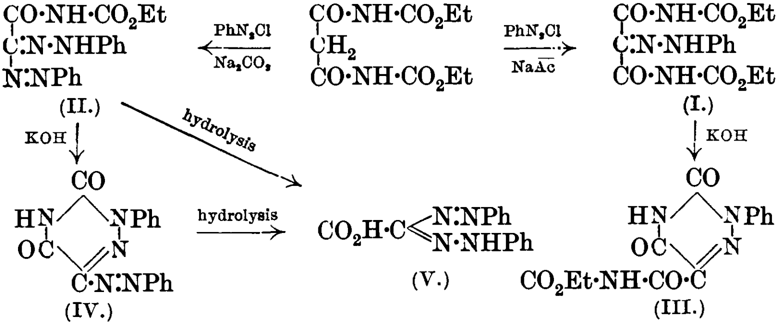
LXXVII.—*The Reaction between Diazonium Salts and Malonyldiurethane.*

By Martha Annie Whiteley and Dorothy Yapp.

Malonyldiurethane condenses with benzenediazonium salts, yielding the *hydrazone* (I) or the *formazyl* derivative (II) according to whether the reaction is carried out in the presence of acetic acid or sodium carbonate, respectively. Each of these compounds undergoes internal condensation by the action of potassium hydroxide whereby alcohol is eliminated between the ethoxyl group



of the urethano-radical and the imino-hydrogen of the hydrazone group, yielding respectively the *carbourethane* (III) and the *benzeneazo-derivative* (IV) of 3 : 5-*diketo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine*. On hydrolysis with hot potassium hydroxide solution, the formazyl compound (II) and the benzeneazotriazine (IV) each yield formazylcarboxylic acid (V).

When the benzenediazonium salt in the above reactions is replaced by certain substituted derivatives, it is found that the nature of the substituent radical and its position in the benzene ring affect the course of the reaction: the *p*-toluene- and the *o*-nitrobenzene-diazonium salt each yield both the hydrazone and the formazyl compound, from which the triazine compounds can be obtained; whereas the *p*-nitrobenzenediazonium salt yields the hydrazone in two isomeric forms, but no formazyl compound, and each of the isomeric hydrazones yields the same triazine compound; *m*-nitrobenzenediazonium salt yields the hydrazone only, from which at present no triazine compound has been obtained.

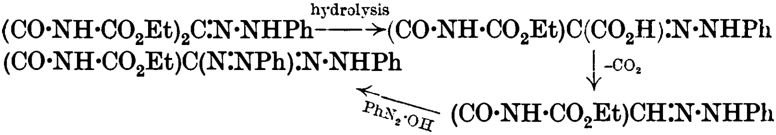
In respect of forming a hydrazone and not an azo-compound by the action of benzenediazonium acetate, malonyldiurethane resembles malonic acid, barbituric acid and other compounds containing the keto-methylene group (compare Meyer, *Ber.*, 1888, **21**, 118; 1891, **24**, 1241; v. Pechmann, *Ber.*, 1892, **25**, 3175; Kuhling, *Ber.*, 1891, **24**, 4140; 1898, **31**, 1972; Bamberger and Wheelwright, *Ber.*, 1892, **25**, 3201), and this constitution of the compound was confirmed by its preparation from monobromomalonyldiurethane and phenylhydrazine, when simultaneous condensation and oxidation occurred (compare v. Pechmann, *loc. cit.*). That

$$\begin{tikzcd} (CO_2Et\cdot NH\cdot CO)_2CHBr \arrow[r, "PhNH\cdot NH_2"] & {[(CO_2Et\cdot NH\cdot CO)_2CH\cdot NH\cdot NHPh]} \arrow[d] \\ & (CO_2Et\cdot NH\cdot CO)_2C{:}N\cdot NHPh \end{tikzcd}$$

this reaction is a general one was shown by the preparation of mesoxamide phenylhydrazone by condensation of (i) dibromomalonamide with phenylhydrazine as described by Ruhemann and Orton (J., 1895, **67**, 1003); (ii) monobromomalonamide with phenylhydrazine; and (iii) benzenediazonium acetate with malonamide:

$$\begin{array}{l} \left.\begin{array}{l}(CO\cdot NH_2)_2CBr_2\\ (CO\cdot NH_2)_2CHBr\end{array}\right\}\xrightarrow{PhNH\cdot NH_2}\searrow \\ (CO\cdot NH_2)_2CH_2 \xrightarrow{PhN_2Cl,Na\overline{Ac}}\nearrow \end{array} (CO\cdot NH_2)_2C{:}N\cdot NHPh.$$

The formation of the formazyl compound when benzenediazonium chloride is added to a solution of malonyldiurethane in sodium carbonate solution is probably due to the further action of the diazonium compound on the phenylhydrazone of glyoxalylurethane produced by the hydrolysis of one of the carbourethano-groups and loss of carbon dioxide from the resulting acid :

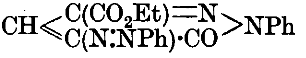


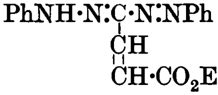
$$\begin{tikzcd}(CO\cdot NH\cdot CO_2Et)_2C{:}N\cdot NHPh \arrow[r, "\text{hydrolysis}"] & (CO\cdot NH\cdot CO_2Et)C(CO_2H){:}N\cdot NHPh \arrow[d, "-CO_2"] \\ (CO\cdot NH\cdot CO_2Et)C(N{:}NPh){:}N\cdot NHPh & (CO\cdot NH\cdot CO_2Et)CH{:}N\cdot NHPh \arrow[l, "PhN_2\cdot OH"]\end{tikzcd}$$

In respect of the above reactions, malonyldiurethane closely resembles malonic acid (v. Pechmann, *loc. cit.*; Busch and Wolbring, *J. pr. Chem.*, 1905, **72**, 366), but whereas the final product of the action of diazonium salts on malonic acid is formazylazobenzene, owing to the readiness with which formazylcarboxylic acid loses carbon dioxide, its urethane derivative resists hydrolysis and forms a stable six-membered ring by loss of alcohol.

There are numerous cases recorded in the literature of internal ring formation in hydrazones and formazyl compounds (see Bamberger and Lorenzen, *Ber.*, 1892, **25**, 3539; Bamberger and de Gruyter, *Ber.*, 1893, **26**, 2385, 2783; Bamberger and Witten, *Ber.*, 1894, **27**, 2786; v. Pechmann, *ibid.*, p. 1679; v. Pechmann and Runge, *ibid.*, p. 2920; Fichter and Schiess, *Ber.*, 1900, **33**, 747), but the researches of Henrich and his collaborators on the formazyl and arylazohydrazone derivatives yielded by glutaconic acid and its esters appear to have a direct bearing on the work described in this paper. These authors found that glutaconic acid reacts with benzenediazonium chloride (2 mols.) in the presence of sodium acetate to form formazylacrylic acid, $CO_2H\cdot CH{:}CH\cdot C(N{:}NPh){:}N\cdot NHPh$ (Henrich and Thomas, *Ber.*, 1907, **40**, 4924); whilst ethyl glutaconate under similar conditions reacts with the diazonium salt (1 mol.) to form a compound which has the constitution of the azo-compound, $CO_2Et\cdot CH{:}CH\cdot CH(CO_2Et)\cdot N{:}NPh$, or that of the tautomeric hydrazone, $CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NHPh$; and when an excess of the diazonium salt is used the arylazohydrazone, ethyl α-keto-γ-benzeneazoglutaconate phenylhydrazone,

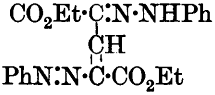
$$CO_2Et\cdot C(N{:}NPh){:}CH\cdot C(CO_2Et){:}N\cdot NHPh,$$

is formed, and this compound differs from the others in that it very readily loses a molecule of alcohol, even on boiling with alcohol, to form the ring compound, ethyl 1-phenyl-5-benzeneazopyridazin-6-one-3-carboxylate,  $CH{<}\begin{matrix}C(CO_2Et)=N\\C(N{:}NPh)\cdot CO\end{matrix}{>}NPh$ (Henrich, Reichenburg, Nachtigall, Thomas, and Baum, *Annalen*, 1910, **376**, 125). In view of the readiness with which the phenylhydrazone of mesoxalyldiurethane and the urethane derivative of formazylglyoxylic acid form rings by the loss of alcohol, and in this respect resemble the arylazohydrazone derivative of ethyl glutaconate, it is the more remarkable that formazylacrylic acid and its ethyl ester are such stable substances and show no tendency to form rings. A simple explanation of this anomalous behaviour would be afforded if it were assumed that the stable forms of these compounds have the *trans*-configuration in respect of the carbethoxy- and hydrazone-groups, whilst that of the arylazohydrazone is *cis*:



$$\begin{array}{c} \mathrm{PhNH{\cdot}N{:}C{\cdot}N{:}NPh} \\ | \\ \mathrm{CH} \\ \| \\ \mathrm{CH{\cdot}CO_2Et} \end{array}$$

Ethyl *trans*-formazylacrylate.



$$\begin{array}{c} \mathrm{CO_2Et{\cdot}C{:}N{\cdot}NHPh} \\ | \\ \mathrm{CH} \\ \| \\ \mathrm{PhN{:}N{\cdot}C{\cdot}CO_2Et} \end{array}$$

Ethyl *cis*-α-keto-γ-benzeneazoglutaconate phenylhydrazone.

The stability of the first product of the action of diazonium acetate on ethyl glutaconate, a compound which can even be distilled without decomposition, may be regarded as evidence of its having the azo-structure, but if it is a hydrazone it probably has the *trans*-configuration.

With reference to the part played by the nature and position of the radical in substituted benzenediazonium derivatives in inhibiting the formation of formazyl derivatives from hydrazones, or of ring compounds from hydrazones or formazyl compounds, the evidence at present available is scanty and of a conflicting nature. The results obtained with malonyldiurethane indicate that a positive substituent in the ortho- or a negative substituent in the para-position offers no hindrance to the formation of the formazyl compound (II) or of the ring compound (III), but that a positive substituent in the para-position prevents the formation of the formazyl, but not of the ring compound, whilst a positive substituent in the meta-position inhibits both formazyl and ring formation. Busch and Wolbring (*loc. cit.*) found that malonic acid gives chiefly the substituted hydrazone of glyoxylic acid and very little of the formazyl hydride when it condenses with certain ortho-substituted derivatives of benzenediazonium salts, such as *o*-nitro-, *o*-chloro-, *o*-bromo-, or *o*-iodo-derivatives, whilst the formazyl compound is the only product when malonic acid condenses with *p*-bromo- or *m*-nitro-benzenediazonium salts, and the chief product when it condenses with *p*-nitroaniline. Henrich and his collaborators (*loc. cit.*), who studied the relative ease of ring formation in the substituted arylazohydrazones of ethyl glutaconate, found that it depended both on the nature and on the position of the substituent in the benzene ring. The more negative the substituent the more readily did ring formation occur, provided that the substituent was not in the ortho-position, as ortho-substitution presented a steric hindrance to the elimination of alcohol.

EXPERIMENTAL.

I. *Phenylhydrazone of Mesoxalyldiurethane* (I).—(i) Into a solution of 5 g. (1 mol.) of malonyldiurethane in 200 c.c. of dilute aqueous sodium acetate cooled in ice, was slowly stirred a cold solution of benzenediazonium acetate prepared by diazotising 1·8 g. (1 mol.) of aniline dissolved in 10 c.c. of dilute hydrochloric acid (1 : 1) and adding excess of sodium acetate. The mixture was kept for 2 hours at 0—5° and the *hydrazone* separated in a crystalline form (yield, 4·8 g.). It is soluble in acetic acid, formic acid, or chloroform, but insoluble, or nearly so, in all the other ordinary organic solvents, and crystallises from acetic acid in pale yellow needles, m. p. 203° (decomp.) (Found: C, 51·3; H, 5·15; N, 16·1. $C_{15}H_{18}O_6N_4$ requires C, 51·4; H, 5·1; N, 16·0%).

(ii) The same compound was also prepared by heating at 100° an alcoholic solution of monobromomalonyldiurethane (1 mol.) and phenylhydrazine (1 mol.).

By replacing the aniline in preparation (i) above by its equivalent of the corresponding base, the following substituted phenylhydrazones of mesoxalyldiurethane were prepared:

(1) The o-*nitrophenylhydrazone*,

$$(CO{\cdot}NH{\cdot}CO_2Et)_2C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

is soluble in acetic acid, acetone, or chloroform, sparingly soluble in ethyl or methyl alcohol or benzene, and insoluble in petroleum; it crystallises from acetic acid in thin, yellow needles, m. p. 208° (decomp.) (Found: N, 17·9. $C_{15}H_{17}O_8N_5$ requires N, 17·7%).

(2) The m-*nitrophenylhydrazone* is very readily soluble in acetic acid, but otherwise resembles the ortho-compound in its solubility. It crystallises from formic acid in very pale yellow needles, m. p. 215° (Found: N, 17·6%).

(3) The p-*nitrophenylhydrazone* crystallises from acetic acid in pale yellow needles, m. p. 218° (decomp.) (Found: N, 17·5%). An isomeric form of this hydrazone is obtained when the condensation of malonyldiurethane with *p*-nitrobenzenediazonium salt is effected in the presence of sufficient sodium carbonate to produce a neutral or slightly alkaline reaction. The *isomeride* crystallises in orange-coloured needles, m. p. 208° (decomp.) (Found: C, 45·4; H, 4·5; N, 17·8. $C_{15}H_{17}O_8N_5$ requires C, 45·5; H, 4·3; N, 17·7%).

(4) The p-*tolylhydrazone*, $(CO{\cdot}NH{\cdot}CO_2Et)_2C{:}N{\cdot}NH{\cdot}C_7H_7$, is readily soluble in all the usual organic solvents with the exception of petroleum; it crystallises from alcohol in pale yellow needles, m. p. 186° (Found: N, 15·5. $C_{16}H_{20}O_6N_4$ requires N, 15·4%).

II. *Urethane Derivative of Formazylcarboxylic Acid* (II).—Into a cold solution of 5 g. (1 mol.) of malonyldiurethane and 8·8 g. (2·5 mols.) of sodium carbonate in 200 c.c. of water was stirred one-half of a cold solution of benzenediazonium chloride, prepared by diazotising 3·6 g. (2 mols.) of aniline in 20 c.c. of dilute hydrochloric acid (1 : 1). The mixture was kept cold and after 2 hours the red precipitate (4·1 g.) was removed by filtration and the filtrate treated with the remainder of the diazonium solution; a further quantity (1 g.) of the product was then obtained. The product consisted of the *urethane* derivative of *formazylcarboxylic acid* (II) containing a small quantity of the triazine compound (III); separation was effected by boiling with water, in which the triazine compound is soluble. The urethane derivative of formazylcarboxylic acid is soluble in all the usual organic solvents except petroleum, it crystallises from alcohol in bright red plates, m. p. 159° (decomp.), and it gives a deep purple coloration when dissolved in concentrated sulphuric acid (Found: C, 60·1; H, 5·1; N, 20·9. $C_{17}H_{17}O_3N_5$ requires C, 60·2; H, 5·0; N, 20·6%). It undergoes hydrolysis when boiled with 10% potassium hydroxide solution, yielding formazylcarboxylic acid (V), m. p. 162° (v. Pechmann, *Ber.*, 1892, **25**, 3175, gives m. p. 162—163°) (Found: C, 63·2; H, 4·6; N, 20·7. Calc.: C, 62·7; H, 4·5; N, 20·9%).

The following substituted formazyl derivatives were similarly prepared:

(1) The *urethane* derivative of *di*-o-*nitroformazylcarboxylic acid*, $CO_2Et{\cdot}NH{\cdot}CO{\cdot}C(N{:}N{\cdot}C_6H_4{\cdot}NO_2){:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, is soluble in all the ordinary organic solvents with the exception of petroleum, and of formic acid, in which it decomposes; it crystallises from acetic acid in red plates with a green reflex, containing acetic acid of crystallisation and melting at 105°, and develops a deep blue coloration when dissolved in concentrated sulphuric acid (Found: C, 46·8; H, 3·9; N, 19·9. $C_{17}H_{15}O_7N_7,C_2H_4O_2$ requires C, 46·6; H, 3·9; N, 20·0%).

(2) The *urethane* derivative of *di*-p-*tolylformazylcarboxylic acid*, $CO_2Et{\cdot}NH{\cdot}CO{\cdot}C(N{:}N{\cdot}C_7H_7){:}N{\cdot}NH{\cdot}C_7H_7$, resembles the *o*-nitro-derivative in its solubility, and crystallises from alcohol in bright red needles that melt at 153°, and give a deep blue coloration with concentrated sulphuric acid (Found: C, 62·3; H, 5·9; N, 19·1. $C_{19}H_{21}O_3N_5$ requires C, 62·15; H, 5·7; N, 19·1%). This compound is hydrolysed by boiling with 10% potassium hydroxide solution, yielding *di*-p-*tolylformazylcarboxylic acid*,

$$HO_2C{\cdot}C(N{:}N{\cdot}C_7H_7){:}N{\cdot}NH{\cdot}C_7H_7,$$

which crystallises from acetic acid in red, rhomboidal crystals, m. p. 182° (Found: N, 19·1. $C_{16}H_{16}O_2N_4$ requires N, 18·9%).

III. The *urethane* derivative of 3 : 5-*diketo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* (III) was prepared by dissolving the phenylhydrazone of mesoxalyldiurethane (I) in warm 10%

aqueous potassium hydroxide and subsequently acidifying the solution with a dilute mineral acid. It is soluble in hot water and crystallises from very dilute alcohol in pale buff-coloured, feathery crystals, m. p. 203° (decomp.) (Found: C, 51·7 *; H, 4·05; N, 18·5. $C_{13}H_{12}O_5N_4$ requires C, 51·3; H, 3·9; N, 18·4%).

The following substituted triazine derivatives were similarly prepared:

(1) The *urethane* derivative of 3 : 5-*diketo*-2-p-*nitrophenyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* is obtained from each of the two isomeric forms of the *p*-nitrophenylhydrazone of mesoxalyldiurethane; it crystallises in garnet-red prisms, m. p. 205° (Found: N, 19·9. $C_{13}H_{11}O_7N_5$ requires N, 20·05%).

(2) The *urethane* derivative of 3 : 5-*diketo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* crystallises from dilute alcohol in pale buff, silky needles, m. p. 218° (decomp.) (Found: C, 53·0 *; H, 4·5; N, 17·6. $C_{14}H_{14}O_5N_4$ requires C, 52·9; H, 4·4; N, 17·6%).

IV. 3 : 5-*Diketo*-6-*benzeneazo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine* (IV) was prepared by two methods: (i) by dissolving the urethane derivative of formazylcarboxylic acid (II) in warm alcoholic potassium hydroxide, diluting the solution with water, and acidifying the mixture with dilute hydrochloric acid; (ii) by the prolonged boiling of the same formazyl compound in xylene solution. The *triazine* crystallises from alcohol in orange needles, m. p. 256° (decomp.), that develop a deep red colour when dissolved in concentrated sulphuric acid (Found: C, 61·9 *; H, 3·8; N, 24·0. $C_{15}H_{11}O_2N_5$ requires C, 61·4; H, 3·75; N, 23·9%). This compound is hydrolysed by boiling with 10% potassium hydroxide solution, yielding formazylcarboxylic acid, m. p. 162°.

The following substituted triazine derivatives were similarly prepared:

(1) 3 : 5-*Diketo*-2-o-*nitrophenyl*-6-o-*nitrobenzeneazotetrahydro*-1:2:4-*triazine* crystallises from acetic acid in red, rhomboidal crystals, m. p. 224° (decomp.) (Found: N, 25·4. $C_{15}H_9O_6N_7$ requires N, 25·6%).

(2) 3 : 5-*Diketo*-6-p-*tolueneazo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine* crystallises from alcohol in orange-red needles, m. p. 246° (Found; C, 64·3 *; H, 4·8; N, 21·75. $C_{17}H_{15}O_2N_5$ requires C, 63·55; H, 4·7; N, 21·8%). When this compound is hydrolysed by hot potassium hydroxide solution the ring is ruptured in two places and di-*p*-tolylformazylcarboxylic acid, m. p. 182°, is formed.

The phenylhydrazone of mesoxamide, $(CO\cdot NH_2)_2C{:}N\cdot NHPh$, was prepared by Ruhemann and Orton (J., 1895, **67**, 1005) by heat-

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* The high values obtained for carbon in the analysis of triazine compounds have been observed by Widman (*Ber.*, 1893, **26**, 2612).

ing an alcoholic solution of dibromomalonamide with the required quantity of phenylhydrazine; it crystallises in long, yellow needles, m. p. 232—233°. The same compound was obtained (i) by heating an alcoholic solution of monobromomalonamide (Backes, West, and Whiteley, J., 1921, **119**, 364) with one equivalent of phenylhydrazine (Found: C, 51·9; H, 4·95; N, 27·2. Calc.: C, 52·4; H, 4·85; N, 27·2%); and (ii) by the action of benzenediazonium chloride on an aqueous solution of malonamide containing excess of sodium acetate; the product crystallised from alcohol in long, yellow needles that melted at 232° and did not depress the melting point of the compound prepared by Ruhemann and Orton's method.

One of us (M. A. W.) desires to thank the Council of the Royal Society for a grant which has covered much of the cost of the materials required for this investigation.

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[*Received, January 5th*, 1927.]