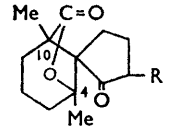
## 687. *Synthetical Studies of Terpenoids. Part IX.* An Unusual Case of Ring-closure with Polyphosphoric Acid.*

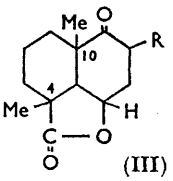
By Soumyendra Lal Mukherjee and Phanindra Chandra Dutta.

The spiroketone (I) is formed in poor yield during cyclisation of the unsaturated acid (XI) with polyphosphoric acid; its structure is established.

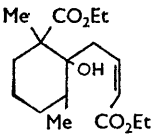
The present investigation deals with experiments leading to the synthesis of the spiroketones (I) and (II), which incorporate a cyclopentane ring as a result of an unusual type of ring-closure during an attempt to synthesise compound (IV),[1] an important degradation product of marrubiin. In view of previous experience [2] of ring-closure of suitably substituted unsaturated compounds with polyphosphoric acid, it was also expected that knowledge of the stereochemistry of the synthetic product (III) would be obtained, had the reaction proceeded in the desired direction. Recently the steric configurations of all the asymmetric centres in the keto-lactone (IV) have been determined [3] on a more or less sure basis, thereby facilitating development of a better synthetic pathway to the desired product, and experiments are in progress to that end.



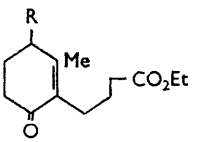
(I) R = H
(II) R = Me



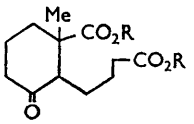
(III) R = H
(IV) R = Me



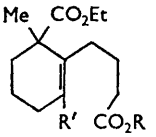
(V)



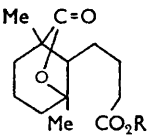
(VI: R = $CO_2Et$)
(VII: R = H)



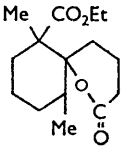
(VIII) R = H
(IX) R = Et



(X) R = Et, R′ = Me
(XI) R = H, R′ = Me
(XVI) R = R′ = H



(XII) R = Et
(XIII) R = H
(XIV) R = Me



(XV)

For the synthesis of the keto-lactone (III), it appeared that the unsaturated acid-ester (XI) might be a useful intermediate which on ring-closure and lactonisation, simultaneous or subsequent, might lead to the product. Methylation of the keto-lactone (III) should lead to compound (IV). To synthesise the unsaturated ester (XI), the most straightforward method appeared to be the condensation of ethyl γ-bromocrotonate with ethyl 1,3-dimethyl-2-oxocyclohexanecarboxylate,[4] but the yield was poor and the desired product (V) was obtained after very careful fractionation. On catalytic reduction, the analytically pure material could not be isolated, probably owing to lactonisation during distillation at high temperature. The next attempt involved the condensation of ethyl γ-iodobutyrate with Hagemann's ester, under controlled conditions; the iodo-ester was prepared from the chloro-ester.[5] The product (VI) was hydrolysed and decarboxylated,

* Part VIII, Narang and Dutta, *J.*, 1964, 1119.

[1] Cocker, Cross, Duff, Edward, and Holley, *J.*, 1953, 2540; Hardy, Rigby, and Moody, 1957, 2955; Burn and Rigby, 2964.

[2] Ghatak, Datta, and Ray, *J. Amer. Chem. Soc.*, 1960, **82**, 1728, and references therein.

[3] Wheeler and Wheeler, *Chem. and Ind.*, 1961, 463, 1832; cf. abstracts of communications, 2nd Int. Symposium on the Chemistry of Natural Products, Prague, 1962, p. 99; Professor Fetizon has suggested that the 4- and the 10-methyl groups in (IV) are *trans*-oriented (personal communication).

[4] Bhattacharyya, *J. Indian Chem. Soc.*, 1945, **22**, 165.

[5] Noyce and Canfield, *J. Amer. Chem. Soc.*, 1954, **74**, 3630.

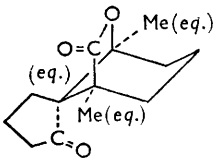
to give the unsaturated keto-ester (VII) in satisfactory yield. Addition of potassium cyanide [6] to the double bond proceeded in excellent yield, and the product, on alkaline hydrolysis *in situ*, afforded the crystalline keto-di-acid (VIII), which was converted into the diester (IX); this reacted with methylmagnesium iodide to afford the corresponding hydroxy-diester, which was dehydrated with thionyl chloride in pyridine, to afford the di-ester (X). The crude ester was boiled with freshly precipitated copper in benzene to remove sulphur. Infrared studies of this dehydration product indicated an appreciable amount of a γ-lactonic material, presumably (XII). This explains the slightly divergent analytical values for the compound (X). The unsaturated di-ester (X) was subjected to partial alkaline hydrolysis, and the crude acidic product was cyclised with polyphosphoric acid,[7] the zinc chloride–acetic anhydride–acetic acid [8] and stannic chloride methods having failed in this case. The product was a complex mixture of acidic and neutral materials. The acidic material has been identified with (XIII), probably the lactonic acid originally present in the reaction mixture. This was esterified with diazomethane to give (XIV), whose infrared spectra indicate the presence of a γ-lactonic function and an ester group, the bands being almost equal in intensity (see below). The ester (XIV), on mild hydrolysis, gave back the acid (XIII), lending further confirmation to its structure. From the neutral fraction, a product subsequently shown to be (I) partly crystallised, and chromatography of the remaining matter yielded compounds (XV) and (I). The structure (XV) has been tentatively assigned to this oily product because of the presence of a broad band at 5·78 μ in the infrared spectrum, and from its behaviour with dilute alkali; it is evidently formed through lactonisation of the unsaturated acid (XI). Compounds (XIII) and (XV) did not afford (I) on treatment with polyphosphoric acid. Since the yield of compound (I) barely exceeds 5% of theory, attempts at ring-closure with polyphosphoric acid were made at a higher temperature. In this case none of the desired product could be isolated, and a small amount of a low-boiling material, with a smell strongly reminiscent of hydrocarbons, could be isolated but not fully characterised. This is parallel to the results [9] of treatment of δ-lactones with phosphorus pentoxide at high temperatures, although cyclopentenone derivatives have recently [10] been obtained by this method.

The keto-lactone (I), so far isolated in poor yield, had the correct analysis for carbon and hydrogen, and $\lambda_{max.}$ (in KBr) 5·65 and 5·80 μ, but, unexpectedly it failed to afford any ketonic derivative. Synthesis was attempted of the α-methylated [11] ketone so that its infrared spectrum might be compared directly with that of the sample (IV) available from natural sources. In order to introduce the methyl group, the keto-lactone (I) was treated with ethyl formate in presence of sodium methoxide in benzene. The formyl derivative was then allowed to react with acetic anhydride, to afford the corresponding acetoxy-derivative, which, on catalytic reduction, afforded the methylated ketone (II) in excellent yield. Incidentally, this indicates the presence of a $-CO\cdot CH_2-$ unit in (I). The infrared spectrum of (II) in carbon tetrachloride not only showed considerable divergence from that of the natural product (IV) (available through the courtesy of Dr. Rigby, formerly of Birkbeck College, London), but the two carbonyl bands appeared at 5·65 and 5·77 μ and the intensity of the latter was only about 50% of that of the former. The presence of the band at 5·77 μ is clearly indicative of a cyclopentanone system. These characteristic features are also discernible for the compound (I) when measured in the same solvent. Attempts to convert (I) into a hydroazulene system through reduction with sodium borohydride and subsequent treatment with acids did not afford any useful information. Further confirmation of the structure (I) came from detailed nuclear

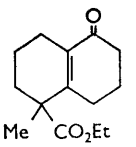
[6] Jilek and Protiva, *Coll. Czech. Chem. Comm.*, 1958, **23**, 692.
[7] King, King, and Topliss, *Chem. and Ind.*, 1956, 113.
[8] Bechmann and Dreiding, *J. Org. Chem.*, 1948, **13**, 316.
[9] Frank and Pierle, *J. Amer. Chem. Soc.*, 1951, **73**, 724.
[10] House and Schellenbaum, *J. Org. Chem.*, 1963, **28**, 34.
[11] Kalvoda and Loeffel, *Helv. Chim. Acta*, 1957, **40**, 2340.

magnetic resonance studies. The spectra showed two sharp singlets at τ 9·0 and 8·72, and multiplets around 7·5—8·5. The ratios of singlet : singlet : multiplet areas (3 : 3 : 12) are in excellent agreement with the distribution of protons as found in structure (I). Singlets at τ 9·0 and 8·72 can be assigned to the quaternary methyl groups at C-4 and C-10, respectively, and multiplets to the twelve protons in structure (I). If the synthetic compound had the structure (III), the tertiary proton at C-6 would have its resonance around or below τ 6·5. The absence of any such signal in the spectrum definitely excludes structure (III). The observed value of τ 9·0 for C-4-methyl resonance is about 0·15—0·2 p.p.m. higher than the observed value for a similarly situated methyl group. The shift upfield of the methyl resonance in (I) is due to the diamagnetic shielding by the carbonyl group. This effect has recently been observed by Chapman *et al.*[12] in α-lumicolchicine and by Crombie and Lown [13] while investigating the chemistry of rotenoids. Confirmation of this viewpoint comes from the n.m.r. spectra of the crude secondary alcohol available from the reduction of (I) with sodium borohydride. The methyl peak at τ 9·0 has now shifted down to the normal position at 8·79, owing to the removal [12] of diamagnetic shielding by the carbonyl group, whilst the position of the other methyl peak at τ 8·72 remained practically constant.

A Dreiding model of (I) shows that it can best be represented by the conformation depicted in (XVII). The axial disposition of the carbonyl group in the spirocyclopentanone ring will be favoured over the equatorial conformation. This is also in keeping with the diamagnetic shielding of the C-4-methyl group as mentioned before. The conformation (XVII) having the 1,3-diaxial lactone ring and two equatorial methyl groups is evidently more favoured energetically than any other conformation assignable to (I). This may explain the formation of (I), although in poor yield, to the complete exclusion of (III) in the present case.

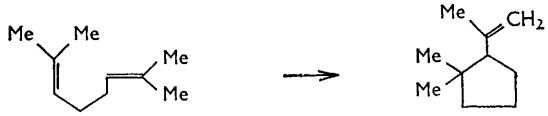



(XVII)




(XVIII)

It may be noted that the unsaturated acid (XVI) undergoes ring-closure with polyphosphoric acid [14] to afford the desired cyclohexenone (XVIII) in satisfactory yield. These observations are quite contrary to those of Cook and Hewett [15] where the absence of methyl groups favours the formation of spirans during the synthesis of polycyclic hydrocarbons. The presence of methyl groups again favours the formation of normal six-membered rings,[16] as is also evident in the case of polyisoprenoids. The formation of the cyclopentane derivative [17] is, however, preferred in the following case as the transition state for the formation of the usual cyclohexane ring is difficult to realise stereoelectronically.




The formation of a spiro-compound, although in poor yield, during acylation is a significant observation and is suggestive of the role of subtle stereoelectronic factors which

[12] Chapman, Smith, and King, *J. Amer. Chem. Soc.*, 1963, **85**, 806; cf. Jackman, " Nuclear Magnetic Resonance Spectroscopy," Pergamon, New York, 1959, pp. 14—20, 121—129.
[13] Crombie and Lown, *J.*, 1962, 775.
[14] Mathew and Dutta, *Proc. Chem. Soc.*, 1963, 135.
[15] Cook and Hewett, *J.*, 1935, 1633.
[16] Cook, Haslewood, and Robinson, *J.*, 1935, 667.
[17] Spadling, *J. Amer. Chem. Soc.*, 1949, **71**, 1681.

are generally operative to a different degree in intramolecular alkylation and acylation processes.

## Experimental

Nuclear magnetic resonance spectra were measured for solutions in deuterochloroform with a Varian A60 instrument, using tetramethylsilane as internal reference. Ultraviolet spectra were measured for ethanol solution. Light petroleum had b. p. 40—60°.

*Ethyl* 2-(3-*Ethoxycarbonylallyl*)-2-*hydroxy*-1,3-*dimethylcyclohexanecarboxylate* (V).—A solution of ethyl 1,3-dimethyl-2-oxocyclohexanecarboxylate (19·8 g.) in benzene (85 c.c.) was added to zinc wool (6 g.), and followed by ethyl γ-bromocrotonate (7 c.c.) and iodine (0·5 g.). The mixture was carefully refluxed in an oil-bath, three additions (3 × 5 g.) of zinc and a trace of iodine were made at 1 hr. intervals, and ethyl γ-bromocrotonate (16 c.c.) was introduced dropwise during 90 min. The mixture was refluxed for a total of 4 hr. The product was decomposed with acetic acid and extracted with ether. The ether–benzene layer was washed with water and 5% ammonium hydroxide solution. The residue, obtained after removal of ether and benzene, was distilled, to give the *product* (4 g.), b. p. 150—160°/0·3 mm. A middle fraction was collected for analysis: (Found C, 65·9; H, 8·6. $C_{17}H_{28}O_5$ requires C, 65·4; H, 8·9%).

*Ethyl* γ-*Iodobutyrate*.—Ethyl γ-chlorobutyrate (140·6 g.) was dissolved in dry acetone (700 c.c.), anhydrous sodium iodide (165 g.) was added, and the mixture refluxed for 6 hr. On removal of acetone from the filtered solution, the residue was diluted with water, whereupon a heavy brownish oil separated; and this yielded a sweet-smelling heavy liquid (182·8 g.), b. p. 122—125°/40 mm.

*Ethyl* 3-(3-*Ethoxycarbonylpropyl*)-2-*methyl*-4-*oxocyclohex*-2-*enecarboxylate* (VI).—Potassium (17·6 g.) was dissolved in an excess of t-butyl alcohol and the solvent distilled off until a solid appeared in the flask. This was cooled, and Hagemann's ester (85·6 g.) added in one lot, with shaking, whereupon the mixture first turned deep red and finally to a yellow mass. After 15 min., ethyl γ-iodobutyrate (130 g.) was added to the mixture and the whole refluxed in an oil-bath for 12 hr. The product was decomposed and extracted with ether. After removal of the solvent the residue afforded a fore-run of the unreacted iodo-ester and Hagemann's ester, and finally the *ester* (VI) (82 g., 59%), b. p. 162—165°/0·2 mm. (Found: C, 64·7; H, 8·3. $C_{16}H_{24}O_5$ requires C, 64·8; H, 8·1%).

Condensations of Hagemann's ester with ethyl γ-bromo- and γ-chloro-butyrate were also attempted. Under the same experimental conditions, with refluxing for 25 hr., the yields were 40·1 and 22·5%, respectively.

2-(3-*Ethoxycarbonylpropyl*)-3-*methylcyclohex*-2-*enone* (VII).—The above keto-di-ester (77 g.) was refluxed with an ethanolic solution of potassium hydroxide (575 c.c.; 15%) for 8 hr. The cooled product was acidified with concentrated hydrochloric acid (110 c.c.), and ethanol was removed from the filtered solution under reduced pressure. The residual liquid was diluted with water and saturated with sodium chloride, whereupon an oily product separated out. This was extracted with ether. The dried residue left after removal of the solvent was esterified with ethanol (385 c.c.) and sulphuric acid (35 c.c.). The usual working-up furnished a greenish-yellow *liquid* (39·3 g.), b. p. 153—155°/0·8 mm. (Found: C, 69·2; H, 8·9. $C_{13}H_{20}O_3$ requires C, 69·6; H, 8·9%), $n_D^{28·5}$ 1·4859, $\lambda_{max.}$ 243 mμ (log ε 4·08). The red 2,4-*dinitrophenylhydrazone* crystallised in long needles (from ethanol), m. p. 119° (Found: C, 56·0; H, 5·9; N, 14·1. $C_{19}H_{24}N_4O_6$ requires C, 56·4; H, 5·9; N, 13·8%).

2-(3-*Carboxypropyl*)-1-*methyl*-3-*oxocyclohexanecarboxylic Acid* (VIII).—A solution of the unsaturated keto-ester (VII) (40 g.) in ethanol (270 c.c.) was added to a solution of potassium cyanide (33·7 g.) in water (190 c.c.), and the solution was refluxed for 12 hr. After addition of a solution of potassium hydroxide (54 g.) in water (540 c.c.) the mixture was refluxed for a further 42 hr. The cooled solution was poured into ice–water, slowly acidified with hydrochloric acid (12N) (200 c.c.), saturated with sodium chloride, and extracted with ether. The solvent was distilled off, and the residue (37 g.) solidified after being dried and left for some time at room temperature. It crystallised from ethyl acetate–light petroleum as white button-shaped crystals, m. p. 161° (Found: C, 59·5; H, 7·4. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4%).

*Ethyl* 2-(3-*Ethoxycarbonylpropyl*)-1-*methyl*-3-*oxocyclohexanecarboxylate* (IX).—The keto-acid

(VIII) (36 g.) was esterified with ethanol (300 c.c.) and sulphuric acid (30 c.c.) by refluxing for 40 hr. The mixture was worked up and extracted with ether. On removal of the solvent, the residue furnished the *product* (IX) as a mobile liquid (29·4 g.), b. p. 180—182°/0·9 mm. (Found: C, 64·8; H, 8·4. $C_{16}H_{26}O_5$ requires C, 64·4; H, 8·7%), $n_D^{28·5}$ 1·4681, $\lambda_{max.}$ (in $CCl_4$) 5·81s and 5·76s μ.

*Ethyl* 2-(3-*Ethoxycarbonylpropyl*)-1,3-*dimethylcyclohex*-2-*enecarboxylate* (X).—Methylmagnesium iodide [from methyl iodide (13 c.c.) and magnesium (3·1 g.)] in ether (54 c.c.) was added with vigorous stirring during 45 min. to a solution of the keto-di-ester (IX) (29·2 g.) in ether (108 c.c.) at −10°. Stirring was continued for about 3 hr. until the bath attained room temperature. The mixture was poured into ice-cold hydrochloric acid and the product taken up in ether. Distillation furnished a viscous liquid (26 g.), b. p. 135—145°/0·2 mm. This was dissolved in dry ether (120 c.c.), and pyridine (13 c.c.) was added. Thionyl chloride (7 c.c.) was added dropwise to the cooled mixture, and the white precipitate which appeared was kept at ice-bath temperature for 2 hr., then at room temperature for 1 hr., and finally decomposed with ice-cold dilute hydrochloric acid; the product was extracted with ether. Distillation gave a mobile yellowish liquid (23 g.) having a pungent smell, b. p. 138—148°/0·2 mm. Freshly precipitated copper (16 g.) was added to a solution of the above product in benzene (650 c.c.) and the mixture was refluxed for 3 hr. The copper was filtered off, benzene was removed, and the residue furnished a mobile liquid (22·6 g.), b. p. 142—148°/0·6 mm., $n_D^{28·5}$ 1·4720, $\lambda_{max.}$ ($CCl_4$) 5·76s and 5·66m μ. The *product* (XI) was carefully re-fractionated for analysis, b. p. 130—132°/0·2 mm. (Found: C, 68·4; H, 8·8. $C_{17}H_{28}O_4$ requires C, 68·9; H, 9·4%).

2-*Carboxy*-6-*hydroxy*-2,6-*dimethylcyclohexanespirocyclopentan*-2′-*one Lactone* (I).—The di-ester (X) (22·6 g.) was added to an ethanolic solution (62 c.c.) of potassium hydroxide (6·1 g.) and the mixture was refluxed for 3 hr., poured into cold water, and the neutral fraction extracted with ether and discarded. The aqueous layer was acidified and again extracted with ether. The red viscous acidic mass (15 g.), left after removal of the solvent, was dried in a vacuum and to this was added polyphosphoric acid [from phosphorous pentoxide (38 g.) and phosphoric acid (33 c.c.; 85%)]. The mixture was heated at 95° on a water-bath for 3 hr. with vigorous stirring; the dark brown mixture was decomposed with ice and extracted with ether. The ethereal layer was thoroughly washed and the acidic materials were removed by washing with cold 5% sodium carbonate solution. Finally, the ethereal extract was washed with water, and dried, and the solvent was removed. The neutral viscous liquid (5 g.) partially solidified on trituration with light petroleum containing a little ethyl acetate, in the cold. The solid was collected and redissolved in ethyl acetate, and the solution quickly passed through a column of neutral alumina (4 g.) and activated charcoal (1 g.); the column was further treated with the same solvent. Ethyl acetate was almost distilled off from the combined eluent, and light petroleum was added until turbidity occurred. Feathery needle-shaped crystals of the *product* (I) (260 mg.) slowly appeared on keeping in the cold. After two crystallisations from light petroleum containing a little ethyl acetate it had m. p. 159—160°. It was soluble in 5% sodium hydroxide solution when warmed on a boiling-water bath (Found: C, 70·2; H, 8·2. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·1%).

γ-(2-*Ethoxycarbonyl*-1-*hydroxy*-2,6-*dimethylcyclohexyl*)*butyric Acid Lactone* (XV).—The oily residue (2 g.), left after separation of the solid, (I) was chromatographed on neutral alumina (35 g.). The column was eluted (*a*) with light petroleum–benzene (1 : 2), fractions 1—7, 100 c.c. each; (*b*) with benzene, fractions 8—10, 100 c.c. each; (*c*) with ether, fractions 11—18, 100 c.c. each. Fractions 11—14 afforded the crystalline keto-lactone, (I), m. p. 159—160°. Fraction 1 gave a yellowish viscous *liquid* (XV) (1·5 g.), b. p. 148—150°/0·4 mm. It was soluble in 5% potassium hydroxide solution on warming, and was regenerated on acidification of the alkaline solution (Found: C, 66·6; H, 9·2. $C_{15}H_{24}O_4$ requires C, 67·1; H, 8·9%).

2-(3-*Carboxypropyl*)-3-*hydroxy*-1,3-*dimethylcyclohexanecarboxylic Acid Lactone* (XIII).—The sodium carbonate washings from polyphosphoric acid treatment were acidified with an excess of hydrochloric acid, and the mixture saturated with sodium chloride and extracted with ether. The ethereal extract was washed and dried. After removal of the solvent, the residue solidified (6 g.) on standing for 48 hr. at room temperature. The adhering tarry matters were removed by passing a solution of the substance in ethyl acetate through a column of neutral alumina (7 g.) and activated charcoal (1·5 g.), and washing the column with the same solvent. The colourless ethyl acetate eluent was concentrated and light petroleum was added until turbidity just appeared. When kept in the cold, this afforded shining prismatic *needles* (4 g.), m. p. 121—

123°. After two crystallisations from light petroleum–ethyl acetate (1 : 1), it had m. p. 123—124° (Found: C, 65·2; H, 8·7. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·7%).

*3-Hydroxy-2-(3-methoxycarbonylpropyl)-1,3-dimethylcyclohexanecarboxylic Acid Lactone* (XIV).—The lactonic-acid (XIII) (4 g.) was esterified with an excess of diazomethane in methanolic solution. The *product* (XIV) was a mobile liquid (4 g.), b. p. 153—155°/0·3 mm. (Found: C, 66·0; H, 8·6. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·6%), $\lambda_{max.}$ (KBr) 5·66s and 5·76s μ $n_D^{24}$ 1·4785.

The methyl ester, on hydrolysis with 5% ethanolic potassium hydroxide solution for 2 hr. on a boiling-water bath gave back the original acid, m. p. and mixed m. p. 123—124°.

*2-Carboxy-6-hydroxy-2,6,3′-trimethylcyclohexanespirocyclopentan-2′-one Lactone* (II).—To an agitated suspension of freshly prepared and well-dried sodium methoxide (2·45 g.) in benzene (70 c.c.), ethyl formate (11 c.c.) was added under nitrogen. After *ca.* 30 min., the keto-lactone (I) (660 mg.) in benzene (35 c.c.) was added dropwise, with cooling. The mixture was agitated for 20 hr. at room temperature, and the resulting clear red solution was poured into ice–water containing hydrochloric acid (12N) (10 c.c.). The benzene layer was separated, and the aqueous portion extracted with ether. The combined organic layer was thoroughly washed with 5% sodium carbonate solution. The alkaline washings were then slowly acidified with cold dilute hydrochloric acid (1 : 1). The acidic solution was saturated with sodium chloride and extracted thrice with ether. The ethereal layer was washed with saturated sodium chloride solution and dried ($Na_2SO_4$). After removal of the solvent, the residue solidified as glistening flakes (630 mg.) which gave a violet colour with an ethanolic ferric chloride solution. The product was acetylated (without further purification) with acetic anhydride (31·5 c.c.) and pyridine (10·5 c.c.), and the solution was allowed to stand at 20° for 18 hr. After dilution of the mixture with cold saturated sodium chloride solution, it was taken up in ether and the organic layer was thoroughly washed with 5% sodium carbonate solution, until it was faintly alkaline, and with water, and finally dried ($Na_2SO_4$). After removal of the solvent, a solid crystalline residue (220 mg.) could be isolated which gave no colouration with ferric chloride. It was dissolved in glacial acetic acid (10 c.c.) and hydrogenated with 10% palladium–charcoal (150 mg.). In 30 min., 2 moles of hydrogen were taken up and then the reaction ceased. There resulted an amorphous product (130 mg.) mixed with some oily impurities. It was dissolved in dry ether and passed through a narrow column of neutral alumina (2 g.). On elution with ether, it afforded a white crystalline product (105 mg.) which, on recrystallisation from a large volume of light petroleum, afforded reflecting flakes of the *lactone* II, m. p. 128—129° (Found: C, 71·1; H, 8·4. $C_{14}H_{20}O_3$ requires C, 71·1; H, 8·4%).

The infrared spectra and some of the n.m.r. spectra were made available through the courtesy of Professor D. H. R. Barton, F.R.S., and others through Dr. Piers (Varian Associates); we are grateful to Dr. U. R. Ghatak for the interpretation of the spectra.

We thank Mrs. Chhabi Dutta for microanalyses, the Council of Scientific and Industrial Research for a maintenance grant to one of us (S. L. M.), and the Chemical Society for financial assistance.

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Buffalo 14, N.Y., U.S.A.] [*Received, November 19th*, 1962; *Amended, May 12th*, 1964.]