445. *A Possible Structure for Eremolactone, a New Type of Diterpene.*

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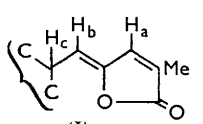
A substance, $C_{20}H_{26}O_2$, eremolactone, from *Eremophila freelingii* appears to be a diterpene of a new biogenetic type. Some evidence is presented concerning parts of the structure and formula (XI) is suggested as a working hypothesis.

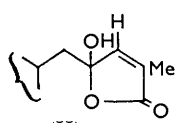
All known diterpenes belong to one biogenetic series, in contrast to sesquiterpenes for which a number of biosynthetic routes must operate. In attempts to find other series of diterpenes we have examined some unusual sources. A compound which appears to be a new type is eremolactone, $C_{20}H_{26}O_2$, m. p. 139°, from prolonged steam-distillation of the leaves of *Eremophila freelingii*.

The compound is shown to contain the lactone system (I) by spectral examination and alkaline hydrolysis. A band at 1765 cm.$^{-1}$ is in accord with an unsaturated γ-lactone, and the ultraviolet absorption ($\lambda_{max.}$ 288 mμ; ε 22,000) indicates two double bonds in linear conjugation with the carbonyl group. The proton magnetic resonance spectrum shows bands for single protons at τ 2·94 (H_a), 4·75 (J = 12 c./sec.) (H_b), and 7·70 (J = 12 c./sec.) (H_c), the splitting of the latter pair indicating the substitution shown. The =C–Me has τ 7·98. Hydrogenation of eremolactone to a tetrahydro-derivative (see below) which has $\nu_{max.}$ 1776 cm.$^{-1}$ confirms the five-ring nature of the lactone.

Mild alkali converted eremolactone into a lactol [partial structure (II)] which was reconverted by phosphorus oxychloride into eremolactone. Prolonged refluxing of



(I)



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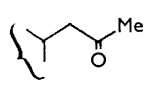


(III)

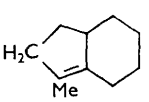
eremolactone in alkali produced, in good yield, pyruvic acid and a ketone, eremone, $C_{17}H_{26}O$ [partial structure (III)]. As expected, eremone contains the group $CH_2{\cdot}CO{\cdot}CH_3$ ($\nu_{max.}$ 1715 cm.$^{-1}$) since its piperonylidene derivative has five ethylenic protons in the range τ 2·35—3·52 and a band due to $CH_2{\cdot}CO$ (τ 7·11—7·32) split by H_c. The spectrum

shows another band, at τ 4·11, also present in eremolactone and the lactol, due to a proton ($\nu_{max.}$ 3020 cm.$^{-1}$) on a trisubstituted nuclear double bond (see below) ($\nu_{max.}$ 825 cm.$^{-1}$).

The nucleus must be tricyclic since it contains only one double bond, as shown by oxidation experiments including the uptake of 0·92 mol. of monoperphthalic acid by eremone. A *gem*-dimethyl group is probably present ($\nu_{max.}$ 1388, 1370 cm.$^{-1}$; τ 9·10, 6 protons), together with a –CHMe group [τ 8·87 (J = 8·5 c./sec.)]. In several derivatives, the two quaternary methyl groups have slightly different chemical shifts. Several attempted dehydrogenation experiments have given no sign of aromatic compounds.

The action, on eremolactone, of boiling 2N-hydrochloric acid in aqueous ethanol, or mild hydrogenation in presence of a palladium catalyst, produced, respectively, isoeremolactone, $C_{20}H_{26}O_2$, and tetrahydroisoeremolactone, $C_{20}H_{30}O_2$, the latter being also obtained by hydrogenation of the former. These reactions involve migration of the nuclear double bond, probably without skeletal rearrangement in view of the mildness of the catalytic method. In the new position, the double bond is tetrasubstituted, since no olefinic proton is detectable spectroscopically, other than in the totally unaffected lactone system; unlike the original double bond it carries a methyl group (τ 8·41). The doublet [τ 8·87 (J = 8·5 c./sec.)] in eremolactone is not present in the spectrum of the isomer. Alkaline hydrolysis of isoeremolactone gave isoeremone, $C_{17}H_{26}O$, also obtained by the action of hot hydrochloric acid on eremone.

Oxidation of the remaining double bond of tetrahydroisoeremolactone with osmium tetroxide gave a diol, $C_{20}H_{32}O_4,H_2O$, which was oxidised by lead tetra-acetate to a diketone, $C_{20}H_{30}O_4$ (also obtained by ozonolysis of tetrahydroisoeremolactone), $\nu_{max.}$ 1776



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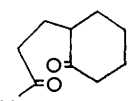

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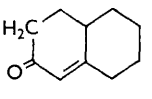


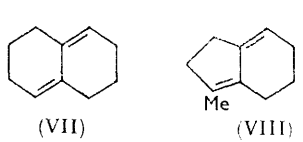
(VI)

(lactone), 1723, and 1718 cm.$^{-1}$. This was shown to be a methyl ketone ($\nu_{max.}$ 1718 cm.$^{-1}$) by a positive iodoform test and by cyclisation (see below). The other carbonyl group ($\nu_{max.}$ 1723 cm.$^{-1}$) appears to be in a six-membered ring, indicating partial structure (V). Treatment of the diketone with mild alkali produced a cyclised product of partial structure (VI), $C_{20}H_{28}O_3$, which has $\lambda_{max.}$ 246 mμ (ε 12,500), $\nu_{max.}$ 1673 and 1625 cm.$^{-1}$, very similar to testosterone [$\lambda_{max.}$ 241 mμ (ε 16,600), $\nu_{max.}$ 1675 and 1615 cm.$^{-1}$]; and its hydroxymethylene derivative, $\lambda_{max.}$ 256 and 304 mμ (ε 6000 and 4000), is also similar to 2-formyltestosterone, $\lambda_{max.}$ 251 and 309 mμ (ε 12,000 and 5300). A single proton band at τ 4·32 confirms the type of substitution of the conjugated double bond and hence the presence of CO·CH_3 in the diketone. Thus, isoeremolactone has partial structure (IV). An attempt to dehydrogenate the unsaturated ketone with dichlorodicyanobenzoquinone to obtain a phenol failed; owing to lack of material it has not been possible to examine other methods.

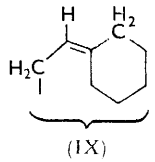
Reduction of the unsaturated ketone with borohydride, followed by dehydration of the alcohol, gave an oil with $\lambda_{max.}$ 243·5 mμ (ε 11,000) and $\lambda_{infl.}$ 239 and 251 mμ. This absorption is very similar to that of 7,9(11)-dienes in both steroids and lanostane-type triterpenoids, but is at a considerably longer wavelength than absorption of 3,5- and 4,6-dienes in the steroid series ($\lambda_{max.}$ about 235 mμ), so that partial structure (VII) seems likely to represent the diene. Oxidation of tetrahydroisoeremolactone by selenium dioxide produced dienic absorption [$\lambda_{max.}$ 244 and 251 mμ (ε 4300 and 4200); $\lambda_{infl.}$ 259 mμ (ε 2300)] consistent with partial structure (VIII), but no pure compound could be obtained.

The diffuseness of the absorption at τ 4·11 in the spectrum of eremolactone and some of its derivatives indicates that the proton on the nuclear double bond of eremolactone itself is coupled to a methylene group. Ozonolysis of eremone gave a small yield of an acid $C_{17}H_{26}O_4,H_2O$, confirming the trisubstituted nature of the double bond. Further information about the environment of the double bond was obtained from the ozonolysis

of tetrahydroeremolactone obtained as an uncrystallisable oil by the reduction of the lactol [partial structure (II)] with lithium in ammonia, and isomerisable by the action of hydrochloric acid (as above) to tetrahydroisoeremolactone. Oxidation of the ozonolysis product with acidic hydrogen peroxide and esterification with diazomethane of the resultant acid gave a gum with $\nu_{max.}$ 1783 (lactone), 1744 (ester), 1727, and 1410 cm.$^{-1}$,


(VII)

(VIII)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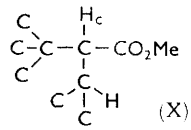
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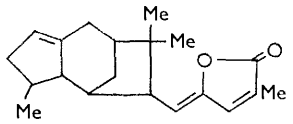
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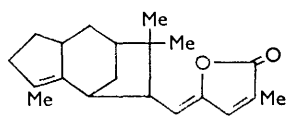
(XII)

the last two bands indicating a six-ring ketone with a methylene group adjacent to the carbonyl group. Thus, eremolcatone appears to contain the partial structure (IX).

Oxidation of isoeremolactone with permanganate gave an acid, $C_{15}H_{22}O_4$, by replacement of the lactonic side-chain by carboxyl and fission of the double bond. Treatment of the derived methyl ester with sodium methoxide gave an αβ-unsaturated keto-ester whose spectra, $\lambda_{max.}$ 246 mμ (ε 12,000), $\nu_{max.}$ 1730 (ester), 1673, and 1625 cm.$^{-1}$, and τ 4·32, are precisely analogous to those of the lactone of partial structure (V). Also present in the proton magnetic resonance spectrum is a sharp doublet [τ 6·63 (J = 6 c./sec.)], corresponding to H_c coupled to one other proton only and thus indicating partial structure (X).

On the basis of the evidence above and by using biogenetic hypotheses and Bredt's rule, it is possible to write only a restricted number of formulæ for eremolactone and isoeremolactone, such as (XI) and (XII), respectively. There is no decisive evidence in favour of any of them, but we suggest that (XI) is at present the best working hypothesis for eremolactone.

In view of lack of material and personal information from Dr. P. R. Jeffries (Perth) that he is working on similar compounds from other *Eremophila* species, one of which appears to be identical with eremolactone (m. p., optical rotation, infrared spectrum), we have stopped work in this field.

Experimental

M. p.s were determined on a Kofler block. Ultraviolet spectra were measured for ethanol solutions. Neutral alumina was Spence's grade " H," stirred with ethyl acetate for 3 days.

Isolation of Eremolactone.—The crude volatile oil of *Eremophila freelingii* was kindly isolated for us by Dr. M. D. Sutherland (University of Queensland). The leaves were distilled in steam for 3 days by a cohobation method, giving a yield of about 1% of crude oil. The oil was kept at −30° for several days, and then the crystalline eremolactone was quickly filtered off and recrystallised from light petroleum (b. p. 40—60°), forming long needles, m. p. 139°, $[\alpha]_D^{25}$ −251° (*c* 1·0), $\lambda_{max.}$ 288 mμ (ε 22,000), $\nu_{max.}$ (in CS_2) 3025, 1765, 1675, 1620, and 825 cm.$^{-1}$ (Found: C, 80·6; H, 8·9. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·9%). The yield of *eremolactone* was generally about 5% of the crude oil.

Action of Alkali on Eremolactone.—(*a*) Eremolactone (250 mg.) was refluxed for 12 hr. with potassium hydroxide (2 g.) in water (10 ml.) and ethanol (10 ml.). The cooled mixture was diluted with water and extracted with ether. Evaporation of the dried extract gave *eremone* (130 mg.), b. p. 145° (bath)/1·2 mm., $\nu_{max.}$ (in CS_2) 3020, 1718, and 825 cm.$^{-1}$ (Found: C, 82·8; H, 10·6. $C_{17}H_{26}O$ requires C, 82·9; H, 10·7%). Eremone reacted with 0·92 mol. of monoperphthalic acid in 24 hr.; it gave a *semicarbazone*, needles (from methanol), m. p. 179—180° (Found: C, 71·3; H, 9·4; N, 13·4. $C_{18}H_{29}N_3O$ requires C, 71·3; H, 9·6; N, 13·8%).

Eremone (100 mg.) was left for 48 hr. with piperonaldehyde (150 mg.) in methanol (5 ml.) containing dissolved sodium (50 mg.). The mixture was diluted with water and extracted

with ether, the extract was evaporated, and the residue recrystallised from aqueous methanol to produce *piperonylidene-eremone* as plates, m. p. 118—120°, $\lambda_{max.}$ 338 mμ (ε 20,000) (Found: C, 78·8; H, 8·0. $C_{25}H_{30}O_3$ requires C, 78·4; H, 8·0%).

The aqueous residue from the alkaline hydrolysis was acidified with sulphuric acid and treated with 2,4-dinitrophenylhydrazine in aqueous sulphuric acid. A yellow precipitate was formed which was filtered off and recrystallised from ethanol, to give yellow flakes, m. p. 214—215° undepressed on admixture with pyruvic acid 2,4-dinitrophenylhydrazone.

(*b*) Eremolactone (250 mg.) was dissolved in pyridine (20 ml.), and water (5 ml.) and potassium hydroxide (250 mg.) were added. After 4 hr. the mixture was poured into ice-cold 2N-hydrochloric acid (20 ml.), left for 30 min., then extracted with ether. The dried extract was evaporated to a hard gum which on crystallisation from light petroleum (b. p. 40—60°) gave laths of the *lactol* [partial structure (II)] (175 mg.), m. p. 122—123°, $\nu_{max.}$ (in Nujol) 3340, 1745, 1668, and 825 cm.$^{-1}$ (Found: C, 75·6; H, 8·8. $C_{20}H_{28}O_3$ requires C, 76·0; H, 8·9%).

The lactol (15 mg.) was left overnight with pyridine (1 ml.) and phosphorus oxychloride (0·2 ml.). The solution was poured on ice, and the mixture extracted with ether. The extract was washed with dilute hydrochloric acid, dried, and evaporated. Recrystallisation of the residue from aqueous ethanol gave eremolactone (10 mg.) as needles, m. p. and mixed m. p. 135—136°.

Action of Acid on Eremolactone.—Eremolactone (100 mg.) was refluxed in ethanol (10 ml.) and 2N-hydrochloric acid (4 ml.) for 2 hr. On cooling, needles were formed which, on recrystallisation from methanol, gave *isoeremolactone* (85 mg.), m. p. 159—160°; $[\alpha]_D^{23}$ +90° (*c* 1·0 in $CHCl_3$), $\lambda_{max.}$ 288 mμ (ε 22,000), $\nu_{max.}$ (in CS_2) 1765, 1668, and 1620 cm.$^{-1}$ (Found: C, 80·3; H, 8·8. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·8%).

Isoeremolactone (210 mg.) on treatment with hot alkali, as for eremolactone, gave *isoeremone* (160 mg.), b. p. 130° (bath)/0·4 mm., $\nu_{max.}$ (in CS_2) 1718 cm.$^{-1}$ (Found: C, 82·8; H, 10·7. $C_{17}H_{26}O$ requires C, 82·9; H, 10·7%). *Isoeremone semicarbazone* separated from methanol as needles, m. p. 182—183° (Found: C, 71·5; H, 9·4. $C_{18}H_{29}N_3O$ requires C, 71·3; H, 9·6%).

The aqueous residue from the alkaline hydrolysis, on treatment as in the experiment (*a*) with eremolactone, gave pyruvic acid 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 214—215°.

Action of Acid on Eremone.—Eremone (30 mg.) was refluxed for 2 hr. with 10N-hydrochloric acid (0·4 ml.) in ethanol (4 ml.). Dilution with water, ether extraction, and evaporation gave an oil (30 mg.), $\nu_{max.}$ 1718 cm.$^{-1}$, the semicarbazone of which, on recrystallisation from methanol, had m. p. 180—181° alone or mixed with isoeremone semicarbazone.

Hydrogenations.—(i) Eremolactone (250 mg.) was shaken with palladium–carbon (100 mg.) in methanol (20 ml.) under hydrogen until uptake became slow, after absorption of 2·1 mol. in about 2 hr. The catalyst was filtered off and the solvent removed, to give a viscous oil (250 mg.), which on crystallisation from light petroleum (b. p. 30—40°) gave *tetrahydroisoeremolactone* as needles (100 mg.) m. p. 130—132°, $\nu_{max.}$ (in CS_2) 1776 cm.$^{-1}$ (Found: C, 79·2; H, 9·8. $C_{20}H_{30}O_2$ requires C, 79·4; H, 10·0%). Concentration of the mother-liquors gave further needles (30 mg.), m. p. 128—131°, of tetrahydroisoeremolactone. The remaining oil (120 mg.) appeared to be mostly hexahydro-compounds, since it had low end-absorption in the ultraviolet region, but no further crystals could be obtained.

(ii) Isoeremolactone (550 mg.) was hydrogenated as described. Filtration and evaporation gave a waxy solid which on crystallisation from light petroleum (b. p. 30—40°) produced tetrahydroisoeremolactone as needles (375 mg.), m. p. and mixed m. p. 129—131°.

Reactions concerning the Isomerised Double Bond.—(i) Tetrahydroisoeremolactone (480 mg.) was left overnight with a 10% solution (4 ml.) of osmium tetroxide in benzene and further benzene (5 ml.) and pyridine (0·5 ml.). The mixture was poured into ether (50 ml.) and shaken with mannitol (10 g.) in 1% sodium hydroxide solution (100 ml.). The osmate was extracted into the aqueous phase but not decomposed. Decomposition of the osmate was achieved by addition of sodium sulphite (1 g.). The mixture was then acidified with dilute hydrochloric acid and the black precipitate was filtered off and washed with ether, the washings being added to the filtered mixture. The aqueous layer was then run off and re-extracted with ether (2 × 50 ml.). Evaporation of the combined, dried ether extracts gave a hard gum (380 mg.) which after chromatography on neutral alumina and recrystallisation from aqueous acetone gave the *diol* as needles, m. p. 158—160°, $\nu_{max.}$ (in Nujol) 3490, 3230, and 1751 cm.$^{-1}$ (Found: C, 67·5; H, 9·5. $C_{20}H_{32}O_4,H_2O$ requires C, 67·7; H, 9·6%).

The diol (160 mg.) in acetic acid (2 ml.) was treated with lead tetra-acetate (300 mg.) for 1 hr. at room temperature with occasional stirring. The product was poured into water and extracted with ether and the extract was washed with sodium carbonate solution and dried. Evaporation gave a gum (145 mg.), $\nu_{max.}$ (in CCl_4) 1783, 1723, and 1718 cm.$^{-1}$ On treatment with Brady's reagent in methanol, the above gum produced a thick yellow precipitate of a *bis*-2,4-*dinitrophenylhydrazone* which separated from chloroform–methanol as an amorphous powder, m. p. 158—165°, recrystallising above 185°, new m. p. 216—219° (Found: C, 54·8; H, 5·2. $C_{32}H_{38}N_8O_{10}$ requires C, 55·2; H, 5·2%).

(ii) Tetrahydroisoeremolactone (350 mg.) was ozonised in ethyl acetate (10 ml.) and acetic acid (5 ml.) at room temperature until 5 min. after iodine was formed in a potassium iodide trap at the end of the gas train. The mixture was then stirred with zinc powder (1 gm.) for 2 hr., filtered, poured into water, and extracted with ether. Evaporation of the dried extract produced a gum (370 mg.), $\nu_{max.}$ (in CCl_4) 1780, 1720, and 1714 cm.$^{-1}$ which on treatment with Brady's reagent gave a derivative, double m. p. 162—167° and 216—218°, undepressed on admixture with the preceding derivative.

(iii) Powdered potassium permanganate was added to isoeremolactone (300 mg.) in " AnalaR " acetone (10 ml.) with stirring, until the pink colour remained for 30 min. The mixture was poured into 0·5N-hydrochloric acid (20 ml.), and solid sodium sulphite added until all the manganese dioxide was dissolved. The solution was then saturated with sodium chloride and extracted with ether (3 × 25 ml.), and the extracts were evaporated to give an acidic gum (250 mg.) (equiv., 240). With ethereal diazomethane the gum gave a viscous oil, $\nu_{max.}$ (in CCl_4) 1730 cm.$^{-1}$ (broad), which with Brady's reagent in methanol gave a *bis*-2,4-*dinitrophenylhydrazone*, needles (from chloroform–methanol), m. p. 227—229° (decomp.), $\nu_{max.}$ (in Nujol) 1730 cm.$^{-1}$ (Found: C, 52·3; H, 4·9. $C_{28}H_{32}N_8O_{10}$ requires C, 52·5; H, 5·0%).

(iv) Tetrahydroisoeremolactone (150 mg.) was refluxed with selenium dioxide (200 mg.) in ethanol (15 ml.) for 12 hr. The solution was filtered, taken into ether (20 ml.), washed with sodium carbonate solution, dried, and evaporated to a gum (135 mg.), $\lambda_{max.}$ 244 and 250 mμ (ε 4300 and 4200), $\lambda_{infl.}$ 259 mμ (ε 2300). No crystals were obtained, even after chromatography on neutral alumina.

Reactions concerning the Original Double Bond.—(i) Eremone (200 mg.) was ozonised in ethyl acetate (5 ml.) at −78° until a permanent blue colour was formed in the solution. The solvent was removed by the passage of air and the residue taken into acetic acid (2 ml.) and hydrogen peroxide (0·5 ml.; 100-vol.) and left overnight. Unused hydrogen peroxide was decomposed and the mixture evaporated. The residue, on crystallisation from methanol, gave an *acid* (25 mg.) as needles, m. p. 174—176° (Found: C, 64·8; H, 8·8. $C_{17}H_{26}O_4,H_2O$ requires C, 65·4; H, 9·0%). The remaining gum, $\nu_{max.}$ 1725—1705 (broad), did not crystallise and further treatment with acetic acid–hydrogen peroxide gave no more of the acid.

(ii) The lactol (200 mg.) was dissolved in liquid ammonia (50 ml.) containing ethanol (1 ml.). Thin slices of lithium were added, with swirling, to keep the solution blue for 1 hr. Unused lithium was then decomposed by addition of solid ammonium chloride, and the ammonia was allowed to evaporate. The residue was mixed with 2N-hydrochloric acid (20 ml.) and ether (20 ml.), and the ether extract was dried and evaporated to an oil whose infrared spectrum [$\nu_{max.}$ (in CS_2) 3025, 1776, and 825 cm.$^{-1}$] indicated that it was tetrahydroeremolactone. The oil (50 mg.) was treated with ethanolic hydrochloric acid as above. The product crystallised from light petroleum (b. p. 30—40°) as needles (35 mg.), m. p. 129—132° alone or mixed with tetrahydroisoeremolactone.

Tetrahydroeremolactone (100 mg.) was ozonised, and the ozonide oxidised as above. The crude non-crystalline acid was esterified with diazomethane, and the ester was chromatographed on neutral alumina, giving a gum (80 mg.), $\nu_{max.}$ (in CCl_4) 1785, 1744, 1727, and 1410 cm.$^{-1}$, from which no crystalline derivative was obtained.

Cyclisations. (i) The diketo-lactone (250 mg.) from the ozonisation (i) preceding was refluxed with potassium hydroxide (250 mg.) in methanol (5 ml.) for 2 hr. The mixture was poured into water, acidified, and extracted with ether. The extract was dried and evaporated to a viscous oil (210 mg.) which crystallised when scratched. Recrystallisation from ether–light petroleum (b. p. 40—60°) gave the αβ-unsaturated *keto-lactone* [partial structure (VI)] as plates, m. p. 107—109°, $\lambda_{max.}$ 246 mμ (ε 12,200), $\nu_{max.}$ (in CCl_4) 1780, 1673, and 1625 cm.$^{-1}$ (Found: C, 75·6; H, 8·6. $C_{20}H_{28}O_3$ requires C, 75·9; H, 8·8%).

(ii) The diketo-ester (150 mg.) was left overnight with sodium methoxide (from sodium,

200 mg.) in methanol (5 ml.). The mixture was poured into water, quickly extracted with ether, and evaporated to an oil (140 mg.), $\lambda_{max.}$ 246 mμ (ε 12,000), $\nu_{max.}$ (in CCl_4) 1732, 1673, and 1625 cm.$^{-1}$ which gave a 2,4-*dinitrophenylhydrazone*, needles (from methanol), m. p. 212—214° (Found: C, 60·1; H, 6·1. $C_{22}H_{26}N_4O_6$ requires C, 59·7; H, 5·9%).

Reactions of the αβ-Unsaturated Keto-lactone.—(i) The keto-lactone (35 mg.) was left overnight with sodium methoxide (100 mg.) in dry ethyl formate (3 ml.). The mixture was poured into water, and the aqueous phase was washed with ether, quickly acidified, and then extracted with ether. The extract was dried and evaporated to a yellow gum (30 mg.), $\lambda_{max.}$ 256 and 304 mμ (ε 6000 and 4000) which did not crystallise or give a crystalline aniline derivative.

(ii) The keto-lactone (25 mg.) was refluxed in benzene (3 ml.) with dichlorodicyanobenzoquinone (20 mg.) for 3 hr. The mixture was diluted with ether and the quinone extracted in sodium carbonate solution. Evaporation of the ether extract and recrystallisation of the residue from ether–light petroleum (b. p. 40—60°) gave unchanged starting material (15 mg.), m. p. and mixed m. p. 106—108°.

(iii) The keto-lactone (23 mg.) was left overnight with sodium borohydride (50 mg.) in methanol (2 ml.). Working up in the standard manner gave a gum (20 mg.), $\nu_{max.}$ (in CCl_4) 3620 and 1775 cm.$^{-1}$, lacking absorption at 1673 cm.$^{-1}$. The gum was left overnight with phosphorus oxychloride (0·5 ml.) in pyridine (2 ml.). Working up gave an oil (17 mg.), $\lambda_{max.}$ 243·5 mμ (ε 5300), $\lambda_{infl.}$ 239 and 251 mμ (ε 4800 and 3500), $\nu_{max.}$ (film) 3010, 1770, 1660, and 835 cm.$^{-1}$, still containing some hydroxylic material ($\nu_{max.}$ 3500 cm.$^{-1}$). Warming this oil with ethanolic hydrochloric acid raised the extinction coefficient at 243·5 mμ to 11,000 without altering the shape of the spectrum. The oil did not crystallise.

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