{C(OH)Me}\\ \quad\mathrm{>O}\\ \mathrm{CH(CO_2H){\cdot}CO}\end{matrix}$

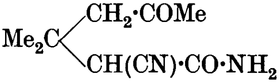
(VI.)

When mesityl oxide is condensed with cyanoacetamide in the presence of a small quantity of sodium ethoxide, 6-*hydroxy*-2-*keto*-3-*cyano*-4 : 4 : 6-*trimethylpiperidine* (VII) is formed. Kohler and Souther, however (*J. Amer. Chem. Soc.*, 1922, **44**, 2906), by the condensation of cyanoacetamide with phenyl styryl ketone (also an αβ-unsaturated ketone), obtained the amide corresponding to the open-chain formula (VIII).

(VII.)

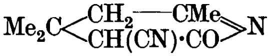


$\mathrm{Me_2C}\Big\langle\begin{matrix}\mathrm{CH_2}\text{——}\mathrm{C(OH)Me}\\ \quad\mathrm{>NH}\\ \mathrm{CH(CN){\cdot}CO}\end{matrix}$



$\mathrm{Me_2C}\Big\langle\begin{matrix}\mathrm{CH_2{\cdot}COMe}\\ \mathrm{CH(CN){\cdot}CO{\cdot}NH_2}\end{matrix}$

(VIII.)

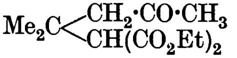
The compound (VII) does not lose ammonia on treatment with dilute sodium hydroxide solution and gives the tetrahydropyridine *derivative*,  $\mathrm{Me_2C}{<}\begin{matrix}\mathrm{CH_2}\text{——}\mathrm{CMe}\\ \mathrm{CH(CN){\cdot}CO}\end{matrix}{>}\mathrm{N}$ (IX), on dehydration with phosphorus oxychloride. The constitution thus indicated is confirmed by the synthesis of the compound from the open-chain *cyano-ester* (X) : this, on treatment with ammonia, gives a crystalline *com-*

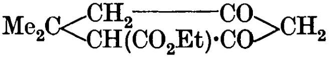
pound (XI) which, on being heated with alcoholic sodium ethoxide, is quantitatively converted into the compound (VII).

(X.) 
$Me_2C<\begin{matrix}CH_2\cdot COMe\\ CH(CN)\cdot CO_2Et\end{matrix}$

 (XI.)
$Me_2C<\begin{matrix}CH_2\cdot CMe(OH)\cdot NH_2\\ CH(CN)\cdot CO\cdot NH_2\end{matrix}$

The compound (VII), when hydrolysed with concentrated aqueous potash, gives as the sole product the acid (V), the ethyl ester (XII) of which, on treatment with alcoholic sodium ethoxide, changes almost quantitatively into ethyl 5 : 5-dimethyl-5 : 6-dihydroresorcinol-4-carboxylate (XIII) (Vorländer, *Annalen*, 1897, **294**, 300).

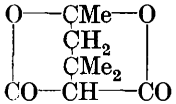
(XII.) 
$Me_2C<\begin{matrix}CH_2\cdot CO\cdot CH_3\\ CH(CO_2Et)_2\end{matrix}$

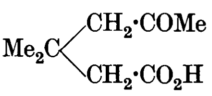
 (XIII.)
$Me_2C<\begin{matrix}CH_2\text{———}CO\\ CH(CO_2Et)\cdot CO\end{matrix}>CH_2$

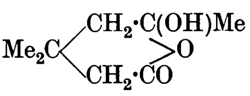
The acid (V) on oxidation with sodium hypobromite solution gives α-carboxy-ββ-dimethylglutaric acid, $CO_2H\cdot CH_2\cdot CMe_2\cdot CH(CO_2H)_2$ (XIV) (Perkin and Goodwin, J., 1896, **69**, 1473), which changes into ββ-dimethylglutaric acid, $CMe_2(CH_2\cdot CO_2H)_2$ (XV), on heating.

Hydrolysis of (VII) with concentrated hydrochloric acid yields as the principal product a neutral crystalline solid, m. p. 137°, which gives the acid (V) when heated with dilute sodium hydroxide solution and is therefore probably the dilactone (XVI) (Vorländer and Gärtner, *Annalen*, 1898, **304**, 16); it is produced from the acid (V) almost quantitatively by heating with concentrated hydrochloric acid and quantitatively by the action of any dehydrating agent.

The acid (V) decomposes at 130—140°, giving a mixture containing the keto-monobasic acid (XVII) and the dilactone (XVI) in relative quantities which suggest that the parent acid is a mixture of the forms (V) and (VI), the generators of (XVII) and (XVI) respectively, approximately in the ratio 3 : 1.


(XVI.)

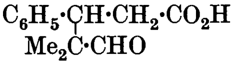

$Me_2C<\begin{matrix}CH_2\cdot COMe\\ CH_2\cdot CO_2H\end{matrix}$
(XVII.)


$Me_2C<\begin{matrix}CH_2\cdot C(OH)Me\\ CH_2\cdot CO\end{matrix}>O$
(XVIII.)

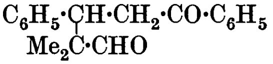
The proof of the existence of the hydroxyl group in the lactol form (VI) of the acid (V) is difficult to obtain. The ease with which lactonisation takes place precludes the formation of the acetyl derivative. It seemed probable that the desired evidence might be obtained if the possibility of dilactone formation were prevented, and therefore the keto-monobasic acid (XVII; lactol form, XVIII) was investigated.

Meerwein and his collaborators have observed (*J. pr. Chem.*, 1927, **116**, 536) that β-phenyl-γγ-dimethylglutaraldehydic acid (XIX) and the δ-keto-aldehyde (XX) sometimes react as their lactol forms (XXI) and (XXII) respectively. It was expected that the acid (XVII) would exhibit similar properties. The acid was prepared, as already mentioned, from the acid (V). It had previously been obtained by Bredt (*Annalen*, 1898, **299**, 177) and by Vorländer and Gärtner (*loc. cit.*). Its constitution was further proved by an independent synthesis of its ethyl ester (XXV) from *ethyl hydrogen* ββ-*dimethylglutarate* (XXIII), through the acid chloride (XXIV) with zinc methyl iodide. The ester was completely converted into Vorländer's dimethyldihydroresorcinol (XXVI) (*Annalen*, 1897, **294**, 314) by alcoholic sodium ethoxide. The acid (XVII), on esterification with alcohol and mineral acid, gave the normal ester (XXV). The identity of the two esters was established by analysis and by the melting point of a mixture of their semicarbazones. The free acid was prepared from the synthetic ester and identified, by means of the semicarbazones, with the acid obtained from (X). Although the free acid appears to have the normal ketonic structure (XVII), it reacts in the isomeric hydroxy-form (XVIII) in presence of acetyl chloride, when, instead of the acetyl compound (XXVII), the unsaturated lactone (XXVIII) is obtained through elimination of the hydroxyl group as water.

(XIX.)



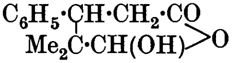
$$\begin{array}{l} C_6H_5\cdot CH\cdot CH_2\cdot CO_2H \\ Me_2C\cdot CHO \end{array}$$



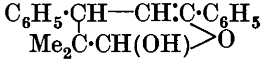
$$\begin{array}{l} C_6H_5\cdot CH\cdot CH_2\cdot CO\cdot C_6H_5 \\ Me_2C\cdot CHO \end{array}$$

(XX.)

(XXI.)

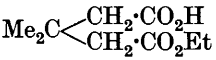


$$\begin{array}{l} C_6H_5\cdot CH\cdot CH_2\cdot CO \\ Me_2C\cdot CH(OH) \end{array}\!\!>O$$



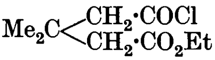
$$\begin{array}{l} C_6H_5\cdot CH{-}CH{:}C\cdot C_6H_5 \\ Me_2C\cdot CH(OH) \end{array}\!\!>O$$

(XXII.)



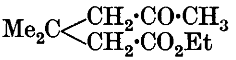
$$Me_2C<\begin{array}{l} CH_2\cdot CO_2H \\ CH_2\cdot CO_2Et \end{array}$$

(XXIII.)



$$Me_2C<\begin{array}{l} CH_2\cdot COCl \\ CH_2\cdot CO_2Et \end{array}$$

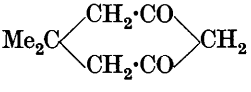
(XXIV.)

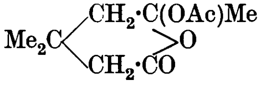


$$Me_2C<\begin{array}{l} CH_2\cdot CO\cdot CH_3 \\ CH_2\cdot CO_2Et \end{array}$$

(XXV.)

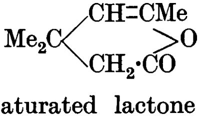
(XXVI.)

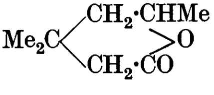




(XXVII.)

(XXVIII.)





(XXIX.)

The unsaturated lactone can be hydrolysed to the keto-acid (XVII) with alcoholic caustic potash. The keto-acid (XVII) on reduction with sodium and alcohol gives a good yield of the saturated *lactone* (XXIX). A study of the action of potassium cyanide on these lactones and of the synthesis of trisubstituted adipic acids is now in progress.

The proximity of a methylene group to the keto-group in the acid (XVII) makes the elimination of a molecule of water an easy matter, and consequently the unsaturated lactone (XXVIII) is readily obtained. But if the γ-carbon atom were substituted, more definite evidence of the existence of the hydroxy-phase of these keto-acids should be obtained. Experiments in this direction are in progress and the δ-keto-acid derived from the acid ester of camphoric acid does actually show interesting properties; the results, however, will form the subject of a future communication.

EXPERIMENTAL.

6-*Hydroxy*-2-*keto*-3-*cyano*-4 : 4 : 6-*trimethylpiperidine* (VII).—When a solution of sodium (2·3 g.) in absolute alcohol (500 c.c.) is mixed with powdered cyanoacetamide (84 g.) and mesityl oxide (108 c.c.) and well shaken, after 10—15 minutes crystals begin to separate and the alcohol sometimes boils. After 12 hours, the crystals are collected and washed with absolute alcohol; the mother-liquor and washings, when neutralised with hydrochloric acid and concentrated, give a few grams more of the same product (total yield, almost theoretical). The solid, after crystallising from ethyl alcohol and drying in the steam-oven, melts at 272° with charring (Found: C, 59·4; H, 7·5. $C_9H_{14}O_2N_2$ requires C, 59·3; H, 7·7%). It is somewhat soluble in water, soluble in hot alcohol, and insoluble in ether, benzene and chloroform. Sodium nitrite in cold acetic acid solution has no action on it.

2-*Keto*-3-*cyano*-4 : 4 : 6-*trimethyl*-2 : 3 : 4 : 5-*tetrahydropyridine* (IX).—The preceding compound (18 g.) is heated with phosphorus oxychloride (15 c.c.) on the steam-bath for 2 hours and the viscous mass obtained on cooling is treated with ice and a slight excess of dilute sodium carbonate solution. The precipitate obtained, after being washed with water and dried (9 g.), crystallises from hot dilute acetic acid in slender short needles, m. p. 253° (Found: C, 65·3; H, 7·1. $C_9H_{12}ON_2$ requires C, 65·8; H, 7·3%), which are very soluble in alcohol, appreciably soluble in dilute mineral acids, but insoluble in ether, chloroform and benzene.

Ethyl α-*Cyano*-γ-*acetyl*-$\beta\beta$-*dimethylbutyrate* (X).—A solution of sodium (1·2 g.) in absolute alcohol (150 c.c.) is mixed with ethyl cyanoacetate (56 g.) and mesityl oxide (54 c.c.) and heated on the steam-bath for 4 hours; the alcohol is then distilled off and the residue poured into water. Ether extracts a liquid which, when washed, dried, and fractionated in a vacuum, gives first unchanged mesityl oxide and ethyl cyanoacetate and then the *ketocyano-ester* (X) as a colourless mobile liquid, b. p. 160°/16 mm., $d_{4^\circ}^{20\cdot3^\circ}$ 1·03705, $n_D^{20\cdot3^\circ}$ 1·44652, whence $[R_L]_D$ 54·39 (calc., 54·43) (Found: C, 62·0; H, 8·0. $C_{11}H_{17}O_3N$ requires C, 62·5; H, 8·0%). The yield is about 70%. The *semicarbazone*, crystallised from dilute methyl alcohol, melts at 166·5° (Found: C, 53·8; H, 7·8. $C_{12}H_{20}O_3N_4$ requires C, 53·7; H, 7·5%).

Action of Aqueous Ammonia on Ethyl α-Cyano-γ-acetyl-ββ-dimethylbutyrate.—When the ester (25 g.) is mixed with aqueous ammonia (24 c.c., *d* 0·880) and occasionally shaken, the separate layers disappear after 24 hours, and after another 24 hours crystals begin to form. Next day, the whole is cooled in a freezing mixture and diluted with acetone and the crystals are collected and dried in the air. On recrystallisation from water, *δ-amino-δ-hydroxy-α-cyano-ββ-dimethylhexoamide* (XI) is obtained in crystals containing $3H_2O$, m. p. 87° (decomp.) (Found: C, 42·7; H, 9·1. $C_9H_{17}O_2N_3,3H_2O$ requires C, 42·7; H, 9·1%). It is soluble in water and in alcohol, but crystallises from the former only when the solution is cooled in ice. It is very sparingly soluble in hot chloroform and acetone and insoluble in ether and benzene. When left in a vacuum desiccator, it loses a part of its water and is converted into a sticky mass. It decomposes in the steam-oven, and loses ammonia when heated with water at 100°. It does not give a semicarbazone.

Hydrolysis of the Condensation Product (VII) *with Concentrated Hydrochloric Acid. Formation of the Dilactone* (XVI).—The powdered condensation product (20 g.) is heated with 100 c.c. of concentrated hydrochloric acid on the steam-bath for 4 hours, and the crystalline product is separated from the cooled, diluted solution and washed with and recrystallised from dilute alcohol, the *dilactone* being obtained in long prismatic needles, m. p. 137° (Found: C, 58·7; H, 6·8. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%), sparingly soluble in cold alcohol, difficultly soluble in ether and hot benzene, and freely soluble in hot alcohol. At 200°, it slowly decomposes with loss of carbon dioxide and production of the unsaturated lactone (XXVIII). The dilactone is also produced by hydrolysis of (IX) or (X) with concentrated hydrochloric acid.

Hydrolysis of the Condensation Product (VII) *with Concentrated Potassium Hydroxide Solution. Formation of α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid* (V).—The compound (VII) (36 g.) is heated with a solution of potassium hydroxide (32 g.) in 130 c.c. of water until ammonia ceases to be evolved (about 28 hours). The cooled, diluted solution is acidified with concentrated hydrochloric acid, with cooling, and saturated with ammonium sulphate. Ether then extracts the acid (V), which crystallises from chloroform–petrol in stout prisms, m. p. 95° (Found: C, 53·4; H, 7·0. Calc. for $C_9H_{14}O_5$: C, 53·4; H, 6·9%. Found: Ag, 51·8. Calc. for $C_9H_{12}O_5Ag_2$: Ag, 51·9%).

The semicarbazone of (V) crystallises from a small quantity of water in short prisms, m. p. 177° (Found : C, 46·3 ; H, 6·8. Calc. : C, 46·3 ; H, 6·6%). The ethyl ester (XII), prepared by means of alcoholic hydrogen chloride, has b. p. 153°/12 mm., $d_{4^\circ}^{20\cdot 2^\circ}$ 1·03921, $n_{\mathrm{D}}^{20\cdot 2^\circ}$ 1·4413, whence $[R_L]_{\mathrm{D}} = 65\cdot59$ (calc. for normal ester, 65·55) (Found : C, 60·0 ; H, 8·5. Calc. : C, 60·4 ; H, 8·5%) ; its semicarbazone melts at 76° (Found : C, 52·8 ; H, 7·9. Calc. : C, 53·3 ; H, 7·9%). The same ester is obtained when the original condensation product is hydrolysed with alcoholic hydrogen chloride.

Oxidation of α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid.—The acid (10 g.) is dissolved in 40 c.c. of 10% sodium hydroxide solution and added to a solution of hypobromite (Br, 12 c.c. ; H_2O, 150 c.c. ; 10% NaOH soln., 200 c.c.), cooled in ice. After 1½ hours, the bromoform is extracted with ether and the alkaline solution is treated with sulphur dioxide, acidified with hydrochloric acid, and saturated with ammonium sulphate. Ether then extracts α-carboxy-ββ-dimethylglutaric acid (XIV), m. p. 173° (decomp.) (compare Perkin and Goodwin, *loc. cit.*).

Behaviour of α-Carboxy-γ-acetyl-ββ-dimethylbutyric Acid (V) *on Heating.*—The acid (5 g.) was heated in a bath at 130—140° for 5 hours. An ethereal solution of the cooled melt, when shaken with dilute sodium carbonate solution, dried, and evaporated, left 1·15 g. (equivalent to 25% of the dibasic acid) of the dilactone (XVI); the alkaline extract gave on acidification a quantity of the acid (XVII) representing 72% of the dibasic acid : 97% of the total material is thus accounted for.

Different quantities of the dibasic acid were heated in this way, but the weight of dilactone isolated always represented 25—27% of the dibasic acid.

γ-Acetyl-ββ-dimethylbutyric acid (XVII), obtained as described above, is a somewhat viscous liquid, b. p. 162°/25 mm., $d_{4^\circ}^{19\cdot 5^\circ}$ 1·03646, $n_{\mathrm{D}}^{19\cdot 5^\circ}$ 1·44652, whence $[R_L]_{\mathrm{D}} = 40\cdot6$ (calc., 40·69) (Found for the *silver* salt : Ag, 40·4. $C_8H_{13}O_3Ag$ requires Ag, 40·7%). The semicarbazone melts at 172° (decomp.) (compare Vorländer and Gärtner, *loc. cit.*).

The ethyl ester (XXV) is obtained by the alcohol–hydrogen chloride method as a colourless mobile liquid with a rather characteristic odour, b. p. 112°/17 mm., $d_{4^\circ}^{19\cdot 8^\circ}$ 0·96248, $n_{\mathrm{D}}^{19\cdot 8^\circ}$ 1·43047, whence $[R_L]_{\mathrm{D}} = 49\cdot97$ (calc. for the normal ester, 50·05) (Found : C, 64·4 ; H, 9·6. Calc. : C, 64·5 ; H, 9·7%) ; its semicarbazone crystallises from dilute methyl alcohol in lustrous flat needles, m. p. 114° (Found : C, 54·6 ; H, 9·3. Calc. : C, 54·3 ; H, 8·6%).

Synthesis of Ethyl γ-Acetyl-ββ-dimethylbutyrate (XXV).—ββ-Dimethylglutaric anhydride is heated with twice the calculated quantity of absolute alcohol on the steam-bath for 3—4 hours; the excess of alcohol is then removed under reduced pressure and water added. The precipitated oil is taken up in ether and shaken with sodium carbonate solution. The alkaline solution on acidification gives *ethyl hydrogen* ββ-*dimethylglutarate*, which is dissolved in ether, dried, and distilled in a vacuum; b. p. 164°/16 mm., $d_{4°}^{18·1°}$ 1·05574, $n_D^{18·1°}$ 1·4403, whence $[R_L]_D = 46·97$ (calc., 46·95) (Found for the *silver* salt: Ag, 36·6. $C_9H_{15}O_4Ag$ requires Ag, 36·6%).

This ester (40 g.) and thionyl chloride (36 c.c.) are heated on the steam-bath for an hour and the product is distilled in a vacuum; the acid chloride is obtained as a colourless mobile liquid (41 g.), b. p. 117°/16 mm.

A well-cooled benzene solution of zinc methyl iodide obtained from 55 g. of zinc–copper couple, 44 c.c. of methyl iodide, 21 c.c. of ethyl acetate, and 50 c.c. of benzene is diluted with 100 c.c. more of the dry solvent and the acid chloride (41 g.) in dry benzene (30 c.c.) is slowly added. After 1 hour, the excess of zinc methyl iodide is decomposed with ice and dilute sulphuric acid, and the benzene solution is washed with water, dilute sodium hydroxide solution, and again with water and then dried and fractionated in a vacuum; the keto-ester (XXV) distils at 126—128°/13 mm. After purification through the semicarbazone it has b. p. 113°/18 mm., $d_{4°}^{20·9°}$ 0·96323, $n_D^{20·9°}$ 1·43067, whence $[R_L]_D = 49·95$ (Found: C, 64·4; H, 9·9%). The semicarbazone prepared from it (Found: C, 54·1; H, 8·6%) melts at 114°, alone or mixed with the semicarbazone of the ester from the acid (XVII).

*Action of Acetyl Chloride on γ-Acetyl-*ββ-*dimethylbutyric Acid.*—After a mixture of the acid (XVII) (15 g.) and acetyl chloride (13 c.c.) has been kept at the ordinary temperature for 2 days, the solution is poured on ice and the oil is extracted with ether, washed with dilute sodium carbonate solution, dried, and distilled. A colourless, mobile liquid with the characteristic odour of the unsaturated lactone (XXVIII) is obtained, b. p. 82°/10 mm., $d_{4°}^{22·2°}$ 0·98658, $n_D^{22·2°}$ 1·45573, whence $[R_L]_D = 38·55$ (calc., 38·13) (Found: C, 68·6; H, 9·0. Calc. for $C_8H_{12}O_2$: C, 68·5; H, 8·6%) (compare Bredt, *Annalen*, 1898, **299**, 179).

Preparation of ββδ-*Trimethylvalerolactone* (XXIX).—The acid (XVII) (10 g.) is reduced with sodium (11 g.) and boiling absolute alcohol (185 c.c.) and after 2½ hours' heating the alcohol is distilled in steam, the residue acidified with concentrated hydrochloric acid, and the oil extracted with ether, washed with sodium carbonate solution, dried, and distilled. The *lactone* (6·6 g.), a colourless mobile liquid with a faint lactonaceous odour, has b. p. 120°/18 mm., $d_{4°}^{17°}$

0·98039, $n_D^{17°}$ 1·44743, whence $[R_L]_D = 38·73$ (calc., 38·70) (Found : C, 67·1 ; H, 9·8. $C_8H_{14}O_2$ requires C, 67·6 ; H, 9·8%).

In conclusion, the author wishes to acknowledge his indebtedness to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in this investigation and to the Government of Bengal for a foreign scholarship and a grant towards the purchase of chemicals. The author also desires to thank Dr. J. C. Bardhan of this laboratory for his friendly advice.

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[*Received, November 6th*, 1928.]