## *The Reaction of Diazonium Salts with α-Aceto-γ-lactones.*

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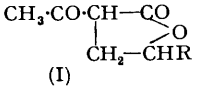
α-Aceto-γ-butyrolactone (I; R = H) reacts with two mols. of an aromatic diazonium salt in strongly alkaline solution to give a 1 : 5-diaryl-3-2′-hydroxyethylformazan (III; R = R′ = H) or a 1-aryl-3-arylazo-Δ²-pyrazoline (V) depending on whether the aryl group contains an *ortho*-substituent. α-Oxo-γ-butyrolactone arylhydrazones (II; R = H) are intermediate in the formation of either type of product but the corresponding acids (VI) give only the formazans.

α-Aceto-γ-valerolactone gives only the 1 : 5-diaryl-3-2′-hydroxypropylformazans (III; R = Me, R′ = H).

The reaction of benzenediazonium salts with α-aceto-γ-butyrolactone (I; R = H) in neutral or weakly alkaline solution is known to give the pale yellow α-oxo-γ-butyrolactone phenylhydrazone (II; R = H, Ar = Ph) (Harradence and Lyons, *J. Proc. Roy. Soc. New South Wales*, 1938, **72**, 221; Feofilaktow and Onischenko, *J. Gen. Chem. U.S.S.R.*, 1939, **9**, 304).

Addition of arenediazonium salts to α-aceto-γ-butyrolactone in strongly alkaline solution at 0—5° gave orange or red products, which were usually precipitated in the crude state as dark tars. Filtration, followed by lixiviation with methanol, gave substantially pure materials which were the result of the interaction of two mols. of the diazonium salt with one of the lactone, and at high pH were the main products even if only one equivalent of the diazonium compound was added (cf. Walker, *J.*, 1923, 2776). The nature of the final product depended upon the aryl group of the diazonium salt, and, of those studied, only that from *p*-nitroaniline failed to give a pure material.

Diazonium salts from *ortho*-substituted anilines gave 3-2′-hydroxyethylformazans (III; R = R′ = H). The type of *ortho*-substituent appeared to have no effect as formazans were obtained from *o*-toluidine, *o*-anisidine, *o*-bromoaniline, and *o*-chloroaniline.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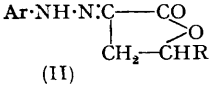
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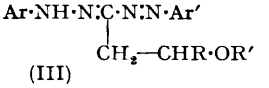
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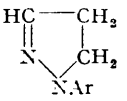
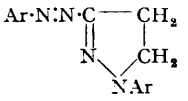
The same products were obtained by treating the arylhydrazones (II; R = H) with diazonium salts in alkaline solution, showing that the hydroxy-acid (VI) is an intermediate stage in the formation of the formazan. An unsymmetrical formazan (III; R = R′ = H, Ar = *o*-tolyl, Ar′ = *o*-chlorophenyl) was prepared by the latter process

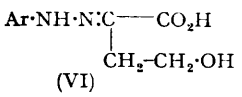
and the same product was obtained when either (II; R = H, Ar = *o*-tolyl) or (II; R = H, Ar = *o*-chlorophenyl) was the starting material. This proves that both the arylazo-groups have entered at the α-carbon atom of the lactone and establishes the structure of the formazans. With acetic anhydride, the formazans gave acetyl derivatives and, as 3-methyl-1 : 5-diphenylformazan was unaffected by such treatment, these compounds must be 3-2′-acetoxyethylformazans (III; R = H, R′ = Ac).

α-Aceto-γ-butyrolactone and aromatic diazonium salts free from *ortho*-substituents gave noticeably paler products, which gave no acetyl derivatives, were identical with the

(IV)   (V)

compounds obtained by treating 1-aryl-$\Delta^2$-pyrazolines (IV) in acetic acid with the appropriate diazonium salts and must therefore be 1-aryl-3-arylazo-$\Delta^2$-pyrazolines (V) (Duffin and Kendall, *J.*, 1954, 408).

Although the arylhydrazones (II; R = H) must be intermediates in the formation of the 3-arylazo-$\Delta^2$-pyrazolines, a number of experiments in which a diazonium salt was added to an alkaline *solution* of the hydrazone (II) (both aryl groups being free from *ortho*-substituents) failed to give any isolatable product. However, addition of benzenediazonium chloride to a *suspension* of α-oxo-γ-butyrolactone phenylhydrazone (II; Ar = Ph, R = H) in 10% aqueous sodium hydroxide gave 1-phenyl-3-phenylazo-$\Delta^2$-pyrazoline (V; Ar = Ph); and diazotised *p*-bromoaniline and alkaline *solution* of α-oxo-γ-butyrolactone *p*-bromophenylhydrazone (II; Ar = *p*-bromophenyl, R = H) gave, not the pyrazoline (V; Ar = *p*-bromophenyl) as obtained from a *suspension* of these reactants, but 1 : 5-di-*p*-bromophenyl-3-2′-hydroxyethylformazan (III; Ar = Ar′ = *p*-bromophenyl, R = H). It appears that isolation of the product in the latter case was aided by its rather low solubility. Therefore, the action of a diazonium salt on the salt of α-oxo-γ-hydroxybutyric acid arylhydrazone (VI) gives the formazan (III) and that with the α-oxo-γ-lactone arylhydrazone gives the 3-arylazo-$\Delta^2$-pyrazoline (V). This was supported by experiments in which diazotised *o*-toluidine and *o*-chloroaniline were condensed with α-aceto-γ-butyrolactone in the presence of the minimum quantity of alkali required to introduce two arylazo-groups, *i.e.*, under conditions in which opening of the lactone ring would be least likely. The products were not the formazans but gave analyses for $C_{19}H_{22}O_3N_4$ and $C_{19}H_{16}O_3N_4Cl_2$ respectively. Either hot alcoholic sodium hydroxide or hydrochloric acid converted these materials into 1-aryl-3-arylazo-$\Delta^2$-pyrazolines (V). There are therefore two possible structures for these substances, namely (VII) or (VIII; R = H); the latter was preferred as attempts to remove the " methanol of crystallization "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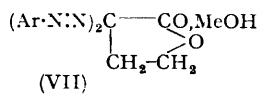
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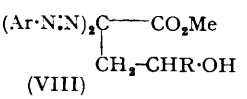
(VIII)

at 80° *in vacuo* resulted in decomposition. The use of ethanol for lixiviation during the isolation of the products was a failure as the materials were too soluble in this solvent. It was further noted that the lixiviation of a crude product from which a pyrazoline was finally obtained was exothermic and of that from which a formazan was obtained was not so. By the method used for isolation, small quantities of alkali must be transferred to the methanol with the crude product and the formation of (VIII; R = H) would appear to be alkali-catalysed, as is the formation of very similar products from arylazomalonyl-2-aminopyridines (Snyder and Robison, *J. Amer. Chem. Soc.*, 1952, **74**, 4910). In a series of experiments, acetic acid was added to the methanol to prevent any alkaline-catalysed reaction at this stage and two important results were obtained. Those reactions which gave formazans (III) were unaffected whereas the crude products from those reactions which would have given pyrazolines (V) gave instead only the α-oxo-γ-butyrolactone arylhydrazones (II; R = H). It is therefore suggested that the pyrazolines are formed by the initial formation of the lactone (VII) in the coupling stage which is then converted,

in the alkaline methanol, into the ester (VIII; R = H) and, if Ar is not *ortho*-substituted, this gives, at room temperature, the final pyrazoline (V) whereas the absence of alkali in the methanol results in the decomposition of bisdiazo-lactone (VII) to the hydrazone (II). The formation of the formazans is seen as the action of the diazonium salt on the sodium salt of the hydrazono-acid (VI) with simultaneous expulsion of the carboxyl group. The *ortho*-substituent may act by assisting the opening of the lactone ring.

α-Aceto-γ-valerolactone (I; R = Me) gave the arylhydrazones (II; R = Me) but the introduction of the second arylazo-group was very slow and from most experiments only the hydrazones (II; R = Me) were obtained even at high pH. The formazan (III; Ar = *o*-chlorophenyl, R = Me) was, however, obtained in good yield, and diazotized *o*-toluidine gave the ester (VIII; Ar = *o*-tolyl, R = Me) which gave no pyrazoline on treatment with hot alcoholic alkali.

## Experimental

*α-Oxo-γ-lactone Arylhydrazones.*—The following exemplifies the procedure: *o*-Toluidine (5·0 ml.) in 5N-hydrochloric acid (25 ml.) was diazotized at 0—5° by sodium nitrite (3·5 g.) in water (10 ml.) with stirring. This solution was added to α-aceto-γ-butyrolactone (6·0 ml.) in water (25 ml.) and pyridine (25 ml.) at 5°. After 1 hr., the precipitated solid was filtered off and recrystallized from acetic acid to give light yellow *α-oxo-γ-butyrolactone o-tolylhydrazone*, m. p. 178° (6·5 g., 64%) (Found: C, 64·6; H, 6·1. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9%). Similar experiments are summarized in Table 1.

Table 1. *α-Oxo-γ-lactone arylhydrazones* (II).

| Ar | R | Yield (%) | M. p. | Found (%) C | Found (%) H | Formula | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|---|---|
| Ph ..... | H | 77 | 228° | 63·2 | 5·1 | Kletz and Lapworth, *J.*, 1915, 1262. | | |
| *o*-$C_6H_4Cl$ ..... | H | 63 | 145 [b] | 53·35 | 3·8 | $C_{10}H_9O_2N_2Cl$ | 53·45 | 4·0 |
| *o*-$C_6H_4{\cdot}NO_2$ ..... | H | 52 | 237 [d] | 50·9 | 3·75 | $C_{10}H_9O_4N_3$ | 51·11 | 3·85 |
| *p*-$C_6H_4Br$ ..... | H | 75 | 257 [d] | 44·7 | 3·65 | $C_{10}H_9O_2N_2Br$ | 44·7 | 3·35 |
| Ph ..... | Me | 49 | 199 [a] | 64·5 | 6·0 | $C_{11}H_{12}O_2N_2$ | 64·7 | 5·9 |
| *o*-$C_6H_4Cl$ ..... | Me | 80 | 162 [c] | 55·2 | 4·35 | $C_{11}H_{11}O_2N_2Cl$ | 55·4 | 4·6 |

[a] Pale yellow leaflets from ethanol. [b] Yellow needles from methanol. [c] Yellow needles from ethanol. [d] Yellow needles from 2-methoxyethanol.

*α-Oxo-γ-hydroxybutyric Acid Phenylhydrazone.*—α-Oxo-γ-butyrolactone phenylhydrazone (5 g.) was heated at 100° for 10 min. with 10% aqueous sodium hydroxide (20 ml.). The solution was filtered and cooled to 0°, and 10N-hydrochloric acid (6 ml.) was added to precipitate the *acid* as colourless leaflets which, dried *in vacuo*, had m. p. 156° (4·8 g., 88%). Very rapid recrystallization from water failed to raise the m. p. (Found: C, 57·5; H, 5·5. $C_{10}H_{12}O_3N_2$ requires C, 57·5; H, 5·7%) but prolonged boiling with water or, better, treatment with ethanolic hydrogen chloride at 0°, gave the lactone again.

3-2′-*Hydroxyalkylformazans.*—The following exemplify the procedures: (A) *From the α-aceto-γ-lactone.* *o*-Toluidine (2·6 ml.) was diazotized in 5N-hydrochloric acid (12·5 ml.) at 5° with sodium nitrite (1·8 g.) in water (8 ml.). The solution was added dropwise to a stirred solution of α-aceto-γ-butyrolactone (1·6 ml.) in 10% aqueous sodium hydroxide (45 ml.) and ice (110 g.). After 1 hr., the precipitated red tar was filtered off and lixiviated with methanol (2 × 25 ml.), to leave a mass of brownish crystals. Recrystallization from methanol gave 3-2′-*hydroxyethyl*-1 : 5-*di*-*o*-*tolylformazan* as orange needles, m. p. 145° (1·24 g., 34%) (Found: C, 69·2; H, 6·75. $C_{17}H_{20}ON_4$ requires C, 68·9; H, 6·95%). Similar experiments are summarized in Table 2.

Table 2. 3-2′-*Hydroxyalkylformazans* (III, R′ = H) (*Method A*).

| Ar = Ar′ | R | Yield (%) | M. p.* | Found (%) C | Found (%) H | Formula | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|---|---|
| *o*-$C_6H_4Cl$ ..... | H | 40 | 147° [a] | 53·5 | 4·2 | See above | | |
| *o*-$C_6H_4Br$ ..... | H | 10 | 157 [a] | 42·3 | 3·5 | $C_{15}H_{14}ON_4Br_2$ | 42·4 | 3·3 |
| *o*-$C_6H_4{\cdot}OMe$ ... | H | 12 | 133 [b] | 61·15 | 5·95 | $C_{17}H_{20}O_3N_4$ | 62·2 | 6·1 |
| *o*-$C_6H_4Cl$ ..... | Me | 17 [d] | 124 [c] | 54·6 | 4·6 | $C_{16}H_{16}ON_4Cl_2$ | 54·7 | 4·55 |

* From MeOH. [a] Dark red needles with green reflex. [b] Red needles with blue reflex. [c] Orange-red needles. [d] With α-oxo-γ-valerolactone *o*-chlorophenylhydrazone (28%).

(B) *From the arylhydrazone.* α-Oxo-γ-butyrolactone *o*-chlorophenylhydrazone (11·2 g.) was dissolved, by warming, in 10% aqueous sodium hydroxide (90 ml.). The solution was cooled and *o*-chlorobenzenediazonium chloride solution [from *o*-chloroaniline (5·3 ml.), 5N-hydrochloric acid (25 ml.) and sodium nitrite (3·5 g.) in water (15 c.c.)] added gradually during 1 hr. at 0°. After 60 hr., the precipitated red solid was filtered off, washed with methanol, and recrystallized from the same solvent, to give 1 : 5-*di*-o-*chlorophenyl*-3-2′-*hydroxyethylformazan* as red needles with a green reflex, m. p. 147° (6·5 g., 38%) (Found: C, 53·4; H, 4·3; Cl, 21·0. $C_{15}H_{14}ON_4Cl_2$ requires C, 53·5; H, 4·2; Cl, 21·1%). Similar experiments are summarized in Table 3.

TABLE 3. 3-2′-*Hydroxyalkylformazans* (III; R′ = H) (*Method B*).

| Arylhydrazone (II) Ar | R | Diazonium cpd. | Yield (%) | M. p. | Found (%) C | H | Formula | Required (%) C | H |
|---|---|---|---|---|---|---|---|---|---|
| *o*-$C_6H_4$·$NO_2$ ..... | H | *o*-$NO_2$·$C_6H_4$·$N_2$ | 4 [a] | 162° | 50·5 | 4·2 | $C_{15}H_{14}O_5N_6$ | 50·2 | 3·9 |
| *o*-$C_6H_4$Me ..... | H | *o*-$C_6H_4Cl$·$N_2$ | 23 [b] | 140 | 60·2 | 5·35 | $C_{16}H_{17}ON_4Cl$ | 60·5 | 5·35 |
| *o*-$C_6H_4Cl$ ..... | H | *o*-$C_6H_4Me$·$N_2$ | 7 [b] | 140 | 60·4 | 5·45 | | | |
| *o*-$C_6H_4Cl$ ..... | Me | *o*-$C_6H_4Cl$·$N_2$ | 15 [c] | 125 | 54·5 | 4·5 | See above | | |
| Ph ..... | Me | Ph·$N_2$ | 4 [d] | 108 | | | | | |

[a] Red needles from MeOH. [b] Dark red needles with green reflex from MeOH. [c] Orange-red needles from MeOH. [d] Dark red needles with blue reflex from light petroleum. Found: N, 19·7. $C_{16}H_{18}ON_4$ requires N, 19·85%.

3-2′-*Acetoxyethyl*-1 : 5-*di*-o-*chlorophenylformazan*.—1 : 5-Di-*o*-chlorophenyl-3-2′-hydroxyethylformazan (0·5 g.), benzene (10 ml.), and acetic anhydride (2 ml.) were warmed on a water-bath for 10 min. and ethanol (10 ml.) added. Evaporation gave reddish crystals which were recrystallized from methanol, to give 3-2′-*acetoxyethyl*-1 : 5-*di*-o-*chlorophenylformazan* as red needles with a green reflex, m. p. 120° (0·15 g., 28%) (Found: C, 53·54; H, 4·2; Cl, 19·1. $C_{17}H_{16}O_2N_4Cl_2$ requires C, 53·7; H, 4·2; Cl, 18·8%). Similar treatment of 3-methyl-1 : 5-diphenylformazan gave unchanged material (92%). The following acetoxy-compounds were prepared from the appropriate formazans: 3-2′-*acetoxyethyl*-1 : 5-*di*-o-*tolylformazan* from methanol as orange plates, m. p. 118° (Found: C, 67·4; H, 6·6. $C_{19}H_{22}O_2N_4$ requires C, 67·5; H, 6·5%), 3-2′-*acetoxyethyl*-1 : 5-*di*-o-*bromophenylformazan* from ethanol as red needles, m. p. 121° (Found: Br, 34·0. $C_{17}H_{16}O_2N_4Br_2$ requires Br, 34·2%), 3-2′-*acetoxyethyl*-1 : 5-*di*-o-*nitrophenylformazan* from ethanol as red needles, m. p. 129° (Found: C, 51·1; H, 3·7. $C_{17}H_{16}O_6N_6$ requires C, 51·0; H, 4·0%), 3-2′-*acetoxyethyl*-1 : 5-*di*-o-*methoxyphenylformazan* from aqueous methanol as red needles, m. p. 97° (Found: C, 61·4; H, 4·9. $C_{19}H_{22}O_4N_4$ requires C, 61·7; H, 4·95%), and 3-2′-*acetoxypropyl*-1 : 5-*di*-o-*chlorophenylformazan* from methanol as orange plates, m. p. 117° (Found: Cl, 18·1. $C_{18}H_{18}O_2N_4Cl_2$ requires Cl, 18·05%).

1-*Aryl*-3-*arylazo*-Δ²-*pyrazolines*.—The following exemplifies the procedure: Aniline (4·65 g.) in 5N-hydrochloric acid (25 ml.) was diazotized at 5—10° with sodium nitrite (3·5 g.) in water (10 ml.) and then added with stirring to a solution of α-aceto-γ-butyrolactone (3·5 ml.) in 10% aqueous sodium hydroxide (80 ml.) during 30 min. After 1 hr. the precipitated red tar was filtered off and left for 16 hr. with methanol (50 ml.). The resulting orange crystals, recrystallized from methanol, gave 1-phenyl-3-phenylazo-Δ²-pyrazoline as orange leaflets, m. p. 156° (1·5 g., 24%) (Duffin and Kendall, *loc. cit.*) (Found: C, 71·95; H, 5·5. Calc. for $C_{15}H_{14}N_4$: C, 72·0; H, 5·6%). Similar experiments are summarized in Table 4.

TABLE 4. 1-*Aryl*-3-*arylazo*-Δ²-*pyrazolines* (V).

| Ar | M. p.* | Yield (%) | Found (%) C | H | Formula | Required (%) C | H |
|---|---|---|---|---|---|---|---|
| *m*-$C_6H_4$Me ..... | 150° | 23 | 73·3 | 6·3 | Duffin and Kendall, *loc. cit.* | | |
| *p*-$C_6H_4$Me ..... | 184 | 10 | 73·45 | 6·6 | | | |
| *p*-$C_6H_4$·OMe ..... | 194 | 24 | 65·8 | 6·00 | $C_{17}H_{18}O_2N_4$ | 65·8 | 5·8 |
| *p*-$C_6H_4Br$ ..... | 206 | 30 | 43·8 | 2·8 | $C_{15}H_{12}N_4Br_2$ | 44·0 | 2·9 |
| *m*-$C_6H_4Cl$ ..... | 135 | 32 | 56·7 | 3·8 | $C_{15}H_{12}N_4Cl_2$ | 56·4 | 3·8 |

* The products form red needles, except the first and fourth which form orange plates; all were crystallized from methanol, except the third and fourth which crystallized from benzene.

*Methyl γ-Hydroxy-αα-di-o-tolylazobutyrate*.—*o*-Toluidine (2·6 ml.) was diazotized in 5N-hydrochloric acid (12·5 ml.) at 5—10° with sodium nitrite (1·8 g.) in water (5 ml.) and added slowly to a stirred solution of α-aceto-γ-butyrolactone (1·6 ml.) in 10% aqueous sodium hydroxide (25 ml.) at 0—5°. After 1 hr., the precipitated tar was filtered off and lixiviated with methanol (2 × 25 ml.) to give the *azo-compound* as red needles with a green reflex, m. p. 98·5° (2·03 g.,

46%); recrystallization from methanol or light petroleum did not change the m. p. [Found: C, 64·4; H, 6·3; N, 16·0%; *M* (ebullioscopic in benzene), 341. $C_{19}H_{22}O_3N_4$ requires C, 64·4; H, 6·25; N, 15·8%; *M*, 354]. By similar processes, *o*-chloroaniline and α-aceto-γ-butyrolactone gave *methyl αα-di-o-chlorophenyl-γ-hydroxybutyrate* as light red needles (from light petroleum), m. p. 91° (15%) (Found: C, 51·8; H, 4·23; Cl, 18·0. $C_{17}H_{16}O_3N_4Cl_2$ requires C, 51·7; H, 4·0; Cl, 18·0%); and *o*-toluidine and α-aceto-γ-valerolactone gave *methyl γ-hydroxy-αα-di-o-tolylazovalerate* as red needles with green reflex, m. p. 82° (30%) [Found: C, 65·25; H, 6·45; N, 15·4%; *M* (ebullioscopic in benzene), 356. $C_{20}H_{24}O_3N_4$ requires C, 65·2; H, 6·5; N, 15·2%; *M*, 368].

1-o-*Tolyl*-3-o-*tolylazo*-Δ²-*pyrazoline*.—Methyl γ-hydroxy-αα-di-*o*-tolylazobutyrate (0·5 g.) was dissolved in ethanol (20 ml.), and 40% aqueous sodium hydroxide (1 ml.) added. After 1 hour's boiling during which the colour changed from violet to orange-yellow, water (100 ml.) was added and the precipitated solid filtered off. Recrystallization from methanol gave 1-*o*-tolyl-3-*o*-tolylazo-Δ²-pyrazoline as red needles, m. p. 92·5° (0·09 g., 25%) (Found: C 73·4; H, 6·6. Calc. for $C_{17}H_{18}N_4$: C, 73·3; H, 6·45%) (Duffin and Kendall, *loc. cit.*). A similar experiment in which the sodium hydroxide was replaced by 10N-hydrochloric acid gave the same product (31%). By similar methods, methyl αα-di-*o*-chlorophenylazo-γ-hydroxybutyrate gave 1-o-*chlorophenyl*-3-o-*chlorophenylazo*-Δ²-*pyrazoline* as red needles, m. p. 95° (28%) (Found: C, 56·5; H, 3·7; Cl, 22·35. $C_{15}H_{12}N_4Cl_2$ requires C, 56·5; N, 3·8; Cl, 22·3%), but no pure product was obtained from methyl γ-hydroxy-αα-di-*o*-tolylazovalerate.

*Experiments on Mechanism of the Reaction*.— (*a*) Aniline (0·93 g.) was diazotized in 5N-hydrochloric acid (5·0 ml.) with sodium nitrite (0·75 g.) in water (3 ml.). α-Oxo-γ-butyrolactone phenylhydrazone (1·9 g.) was suspended in 10% aqueous sodium hydroxide (15 ml.) at 0° and the diazonium solution added slowly. After 2 hr. the mixture was diluted with water (100 ml.) and the precipitated tar filtered off. After 60 hr. in methanol, a mass of orange crystals was filtered off and recrystallized from methanol, to give 1-phenyl-3-phenylazo-Δ²-pyrazoline, m. p. 156° (0·30 g., 12%) (Found: C, 71·6; H, 5·7%). A similar experiment in which the lactone was dissolved in warm alkali and then cooled to 0° before coupling gave no pure product.

(*b*) In a similar manner *p*-bromoaniline and α-oxo-γ-butyrolactone *p*-bromophenylhydrazone gave 1-*p*-bromophenyl-3-*p*-bromophenylazo-Δ²-pyrazoline (11%) identical with the product obtained previously.

(*c*) *p*-Bromoaniline (3·45 g.) in 3N-hydrochloric acid (15 ml.) was diazotized at 0—5° with sodium nitrite (1·5 g.) in water (5 ml.) and then added to a solution (prepared by warming) of α-oxo-γ-butyrolactone *p*-bromophenylhydrazone (5·5 g.) in 4% aqueous sodium hydroxide (100 ml.) and ice (200 g.). After 1 hr., the precipitated solid was filtered off, washed with water, and lixiviated with methanol (2 × 25 ml.) to give an orange solid. Recrystallization from benzene gave 1 : 5-*di*-p-*bromophenyl*-3-2′-*hydroxyethylformazan* as orange needles, m. p. 152° (2·05 g., 24%) (Found: C, 42·2; H, 3·4. $C_{15}H_{14}ON_4Br_2$ requires C, 42·4; H, 3·3%).

(*d*) *m*-Toluidine (5·3 ml.) in 5N-hydrochloric acid (25 ml.) was diazotized at 0—5° with sodium nitrite (3·5 g.) in water (10 ml.) and added with stirring to a solution of α-aceto-γ-butyrolactone (3·5 ml.) in 10% aqueous sodium hydroxide (60 ml.) at 0—5°. After 1 hr., the precipitated solid was filtered off and added to a mixture of methanol (50 ml.) and acetic acid (2 ml.). The initial red colour became rapidly paler and after 15 hr. a pale yellow solid was present. Filtration and recrystallization from ethanol gave *α-oxo-γ-butyrolactone m-tolylhydrazone* (3·3 g., 65%) as yellow leaflets, m. p. 197° (Found: C, 64·5; H, 6·0. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9%). Similarly, α-aceto-γ-butyrolactone with *p*-bromoaniline gave the hydrazone (II; R = H, Ar = *p*-bromophenyl), and with *o*-chloroaniline the formazan (III; R = R′ = H, Ar = *o*-chlorophenyl).

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