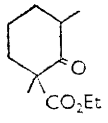
Reactions of 2-Ethynyl-2-hydroxy-1,3-dimethylcyclohexanecarboxylic Acid

By A. C. Riemer and W. Rigby

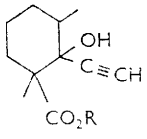
2-Ethynyl-2-hydroxy-1,3-dimethylcyclohexanecarboxylic acid has been synthesised and its reduction and its reactions with acidic and mercury catalysts and with other reagents have been studied. Some reactions of this and related compounds involve molecular rearrangements including an α-ketol ring enlargement, and steric hindrance of the functional groups is often manifest. Some infrared and n.m.r. data are given; several of the acids and esters encountered show abnormal infrared frequencies.

In connexion with work being done on degradation products of marrubiin, 2-ethynyl-2-hydroxy-1,3-dimethylcyclohexanecarboxylic acid (IIa) has been synthesised from ethyl 1,3-dimethyl-2-oxocyclohexanecarboxylate (I), and some of its transformation products have been examined.

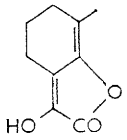
The enol-lactone (III) of 2-methyl-6-oxalocyclohexanone [1] which is encountered as a by-product in the first stage of the synthesis (condensation of 2-methylcyclohexanone with ethyl oxalate) titrates as a monobasic acid and has $\nu_{max.}$ ($CHCl_3$) 1740 (broad), 1684 (sharp) cm.$^{-1}$. When ethyl 1,3-dimethyl-2-oxocyclohexanecarboxylate was condensed with sodium acetylide in liquid ammonia, ethyl hydrogen αε-dimethylpimelate (IVa) and ethyl αε-dimethylpimelamate (IVb) were formed along with the ester (IIb), presumably arising from hydrolysis or ammonolysis of the cyclic ketone: examined gas chromatographically, the crude amic ester appeared to consist of only one isomer, and



(I)



(IIa: R = H)
(IIb: R = Et)
(IIc: R = Me)



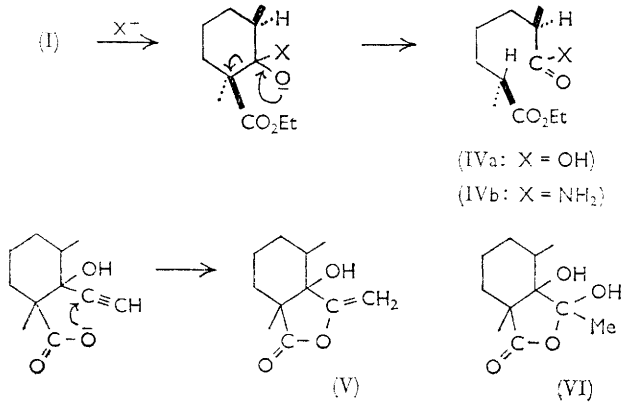
(III)

on hydrolysis it yielded, largely, *meso*-αε-dimethylpimelic acid [2] (dianilide, m. p. 193·5—194·5°: the lit.[2] m. p., 183—184°, is presumably an error of transcription). The virtual absence of *dl*-isomer indicates that

[1] A. Kötz, K. Blendermann, and J. Meyer, *Ber.*, 1912, **45**, 3702.

[2] A. Fredga and B. Östman, *Acta Chem. Scand.*, 1956, **10**, 703; F. S. Kipping, *J. Chem. Soc.*, 1895, **67**, 139.

the cyclic ketone reacts as a single species, that racemisation at C-2 or C-6 does not occur duing the ring-opening, and that the ring-opening takes place either with high retention or high inversion of configuration: reverse aldol condensations commonly occur with retention of configuration [3] (but ring-opening has been little investigated) and if that is the case here the methyl groups will be *trans* to one another in the reacting cyclic ketone.

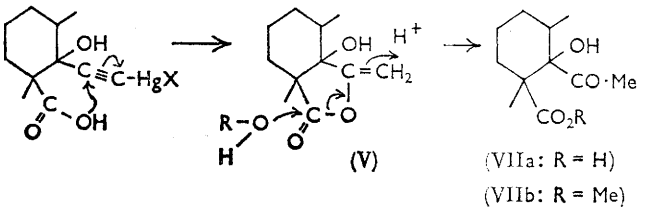


It was necessary that the acetylenic compound should be stereochemically pure, and to ensure this the (liquid) ethyl ester was converted into the crystalline acid (IIa). Hydrolysis of the ester led to undesired results except under controlled conditions. It has been noted [4] that an acetylenic bond $\gamma\delta$ with respect to a carboxylic ester may become hydrated to give the γ-oxo-acid on hydrolysis of the ester—we suggest that this will be by attack of the carboxylate ion to give the enol-lactone [(V) in this case]—and that the oxo-acid may then form its lactol (VI). Fairly vigorous hydrolysis of the ester (IIb) led to a mixture which probably contained such products: vigorous hydrolysis degraded the molecule to 2,6-dimethylcyclohexanone. However, conditions were found whereby it was hydrolysed in 92% yield to the acid (IIa), m. p. 134°. The high yield from this hydrolysis indicated that the reaction giving rise to the ethyl ester (IIb) had been stereospecific, the product being one *dl*-pair.

The methyl ester (IIc), m. p. 81°, did not give a precipitate with ammoniacal or ethanolic silver nitrate; formation of the mercury derivative, m. p. 177°, of the ester was also difficult and this low reactivity recalls that of 2,2,6-trimethyl-1-ethynylcyclohexanol which has been reported as giving [5a] and as not giving [5b] such reaction. The carbonyl stretching frequencies of the acid and its ester, those of the vinyl and ethyl compounds derived from them by hydrogenation, and those of methyl ketones derived by hydration, were of interest in that they were unusually low [6] and some were multiple [*e.g.*, the acetylenic acid (IIa) had $\nu_{max.}$ (KBr) 1701, 1670 cm.$^{-1}$ and its ester (IIc) had $\nu_{max.}$ (CCl_4) 1698 cm.$^{-1}$; the olefinic acid (XIVa) had $\nu_{max.}$ (CCl_4) 1680 cm.$^{-1}$: as was not unexpected, this spectral region was sometimes far more complex with chloroform solutions]. Similar low frequencies (1693 and 1675 cm.$^{-1}$, measured on a paraffin suspension) in the spectrum of an acid derived from atisine were attributed by Edwards and Howe [6] to extreme steric hindrance at the carboxyl group. Hydrogen bonding in compounds such as (IIa) and (IIc) could be fairly normal, to give decalin-like structures. The ester (IIc) and acid (XVI) had ε *ca.* 120 at 2170 Å (see ref. 6).

Heated with aluminium phosphate, the ester (IIc) gave the (unpurified) vinylacetylene.

When the acetylenic acid (IIa) was heated with mercuric sulphate in methanol, the main product was its isomer the enol-lactone (V) of 2-acetyl-2-hydroxy-1,3-dimethylcyclohexanecarboxylic acid, m. p. 119°, which, in the infrared had two hydroxyl frequencies [3598 (sharp) and 3490 cm.$^{-1}$ (fairly sharp)] and double-bond frequencies appropriate to a vinyl ester [1815 (strong) and 1672 cm.$^{-1}$ (medium-strong)]; a *cis* or a *trans* ring-junction is feasible for the compound. The other products isolated were the ester (VIIb) and a small amount of the corresponding oxo-acid (VIIa); the acetylenic methyl ester (IIc) was apparently absent. When the catalyst was modified by the addition of sulphuric acid the enol-lactone (V) could no longer be found among the products. Compound (V) is thus the primary product, suffering acid-catalysed alcoholysis and hydrolysis. Use of a boron trifluoride–mercuric



oxide catalyst [7] with the acid (IIa) gave the mercury derivative, m. p. 163°, of the acid (IIa); but from its methyl ester, (IIc), the oxo-ester (VIIb) and the mercury derivative of the starting material were obtained.

Alkali hydrolyses the enol-lactone (V) to the oxo-acid (VIIa), m. p. 165°: this acid, its methyl ester, and other methyl ketones of this series are hindered ketones, not giving oximes or 2,4-dinitrophenylhydrazones or responding to the iodoform test (see ref. 8). Hydrolysis of the methyl ester (VIIb) regenerated the acid (VIIa). The moderate (*ca.* 60—70%) yields of the acid (VIIa) obtained in the hydrolysis of the enol-lactone (V) and

[3] (*a*) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Amer. Chem. Soc.*, 1959, **81**, 5774, and preceding Papers by D. J. Cram *et al.*; (*b*) R. B. Woodward, *Angew. Chem.*, 1960, **72**, 651.

[4] N. R. Easton and R. D. Dillard, *J. Org. Chem.*, 1962, **27**, 3602.

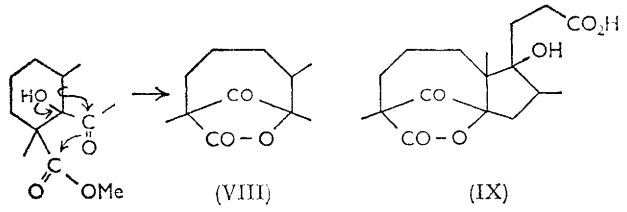
[5] (*a*) H. Sobotka and J. D. Chanley, *J. Amer. Chem. Soc.*, 1949, **71**, 4136; (*b*) N. A. Milas, N. S. MacDonald, and D. M. Black, *ibid.*, 1948, **70**, 1829.

[6] O. E. Edwards and R. Howe, *Proc. Chem. Soc.*, 1959, 62.

[7] J. C. Hamlet, H. B. Henbest, and Ewart R. H. Jones, *J. Chem. Soc.*, 1951, 2652; G. F. Hennion, R. B. Davis, and D. E. Maloney, *J. Amer. Chem. Soc.*, 1949, **71**, 2813.

[8] H. B. Henbest and G. Woods, *J. Chem. Soc.*, 1952, 1150.

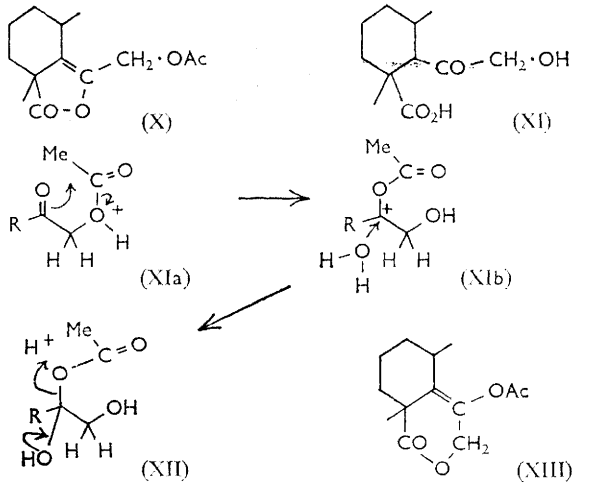
the ester (VIIb) are no doubt a consequence of competition from an α-ketol rearrangement comparable with that giving rise to compound (VIII) (below), and possibly from lactol formation [cf. (VI)]. When the ester (VIIb) was heated with aluminium phosphate at 350°, rearrangement with ring-enlargement occurred to give the trimethylcycloheptanone lactone (VIII) [$\nu_{max.}$ (CCl_4) 1790, 1747 cm.$^{-1}$; cf. 1794, 1743 cm.$^{-1}$ for the corresponding frequencies [9] in the lactone (IX)]. Surface catalysis of α-ketol rearrangements is known,[10] but aluminium phosphate appears not to have been recorded as a catalyst for the reaction. The oxo-lactone (VIII) did not respond to the iodoform test, but was unhindered, giving a precipitate with 2,4-dinitrophenylhydrazine; alkaline hydrolysis opened the lactone, but the resulting β-oxo-acid was decarboxylated on warming to give the unhindered 2-hydroxy-2,3,7-trimethylcycloheptanone (oxime, m. p. 117°).



(VIII) (IX)

When the enol-lactone (V) was heated with aluminium phosphate an oxo-lactone, possibly (VIII), was formed together with a small amount of a crystalline αβ-unsaturated ketone.

Acetylation of the enol-lactone (V) with acetic anhydride–acetyl bromide gave the product of allylic rearrangement, (X), m. p. 55°. The n.m.r. spectrum of the product showed a single, unsplit signal at −4·7 p.p.m., representing two protons, and a one-proton multiplet centred near −3 p.p.m., in contrast with that of the enol-lactone (V) with its two one-proton doublets at −4·49 and −4·80 p.p.m. and no signal near −3 p.p.m.: the infrared spectrum had $\nu_{max.}$ (CCl_4) 1795, 1748, 1229 cm.$^{-1}$. The spectral data are consistent with the structure (X) (lactone carbonyl 1795, acetate 1748 cm.$^{-1}$) if it is reasonably assumed that the degree of n.m.r. non-equivalence to be expected for the ester methylene protons is too slight to affect their signal. Acid-catalysed hydrolysis of the acetate-lactone (X) was easy, to give the α-ketol (XI) [$\nu_{max.}$ (KCl) 3485, 1709, 1052 cm.$^{-1}$] the hydrolysis of the acetate group occurred much more readily than was to have been expected for a simple ester.[11a] The acid-catalysed hydrolysis of some allylic esters has been shown to be considerably faster than that of related saturated esters, and to involve alkyl–oxygen fission [11b] (contrast ref. 11c). This could be the case here; but alternatively the lactone may undergo the rapid hydrolysis characteristic of lactones, to give the α-ketol acetate, and we suggest that the acid-catalysed hydrolysis of the esters of α-ketols can be assisted by the neighbouring carbonyl group forming an acylhemiacetal intermediate (as XII).



A substance of structure (XIII), which is essentially an ester-interchanged version of the molecule (X), might conceivably be generated from compound (X) under the conditions obtaining in the original acetylation (though the ketone would have to be an intermediate), and it might be expected to have n.m.r. spectrum rather similar to that of (X): however, its enol-ester carbonyl frequency would probably be appreciably lower than the observed 1795 cm.$^{-1}$.

Hydrogenation of the acid (IIa) yielded the olefinic acid (XIVa), m. p. 91° (palladium catalyst), or the saturated acid (XV), (m. p. 106°) (Adams catalyst): the methyl ester (IIb) behaved analogously.

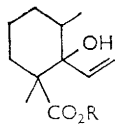
The olefinic acid (XIVa), with acetic anhydride–pyridine gave an acetate $C_{13}H_{20}O_4$, m. p. 124 (decomp.), which was not extracted from ether by aqueous sodium hydrogen carbonate and which has $\nu_{max.}$ (CCl_4) 1743 and 1701 cm.$^{-1}$. Although not extracted by sodium hydrogen carbonate, the compound is an acid, the carboxyl group being represented in the infrared spectrum by the lower-frequency carbonyl band and by the usual feature in the region of 2650 cm.$^{-1}$, and in the n.m.r. spectrum by a broad signal at −9·65 p.p.m. Other features of the n.m.r. spectrum are compatible with the structure (XVI), but the signal of the proton geminal with the methyl group occurs near −3·3 p.p.m., whereas the parent tertiary alcohol gives no signals between −2·3 and −5 p.p.m.: presumably an effect of the introduced carbonyl group, or perhaps acetylation of the tertiary hydroxyl group has been accompanied by a conformational change which allows deshielding of the methyl-geminal proton by the vinyl group. The structure (XVII), resulting from allylic rearrangement,

[9] D. G. Hardy, W. Rigby, and D. P. Moody, *J. Chem. Soc.*, 1957, 2955.

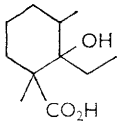
[10] *E.g.*, C. W. Shoppee and D. A. Prins, *Helv. Chim. Acta*, 1943, **26**, 201; D. Taub and N. L. Wendler, *Chem. and Ind.*, 1959, 902.

[11] (*a*) B. Loev, *Chem. and Ind.*, 1964, 193; (*b*) H. L. Goering and E. F. Silversmith, *J. Amer. Chem. Soc.*, 1955, **77**, 6249; (*c*) E. A. Braude, *J. Chem. Soc.*, 1948, 794.

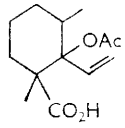
would accommodate a signal similar to that found at −3·3 p.p.m., but the pattern of the low-field signals seems more appropriate to a vinyl group than to the three relevant protons (a and b) of (XVII); the split



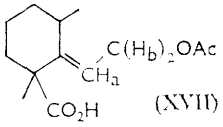
(XIVa: R = H)
(XIVb: R = Me)



(XV)



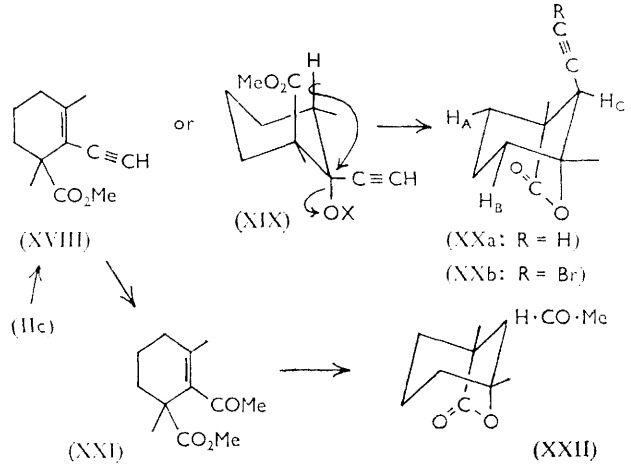
(XVI)



(XVII)

methyl signal of the acetate (XVI) corresponds in position (−0·8 p.p.m.) with that of its precursor (XIVa), whereas that of the rearrangement product (X) is at appreciably lower field (−1·15 p.p.m.).

The acid (XIVa) gave much of its acetate (XVI) when boiled with acetic anhydride, whereas in similar circumstances the ester (XIVb) was almost unaffected; this



indicates that the acetylation is an intramolecular process involving the mixed anhydride of the acid (XIVa).

When a solution of the acetylenic ester (IIc) in 80% formic acid was boiled, absorption near 2280 and 2400 Å suggested that the αβ-unsaturated acetylene [5] (XVIII) and the αβ-unsaturated ketone [8] (XXI) were simultaneously present, the latter building up in one hour to a maximum concentration of 10% [estimated from the overall value of ε (*ca.* 400) at 2420 Å] and then slowly falling off: the product after eight hours' reaction time yielded the lactone (XXII) of 2-acetyl-3-hydroxy-1,3-dimethylcyclohexanecarboxylic acid (*ca.* 50%), and the lactone (XXa) of 2-ethynyl-3-hydroxy-1,3-dimethylcyclohexanecarboxylic acid (*ca.* 12%). The acid (IIa) gave the same products, but with a smaller proportion of the acetylenic lactone (5%); up to 25% of starting material could be recovered from the acidic fraction and, capriciously, the lactol, (VI), $C_{11}H_{18}O_4$ (m. p. 162°) of the oxo-acid (VIIa) was also obtained in small amount. [With aqueous–ethanolic sulphuric acid the acid (IIa) gave a lower yield (9%) of the oxo-lactone (XXII); the acetylenic lactone (XXa) was not detected among the products.]

The oxo-acid (VIIa), its methyl ester (VIIb), and the acetylenic lactone (XXa) were all stable to formic acid under these conditions, and the enol-lactone (V) was not converted into the lactone (XXII) by formic acid; so these cannot be intermediates in the formation of the oxo-lactone (XXII). Dehydration therefore precedes hydration in the formation of the oxo-lactone (XXII), which is in line with previous findings.[7]

The acetylenic lactone (XXa), however, might be formed *via* the enyne (XVIII). Its ethynyl group will be axial, as the n.m.r. signal from the proton geminal with it, doubled by coupling with the acetylenic proton, was further subdivided by incompletely resolved small couplings: the "M rule" of Rassat, Jefford, Lehn, and Waegell [12] would predict long-range ($^4J_{HH}$) coupling of an equatorial proton at this point, but not of an axial proton, with the (non-equivalent) protons H_A and H_B of (XXa). Formation of this lactone (XXa) from the enyne (XVIII) involves *cis* addition at the double bond, which might well be more accessible to the carboxylic proton than to external ones. But an alternative to the enyne route would be loss of the hydroxyl group and concomitant 1,2-hydride shift; the structure, (XXa), of the product would imply the structure (XIX) for its precursor—the ethynyl group originally *cis* to the carboxyl group becoming *trans* to it in the product (see ref. 13). An attempt to demonstrate that the enyne was the intermediate failed.

When compound (XXa) was heated with dilute alkali, the lactone ring opened quantitatively, but it closed spontaneously when the solution was acidified. Prolonged boiling with mercuric sulphate and sulphuric acid in methanol merely formed the mercury derivative, and boiling with 80% formic acid was without effect. An attempt to transform this acetylene into the corresponding methyl ketone through the product of Favorskii bromination,[14] by the use of *N*-bromoacetamide,[14b] also failed—mere substitution of the acetylenic proton occurred, giving the corresponding bromoacetylene (XXb): the formation of a bromoacetylene under these conditions is unusual. The infrared spectrum of the bromo-compound was very similar to that of the parent acetylene (apart from the ≡C–H bands of the latter, at

[12] A. Rassat, C. W. Jefford, J. N. Lehn, and B. Waegell, *Tetrahedron Letters*, 1964, 233 (cf. *inter alia* F. A. L. Anet, *Canad. J. Chem.*, 1961, **39**, 789; J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 2769; L. D. Hall and L. Hough, *Proc. Chem. Soc.*, 1962, 382; C. W. Jefford and B. Waegell, *Tetrahedron Letters*, 1963, 1981).

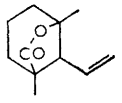
[13] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562.

[14] (*a*) A. Favorskii, *J. prakt. Chem.*, 1895, [2], **51**, 533; (*b*) J. S. Mills, H. J. Ringold, and C. Djerassi, *J. Amer. Chem. Soc.*, 1958, **80**, 6118.

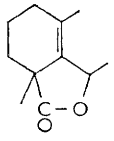
ca. 640 and 3320 cm.$^{-1}$): in the n.m.r. spectrum, the signal of the proton geminal with the acetylene group (at −2·74 p.p.m. in CCl_4) was broadened, but $^4J_{HH}$ coupling was not so distinct as in the case of the parent acetylene.

The inertness, relative to the acetylenes (IIa) and (IIc), of the lactone (XXa) to reaction at the subterminal carbon atom of its ethynyl group implies that the intramolecular mechanism which held for the hydration of (IIa) and (IIc) is not available here: it must be supposed that the conformer of the corresponding hydroxy-acid with axial ethynyl is highly favoured, probably because its other 1,3-axial groups are mutually reactive whereas the alternative chair form would have 1,3-axial methyls.

Partial hydrogenation of the acetylenic lactone (XXa) could be made to yield the corresponding vinyl compound, the lactone (XXIII) of 3-hydroxy-1,3-dimethyl-2-vinylcyclohexanecarboxylic acid; the possible alternative structure (XXIV) is ruled out by n.m.r. (and other) evidence. One of the presumed $=CH_2$ frequencies is unusually high (929 cm.$^{-1}$; in CCl_4) for a vinyl compound unsubstituted by a functional group at the allylic position,[15] and while it could be surmised that the lactone



(XXIII)



(XXIV)

bridge might thus affect the vinyl group if it were equatorial, interaction in the remote axial situation seems unlikely; however, strong bands near here are not uncommon among compounds encountered in this work, for instance the acetylene (XXa) and its bromo-derivative (XXb) have similar strong bands (at 928 and 924 cm.$^{-1}$, respectively; in CCl_4). The n.m.r. signal of the allylic proton showed no clear evidence of ^4J coupling. The lactone ring of the vinyl compound could be opened by hot dilute alkali, but it closed again spontaneously when the solution was acidified.

The oxo-lactone (XXII) had infrared absorption maxima at 1786 and 1709 cm.$^{-1}$. Its n.m.r. spectrum showed unsplit methyl signals at −2·22, −1·48, and −1·35 p.p.m., and a 1-proton signal at −2·97 p.p.m.; this last, which will originate in the proton α to the ketone group, showed no distinct splitting but was rather broad; it is not clear whether long-range (^4J) coupling is occurring, and the stereochemistry here must remain in doubt.

EXPERIMENTAL

Unless otherwise stated, ultraviolet spectra were determined for ethanol solutions. N.m.r. spectra were determined at 60 Mc./sec. (Varian A-60 instrument) for deuteriochloroform solutions, with tetramethylsilane as internal standard; signal positions are measured downfield from the standard signal and are expressed in units of millionths (p.p.m.) of that magnetic field which corresponds to the standard signal.

Ethyl 1,3-*Dimethyl*-2-*oxocyclohexanecarboxylate* (I).—2,6-Dimethyl-2-ethoxycarbonylcyclohexanone was prepared[16,17] from 2-methylcyclohexanone (450 g.): the crude 6-ethoxalyl-2-methylcyclohexanone[17] deposited crystals of the enol-lactone (III) of 2-methyl-6-oxalylcyclohexanone[1] (127 g.) which, after recrystallisation from benzene and from ether formed needles, m. p. 141° (slow decomp.) (lit.,[1] 141°), $\lambda_{max.}$ 2900 Å (ε 23,000), $\nu_{max.}$* ($CHCl_3$) 1720br, 1684s cm.$^{-1}$ [Found: C, 64·9; H, 6·0%; Equiv. (direct titration), 165. Calc. for $C_9H_{10}O_3$: C, 65·05; H, 6·1%; *M*, 166). The lactone kept reasonably well for a year, under nitrogen at 0°. The ethoxalyl compound was not purified further than by the removal of this lactone; the ethyl 3-methyl-2-oxocyclohexanecarboxylate resulting from its decarbonylation was distilled, 252 g., b. p. 117—118°/15 mm. (lit.,[17a] 115°/12 mm.) and methylated[16] to give the ester (I) (224 g.), b. p. 114—115°/15 mm. (lit.,[16] 111—112°/15 mm.).

Ethyl 2-*Ethynyl*-2-*hydroxy*-1,3-*dimethylcyclohexanecarboxylate* (IIb).—Acetylene was passed into liquid ammonia (1 l.) containing sodamide (from sodium, 29 g.) until the reaction appeared to be complete,[18] and the foregoing ester (224 g.) in ether (100 ml.) was added during ½ hr., with stirring, at −50°. The thick suspension was stirred for 2 hr. while acetylene was passed into it, ammonium chloride (87 g.) was added, and after ammonia had evaporated the residue was taken up in ether and water, and the aqueous solution, A, was reserved.

Distillation of the ether solution yielded *ethyl* 2-*ethynyl*-2-*hydroxy*-1,3-*dimethylcyclohexanecarboxylate* (IIb), 113 g., b. p. 104—105·5°/2·5 mm. (Found: C, 70·0; H, 9·2. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%). Continuation of the distillation gave a variable amount (up to 20% yield) of *ethyl* αα′-*dimethylpimelamate* (IVb), b. p. 168/1 mm., $\nu_{max.}$ (film) 3425, 3345, 3195, 1725, 1660, 1618 cm.$^{-1}$ (Found: C, 60·9; H, 9·8; N, 6·3. $C_{11}H_{21}NO_3$ requires C, 61·4; H, 9·8; N, 6·5%). When hydrolysed by sodium hydroxide this yielded slightly impure *meso*-αα′-dimethylpimelic acid: its m. p. (79—80·5°) did not quite exclude the possibility of its being the *dl*-compound (lit.,[2] *dl*, m. p. 76—76·5°; *meso*, m. p. 81—81·5°) but the acid is difficult to purify directly; it was converted (thionyl chloride, aniline) in high yield into the dianilide, m. p. 193·5—194·5° (lit.,[2] *meso*, m. p. 183—184°, *dl*, m. p. 154—155°), $\nu_{max.}$ (KCl) 3247, 1656, 1608, 1530 cm.$^{-1}$ (Found: C, 74·4; H, 7·7; N, 8·35. Calc. for $C_{21}H_{26}O_2N_2$: C, 74·5; H, 7·75; N, 8·3%).

The aqueous solution, A, when acidified gave *ethyl hydrogen* αα′-*dimethylpimelate* (IVa), b. p. 143/0·5 mm., in 14% yield (Found: C, 61·5; H, 9·6%; Equiv., 216. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%; *M*, 216). Hydrolysis gave slightly impure *meso*-αα′-dimethylpimelic acid, m. p. 79—80° (Found: C, 57·7; H, 8·5%; Equiv., 94. Calc. for $C_9H_{16}O_4$: C, 57·4; H, 8·6%; *M*, 188).

2-*Ethynyl*-2-*hydroxy*-1,3-*dimethylcyclohexanecarboxylic Acid* (IIa).—The ethyl ester (IIb) (113 g.) was boiled with

* br = broad, s = sharp, w = weak, sh = shoulder.

[15] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1957, p. 49.

[16] R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1939, 1299.

[17] (*a*) A. Kötz and A. Michels, *Annalen*, 1906, **348**, 94; (*b*) cf. A. Kötz and L. Hesse, *ibid.*, 1905, **342**, 315.

[18] I. M. Heilbron, Ewart R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1945, 81.

3N-aqueous sodium hydroxide (500 ml.), ethanol (40 ml.), and Teepol (2 ml.) until the mixture became homogeneous (9 hr.). The solution was washed with ether, acidified, and extracted with ether, evaporation of which left the crystalline acid (yield 92%). Recrystallisation from ether–light petroleum (b. p. 40—60°) gave *2-ethynyl-2-hydroxy-1,3-dimethylcyclohexanecarboxylic acid* (IIa), prisms, m. p. 134°. $\nu_{max.}$ (KBr) 3288 (≡CH), 3100 (OH), 2102vw (C≡C), 1701, 1670 cm.$^{-1}$; ($CHCl_3$) 3319 (≡CH), 1755, 1722, 1682 cm.$^{-1}$ (with further shoulders on the carbonyl bands in both spectra); n.m.r. (p.p.m.) *ca.* −7·7 (2 OH), −2·55 (≡CH), −1·51 (CH_3), −1·12 (doublet; J = 5·8 c./sec.) (CH_3) (Found: C, 67·8; H, 8·4. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%). After the acid had been boiled in methanol with a mercuric oxide–boron trifluoride catalyst (see below) some was recovered as its mercuric derivative, which formed prisms (from ether), m. p. 163°. Hydrogen sulphide in acidified ethanol regenerated from it the acetylenic acid (IIa), m. p. and mixed m. p. 134°.

With diazomethane the acid gave its *methyl ester* (IIc), prisms from light petroleum, m. p. 81°, $\nu_{max.}$ (CCl_4) 3470 (OH), 3280 (≡CH), 1698 cm.$^{-1}$; n.m.r. (p.p.m.) −3·91 (1H), −3·7 (OMe), −2·3 (1H), −1·42 (CH_3), −1·08 (doublet; J = 5·5 c./sec.) (CH_3) (Found: C, 68·65; H, 8·25. $C_{12}H_{18}O_3$ requires C, 68·55; H, 8·6%), ε 120 (shoulder) at 2170 Å.

After the ester had been boiled in methanol with a mercuric oxide-boron trifluoride catalyst (see below), some was recovered as its *mercuric derivative*, prisms (from ether), m. p. 177°, $\nu_{max.}$ (KBr) 3460 (OH), 2154w (C≡C), 1681 cm.$^{-1}$ (Found: C, 46·75; H, 5·55. $C_{24}H_{34}HgO_6$ requires C, 46·55; H, 5·55%). Hydrogen sulphide in acidified ethanol regenerated the methyl ester (IIc) from it. The ester gave no precipitate with ammoniacal or ethanolic silver nitrate. When the ester was heated (350°; in N_2; 1 hr.) with aluminium phosphate catalyst [19] and the product extracted with ether and chromatographed on silica, benzene containing 1% of ethanol eluted about 20% of material which had $\lambda_{max.}$ 2200 Å (ε *ca.* 900), $\nu_{max.}$ *ca.* 3440 cm.$^{-1}$ and which therefore probably contained about 70% of a vinylacetylene: but it did not crystallise.

Vigorous Hydrolysis.—The acid (IIa) (0·3 g.) was boiled (135°) with a solution of sodium hydroxide (0·3 g.) in water (0·4 ml.) and ethylene glycol (3 ml.) for 2½ hr. and, after the addition of a little more water, for a further 2½ hr. (115°). Working up gave a neutral oil and *ca.* 15% of acidic material. The oil, when (*a*) heated (*ca.* 90°, 2 hr.) with hydroxylamine hydrochloride in pyridine, yielded the oxime of *trans*-2,6-dimethylcyclohexanone as stout needles (from methanol), m. p. and mixed m. p. 116—118° (lit.,[20] 118°); or (*b*) warmed with aqueous hydroxylamine yielded the oxime of *cis*-2,6-dimethylcyclohexanone, m. p. 70—74° (Pyrex tube) (lit.,[20] 79°). The n.m.r. spectrum of the acidic material showed that it was essentially starting material, and not the oxo-acid (VIIa).

Hydrogenation of the Acetylenic Acid (IIa).—With hydrogen and platinum oxide in ethyl acetate at room temperature and pressure the acetylenic acid (IIa) readily gave *2-ethyl-2-hydroxy-1,3-dimethylcyclohexanecarboxylic acid* (XV); prisms [from benzene–light petroleum (b. p. 60—80°)], m. p. 106°, $\nu_{max.}$ (KCl) 3300 (OH), 1677; ($CHCl_3$) 1739, 1725 (infl.), 1684 cm.$^{-1}$; n.m.r. (p.p.m.) −7·55 (OH and CO_2H), −1·30 (CH_3), −1·00 (doublet; J = 6·6 c./sec.) (CH_3), −1·00 (triplet; J = 7 c./sec.) (CH_3) (Found: C, 65·7; H, 9·8. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·1%).

With palladium–calcium carbonate as catalyst, used similarly, uptake of hydrogen virtually ceased when 1 mole had been taken up to give *2-hydroxy-1,3-dimethyl-2-vinylcyclohexanecarboxylic acid* (XIVa); prisms [from light petroleum (b. p. 60—80°)], m. p. 91°; $\nu_{max.}$ (paraffin) 3280 (OH), 1686; (CCl_4) 3534 (OH), 1860w, 1680, 995, 932; ($CHCl_3$) 1750, 1735sh, 1724sh, 1687 cm.$^{-1}$; n.m.r. (p.p.m.) complex region *ca.* −6·3 to −5·2 (3H) (vinyl), −1·19 (CH_3), −0·84 (doublet; J = 6 c./sec.) (CH_3) (Found: C, 66·65; H, 9·2. $C_{11}H_{18}O_3$ requires C, 66·65; H, 9·15%).

Diazomethane converted the olefinic acid (XIVa) into its *methyl ester* (XIVb); prisms [from light petroleum (b. p. 60—80°)], m. p. 31° $\nu_{max.}$ (CCl_4) 3525 (OH), 1860w, 1706, 994, 930 cm.$^{-1}$ (Found: C, 67·7; H, 9·4. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%). The same product resulted when the methyl ester (IIc) was hydrogenated in the presence of palladium–calcium carbonate.

A solution of the olefinic acid (XIVa) (0·2 g.) in pyridine (2 ml.) and acetic anhydride (2 ml.) was heated at 80° for 2 hr., acidified, and extracted with ether. The ether solution was washed with aqueous sodium hydrogen carbonate, the bicarbonate extract yielding an oil (0·06 g.) which was not investigated. Evaporation of the ether solution yielded *2-acetoxy-1,3-dimethyl-2-vinylcyclohexanecarboxylic acid* (XVI) (35%); needles (from ethyl acetate), m. p. 124° (decomp.), $\lambda_{max.}$ 2175 Å (ε 110), $\nu_{max.}$ (CCl_4) 1743, 1701, 1637w, 1267, 1241, 1233 cm.$^{-1}$; [($CHCl_3$) 1733, 1700 cm.$^{-1}$; on addition of triethylamine, the 1700-cm.$^{-1}$ band was replaced by a broad one near 1635 cm.$^{-1}$], n.m.r. (p.p.m.) −9·66 (1H), *ca.* −6 (1H) (quartet; J = 18, 9·5 c./sec.) and *ca.* −5·4 (2H) (J = 18, 9·5, 2·7 c./sec.) (vinyl), *ca.* −3·4 (multiple) (1H), −2·1 (OAc), −1·22 (CH_3), −0·8 (doublet; J = 6·5 c./sec.) (CH_3) (Found: C, 65·1; H, 8·5; Ac, 21·3. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·4; Ac, 17·9%).

The acid (XIVa) boiled with acetic anhydride for 1½ hr. gave a mixture which contained the acetate (XVI), but the method of preparation involving pyridine was much better: the ester (XIVb) was recovered (93%) after it had been boiled for 2 hr. with acetic anhydride.

Action of Mercury Catalysts on the Acetylenic Acid (IIa).—The acid (IIa) (20 g.) and mercuric sulphate (7 g.) were boiled together in methanol (800 ml.) for 8 hr., much of the alcohol was removed, ether was added, and the solution was extracted with aqueous sodium hydrogen carbonate. Acidification of the extract gave *2-acetyl-2-hydroxy-1,3-dimethylcyclohexanecarboxylic acid* (VIIa) (9% yield), prisms [from ether–light petroleum (b. p. 40—60°)], m. p. 165°, $\lambda_{max.}$ 2900 Å (ε 39); $\nu_{max.}$ (paraffin) 1677 cm.$^{-1}$; (CCl_4) 1709, 1681 cm.$^{-1}$; ($CHCl_3$) 3546 (OH), 1701, 1684 cm.$^{-1}$ [sodium salt $\nu_{max.}$ (paraffin) 1696, 1612 cm.$^{-1}$], n.m.r. (p.p.m.) −2·29 (Ac), −1·29 (CH_3), −0·94 (doublet; J = 6·2 c./sec.) (CH_3) (OH/CO_2H signal very diffuse) (Found: C, 61·5; H, 8·6. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·5%). With ethereal diazomethane, the acid gave its *methyl ester* (VIIb), prisms [from light petroleum (b. p. 60—80°)], m. p. 31°, $\lambda_{max.}$ 3000 Å (ε 39); $\nu_{max.}$ (CCl_4) 3505 cm.$^{-1}$ (OH); (KBr or CCl_4) 1698 cm.$^{-1}$ (Found: C, 63·1; H, 8·95. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·8%).

[19] I. M. Heilbron, Ewart R. H. Jones, and R. W. Richardson, *J. Chem. Soc.*, 1949, 287.

[20] R. Cornubert, P. Anziani, A. Aubry, P. Hartmann, and M. Lemoine, *Bull. Soc. chim. France*, 1950, 636.

Evaporation of the initial, bicarbonate-washed ethereal solution gave an oil (18 g.). A solution of this in light petroleum (b. p. 40—60°) when cooled to −50° deposited crystals (4·9 g.) which, recrystallised from ether–light petroleum (b. p. 40—60°), gave the *enol-lactone* (V) as needles, m. p. 119°, $\nu_{max.}$ (paraffin) 1786, 1669 cm.$^{-1}$; (CCl_4) 3598s, 3490, 1815, 1672, 990, 951 cm.$^{-1}$, n.m.r. (p.p.m.) −4·80 (doublet; J = 3 c./sec.), 4·49 (doublet; J = 3 c./sec.), −1·32 (CH_3), −1·19 (doublet; J = 7·5 c./sec.) (CH_3) (Found: C, 67·5; H, 8·5. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%). More of this lactone was obtained by working up the mother-liquors (see below): total 47%. When hydrolysed by boiling it with aqueous ethanolic 3N-sodium hydroxide, the lactone gave the oxo-acid (VIIa), m. p. and mixed m. p. 165°.

The evaporated mother-liquors from the isolation of the enol-lactone were chromatographed on silica; light petroleum–benzene (4 : 1) eluted the methyl ester (VIIb) (36%), m. p. and mixed m. p. 31°, and benzene then eluted the enol-lactone (V), m. p. and mixed m. p. 119°.

When the mercuric sulphate catalyst was similarly used in acid solution (5 ml. of 2N-sulphuric acid added per 100 ml. of methanol), the products obtained were the oxo-acid (VIIa) (20%) and its methyl ester (VIIb) (38%).

The acetylenic acid (IIa) (2·5 g.), mercuric oxide (0·3 g.), boron trifluoride–acetic acid (40%; 3·6 ml.), and trichloracetic acid [7] (0·01 g.) were boiled together in methanol (6 ml.) for 4 hr., and ether and 6N-sulphuric acid were added. The ether solution, washed with 6N-sulphuric acid and with water, on evaporation gave an oil which crystallised in the presence of light petroleum (b. p. 40—60°) to give the mercury derivative, m. p. 163°, of the acetylenic acid (IIa) (see above).

The methyl ester (IIc) was similarly treated with the boron trifluoride–mercuric oxide catalyst, except that the reaction time was reduced to 2½ hr. The oil which was obtained by evaporation of the acid-washed ether solution was chromatographed on silica. Light petroleum (b. p. 40—60°) eluted an oil which was resolved by chromatography on alumina into starting material and the oxo-ester (VIIb), m. p. 31° (30%). Benzene then eluted the mercury derivative, m. p. 177°, of the acetylenic methyl ester (IIc) (see above).

Neither the acid (VIIa) nor its methyl ester (VIIb) gave a precipitate with 2,4-dinitrophenylhydrazine phosphate reagent; the ester gave no oxime when kept for 6 days with hydroxylamine hydrochloride in pyridine at 86°; both were unaffected by boiling with 80% formic acid for 8 hr. A mixture of the ester (VIIb) (0·2 g.), ethanol (1 ml.), and 3N-sodium hydroxide became homogeneous when boiled for 10 hr., and yielded (*ca.* 70%) the oxo-acid (VIIa) on acidification.

Ring-expansion of the Oxo-ester (VIIb).—The ester (VIIb) (1 g.) was heated at 350° under nitrogen with aluminium phosphate catalyst [19] for ¾ hr. The product, extracted by ether, was recrystallised from light petroleum (b. p. 60—80°) to give the *lactone* (VIII) *3-hydroxy-1,3,4-trimethyl-2-oxocycloheptanecarboxylic acid* (93%), needles, m. p. 88°, $\lambda_{max.}$ 2900 (ε 38); $\nu_{max.}$ (CCl_4) 1790, 1747 cm.$^{-1}$, n.m.r. (p.p.m.) −1·43 (CH_3), −1·19 (CH_3), −0·95 (doublet; J = 7 c./sec.) (CH_3) [Found: C, 67·1; H, 8·5%; Equiv. (hydrolytic), 211. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%; *M*, 196]. The compound gave a precipitate with 2,4-dinitrophenylhydrazine, but did not respond to the ferric chloride or iodoform tests.

2-Hydroxy-2,3,7-trimethylcycloheptanone.—The lactone (VIII) (0·25 g.) was heated with 0·1N-sodium hydroxide (20 ml.) and ethanol (2 ml.) at 100° for 1½ hr., 0·1N-hydrochloric acid (20 ml.) was added and the solution was distilled. Ether extraction of the distillate gave *2-hydroxy-2,3,7-trimethylcycloheptanone* as an oil (69%), $\lambda_{max.}$ 2900 Å (ε 40), $\nu_{max.}$ (film) 3450, 1700 cm.$^{-1}$ (Found: C, 70·8; H, 10·7. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%). Even careful addition, at 0°, of the calculated amount of hydrochloric acid to the alkaline hydrolysis product brought about immediate evolution of carbon dioxide and separation of the ketone. The compound gave a precipitate with 2,4-dinitrophenylhydrazine. The *oxime* (prepared by the pyridine method) crystallised as needles, m. p. 117°, $\nu_{max.}$ (KCl) 3520, 2907, 1645w cm.$^{-1}$ (Found: C, 64·6; H, 10·1; N, 7·2. $C_{10}H_{19}NO_2$ requires C, 64·8; H, 10·3; N, 7·6%).

Reactions of the Enol-lactone (V).—*Action of aluminium phosphate.* The enol-lactone (V) (0·1 g.) was heated under nitrogen with aluminium phosphate catalyst [19] for ¼ hr. (or, with similar results, ¾ hr.) and the ether-extracted product was chromatographed on silica: after light petroleum–benzene had eluted an oil (3 mg.; $\lambda_{max.}$ 2350, ε 7200), benzene eluted successively a crystalline αβ-unsaturated ketone (4 mg.; $\lambda_{max.}$ 2480, ε 8900) and an oil which contained a γ-lactone ($\nu_{max.}$ *ca.* 1785 cm.$^{-1}$) and which gave a precipitate with 2,4-dinitrophenylhydrazine and could therefore have been a crude specimen of the oxo-lactone (VIII).

Acetylation. The enol-lactone (V) (8 g.) was heated with acetic anhydride (10·4 g.) and acetyl bromide (0·5 g.) at 100° for 17 hr. Chromatography (light petroleum–benzene/silica) of the washed product gave the *enol-lactone* (X) (3 g.); needles from light petroleum (b. p. 40—60°)–ether, m. p. 55°, $\nu_{max.}$ (CCl_4) 1795, 1748, 1229, 1020, 980, 938, 881w cm.$^{-1}$; n.m.r. (p.p.m.) −4·70 (2H; sharp), −3·0 (1H; multiple), −2·07 (OAc), −1·40 (CH_3), −1·15 (doublet; J = 7·5 c./sec.) (CH_3) (Found: C, 65·9; H, 7·9; Ac, 17·1. $C_{13}H_{18}O_4$ requires C, 65·5; H, 7·6; Ac, 18·1%).

The acetoxy-lactone (X) (0·05 g.) was heated at 100° for 20 min. with dioxan (1 ml.) and 2N-hydrochloric acid (0·5 ml.), and the mixture was evaporated to dryness under reduced pressure. The residue was crystallised from acetone–carbon tetrachloride, giving *2-hydroxyacetyl-1,3-dimethylcyclohexanecarboxylic acid* (XI), m. p. 128—130°, $\nu_{max.}$ (KCl) 3475 (OH) 3145, 1709, 1052 cm.$^{-1}$, n.m.r. (p.p.m.) −4·22 (singlet) (2H), −3·28 (doublet; $J \sim 4·5$ c./sec.) (1H), −1·12 (CH_3), −0·89 (doublet; J = 6 c./sec.) (CH_3), CH with CO_2H diffuse (*ca.* −7·1 when sharpened with a trace of $CF_3 \cdot CO_2H$) (Found: C, 61·7, H, 8·5. $C_{11}H_{18}O_4$ requires C, 61·65; H, 8·45%).

Action of Acids on the Acetylenic Acid (IIa) *and its Methyl Ester* (IIc).—*Formic acid.* (*a*) A solution of the ester (IIc) in 80% formic acid was boiled and 0·3-ml. portions were evaporated (room temp.; N_2) from time to time. The reaction time (hr.), $\lambda_{max.}$ and ε for each product are bracketed: (¼; 2250—2400 Å; 200) (½; 2420 Å; 365) (1; 2420 Å; 410) (1·5; 2420 Å; 410) (2; 2420 Å; 410) (3; 2420 Å; 250) (4; *ca.* 2350sh Å; 350); subsequent products (6—15 hr.) showed no absorption maxima above 2200 Å. A similar experiment with the acid (IIa) was less easy to follow in the earlier stages.

(*b*) A solution of the acid (IIa) (5 g.) in 80% formic acid (150 ml.) was boiled for 8 hr. The formic acid was removed under reduced pressure and an ethereal solution of the

residue was washed with aqueous sodium hydrogen carbonate.

Evaporation of the ether gave a crystalline residue which was recrystallised from light petroleum (b. p. 60—80°) to give the *lactone* (XXII), as needles, m. p. 82° (2 g.): [more was recovered from the mother-liquors (see below); total yield 48%], $\lambda_{max.}$ 2870 Å (ε 30) changed on the addition of a little aqueous sodium hydroxide to 2440 Å (ε *ca.* 2400), $\nu_{max.}$ (CCl_4) 1786, 1709 cm.$^{-1}$, n.m.r. (p.p.m.) −2·97 (1H), −2·22 (Ac.), −1·48 (CH_3), −1·35 (CH_3) [Found: C, 67·4; H, 8·3%; Equiv. (back-titration), 199. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%; *M*, 196]. The compound did not respond to the iodoform test and gave no precipitate with 2,4-dinitrophenylhydrazine phosphate reagent.

The mother-liquors from which the lactone (XXII) had crystallised were chromatographed on silica; benzene–light petroleum (b. p. 60—80°) (3 : 1) eluted the *lactone* (XXa) (*ca.* 12%); needles (from ether), m. p. 153°, $\nu_{max.}$ (CCl_4) 3307 (≡CH), 1777, 642, 635 cm.$^{-1}$, n.m.r. (p.p.m.) −2·79 (unresolved multiplet) (1H), −2·36 (doublet; J = 2·5 c./sec.) (≡CH), −1·47 (CH_3), −1·20 (CH_3) [Found: C, 74·0; H, 8·0%; Equiv. (back-titration; see below), 183. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%; *M*, 178]. Benzene then eluted more of the oxo-lactone (XXII), m. p. 82°.

Acidification of the bicarbonate extract usually gave starting material (*ca.* 25% recovery), but sometimes the *lactol* (VI), $C_{11}H_{18}O_4$, was obtained, forming needles (from ethyl acetate), m. p. 162° [depressed by mixing with the oxo-acid (VIIa)], $\nu_{max.}$ ($CHCl_3$) 1780 cm.$^{-1}$ (Found: C, 61·5; H, 8·4. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·5%). On recrystallisation the lactol sometimes turned into the oxo-acid (VIIa).

(*c*) The methyl ester (IIc) boiled with 80% formic acid for 8 hr. similarly gave the oxo-lactone (XXII) (50%), m. p. 82°, and the ethynyl lactone (XXa) (12%), m. p. 144°.

(*d*) The methyl ester (IIc) was boiled with 80% formic acid for 1 hr., a bicarbonate-washed ethereal solution of the products was evaporated, and when light petroleum (b. p. 60—80°) was added to the residue some starting-material crystallised (43% recovery). Chromatography of the mother-liquors on silica yielded some more starting material [eluted by benzene–light petroleum (1 : 1)], then oils (*ca.* 25% yield) with $\lambda_{max.}$ 2750 Å (ε *ca.* 900), 2250 Å (ε *ca.* 5500), and finally an oil with $\lambda_{max.}$ 2400 Å (ε 3700) (*ca.* 4% yield; eluted by 0·25% ethanol in benzene). The oils with $\lambda_{max.}$ 2750, 2250 Å were boiled with 80% formic acid for a further 7 hr., but no crystalline products were obtained.

Sulphuric acid. The acid (IIa) (1 g.) was heated in a mixture of ethanol, water, and sulphuric acid (11 ml. each) for 9 hr. at 60° and then for 1 hr. at 70°. The diluted solution was extracted with ether and starting material (*ca.* 40% recovery) was extracted from the ethereal solution by aqueous sodium hydrogen carbonate. Evaporation of the ethereal solution and chromatography of the residue yielded the oxo-lactone (XXII), m. p. 82°; yield 28%, allowing for recovered starting material.

Reactions of the Acetylenic Lactone (XXa).—(*a*) The compound was unaltered by boiling it for 8 hr. with 80% formic acid, and more than 90% was recovered after 0·1 g. had been boiled for 8 hr. with mercuric sulphate (0·03 g.), sulphuric acid (0·01 ml.), and 95% methanol (2·2 ml.).

(*b*) *Hydrolysis.* The lactone (0·05 g.), 0·1N-sodium hydroxide (5 ml.), and ethanol (2 ml.) were heated together at 100° for 1¾ hr., and the solution (after titration at 0° for equivalent-wt. determination) was acidified, yielding starting-material, m. p. 142—143° (0·04 g.).

(*c*) *Hydrogenation.* The lactone (0·45 g.) was hydrogenated in ethyl acetate in the presence of prereduced palladium (2%) on calcium carbonate (0·05 g.) and the reaction was stopped when *ca.* 1·05 mol. of hydrogen had been absorbed: there was no marked change in absorption rate at this point. The product, recrystallised from light petroleum (b. p. 60—80°) gave the *lactone* (XXIII) (59%), as needles, m. p. 73°, $\nu_{max.}$ (CCl_4) 1860w, 1780, 1640w, 929 cm.$^{-1}$ [Found: C, 73·3; H, 9·0%; Equiv. [hydrolytic, as with lactone (XXa)], 185. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%; Equiv., 180]. The lactone (XXIII) re-formed quantitatively when the solution produced during the equivalent-wt. determination was acidified.

(*d*) *Bromination.* A solution of the lactone (XXa) (0·066 g.), anhydrous sodium acetate (0·187 g.), and *N*-bromoacetamide (0·187 g.) in acetic acid (3·5 ml.) and water (0·7 ml.) was kept at room temperature for 5 days (negligible reaction had occurred after 4 hr.): dilution with water precipitated the *bromoethynyl-lactone* (XXb) in high yield. It formed prisms (from cyclohexane or by sublimation at 130°), m. p. 144° [mixed m. p. with the acetylene (XXa) <130°]; $\nu_{max.}$ (CCl_4) 1780 cm.$^{-1}$, the spectrum being markedly similar to that of the acetylene (XXa) but with no bands near 3300 or 640 cm.$^{-1}$, n.m.r. (p.p.m.) −2·74 (1H), −1·43 (CH_3), −1·15 (CH_3) (Found: C, 51·6; H, 4·9. $C_{11}H_{13}BrO_2$ requires C, 51·4; H, 5·1%).

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