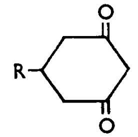
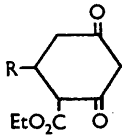
582. cyclo*Hexane*-1 : 3-*diones. Part I. Hydrolysis of Ethyl 2 : 4-Dioxo-6-styryl*cyclo*hexanecarboxylate.*

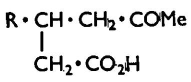
By G. R. Ames and W. Davey.

Vigorous hydrolysis of ethyl 2 : 4-dioxo-6-styryl*cyclo*hexanecarboxylate gave 5-oxo-3-phenethylhex-2-enoic acid (VI) instead of the expected 5-oxo-3-styrylhexanoic acid. Wolff–Kishner reduction of the acid (VI) yielded 3-phenethylhex-2-enoic acid (VII), the geometrical isomer of which was synthesised from 1-phenylhexan-3-one. Evidence regarding the configuration of these isomers is presented.

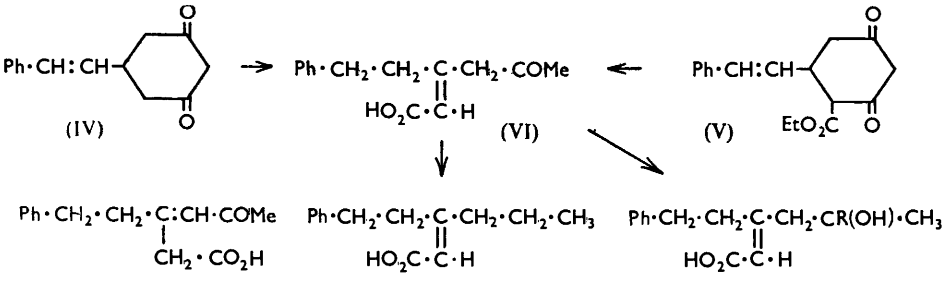
Vorländer[1,2] showed that hydrolysis of *cyclo*hexane-1 : 3-diones (I) and the derived carboxylic esters (II) afforded δ-keto-acids (III). The hydrolysis of the diones (I and II; R = Ph) has been thoroughly investigated by Vorländer,[2] Knoevenagel,[3] and Michael.[4] The styryl diones (IV) and (V) were prepared by Vorländer [5,6] by addition of diethyl malonate to cinnamylideneacetone, and their structures were proved by oxidation of the former to β-styrylglutaric acid, which was further oxidised to tricarballylic acid, but no further work on them has been reported. The present work constitutes an investigation of the hydrolysis of the dione (V). First, the following evidence in support of the structure (V) was adduced: ozonolysis gave benzaldehyde, and treatment with perbenzoic acid resulted in the uptake of 1 mol. of oxygen.


(I)


(II)


$$R\cdot\underset{\displaystyle CH_2\cdot CO_2H}{CH}\cdot CH_2\cdot COMe$$
(III)

Hydrolysis of either dione (IV) or (V) with hydrochloric acid yielded a keto-acid, subsequently identified as (VI), which was reduced by the modified Wolff–Kishner or the Clemmensen method to the olefinic acid (VII), characterised as its amide and nitrile.



The ultraviolet spectra of these acids (VI) and (VII) (see Table) do not show the intense absorption at about 250 mμ expected for the styryl chromophore,[7] but show a series of weak bands characteristic of an unconjugated benzene ring. In the diones (IV) and (V) the styryl absorption coincides with the β-diketone band, although comparison with the phenyl homologues (I and II; R = Ph) shows that in compounds of this type the styryl group contributes *ca.* 20,000 to the molecular extinction coefficient at 255 mμ. Bands at 1679

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[1] Vorländer, *Ber.*, 1894, **27**, 2053.
[2] *Idem, Annalen*, 1896, **294**, 253.
[3] Knoevenagel, *Ber.*, 1894, **27**, 2337.
[4] Michael, *ibid.*, p. 2126.
[5] Vorländer, *Annalen*, 1896, **294**, 273.
[6] Vorländer and Groebel, *ibid.*, 1906, **345**, 206.
[7] Overberger and Tanner, *J. Amer. Chem. Soc.*, 1955, **77**, 369.

and 1687 cm.$^{-1}$ in the infrared spectra of the acids (VI) and (VII) respectively confirm the conjugation of the carboxyl groups. The alternative structure (VIII) for the keto-acid can be ruled out because the semicarbazone has maximum absorption at 230 mμ (ε 16,700) characteristic of an unconjugated ketone.

The hydroxy-acid (IX; R = H) was obtained from the keto-acid by reduction with potassium borohydride and by hydrogenation in alkali with a Raney nickel catalyst. The homologous acid (IX; R = Me) was produced by the action of methylmagnesium iodide on the parent (VI). These hydroxy-acids are not lactonised when heated above the melting point, which indicates that the carboxyl group has the *trans*-configuration with respect to the acetonyl group, as shown in (VI).

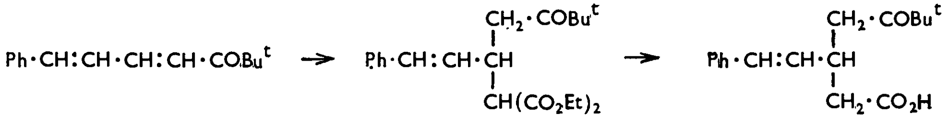
Palladium-catalysed hydrogenation of the styryl-diones (IV) and (V) yielded the phenethyl-diones (I and II; $R = CH_2Ph{\cdot}CH_2$), both of which were hydrolysed to the saturated keto-acid (III; $R = CH_2Ph{\cdot}CH_2$), whence Clemmensen reduction afforded 3-phenethylhexanoic acid.

*Ultraviolet light absorption in ethanol.**

Compound	$\lambda_{max.}$ (mμ)	ε	Compound	$\lambda_{max.}$ (mμ)	ε	Compound	$\lambda_{max.}$ (mμ)	ε
IV	254	33,900	Me ester from XVI	*259*	389	XII	252	17,800
V	255	42,500		265	479		284	1780
VI	*243*	117		273	437		292·5	1200
	248	153	I; R = Ph	257·5	15,100	XV	248	280
	253	200	II; R = Ph	257	16,600		253	300
	258·5	243	VII	*237*	71		259	320
	260	215		*243*	89		264	260
	264	193		248	138		268	240
	268	156		253	191			
	285	44		*255*	182			
XIV; R=Et	233·5	12,000		258·5	224			
XIV; R = H	235	11,500		261	219			
Amide from XVI	*253*	246		264	170			
	257	372		268	162			
	266	525						
	273	550						

* Italicised figures denote inflexions.

No isomerisation similar to that described above occurred on hydrolysis of the Michael adduct (X) obtained from 2 : 2-dimethyl-7-phenylhepta-4 : 6-dien-3-one (cinnamylidene-pinacolone) (XI). The acid (XII) thus obtained gave benzaldehyde on ozonolysis, and the ultraviolet spectrum confirmed the presence of the styryl group. The absence of isomerisation during hydrolysis of the ester (X) suggests that the isomerisation with the cyclic compound (V) depends on the cleavage of the ring.



$$Ph{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COBu^t \longrightarrow Ph{\cdot}CH{:}CH{\cdot}\underset{CH(CO_2Et)_2}{\overset{CH_2{\cdot}COBu^t}{CH}} \longrightarrow Ph{\cdot}CH{:}CH{\cdot}\underset{CH_2{\cdot}CO_2H}{\overset{CH_2{\cdot}COBu^t}{CH}}$$

(XI) (X) (XII)

Confirmation of the structure (VII) assigned above was sought by independent synthesis. Condensation of 1-phenylhexan-3-one (XIII) with ethyl cyanoacetate yielded the cyano-ester (XIV; R = Et) which, on hydrolysis with hydrochloric acid, unexpectedly afforded the cyano-acid (XIV; R = H). The structure of the latter was shown by the similarity of its ultraviolet spectrum to that of its ester (see Table).

The cyano-acid (XIV; R = H) was decarboxylated at 200°; but the nitrile obtained was not pure, so its identity, or isomerism, with the nitrile derived from the acid (VII) could not be established. Both nitriles showed an infrared band at 2224 cm.$^{-1}$; Kitson and Griffith [8] give 2225 ± 8 cm.$^{-1}$ for conjugated nitriles. In order to correlate the structures of the two nitriles, the conversion of the nitrile from the cyano-acid (XIV; R = H) into the amide with alkaline hydrogen peroxide was attempted, but unchanged

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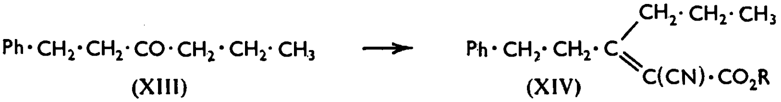
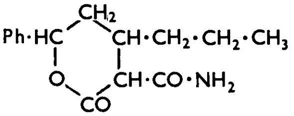
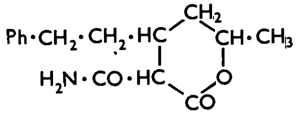
[8] Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334.

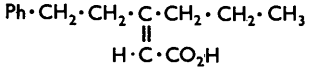
nitrile was recovered; and the cyano-acid itself was also unaffected by this treatment. Alkaline hydrogen peroxide converted the cyano-ester (XIV; R = Et) into a compound $C_{15}H_{19}O_3N$, isolated as the hemihydrate, which was not decarboxylated at 200° and whose ultraviolet spectrum (see Table) is characteristic of an unconjugated benzene ring. The infrared spectrum in Nujol mull shows bands attributed to amide (3352, 3180, 1670, 1645, 1422 cm.$^{-1}$), lactone (1747 cm.$^{-1}$), and phenyl (1607, 1493 cm.$^{-1}$) systems; in chloroform the lactone band is at 1737 cm.$^{-1}$. Grove and Willis[9] and Berson[10] assign 1740 cm.$^{-1}$ to δ- and 1770 cm.$^{-1}$ to γ-lactone systems. The spectroscopic evidence is therefore compatible with formula (XVa or b) rather than the corresponding γ-lactones. Structure (XVb) is tentatively assigned to the lactone-amide, the alternative (XVa) being considered unlikely since the compound was not reduced by hydrogen in the presence of palladised charcoal.


(XIII) (XIV)


(XVa)


(XVb)

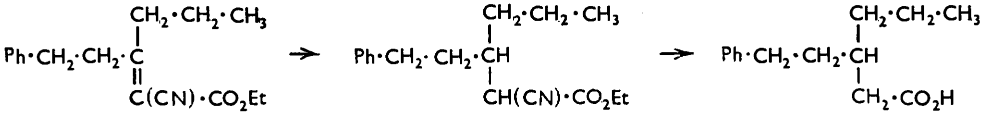
Because of the incomplete hydrolysis of the cyano-ester (XIV; R = Et) by hydrochloric acid, the use of hydrobromic acid was examined. The oily acid (XVI) produced was converted directly into the amide, m. p. 140°, which was not identical with the amide, m. p. 145°, of the unsaturated acid (VII). The ultraviolet spectra of the new amide and the methyl ester (see Table) showed no strong absorption above 220 mμ. In view of the configuration (VII) assigned above, this acid must be the *cis*-isomer (XVI).


(XVI)

$$Ph\cdot CH_2\cdot CH_2\cdot \underset{\underset{H\cdot C\cdot CO_2H}{\|}}{C}\cdot CH_2\cdot CH_2\cdot CH_3$$

Attempts to interconvert the amides of the isomers (VII) and (XVI) by ultraviolet light in the presence of iodine[11] were unsuccessful, and the acids were not isomerised by hydrobromic acid or aqueous sodium hydroxide.

Finally, 3-phenethylhexanoic acid was obtained from the cyano-ester (XIV; R = Et) by hydrogenation and hydrolysis. Comparison of the amides showed that the product was identical with the sample obtained from the cyclic ester (II; R = $CH_2Ph\cdot CH_2$).



EXPERIMENTAL

Ultraviolet spectra were determined in 96% EtOH with a Unicam SP 500 spectrophotometer. Infrared spectra were measured for Nujol mulls unless stated otherwise.

trans-5-*Oxo*-3-*phenethylhex*-2-*enoic Acid* (VI).—Ethyl 2 : 4-dioxo-6-styryl*cyclo*hexanecarboxylate[6] (162 g.) was refluxed with concentrated hydrochloric acid (1200 c.c.), acetic acid (800 c.c.), and water (800 c.c.) for 15 hr. Concentration under reduced pressure followed by dilution with water gave trans-5-*oxo*-3-*phenethylhex*-2-*enoic acid* as pale yellow crystals (102 g., 78%), m. p. 120—122°. Recrystallisation from aqueous alcohol afforded colourless plates, m. p. 127—128° (Found: C, 72·1; H, 6·6. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). The *semicarbazone* formed prisms, m. p. 211°, from methanol (Found: N, 14·2. $C_{15}H_{19}O_3N_3$ requires N, 14·5%).

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[9] Grove and Willis, *J.*, 1951, 881.

[10] Berson, *J. Amer. Chem. Soc.*, 1954, **76**, 4974.

[11] Cawley and Nelan, *ibid.*, 1955, **77**, 4130.

Successive treatment of the acid with ethereal diazomethane and aqueous ammonia yielded the *amide*, needles, m. p. 166—167°, from water (Found: C, 72·2; H, 7·4; N, 6·6. $C_{14}H_{17}O_2N$ requires C, 72·7; H, 7·4; N, 6·1%). The keto-acid was not lactonised when heated with 50% sulphuric acid.

trans-3-*Phenethylhex-2-enoic Acid* (VII).—(a) *By the modified Wolff–Kishner method.*[12] A mixture of the acid (VI) (12 g.), sodium hydroxide (6 g.) in water (6 c.c.), 80% hydrazine hydrate (15 c.c.), and ethylene glycol was boiled under reflux for 1·5 hr., distilled until the temperature of the mass reached 200°, and then refluxed for 6 hr. Pouring into water and acidification gave the acid, m. p. 80—85°. On recrystallisation from light petroleum (b. p. 60—80°), trans-3-*phenethylhex-2-enoic acid* formed needles, m. p. 97—98° (10·3 g., 82%) (Found: C, 76·5; H, 8·2%; equiv., by titration, 215. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%; equiv., 218).

(b) *By the Clemmensen procedure.* Reduction of the keto-acid (VI) with amalgamated zinc (10 g.) in concentrated hydrochloric acid (10 c.c.) and acetic acid (20 c.c.) gave the acid (VII) (1·1 g.), m. p. and mixed m. p. 96—98°. The p-*bromophenacyl ester* formed needles, m. p. 102—103°, from aqueous ethanol (Found: C, 64·0; H, 5·6. $C_{22}H_{23}O_3Br$ requires C, 63·6; H, 5·6%). The acid (VII) was not oxidised by performic or perbenzoic acid. No recognisable products were obtained on oxidation with potassium permanganate or ozonolysis.

Methyl trans-3-*phenethylhex-2-enoate*, obtained by the action of diazomethane on the acid, had b. p. 135—136°/2 mm., n_D^{19} 1·5220 (Found: C, 77·8; H, 8·6. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·7%). Ultraviolet absorption: $\lambda_{max.}$ *237*, *242*, 248, 253, 259, 261, 264, 268 mμ (ε 95, 117, 159, 209, 240, 234, 182, 174 respectively).

trans-3-*Phenethylhex-2-enoamide*, obtained by treatment of the acid with thionyl chloride and then with ammonia, formed needles, m. p. 145°, from benzene (Found: C, 77·6; H, 8·6; N, 6·75. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·75; N, 6·5%). Ultraviolet absorption: $\lambda_{max.}$ *242*, 248, 253, 259, 261, 264, 268 mμ (ε 170, 214, 269, 302, 295, 240, 234 respectively).

trans-3-*Phenethylhex-2-enonitrile*, obtained when the amide was refluxed with thionyl chloride for 2 hr., had b. p. 126—128°/0·6 mm., n_D^{18} 1·5396 (Found: C, 84·0; H, 8·8; N, 6·8. $C_{14}H_{17}N$ requires C, 84·4; H, 8·6; N, 7·0%).

trans-5-*Hydroxy-3-phenethylhex-2-enoic Acid* (IX; R = H).—(a) *By potassium borohydride.* A solution of the keto-acid (VI) (5 g.) and potassium borohydride (3 g.) in water (50 c.c.) was set aside for 3 days. Acidification then yielded the *hydroxy-acid*, needles, m. p. 115—117°, from benzene (Found: C, 71·3; H, 7·7. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). Ultraviolet absorption: $\lambda_{max.}$ 238, 243, 249, *252*, 254·5, *258*, 261, *265*, 268 mμ (ε 111, 134, 187, 176, 235, 204, 242, 155, 133 respectively).

(b) *By catalytic hydrogenation.* When a solution of the keto-acid (6 g.) in ethanol (150 c.c.) and 2N-sodium hydroxide (20 c.c.) was shaken under hydrogen in the presence of Raney nickel (W 7; *ca.* 5 g.), absorption ceased after the uptake of 1 mol. Removal of the catalyst, concentration, and acidification gave the hydroxy-acid (5·7 g.), m. p. and mixed m. p. 114—116°.

trans-5-*Hydroxy-5-methyl-3-phenethylhex-2-enoic Acid* (IX; R = Me).—Methylmagnesium iodide (5 mol.) in ether (100 c.c.) was added during 1 hr. to a suspension of the keto-acid (VI) (5 g.) in ether. After 2 hr. at room temperature, the mixture was heated on a steam-bath for 30 min. Working up in the usual manner gave 3·2 g. of material, m. p. 149—152°. Recrystallisation from benzene afforded the *hydroxy-acid* as needles, m. p. 154—155° (Found: C, 72·6; H, 7·9. $C_{15}H_{20}O_3$ requires C, 72·6; H, 8·1%).

Ethyl 2 : 4-*Dioxo-6-phenethyl*cyclo*hexanecarboxylate* (II; R = $CH_2Ph{\cdot}CH_2$).—When the styryl analogue was hydrogenated in ethanol in the presence of palladised charcoal, 1 mol. was taken up; the *product* crystallised from benzene–light petroleum (b. p. 60—80°) as needles, m. p. 93—94° (Found: C, 70·1; H, 6·9. $C_{17}H_{20}O_4$ requires C, 70·8; H, 6·9%). Ultraviolet absorption: $\lambda_{max.}$ 258 mμ (ε 18,200).

5-*Phenethyl*cyclo*hexane*-1 : 3-*dione* (I; R = $CH_2Ph{\cdot}CH_2$).—Similar hydrogenation of 5-styryl*cyclo*hexane-1 : 3-dione gave the saturated *dione*, needles, m. p. 148—149°, from benzene (Found: C, 78·0; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·7; H, 7·5%). The ultraviolet spectrum had $\lambda_{max.}$ 255 mμ (ε 24,000).

5-*Oxo-3-phenethylhexanoic Acid* (III; R = $CH_2Ph{\cdot}CH_2$).—5-Phenethyl*cyclo*hexane-1 : 3-dione (3 g.) was boiled under reflux with concentrated hydrochloric acid (45 c.c.) and acetic acid (15 c.c.) for 20 hr. Isolation of the acidic fraction with ether furnished the *acid* as an oil (2·7 g.) (Found: C, 71·6; H, 7·6. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene as orange-yellow needles, m. p. 146—147° (Found: C, 57·6;

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[12] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

H, 5·3; N, 13·0. $C_{20}H_{22}O_6N_4$ requires C, 58·0; H, 5·4; N, 13·5%). Similar hydrolysis of the dione-ester (II; R = $CH_2Ph{\cdot}CH_2$) afforded an oily acid, which gave the same 2 : 4-dinitrophenylhydrazone.

3-*Phenethylhexanoic Acid.*—The foregoing keto-acid (5 g.) in acetic acid (50 c.c.) was reduced by amalgamated zinc wool (25 g.) in boiling concentrated hydrochloric acid (25 c.c.) for 16 hr. After concentration under reduced pressure, the product was isolated with ethyl acetate. 3-*Phenethylhexanoic acid* had b. p. 154—156°/1·2 mm., n_D^{21} 1·5202 (Found: C, 76·4; H, 8·5. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·1%). The *amide*, prepared by successive treatment with thionyl chloride and ethereal ammonia, crystallised from water as needles, m. p. 91—92° (Found: C, 77·0; H, 9·8; N, 6·0. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·7; N, 6·4%). Ultraviolet absorption: $\lambda_{max.}$ 237, *243*, *253*, 255, 259, 261, *265*, 268 mμ (ε 100, 120, 224, 229, 263, 269, 200, 219 respectively). The acid with ethereal diazomethane yielded the *methyl ester*, b. p. 105°/0·6 mm., n_D^{16} 1·4935 (Found: C, 77·4; H, 9·4. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). Ultraviolet absorption: $\lambda_{max.}$ *243*, *248*, 254·5, 259, 261, *264*, 268 mμ (ε 91, 138, 191, 229, 178, 182 respectively).

2 : 2-*Dimethyl*-7-*phenylhepta*-4 : 6-*dien*-3-*one* (XI).—A mixture of pinacolone (26·1 g.), cinnamaldehyde (37·8 g.), ethanol (100 c.c.), and N-sodium hydroxide (60 c.c.) was shaken for 3 days. Isolation of the products with benzene followed by distillation gave the *dienone*, b. p. 134—136°/0·8 mm. (20 g.), which crystallised from light petroleum (b. p. 60—80°) as pale yellow prisms, m. p. 58—60° (Found: C, 84·2; H, 8·5. $C_{15}H_{18}O$ requires C, 84·1; H, 8·5%). Ultraviolet absorption: $\lambda_{max.}$ 231, 325 mμ (ε 7900, 34,700 respectively). The *semicarbazone* formed prisms, m. p. 128—129°, from benzene–light petroleum (b. p. 60—80°) (Found: N, 15·6. $C_{16}H_{21}ON_3$ requires N, 15·5%); ultraviolet max. at 227, 302, 308 mμ (ε 14,400, 26,900, 26,300 respectively).

6 : 6-*Dimethyl*-5-*oxo*-3-*styrylheptanoic Acid* (XII).—The above ketone (8·8 g.) was added to a suspension of diethyl sodiomalonate (from sodium, 1·0 g., and diethyl malonate, 6·9 g.) in ether. After boiling for 6 hr., the solution was evaporated; the residue was taken up in ethanol (100 c.c.) and refluxed with potassium hydroxide (15 g.) in water (50 c.c.) for 4 hr. Isolation of the acidic products gave the crude diacid which was decarboxylated by heating it to 170°. The *acid* (6·3 g.) obtained crystallised from water as the *hemihydrate*, needles, m. p. 93—94° (Found: C, 72·3; H, 7·8. $C_{17}H_{22}O_3,\frac{1}{2}H_2O$ requires C, 72·0; H, 8·2%). The *semicarbazone* formed rhombs, m. p. 115—117°, from benzene (Found: N, 13·2. $C_{18}H_{25}O_3N_3$ requires N, 12·7%).

Ozonolysis of the acid in acetic acid afforded benzaldehyde, identified as the 2 : 4-dinitrophenylhydrazone, as the only steam-volatile product.

1-*Phenylhexan*-3-*one* (XIII).—Condensation of β-phenylpropionyl chloride with di-*n*-propylcadmium according to Cason's general procedure[13] gave a 71% yield of 1-phenylhexan-3-one, b. p. 93—96°/2 mm., n_D^{20} 1·5010. Rupe and Hirschmann[14] give b. p. 133—135°/8 mm. The 2 : 4-*dinitrophenylhydrazone*, orange prisms from methanol–ethyl acetate, had m. p. 170—172° (Found: N, 15·8. $C_{18}H_{20}O_4N_4$ requires N, 15·7%). The semicarbazone formed needles, m. p. 87—88°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 66·7; H, 8·2. Calc. for $C_{13}H_{19}ON_3$: C, 66·9; H, 8·2%); Rupe and Hirschmann[14] give m. p. 79°.

Ethyl 2-*Cyano*-3-*phenethylhex*-2-*enoate* (XIV; R = Et).—A mixture of 1-phenylhexan-3-one (28·4 g.), ethyl cyanoacetate (22·4 g.), and acetic acid (8·0 g.) in benzene (200 c.c.) was refluxed for 45 hr. under a Dean and Stark separator. Ammonium acetate (9·0 g.) was added in 0·5 g. portions at intervals.[15] The solution was washed with sodium hydrogen carbonate solution, dried, and evaporated. Fractionation yielded *ethyl* 2-*cyano*-3-*phenethylhex*-2-*enoate* (31·8 g., 73%), b. p. 159—160°/1·4 mm., n_D^{19} 1·5227 (Found: C, 75·5; H, 7·7; N, 5·1. $C_{17}H_{21}O_2N$ requires C, 75·3; H, 7·8; N, 5·2%).

The ester (2·3 g.) was boiled with concentrated hydrochloric acid (30 c.c.), acetic acid (50 c.c.), and water (20 c.c.) for 15 hr. Evaporation and crystallisation from light petroleum (b. p. 60—80°) afforded the *cyano-acid* (0·9 g.), needles, m. p. 101—102° (Found: C, 73·8; H, 7·0; N, 5·8. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0; N, 5·8%).

Decarboxylation of the Cyano-acid.—When heated to 200°, the cyano-acid yielded, probably, *cis*-3-phenethylhex-2-enonitrile, b. p. 125—127°/0·8 mm., n_D^{19} 1·5223 (Found: C, 84·0; H, 8·5; N, 6·6. Calc. for $C_{14}H_{17}N$: C, 84·4; H, 8·6; N, 7·0%). Although the analysis was satisfactory, this sample could not have been pure as the infrared spectrum showed the presence of hydroxylic and lactonic impurities; the material became yellow on storage.

[13] Cason, *J. Amer. Chem. Soc.*, 1946, **68**, 2078.

[14] Rupe and Hirschmann, *Helv. Chim. Acta*, 1931, **14**, 687.

[15] Cf. Cragoe, Robb, and Sprague, *J. Org. Chem.*, 1950, **15**, 381.

Action of Alkaline Hydrogen Peroxide on Ethyl 2-Cyano-3-phenethylhex-2-enoate.—To the cyano-ester (3 g.) in acetone (30 c.c.) were added 10% hydrogen peroxide (15 c.c.) and 10% sodium carbonate solution (2·5 c.c.), and the solution was set aside for a week. Isolation with chloroform gave 2·9 g. of, probably, *2-carbamoyl-5-hydroxy-3-phenethylhexanoic lactone* (XVb), needles, m. p. 60—62°, from light petroleum (b. p. 60—80°) (Found: C, 67·0; H, 7·5; N, 4·8. $C_{15}H_{19}O_3N,0·5H_2O$ requires C, 66·7; H, 7·5; N, 5·2%). This compound could not be hydrogenolysed in the presence of a palladium catalyst.

cis-3-*Phenethylhex-2-enoamide.*—Ethyl 2-cyano-3-phenethylhex-2-enoate (6·2 g.) was refluxed with hydrobromic acid (48%; 75 c.c.) and acetic acid (30 c.c.) for 20 hr., and the solution evaporated *in vacuo*. The acidic fraction (1·8 g.), isolated with aqueous sodium carbonate, did not crystallise. Successive treatment with thionyl chloride and ethereal ammonia gave the *amide*, rods, m. p. 140° (from benzene) (Found: C, 77·3; H, 8·5; N, 6·4. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8; N, 6·5%).

Methyl cis-3-*Phenethylhex-2-enoate.*—Treatment of the preceding crude acid with ethereal diazomethane afforded the *methyl ester*, b. p. 113—115°/0·6 mm., n_D^{20} 1·5244 (Found: C, 77·1; H, 8·7. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%).

Ethyl 2-Cyano-3-phenethylhexanoate.—Hydrogenation of ethyl 2-cyano-3-phenethylhex-2-enoate in ethanol with palladised strontium carbonate catalyst yielded *ethyl 2-cyano-3-phenethylhexanoate*, b. p. 156—159°/1·3 mm., n_D^{19} 1·4967 (Found: C, 75·2; H, 8·6; N, 4·7. $C_{17}H_{23}O_2N$ requires C, 74·7; H, 8·5; N, 5·1%).

The cyano-ester (4·1 g.) was added to ethylene glycol (25 c.c.) and 50% potassium hydroxide solution (5 c.c.); the mixture was distilled until the b. p. reached 200° and then refluxed for 18 hr. The acidic fraction (3·0 g.), b. p. 133—135°/0·2 mm., was converted into 3-phenethylhexanoamide, identical with that obtained previously.

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