420. *The Chemistry of Reductone. Part II.* Some Condensation Products of Reductone with Amino-compounds.*

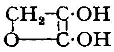
By Wesley Cocker, R. A. Q. O'Meara, J. C. P. Schwarz, and E. R. Stuart.

Reductone has been condensed with various aromatic primary and secondary amines and certain α-amino-acids. The structures of these condensation products are discussed.

In view of the biological significance of the condensation products of reductone with amino-compounds (Forrest and Walker, *J.*, 1949, 2002; Angier *et al.*, *J.*, *Amer. Chem. Soc.*, 1948, **70**, 25; Bell, Cocker, and O'Meara, *Biochem. J.*, 1949, **45**, 373), it seemed desirable to investigate the formation and chemistry of these compounds in greater detail.

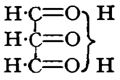
Although reductone can, theoretically, exist in a number of tautomeric modifications and a number of such structures have been suggested, *e.g.*, (I) (Norrish and Griffiths, *J.*, 1928, 2829), (II), (IV), and (V) (von Euler, Hasselquist, and Lööv, *Arkiv Kemi, Mineral., Geol.*, 1948, **26**, *A*, 17; von Euler and Hasselquist, *Arkiv Kemi, Mineral., Geol.*, 1949, **26**, *A*, 25), structure (III) (von Euler and Martius, *Annalen*, 1933, **505**, 73) seems to us, with our present information, to be the most acceptable. Incidentally, (V) is really the chelated *trans*-form of (III) : molecular models show that chelation of the *cis*-form is stereochemically impossible.

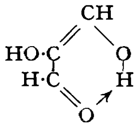
$HO{\cdot}CH_2{\cdot}CO{\cdot}CHO$
(I.)


(II.)

$HO{\cdot}CH{=}C(OH){\cdot}CHO$
(III.)

$HO{\cdot}\overset{+}{C}H{\cdot}C(OH){=}CH{\cdot}OH$
(III*a*.)


(IV.)


(V.)

Reductone has been shown to condense, in the cold, with a number of amines, both in presence and in absence of mineral acid. Undoubtedly, in the latter conditions the yields and quality of products are inferior to those obtained when mineral acid is employed. This may be associated with the necessity for the opening of an acid-labile ring system such as (II), as suggested by von Euler, Hasselquist, and Lööv (*loc. cit.*), but it may be that the acid favours the formation of the reactive, symmetrical ion (III*a*).

The products obtained from reductone and aniline, *p*-chloroaniline, 2-naphthylamine, and sulphanilic acid are, respectively, 3-anilino- (VI; R = H), 3-*p*-chloroanilino- (VI; R = Cl), 3-2'-naphthylamino- (VI*a*), and 3-*p*-sulphoanilino-2-hydroxyprop-2-enal (VI; R = SO_3H). Compounds (VI; R = H and R = Cl) and (VI*a*) give the ene-diol colour reaction of Fearon and Kawerau (*Biochem., J.*, 1943 **37**, 326), but the reaction with (VI; R = SO_3H) was unsatisfactory. The compounds (VI; R = H) and (VI*a*) were shown to be completely enolic by titration with dichlorophenol-indophenol (Tillmans's reagent) in acid solution and this result was confirmed for (VI; R = H) by titration with iodine. Titration with iodine reveals that (VI; R = SO_3H) is only 50% enolic.

When reductone is condensed with methylaniline in presence of dilute acetic acid, 3-*N*-methylanilino-2-hydroxyprop-2-enal (VII) is obtained. Although this compound does not

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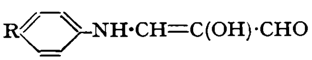
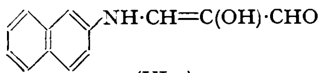
* The paper by Bell, Cocker, and O'Meara (*loc. cit.*) can be considered as Part I of this series.

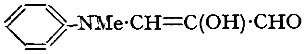
give Fearon and Kawerau's ene-diol reaction (*loc. cit.*) it can be quantitatively titrated with iodine or with Tillmans's reagent in acid solution. Oxidation of the groups $-C(OH){=}C(OH)-$ and $-C(OH){=}C(NHR)-$ by *o*-dinitrobenzene would, on Fearon and Kawerau's view (*loc. cit.*), yield the systems $O{=}\dot{C}{-}\dot{C}{=}O$ and $O{=}\dot{C}{-}\dot{C}{=}NR$, but no such oxidation of $-C(OH){=}C(NRR')-$ is possible; oxidation of the three enol systems with iodine or Tillmans's reagent, which proceeds in acid solution, may involve the production of $O{=}\dot{C}{-}\dot{C}{=}O$, $O{=}\dot{C}{-}\dot{C}{=}NR$, and $O{=}\dot{C}{-}\dot{C}{=}\overset{+}{N}RR'$ respectively, thus affording an explanation of the oxidation of $-C(OH){=}C(NRR')-$, as in (VII), with iodine and Tillmans's reagent despite failure to react with *o*-dinitrobenzene.



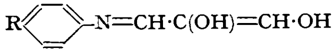
(VI.)



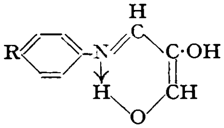
(VI*a*.)



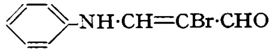
(VII.)



(VIII.)



(IX.)



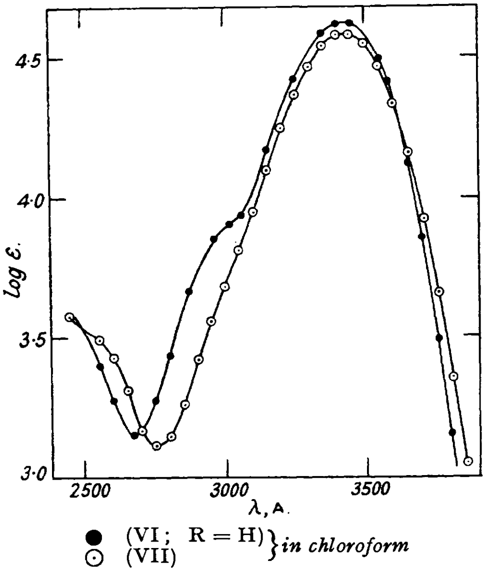
(X.)

$CH_3\cdot CO\cdot CH{=}CH\cdot NHPh$

(XI.)

The ultra-violet light absorption characteristics of a number of the amine and related condensation products are recorded in the Table and Fig. 1. The spectra of the condensation products of the primary amines are similar to that of the product from methylaniline and reductone which, if condensation is at an end carbon atom (see below), can only be of type (VII). The general structure (VI) has, therefore, been assigned to these products rather than (VIII) previously accepted by Angier *et al.* (*loc. cit.*) and by Bell, Cocker, and O'Meara (*loc. cit.*). It is clear, however, that in the chelated state (IX), the two forms of the primary amine derivatives become identical.

Fig. 1.



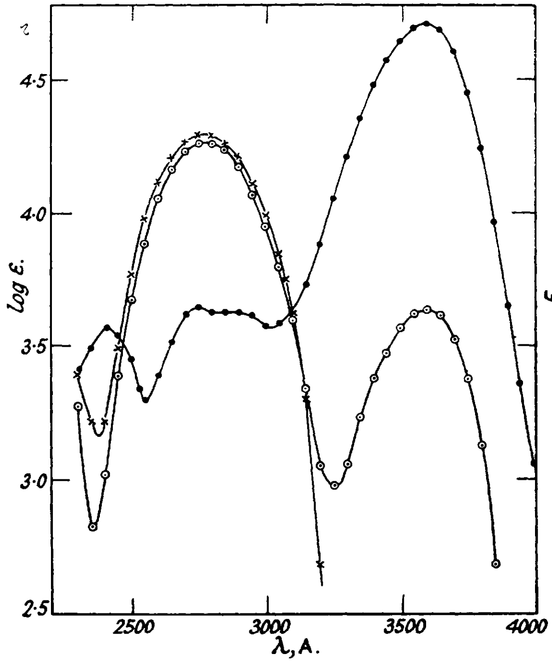
	In chloroform.		In ethanol.	
	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.	$\lambda_{max.}$, A.	log $\varepsilon_{max.}$.
$C_6H_5\cdot NH\cdot CH{=}C(OH)\cdot CHO$	3420	4·63	2320 3420	3·74 4·58
$C_6H_5\cdot NMe\cdot CH{=}C(OH)\cdot CHO$	3420	4·59	2360 3420	3·65 4·57
$C_6H_5\cdot NH\cdot CH{=}CBr\cdot CHO$	3230	4·61	—	—
$C_6H_4Cl\cdot NH\cdot CH{=}C(OH)\cdot CHO$	3460	4·68	—	—
$EtO_2C\cdot C_6H_4\cdot NH\cdot CH{=}C(OH)\cdot CHO$	2650 3570	3·46 4·82	2420 2760 3580	3·57 3·65 4·71
$BzO\cdot CH{=}C(OBz)\cdot CHO$	—	—	2370 2540	4·46 4·47
$C_6H_5\cdot N{=}CH\cdot C(OH){=}CH\cdot OBz$	—	—	(2920) 3230	4·13 4·59
$C_6H_5\cdot NMe\cdot CH{=}C(OBz)\cdot CHO$	—	—	2310 3050	4·29 4·48
$C_6H_5\cdot N{=}CH\cdot C(OBz){=}CH\cdot OBz$	—	—	2290 (2920) 3250	4·42 4·04 4·47

We have examined the light absorption characteristics of 2-bromo-3-anilinoprop-2-enal (X) obtained from bromomalonaldehyde and aniline (Dieckmann and Platz, *Ber.*, 1904, **37**, 4637) and compared them with those of 1-anilinobut-1-en-3-one (XI) and related compounds (Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45). The spectra of these compounds are very similar to those of our condensation products, thus adding weight to the view accepted by most workers in this field that condensation of reductone with one molecule of amine takes place at an end carbon atom. If the ion (III*a*) is taken as a reactive form of reductone in acid solution, a possible mechanism of reaction with one molecule of amine is as follows :

$$\mathrm{HO{\cdot}\overset{+}{C}H{\cdot}C(OH){=}CH{\cdot}OH + Ph{\cdot}NH_2 \longrightarrow Ph{\cdot}\overset{+}{N}H_2{\cdot}CH(OH){\cdot}C(OH){=}CH{\cdot}OH \longrightarrow}$$
$$\mathrm{Ph{\cdot}NH{\cdot}CH{=}C(OH){\cdot}CHO + H^+ + H_2O}$$

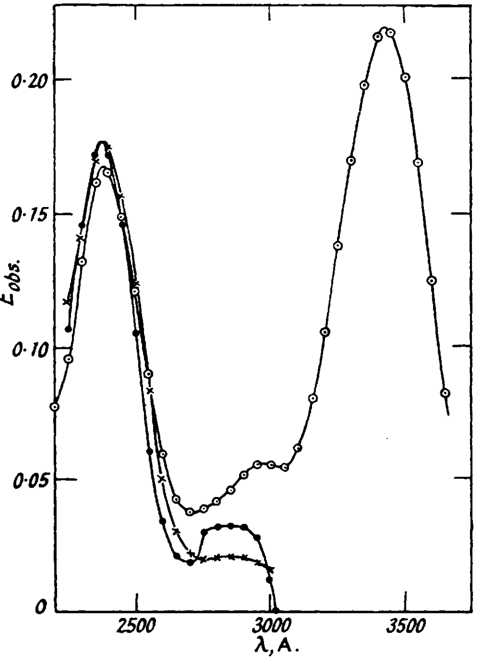
An interesting change in light-absorption characteristics took place, with time, in solutions of (VI; R = H, CO_2Et) in a large volume of alcohol (see Fig. 2*a*), but no similar change was observed in chloroform nor did alcoholic solutions of (VII) or of the dibenzoyl derivative (XVI) of reductone undergo any change. In the latter cases, the reducing system is, of course, blocked. The change is apparently associated with oxidation, since when (VI; R = H) was dissolved in alcohol, from which oxygen had been expelled by a current of nitrogen, the change in absorption characteristics was slowed and, on the contrary, the change was considerably accelerated when the solution was made up by using alcohol through which oxygen had been bubbled (Fig. 2*b*). The spectrum of the solution after a long period of time closely resembled that of formanilide, but attempts to isolate this compound from the oxidation of (VI; R = H) with alkaline or neutral hydrogen peroxide were unsuccessful, although a strong carbylamine odour was noted.

FIG. 2*a*.



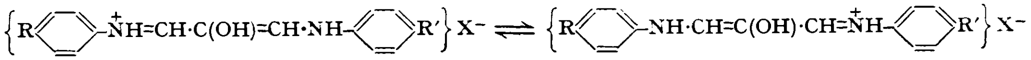
(VI; R = CO_2Et) *in alcohol.*
● *after* 1 *hr.*
⊙ ,, 18 *hrs.*
× ,, 24 *hrs.*

FIG 2*b*.

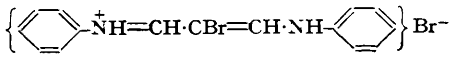


(VI; R = H.)
× " O_2 " *alcohol* (4½ *hrs.*).
● " *Stock* " *alcohol* (24 *hrs.*)
⊙ " N_2 " *alcohol* (24 *hrs.*).

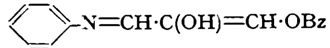
Compounds (VI; R = H) and (VII) give intense violet colours with ferric chloride. Concentrated sodium hydroxide converts them into their sodium salts which, when dried and shaken in dry ether with benzoyl chloride, yield 3-anilo-1-benzoyloxyprop-1-en-2-ol (XIV) and 3-*N*-methylanilino-2-benzoyloxyprop-2-enal (XV) respectively. The spectrum of (XIV) differs from that of (XV) (Fig. 3), but resembles that of the condensation product of aniline with the dibenzoyl derivative (XVI; see below) of reductone; this product must obviously be (XVII). It is for this reason that we assign the structure (XIV) to the benzoylation product of (VI; R = H).



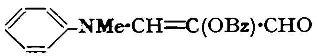
(XII.)



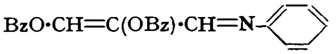
(XIII.)



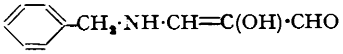
(XIV.)



(XV.)



(XVII.)



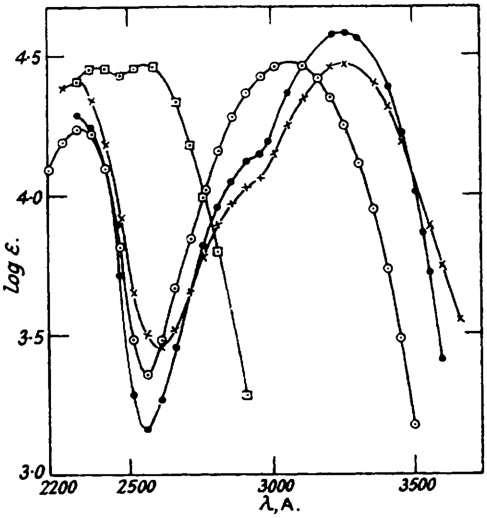
(XVIII.)

$BzO{\cdot}CH{=}C(OBz){\cdot}CHO$ (XVI.)

When (VI; R = H) is heated with aniline in dilute hydrochloric acid, it affords 3-anilino-1-aniloprop-2-en-2-ol hydrochloride (XII; R = H, R′ = H, X = Cl). This compound probably has the symmetrical resonance structure and this is supported by the fact that (XII; R = H, R′ = Cl, X = Cl) is obtained by condensation of (*a*) (VI; R = H) with *p*-chloroaniline or (*b*) (VI; R = Cl) with aniline (see below). The compound (XII; R = H, R′ = H, X = Cl) is also obtained when reductone is ***heated*** with one or two equivalents of aniline in the presence of hydrochloric acid or from (VI; R = H) by disproportionation with hydrochloric acid. 2-Bromo-3-anilinoprop-2-enal (X) disproportionates in a similar manner when heated with hydrobromic acid, giving 2-bromo-3-anilino-1-aniloprop-2-ene hydrobromide (XIII; Dieckmann and Platz, *loc. cit.*).

Von Euler, Hasselquist, and Lööv (*loc. cit.*) obtained a compound, m. p. 260°, by heating reductone with aniline in 4N-hydrochloric acid, which they considered to be the hydrochloride of a monoaniline derivative of reductone. They do not give an analysis of this compound, but base their structure solely on a titration of the crude material with Tillmans's reagent. Working under these conditions we obtained (XII; R = H, R′ = H, X = Cl) and this compound decolorised one mole (two atoms) of iodine per mole, and its titration with Tillmans's reagent agreed with this. We were also unable to obtain the "free base," m. p. 64° (again, no analyses were recorded), described by von Euler and his co-workers (*loc. cit.*). In our hands, basification of (XII; R = H, R′ = H, X = Cl) with alkali or sodium acetate gave a red precipitate which could not be purified; further, the odour of carbylamine was noticed.

FIG. 3.



● (XIV). ⊙ (XV). ⊡ (XVI). × (XVII).

Attempts to cyclise (VI; R = H) or (XII; R = H, R′ = H, X = Cl) to an indole or quinoline were unsuccessful. Concentrated sulphuric acid converted both compounds into (VI; R = SO_3H).

We have also obtained 3-*p*-toluidino-1-*p*-tolyliminoprop-2-en-2-ol hydrochloride (XII; R = Me, R′ = Me, X = Cl), 3-*p*-chloroanilino-1-*p*-chloroaniloprop-2-en-2-ol hydrochloride (XII; R = Cl, R′ = Cl, X = Cl), and 3-anilino-1-aniloprop-2-en-2-ol sulphate and acetate (XII; R = H, R′ = H, X = $\frac{1}{2}SO_4$ and OAc respectively) by condensation of the appropriate amine with reductone in presence of the appropriate hot dilute acid.

It is interesting that, when (VII) was heated with aniline in presence of hydrochloric acid, the methylaniline residue was eliminated and the dianilino-compound (XII; R = H, R′ = H, X = Cl) was obtained.

Benzylamine reacts with reductone in alcohol to give the benzylamine salt which is transformed, in aqueous solution on storage, into 3-benzylamino-2-hydroxyprop-2-enal (XVIII).

The dibenzoyl derivative of reductone (XVI) is obtained either from the dry sodium salt and benzoyl chloride in ether or by shaking reductone with benzoyl chloride in aqueous sodium acetate. The monobenzoyl derivative was not encountered.*

Reductone condenses readily with primary or secondary α-amino-acids in the presence or absence of hydrochloric acid. Except in the case of alanine, condensation products of the type (XIX) are produced, *e.g.*, from glycine, ($\pm$)-α-aminobutyric acid, and ($\pm$)-β-phenylalanine, we have obtained respectively (XIX; $R = R' = H$: XIX; $R = H$, $R' = Et$: and XIX; $R = H$, $R' = CH_2Ph$). These compounds give Fearon and Kawerau's ene-diol test and are quantitatively oxidised by iodine and Tillmans's reagent. In water they titrate as monobasic acids; in alcohol, slightly higher figures are obtained.

N-Phenyl- and *N*-benzyl-glycine respectively yield (XIX; $R = Ph$, $R' = H$; and $R = CH_2Ph$, $R' = H$). These compounds titrate normally with iodine and Tillmans's reagent and as monobasic acids with sodium hydroxide, but the ene-diol colour only appears after some time, during which hydrolysis probably occurs.

($\pm$)-Alanine reacts abnormally with reductone yielding a compound which analyses as $C_9H_{11}O_6N$ or $C_9H_{13}O_6N$. This compound is not oxidised by iodine or Tillmans's reagent, nor does it give the ene-diol reaction. It titrates as a dibasic acid and gives a powerful red-brown ferric reaction. Structure (XX) or (XXI) seems likely for this compound. However, attempts to condense reductone with $\alpha\alpha'$-iminodipropionic acid, which could afford (XXI), have so far been unsuccessful and it has not been possible to condense (XIX; $R = R' = H$) or (VI; $R = H$) with another molecule of reductone.

(XIX.) $OHC{\cdot}C(OH){=}CH{\cdot}NR{\cdot}CHR'{\cdot}CO_2H$ $\qquad$ $[OHC{\cdot}C(OH){=}CH]_2N{\cdot}CHMe{\cdot}CO_2H$ (XX.)

$OHC{\cdot}C(OH){=}CH{\cdot}N(CHMe{\cdot}CO_2H)_2$ (XXI.)

We were unable to obtain a product from (−)-L-leucine and reductone as described by von Euler, Hasselquist, and Lööv (*Arkiv Kemi, Mineral., Geol.*, 1948, **26**, *A*, 17).

Further work on the condensation of reductone with amino-acids is in progress.

EXPERIMENTAL.

Reductone.—This compound was obtained by a modification of the method described by von Euler, Hasselquist, and Lööv (*ibid.*, 1948, **26**, *B*, 5). The dried lead salt of reductone was suspended in acetone and decomposed with phosphoric acid. After filtration the solution was concentrated under reduced pressure and cooled. Reductone separated and was washed with a little acetone.

Tillmans's Reagent.—10 Tablets of dichlorophenol-indophenol (B.D.H.; each tablet equiv. to 1 mg. of ascorbic acid) were dissolved in distilled water (50 c.c.) giving a 0·00227N-solution. Titrations were carried out in presence of hydrochloric acid.

3-*Anilino-2-hydroxyprop-2-enal* (VI; $R = H$).—A mixture of reductone (0·5 g.), aniline (0·5 c.c.), concentrated hydrochloric acid (0·5 c.c.) and water (7 c.c.) was set aside at 0° for 2 hours and the product (0·7 g.; m. p. 116—118°) was collected. The *aldehyde* was obtained as colourless needles, m. p. 118—120°, by crystallisation from chloroform–light petroleum (Found: C, 66·3; H, 5·5; N, 7·8. $C_9H_9O_2N$ requires C, 66·2; H, 5·5; N, 8·6%). The same product was obtained (0·5 g.; m. p. 95—96°) when a mixture of reductone (0·5 g.), aniline (0·5 c.c.) in alcohol (1·5 c.c.) and water (30 c.c.) was shaken for 2 hours. The compound (1·26 mg.) in acidified alcohol required 6·4 c.c. of Tillmans's reagent (2 equivs. require 6·8 c.c.). The compound (15·3 mg.) required 18·6 c.c. of N/100-iodine, benzene being used as indicator (2 equivs. require 18·8 c.c.).

3-p-*Chloroanilino-2-hydroxyprop-2-enal* (VI; $R = Cl$) was obtained (0·95 g.) when a mixture of reductone (0·5 g.), *p*-chloroaniline (0·7 g.), concentrated hydrochloric acid (1 c.c.) and water (10 c.c.) was kept at 0° for 2 hours. The *aldehyde* crystallised from very dilute alcohol (charcoal) as pale yellow needles, m. p. 168—170° (Found: C, 54·8; H, 4·3; N, 6·8. $C_9H_8O_2NCl$ requires C, 54·7; H, 4·1; N, 7·1%).

3-(2-*Naphthylamino*)-2-*hydroxyprop*-2-*enal* (VI*a*) was obtained (0·8 g., m. p. 145—150°) from reductone (0·5 g.) as described for the above compounds. It crystallised from chloroform as golden plates, m. p. 151—152° after shrinking at 145° (Found: C, 72·7; H, 5·0; N, 6·4. $C_{13}H_{11}O_2N$ requires C, 73·2; H, 5·2; N, 6·6%).

3-(p-*Sulphoanilino*)-2-*hydroxyprop*-2-*enal* (VI; $R = SO_3H$), obtained by warming equivalent quantities of reductone and sulphanilic acid in water, crystallised from water as yellow small needles, m. p. 298° (decomp.) (Found: C, 41·2; H, 4·2; N, 5·4; S, 12·6. $C_9H_9O_5NS,H_2O$ requires C, 41·4; H, 4·2; N, 5·4; S, 12·3%).

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* [*Added, May 4th,* 1950.] Since this paper was submitted, the monobenzoyl derivative of reductone has been obtained by shaking the sodium salt of reductone with benzoyl chloride in dry benzene. Details will be published later.

The same compound was obtained when (VI; R = H) (0·2 g.) was treated with concentrated sulphuric acid (*a*) in the cold for 2 hours or (*b*) at 100° for 15 minutes. Pouring the solutions into water gave (VI; R = SO_3H).

3-N-*Methylanilino*-2-*hydroxyprop*-2-*enal* (VII).—A mixture of reductone (1 g.), methylaniline (1 c.c.), acetic acid (4 c.c.) and water (9 c.c.) was kept at 0° for 5 days. The *aldehyde* (0·7 g.; m. p. 100—103°) crystallised from dilute alcohol as colourless plates, m. p. 106—107° (Found: C, 68·3; H, 6·5; N, 7·8. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2; N, 7·9%). 1·97 Mg., titrated in alcohol containing hydrochloric acid, required 10 c.c. of Tillmans's reagent (2 equivs. require 9·8 c.c.).

Benzylamine Salt of Reductone.—The *salt* separated when benzylamine (0·22 c.c.) was added to reductone (0·2 g.) in alcohol (4 c.c.), as plates, m. p. 77—79° (Found: C, 61·6; H, 6·3; N, 7·3. $C_7H_9N,C_3H_4O_3$ requires C, 61·5; H, 6·7; N, 7·2%). Its solution in water gradually deposited a solid, m. p. 70—90°, which could not be crystallised. This is probably 3-*benzylamino*-2-*hydroxyprop*-2-*enal* (XVIII) (Found: C, 64·3; H, 6·0. $C_{10}H_{11}O_2N,\frac{1}{2}H_2O$ requires C, 64·5; H, 6·5%).

3-*Anilo*-1-*benzoyloxyprop*-1-*en*-2-*ol* (XIV).—The substance (VI; R = H), dissolved in a minimum quantity of alcohol, was treated with excess of sodium hydroxide (25%). The precipitated sodium salt was collected, washed with alcohol, and dried with ether. The finely powdered salt (0·55 g.) was suspended in ether (20 c.c.), shaken with benzoyl chloride (0·34 c.c.) for 18 hours and then with sodium hydrogen carbonate solution, and filtered. The pale yellow *residue* (0·2 g.; m. p. 156—158°) crystallised from benzene as colourless prisms, m. p. 157—158° (Found: C, 72·9; H, 5·1; N, 4·9%; *M*, 247. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9; N, 5·2%; *M*, 267). It gave a reddish-brown colour with ferric chloride.

3-N-*Methylanilino*-2-*benzoyloxyprop*-2-*enal* (XV), similarly obtained from (VII) in 70% yield, crystallised from dilute alcohol as pale yellow prisms, m. p. 151° (Found: C, 72·2; H, 5·5; N, 4·3. $C_{17}H_{15}O_3N$ requires C, 72·6; H, 5·3; N, 5·0%).

3-*Anilino*-1-*aniloprop*-2-*en*-2-*ol Hydrochloride* (XII; R = H, R′ = H, X = Cl), *etc*.—A mixture of reductone (1 g.), aniline (2 c.c.), hydrochloric acid (3·4 c.c.), and water (10 c.c.) was heated at 65° for 10 minutes. On cooling, the *hydrochloride* (1·5 g.) was deposited and crystallised from dilute alcohol as golden yellow needles, m. p. 245—255° (decomp.) according to the rate of heating (Found: C, 65·6; H, 5·6; N, 9·5. $C_{15}H_{14}ON_2,HCl$ requires C, 65·6; H, 5·5; N, 10·2%). The same compound was obtained when (VI; R = H) (0·5 g.) was heated with hydrochloric acid (2 c.c.) and water (3 c.c.) for 10 minutes on the water-bath. The corresponding *sulphate* was obtained when the reaction was performed in sulphuric acid (*ca.* 15%). It crystallised from dilute alcohol as yellow needles, m. p. 203—208° (decomp.) [Found: C, 59·2; H, 5·7; N, 9·4. $(C_{15}H_{14}ON_2)_2,H_2SO_4,2H_2O$ requires C, 59·0; H, 5·6; N, 9·2%]. The *acetate* was obtained when reductone (0·5 g.), aniline (1 c.c.), water (9 c.c.), and acetic acid (5 c.c.) were heated gently for 5 minutes; it crystallised from chloroform as yellow needles, m. p. 150—153° (Found: C, 63·5; H, 5·9; N, 7·9; $CH_3{\cdot}CO_2H$, 34·4. $C_{15}H_{14}ON_2,2C_2H_4O_2$ requires C, 63·7; H, 6·1; N, 7·8; $CH_3{\cdot}CO_2H$, 33·5%).

3-p-*Toluidino*-1-**p**-*tolyliminoprop*-2-*en*-2-*ol Hydrochloride* (XII; R = Me, R′ = Me, X = Cl), prepared in a similar manner to the aniline analogue, crystallised from dilute alcohol as yellow needles, m. p. 264° (decomp.) (Found: C, 67·5; H, 6·1; N, 9·0. $C_{17}H_{18}ON_2,HCl$ requires C, 67·4; H, 6·3; N, 9·3%).

3-p-*Chloroanilino*-1-p-*chloroaniloprop*-2-*en*-2-*ol hydrochloride* (XII; R = Cl, R′ = Cl, X = Cl) crystallised from glacial acetic acid as yellow needles, m. p. 274—276° (decomp.) (Found: C, 52·5; H, 4·1; N, 8·4. $C_{15}H_{12}ON_2Cl_2,HCl$ requires C, 52·4; H, 3·8; N, 8·2%).

3-p-*Chloroanilino*-1-*aniloprop*-2-*en*-2-*ol hydrochloride* (XII; R = H; R_1 = Cl; X′ = Cl) was obtained when (VI; R = Cl) (0·6 g.) in alcohol (15 c.c.) was heated with aniline hydrochloride (0·5 g.) and concentrated hydrochloric acid (1 c.c.) for 5 minutes on the water-bath. It crystallised from a large volume of alcohol as golden-yellow prisms, m. p. 262—265° (decomp.) (Found: C, 57·4; H, 4·2; N, 8·9. $C_{15}H_{13}ON_2Cl,HCl$ requires C, 58·3; H, 4·5; N, 9·1%). The same compound is obtained when (VI); R = H is heated with *p*-chloroaniline hydrochloride.

2 : 3-*Dibenzoyloxyprop*-2-*enal* (XVI).—The sodium salt of reductone (von Euler, Hasselquist, and Lööv, *Arkiv Kemi, Mineral., Geol.*, 1948, **26**, *B*, 8), finely powdered (3·7 g.), benzoyl chloride (3·8 c.c.), and ether (70 c.c.) were shaken for 10 hours. After being shaken with water and sodium hydrogen carbonate solution, the mixture was filtered. The residue crystallised from alcohol as needles, m. p. 115—125° (Found: C, 69·1; H, 4·3%; *M*, 314. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%; *M*, 296). It gave no ferric reaction.

2 : 3-*Dibenzoyloxyprop*-2-*enylideneaniline* (XVII).—This *anil* was obtained when the previous compound (XVI) (0·5 g.) in benzene (6 c.c.) was warmed gently for 3 minutes with aniline (0·16 c.c.). It separated on cooling and crystallised from benzene as yellow needles, m. p. 126—128° (Found: C, 74·0; H, 5·3; N, 5·1. $C_{23}H_{17}O_4N$ requires C, 74·4; H, 4·6; N, 3·8%). It gave no ferric reaction.

When (VII) (0·54 g.) was heated in water (6 c.c.) with hydrochloric acid (1 c.c.) and aniline hydrochloride (0·42 g.) for 5 minutes on the water-bath, it yielded (XII; R = H, R′ = H, X = Cl) (Found: C, 65·7; H, 5·3%).

Condensation of Reductone with α-Amino-acids.—(a) *With glycine*. A mixture of reductone (0·5 g.), glycine (0·5 g.), N-hydrochloric acid (1 c.c.), and water (4 c.c.) was heated in the water-bath for 3 minutes. On cooling, the N-(2-*hydroxy*-2-*formylvinyl*)*glycine* (XIX; R = R′ = H) (0·3 g.) was deposited. It crystallised from water as colourless prisms, m. p. 171—173° (decomp.) (Found: C, 41·6; H, 5·3; N, 9·0. $C_5H_7O_4N$ requires C, 41·4; H, 4·8; N, 9·6%).

(b) *With* (±)-*a-aminobutyric acid.* a-N-(2-*Hydroxy-2-formylvinyl*)*aminobutyric acid* (XIX; R = H, R′ = Et) crystallised from water as prisms, m. p. 171° (decomp.) (Found: C, 48·8; H, 6·0; N, 8·2. $C_7H_{11}O_4N$ requires C, 48·6; H, 6·4; N, 8·1%). During the preparation of this compound, the odour of propaldehyde was noticed; no doubt this arose from the oxidation of the amino-acid by an oxidised form of reductone (cf. Schönberg, Moubasher, and Mostafa, *J.*, 1948, 176).

(c) *With* (±)-*β-phenylalanine.* This condensation, with reductone (0·5 g.), was performed in more dilute solution (15 c.c. of water) and heating was extended to 10 minutes. a-N-(2-*Hydroxy-2-formylvinyl*)*amino-β-phenylpropionic acid* (XIX; R = H, R′ = CH_2Ph) (0·6 g.) crystallised from water as prisms, m. p. 181° (decomp.) (Found: C, 61·1; H, 5·0; N, 6·1. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·5; N, 6·0%).

(d) *With* N-*phenylglycine.* The condensation, performed as in (a), gave N-*phenyl*-N-(2-*hydroxy-2-formylvinyl*)*glycine* (XIX; R = Ph, R′ = H), first as an oil; this solidified to a yellow solid (1·0 g. from 0·6 g. of reductone) and crystallised from water as pale orange prisms, m. p. 137—138° (Found: C, 59·6; H, 4·9; N, 6·6. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0; N, 6·3%).

(e) *With* N-*benzylglycine.* From reductone (0·6 g.), N-*benzyl*-N-(2-*hydroxy-2-formylvinyl*)*glycine* (XIX; R = CH_2Ph, R′ = H) (0·5 g.) was obtained, which crystallised from 50% alcohol as colourless rhombs, m. p. 159° (decomp.) (Found: C, 61·6; H, 5·3. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·5%).

(f) *With* (±)-*alanine.* The requisite conditions in this case seem to be more specific. Reductone (0·5 g.) and a-alanine (0·5 g.) in water (4 c.c.) containing N-hydrochloric acid (1 c.c.) were heated on the water-bath for 10 minutes. On cooling and scratching, the *product*, probably (XX) or (XXI) (0·1 g.), separated. It crystallised from water as pale yellow rhombs, m. p. 220° (decomp.) (Found: C, 47·5; H, 4·1; N, 6·4. $C_9H_{13}O_6N$ requires C, 46·8; H, 5·6; N, 6·1. $C_9H_{11}O_6N$ requires C, 47·2; H, 4·8; N, 6·1%).

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