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ASYMMETRIC TRIAZINES—XIII

REACTION OF PHOSPHORUS PENTACHLORIDE WITH 4-NITROSOPYRAZOLES

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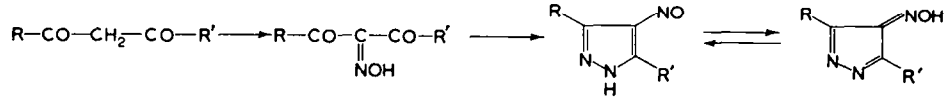
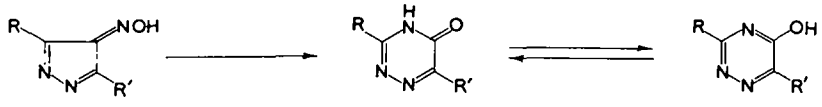
Abstract—The reaction of phosphorus pentachloride with some 3:5-disubstituted-4-nitrosopyrazoles (dimethyl, diphenyl, methyl phenyl and phenyl carbomethoxy) has been investigated. Formation of a new class of compounds, 1-chloro-4-cyano-2:3-diazabuta-1:3-dienes, is described. By treatment with ammonia and subsequent alkali-induced cyclisation these substances are converted into 5-amino-*as*-triazines and reactions of the latter have been investigated.

THE present investigation was undertaken in order to establish if expansion of a pyrazole nucleus to an *as*-triazine ring was feasible by means of a Beckmann rearrangement performed on 4-nitrosopyrazoles unsubstituted at position 1 (III). As it is known these substances, of which only a few examples are described, can be obtained by a general procedure from β-diketones (I) through their *iso*nitroso derivatives (II).



I II III a III b

4-Nitrosopyrazoles are to be considered, owing chiefly to their deep colours, as true nitroso derivatives (IIIa), but a tautomeric *iso*nitroso form (IIIb) is also possible. On the basis of a formal analogy a Beckmann rearrangement operating on 4-nitrosopyrazoles would then afford 5-hydroxy-*as*-triazines (IV). A similar reaction has been



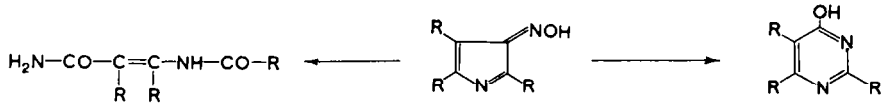
III b IV

reported by Ajello,[1] who allowed phosphorus pentachloride to react with some β-*iso*nitrosopyrroles with substituents at positions 2,4 and 5 (general formula V).

As foreseen, Ajello obtained from (V) the corresponding pyrimidines (VI); however, having observed among the reaction products also open-chain compounds

* The results of this investigation have been anticipated in a short communication published in *Mem. Accad. Lincei* **21**, 208 (1956) and presented at the Sixteenth International Congress of Pure and Applied Chemistry, Paris, 17–24 July 1957. Previous papers of this series appeared in *Gazz. Chim. Ital.* **83**, 133 (1953); **84**, 373 (1954); **86**, 484 (1956); **87**, 438 (1957); *Farmaco* **10**, 619 (1955); *R.C. Ist Lombardo* **88**, 173, 185 (1955); **91**, 186 (1957); **91**, 936 (1957).

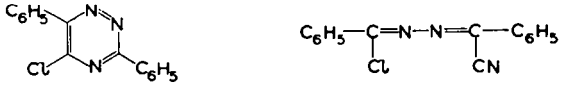
[1] T. Ajello, *Gazz. Chim. Ital.* **69**, 460 (1939); **70**, 504 (1940); **72**, 325 (1942).



VII V VI

(VII), he inferred the process to be a modification of the true Beckmann rearrangement. Without taking into discussion this reaction mechanism or the origin of products (VII), Ajello's experiments looked encouraging for a new synthesis of the *as*-triazine ring.

The investigation was begun by using 3:5-diphenyl-4-nitrosopyrazole (III, R = R′ = C_6H_5), recently described,[2] prepared by reacting *iso*nitrosodibenzoylmethane (II, R = R′ = C_6H_5) with hydrazine in methanol solution. When a chloroform solution of 3:5-diphenyl-4-nitrosopyrazole was treated with phosphorus pentachloride, the emerald-green characteristic colour of the nitroso compound quickly disappeared with evolution of hydrogen chloride and from the crude reaction product a crystalline yellow solid with empirical formula $C_{15}H_{10}N_3Cl$ was isolated. Alternative structures for this product are 3:6-diphenyl-5-chloro-*as*-triazine (VIII) or the open-chain one corresponding to the chloronitrile (IX).



VIII IX

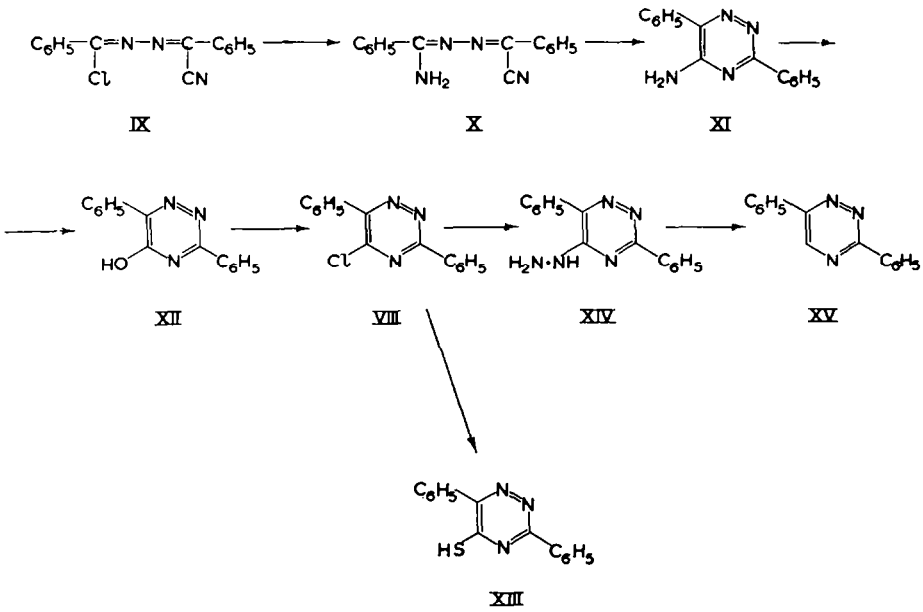
The deep-yellow colour like that observed for $C_{15}H_{10}N_3Cl$ is not easily explained in a cyclic structure such as (VIII). This fact, and chiefly the chemical evidence that will be discussed later, are in favour of the open-chain structure (IX). Compound (IX), presenting rather uncommon structural features, has been related, for its nomenclature, to the corresponding non-nitrogenous system of buta-1:3-diene and consequently identified as 1:4-diphenyl-1-chloro-4-cyano-2:3-diazabuta-1:3-diene.

The formation of the halogenated nitrile (IX) is consistent with results obtained from the so called Beckmann reaction "of the second order".[3] This reaction is typical of those cyclic compounds in which a carbonyl group is contiguous to a ketoximic function.

The halogen atom in (IX) is reactive and can be substituted by an amino group when treated with ammonia in dioxan. The resulting aminonitrile (X) is a yellow coloured crystalline solid, which, when treated with hot strong alkalis, rapidly isomerises to yield a colourless substance. This is a new base, which resists chemical attack, particularly oxidising agents; it forms stable salts with strong mineral acids and even a sparingly soluble permanganate. The formation of this base with simultaneous disappearance of the yellow colour must be interpreted as a cyclisation of the aminonitrile (X) and its structure is therefore that of 3:6-diphenyl-5-amino *as*-triazine (XI).* Ultra-violet and visible region absorption spectra of (X) and (XI) are

* For this and for other *as*-triazine derivatives reported in this work only the "aromatic" structures will be written and no account will be taken of other theoretically possible tautomeric forms.

[2] R. Hüttel, F. Büchele and P. Jochum, *Chem. Ber.* **88**, 1577 (1955).
[3] W. Borsche and W. Sander, *Ber. Dstch. Chem. Ges.* **47**, 2815 (1914).



shown in Fig. 1. On account of its chemical inertness the amino group in (XI) can be hydrolysed only by prolonged boiling in concentrated hydrobromic acid. In this way 5-hydroxy-3:6-diphenyl-*as*-triazine (XII) is produced as a high-melting colourless solid, soluble in strong alkalis and insoluble in water and most organic solvents.

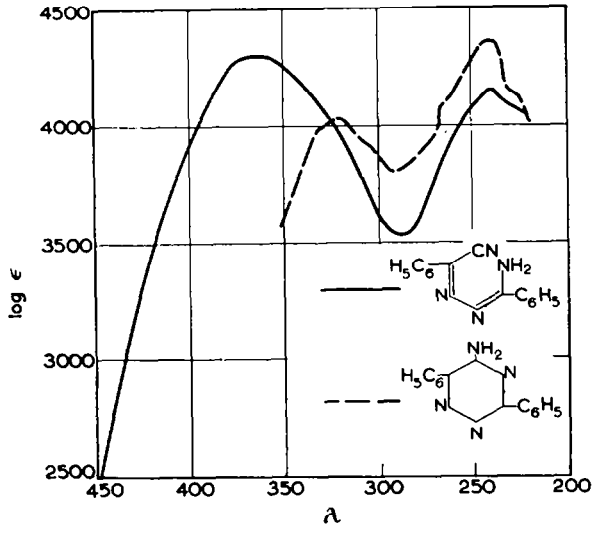


FIG. 1.

5-Hydroxy-3:6-diphenyl-*as*-triazine can be chlorinated by phosphorus pentachloride and the 5-chloro derivative (VIII) on reaction with hydrazine hydrate gives the corresponding 5-hydrazino derivative (XIV).

3:6-Diphenyl-5-chloro-*as*-triazine (VIII) is the cyclic isomer of the chloronitrile (IX) originally produced by the interaction of phosphorus pentachloride and nitrosodiphenyl-pyrazole. As expected, the new substance is colourless and its preparation

indirectly proves the correctness of the open chain structure previously postulated for (IX). Ultra-violet and visible region absorption spectra of the two isomers are shown in Fig. 2.

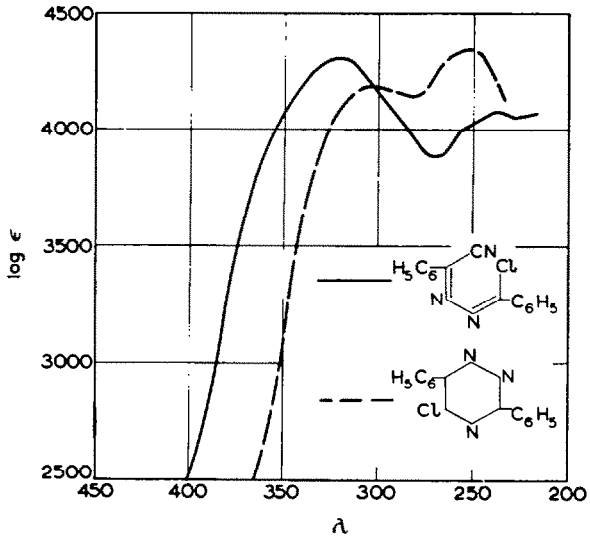


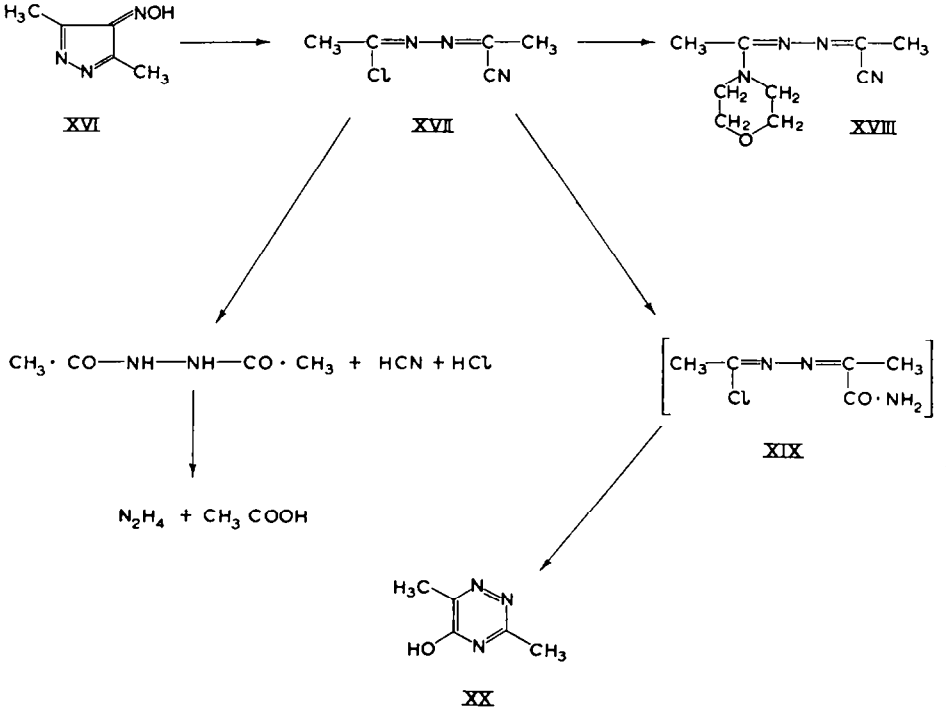
FIG. 2.

5-Hydrazino-3:6-diphenyl-*as*-triazine (XIV) is a high-melting yellow solid, which, unlike the *isomeric* 3-hydrazino-5:6-diphenyl-*as*-triazine, gives no colour reaction in presence of the ferrous ion.[4] Oxidation of (XIV) by yellow mercuric oxide in alcoholic solution by a procedure previously employed in this laboratory[5] yields 3:6-diphenyl-*as*-triazine (XV).

The above series of reactions opens a new sythetic route to the *as*-triazine nucleusn which is only limited by the availability of 4-nitrosopyrazoles. Chlorotriazine (VIII) on treatment with alcoholic sodium hydrosulphide was also transformed into the corresponding 5-thiol derivative (XIII). This substance is the first example of an *as*-triazine with a sulphydryl group at position 5.

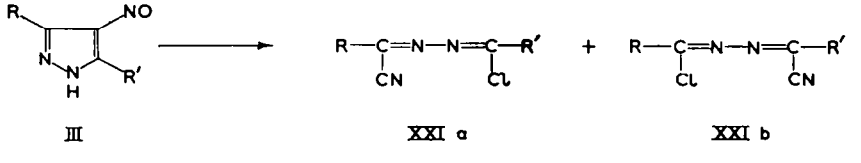
The pyrazole ring cleavage reaction was also applied to 3:5-dimethyl-4-nitroso-pyrazole (III, R = R′ = CH_3 = XVI) prepared in the usual way from acetylacetone (I, R = R′ = CH_3). Phosphorus pentachloride reacts briskly upon dimethyl-nitrosopyrazole (XVI) and the intense blue colour of the nitroso compound immediately disappears. At the same time tarry brown by-products separate, the formation of which can be limited only by employing dimethylnitrosopyrazole of high purity. The main product is a pungent liquid containing chlorine in a highly reactive form. Consistently with the experiment on the diphenyl derivative, this substance has been designated as 2-chloro-5-cyano-3:4-diazahexa-2:4-hexadiene (XVII). Heated with diluted mineral acids (XVII) envolves hydrogen cyanide, while hydrazine and acetic acid can be detected in the solution and further, it reacts smoothly with amines to give bases that are easily purified solids. Morpholine for instance yields base (XVIII),

[4] R. Fusco and R. Trave, *R.C. Ist. Lombardo* **91**, 202 (1957).
[5] S. Rossi, *R.C. Ist. Lombardo* **88**, 187 (1955).

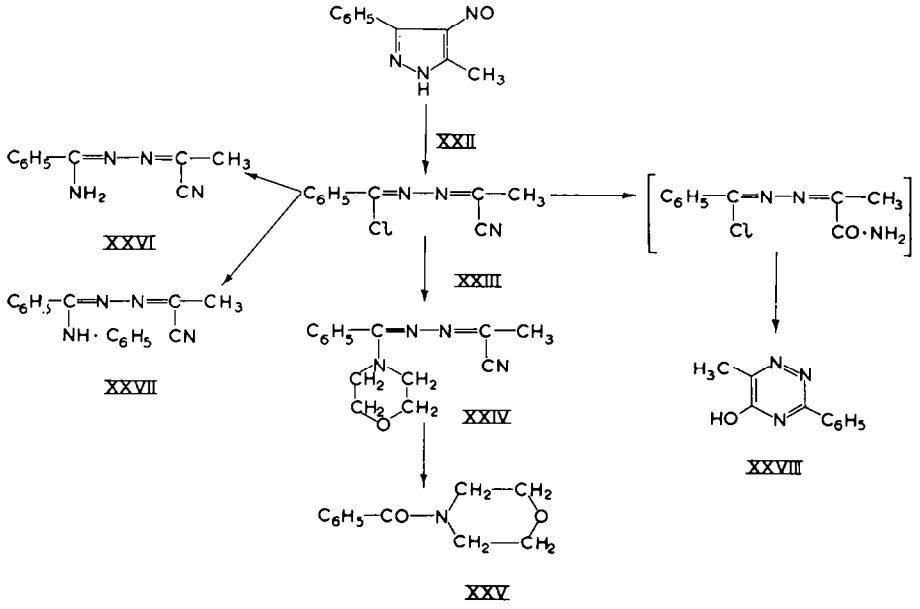


whose structure is confirmed by analytical data. Substance (XVII) undergoes a more complex transformation when exposed to air for a long time. Under these conditions a new colourless sublimable material, m.p. 138°, is slowly formed. This substance, of empirical formula $C_5H_7ON_3$, can be regarded as derived from (XVII) by addition of a molecule of water and loss of hydrogen chloride. Being stable to hydrolytic agents, $C_5H_7ON_3$ does not yield hydrogen cyanide on either acid or alkaline hydrolysis and it cannot be considered as a product derived from simple substitution of chlorine in (XVII) by a hydroxyl group. The new substance is assigned the structure of 3:6-dimethyl-5-hydroxy-*as*-triazine (XX), which could be formed by partial hydrolysis of the nitrile group of (XVII) followed by loss of hydrogen chloride from intermediate amide (XIX). Unfortunately, it has not been possible to extend this investigation owing to poor yields obtained in the dimethylnitrosopyrazole cleavage reaction, to the instability of the resulting chloronitrile and to difficulties in its purification.

It should be noted that up to this point the investigation was carried out on symmetrical nitrosopyrazoles substituted at positions 3 and 5 by identical groups and consequently only one chloro derivative could be obtained. Starting from asymetrically substituted nitrosopyrazoles (III, $R \neq R'$), two isomeric chloronitriles (XXIa and XXIb) could theoretically arise by reaction with phosphorus pentachloride.



In order to investigate this point 4-nitroso-3-phenyl-5-methylpyrazole (XXII), prepared from benzoylacetone (I, R = C_6H_5; R′ = CH_3), was treated with phosphorus pentachloride. The reaction, carried out by the procedure already described gives a chlorine-containing yellow solid with a pungent odour, whose chemical behaviour gives evidence of an open structure and whose chlorine atom reacts quantitatively with silver nitrate in the cold. Derivatives have been obtained by substituting chlorine with nitrogen-containing groups (amino, anilino and morpholine).



On acid hydrolysis substance (XXI) (R = C_6H_5; R′ = CH_3) behaves like the dimethyl derivative (XVII) and forms hydrogen cyanide, hydrogen chloride, benzoic acid, hydrazine and acetic acid, both isomeric structures (XXIa) and (XXIb) (R = C_6H_5; R′ = CH_3) being consistent with such degradation products. Hydrolysis of the morpholine derivative (XXIV) furnishes a clue in favour of structure (XXIb) (R = C_6H_5; R′ = CH_3) as the formation of benzoylmorpholine (XXV) is consistent only with structure (XXIII).

Analogous nitrogen-containing derivatives prepared by reaction with ammonia and and aniline are assigned structures (XXVI) and (XXVII)*. On prolonged exposure to air, compound (XXIII) undergoes a change similar to that observed for the dimethyl derivative (XVII) and yields a new substance with the empirical formula $C_{10}H_9ON_3$. Considering its thermal stability and its resistance to hydrolytic agents, this product is to be assigned structure (XXVIII) of 3-phenyl-6-methyl-5-hydroxy-*as*-triazine. Yields of the product of the cleavage reaction of phosphorus pentachloride on nitrosopyrazole (XXII) and subsequent formation of the triazine compound are lower than those observed for 3:6-diphenylpyrazole. It is to be noted that 3-phenyl-6-methyl-5-hydroxy-*as*-triazine (XXVIII) as well as 3:6-dimethyl-5-hydroxy-*as*-triazine

* Formation of the isomer corresponding to structure (XXIa) (R = C_6H_5; R′ = CH_3) can not be ruled out, and, owing possibly to very poor yields from the cleavage reaction or to its chemical instability, it has not been possible to detect it. Further, one of the structures (XXIa) and (XXIIb) could arise from the *syn* or *anti* configuration of the nitrosopyrazole (IIIb).

(XX) and the triazines of the 3:6-diphenyl series (XI to XV) belong to a new family of *as*-triazines not available through previously known synthetic routes. It has now been shown that the cleavage of the pyrazole ring can be used to obtain *as*-triazines. The preparation of simpler *as*-triazines was undertaken in order to study the chemical behaviour of this heterocyclic structure. For this purpose the action of phosphorus pentachloride on 4-nitrosopyrazoles with substituents in positions 3 and 5 which could be subsequently replaced or eliminated was investigated.

This project was started by synthesising 3-phenyl-5-carbomethoxy-4-nitroso-pyrazole (XXIX).

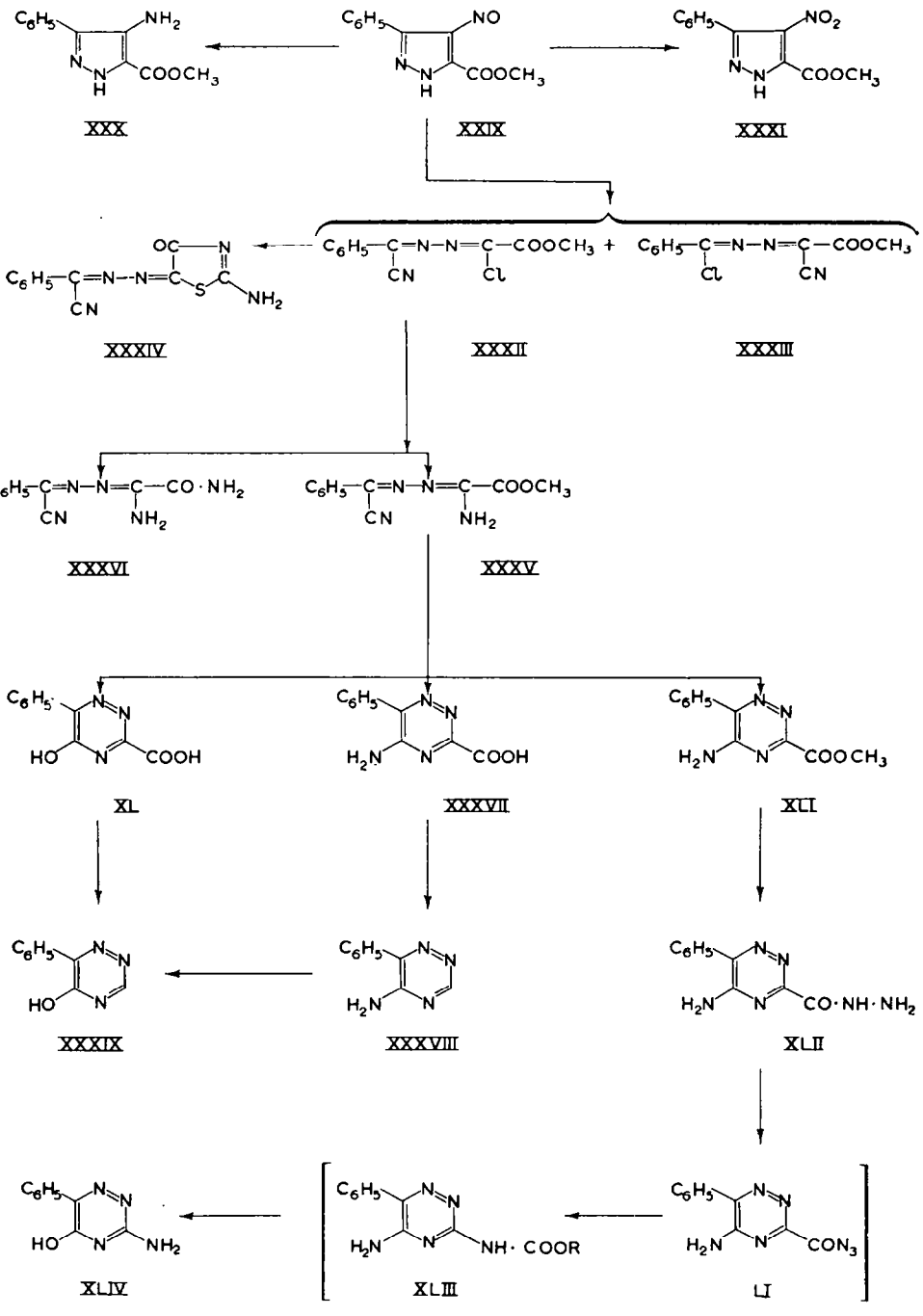
When nitrous acid and hydrazine are allowed to react in rapid succession on methyl acetophenonoxalate (I, R = C_6H_5, R′ = $COOCH_3$) in acetic acid, the solution develops in a short time a characteristic green colour. After dilution in the cold a colourless crystalline solid separates. Satisfactory yields of nitrosopyrazole (XXIX) are obtained only when the intermediate nitrosodiketone (II, R = C_6H_5, R′ = $COOCH_3$) is treated with hydrazine immediately after its formation. Although colourless in the solid state, 3-phenyl-4-nitroso-5-carbomethoxypyrazole (XXIX) shows an intense emerald-green colour when melted or dissolved in organic solvents. This behaviour, which is common to several nitroso compounds, is probably due to the existence in the solid state of a dimeric colourless form. The structure of nitroso-pyrazole (XXIX) has been confirmed through reduction to 3-phenyl-4-amino-5-carbomethoxypyrazole (XXX) and oxidation to 3-phenyl-4-nitro-5-carbomethoxy-pyrazole (XXXI).

With phosphorus pentachloride in chloroform nitrosopyrazole (XXIX) affords a crystalline material, the melting point indicating it to be a mixture of the two isomers, 1-phenyl-1-cyano-4-chloro-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXII) and 1-phenyl-1-chloro-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXIII). The isomers can be separated by fractional crystallisation from benzene and (XXXII), containing an α-chlorocarbomethoxyl group, reacts quantitatively with thiourea to yield a sparingly soluble thiazole derivative (XXIV), which was isolated and analysed. By means of this very sensitive test purification of the higher-melting less-soluble isomer (XXXII) can be controlled.

The lower-melting isomer (XXXIII) is obtained in less pure condition. By reaction with ammonia 1-cyano-1-phenyl-4-chloro-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXII) gives the corresponding aminonitrile (XXXV) in 90 per cent yields. With higher temperatures or prolonged contact of gaseous ammonia with the chloro-nitrile the amino amide (XXXVI) is produced. After treatment with potassium carbonate solution amino ester (XXXV) cyclises with simultaneous hydrolysis of the carbomethoxyl group and 5-amino-6-phenyl-*as*-triazine-3-carboxylic acid (XXXVII) is obtained in theoretical yields. On heating (XXXVII) decarboxylates to the triazino-amine (XXXVIII), which in turn can be hydrolysed by hot diluted alkalis to 5-hydroxy-6-phenyl-*as*-triazine (XXXIX).

5-Hydroxy-6-phenyl-*as*-triazine (XXXIX) has also been prepared by an independent synthesis and so additional evidence of the structures of all triazine derivatives described in this work was obtained. 3-Mercapto-5-hydroxy-6-phenyl-*as*-triazine (XLV), prepared by the method of Bougault,[6] yields the corresponding 3-hydrazino-*as*-triazine (XLVI) when treated with hydrazine in boiling butanol. Oxidation of the

[6] J. Bougault and L. Daniel, *C.R. Acad. Sci., Paris* **186**, 151 (1928).


XXX
XXIX
XXXI
XXXIV
XXXII
XXXIII
XXXVI
XXXV
XL
XXXVII
XLI
XXXIX
XXXVIII
XLII
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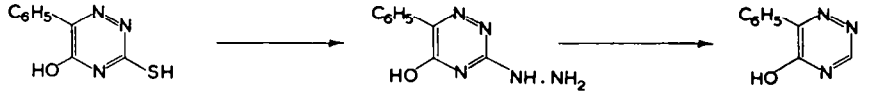
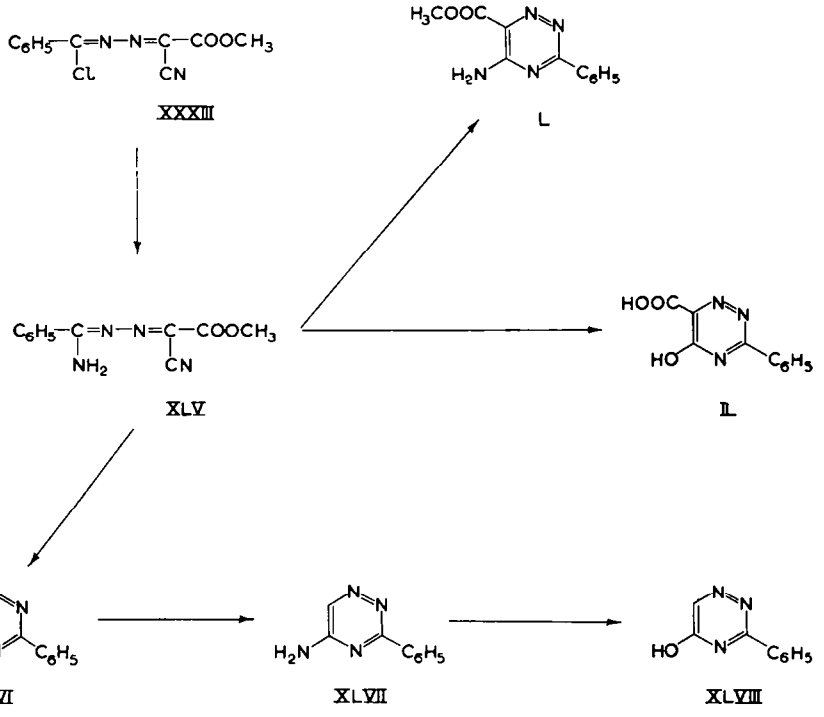
LI

hydrazine group by yellow mercuric oxide gives 5-hydroxy-6-phenyl-*as*-triazine (XXXIX) identical with the product obtained by decarboxylating acid (XL).



XLV XLVI XXXIX

Formation of the *as*-triazine nucleus from the amino ester (XXXV) is also possible without affecting the carbomethoxyl group by operating in anhydrous ethanol in presence of a sodium alkoxide. 3-Carbomethoxy-5-amino-6-phenyl-*as*-triazine (XLI) can be converted into the corresponding hydrazide (XLII) and Curtius degradation of the latter affords 3-amino-5-hydroxy-6-phenyl-*as*-triazine (XLIV). Alkaline hydrolysis of the carbamate (XLIII) also affects the 5-amino group to give the 5-hydroxy derivative.



XXXIII L

XLV IL

XLVI XLVII XLVIII

From benzene mother-liquors of chloronitrile (XXXII) the lower-melting more-soluble isomer 1-phenyl-1-chloro-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXIII) can be isolated. Experiments carried out in order to purify it having failed, the crude isomer (XXXIII) was treated with ammonia in dioxan solution so that the resulting aminonitrile (XLV) could then be more easily purified by crystallisation from ethanol.

(XLV) when treated with potassium carbonate yields 3-phenyl-5-amino-6-carboxy-*as*-triazine (XLVI) and, by decarboxylation of the latter, 3-phenyl-5-amino-*as*-triazine (XLVI) is obtained. Hydrolysis of the aminotriazine (XLVII) affords 3-phenyl-5-hydroxy-*as*-triazine (XLVIII) while 3-phenyl-5-hydroxy-*as*-triazine-6-carboxylic acid (IL) is obtained by treatment of the amino ester (XLV) with caustic alkalis.

3-Phenyl-5-hydroxy-*as*-triazine-6-carboxylic acid (IL) behaves like a strongly acidic substance and it can be displaced from its salts only by strong mineral acids and furnishes sparingly soluble salts with calcium and barium. Sodium ethoxide affords closure of the *as*-triazine nucleus from the amino ester (XLV) without affecting the carbomethoxyl group and yields 3-phenyl-5-amino-*as*-triazine-6-carboxylic acid methyl ester (L).

EXPERIMENTAL*

1:4-*Diphenyl*-1-*chloro*-4-*cyano*-2:3-*diazabuta*-1:3-*diene* (IX). To a stirred solution of 3:5-diphenyl-4-nitrosopyrazole (III, R = R′ = C_6H_5) (10 g) in 300 ml of boiling anhydrous chloroform, phosphorus pentachloride (13 g) in 100 ml of chloroform was added in small portions. After being set aside for a few hours at room temperature, the solution was repeatedly washed with cold water, dried over calcium chloride and evaporated. The golden-yellow residue crystallised as needles from ethanol (yield 8·2 g), m.p. 138° (Found: C, 67·61; N, H, 3·81; N, 15·33. $C_{15}H_{10}N_3Cl$ requires C, 67·41; H, 3·74; N, 15·73 per cent).

1:4-*Diphenyl*-1-*amino*-4-*cyano*-2:3-*diazabuta*-1:3-*diene* (X). 1:4-Diphenyl-1-chloro-4-*cyano*-2:3-diazabuta-1:3-diene (IX) (15 g) was dissolved in 150 ml of dioxan and treated with dry ammonia gas. Ammonium chloride separated, and after 30 min the flow of ammonia was discontinued, water was added (100 ml) and the yellow precipitate was collected, and recrystallised from ethanol, m.p. 170° (yield 12·5 g) (Found: N = 22·35. $C_{15}H_{12}N_4$ requires N = 22·58 per cent).

3:6-*Diphenyl*-5-*amino*-as-*triazine* (XI). 1:4-Diphenyl-1-amino-4-cyano,-2:3-diazabuta-1:3-diene (X) (12·5 g) was dissolved in 150 ml ethanol and 6 ml of 30% sodium hydroxide were added. After being heated under reflux for 15 min, the solution was completely decolorised and on cooling 10·5 g of the triazine separated as needles, which were recrystallised from ethanol, m.p. 219° (Found: N, 22·57. $C_{15}H_{12}N_4$ requires N, 22·58 per cent).

The aminotriazine gives stable salts with several strong mineral acids. When treated with potassium permanganate in dilute sulphuric acid solution, the violet-red permanganate was precipitated (Found: Mn, 14·81. $C_{15}H_{13}O_4N_4Mn$ requires Mn, 14·94 per cent).

3:6-*Diphenyl*-5-*hydroxy*-as-*triazine* (XII). 3:6-Diphenyl-5-amino-*as*-triazine (XI) (10·5 g) was dissolved in 90 ml of 48% hydrobromic acid and heated under reflux for 3 hr. After cooling, the precipitate was collected on a sintered-glass funnel and recrystallised from acetic acid, m.p. 274–276° (yield 9·5 g); colourless crystals, soluble in alkalis, insoluble in water and sparingly in the usual organic solvents were obtained (Found: N, 16·75. $C_{15}H_{11}ON_3$ requires N, 16·86 per cent).

3:6-*Diphenyl*-5-*chloro*-as-*triazine* (VIII). A mixture of 3-6-diphenyl-5-hydroxy-*as*-triazine (XII) (4 g) and phosphorus pentachloride (5·6 g) in 8 ml of dry toluene was heated under reflux for 3 hr. The toluene solution was thoroughly washed with water, dried over calcium chloride and then evaporated. The residual material (3·3 g) was crystallised from benzene, m.p. 132–134° (Found: N, 15·59. $C_{15}H_{10}N_3Cl$ requires N, 15·73 per cent).

3:6-*Diphenyl*-5-*hydrazino*-as-*triazine* (XIV). 3:6-Diphenyl-5-chloro-*as*-triazine (VIII) (0·64 g) was dissolved in anhydrous ice-cold dioxan (50 ml) and treated with

* Melting points are not corrected.

8 ml of a 5% solution of hydrazine hydrate in dioxan. The mixture was left at room temperature for 2 days, and evaporated to dryness under reduced pressure. The residual solid was collected and crystallised from ethanol. Orange needles soluble into dilute acids, sintering at 217–218°, and melting over 300° were obtained (Found: N, 26·86. $C_{15}H_{13}N_5$ requires 26·61 per cent).

3:6-*Diphenyl*-as-*triazine* (XV). 3:6-Diphenyl-5-hydrazino-*as*-triazine (XIV) (0·15 g) was dissolved in 6 ml of ethanol containing 0·29 g of yellow mercuric oxide and heated under reflux for 1 hr. The cooled suspension was filtered and diluted with water, and the crude precipitate was collected, dried under vacuum and slowly sublimed at 150° and a pressure of 16 mm, m.p. 156–157° (Found: N, 17·93. $C_{15}H_{11}N_3$ requires N, 18·03 per cent).

3:6-*Diphenyl*-5-*thiol*-as-*triazine* (XIII). Sodium (10 mg) was dissolved in 20 ml anhydrous ethanol and the resulting sodium ethoxide solution was first saturated in the cold with hydrogen sulphide and then treated with 3:6-diphenyl-5-chloro-*as*-triazine (VIII) (0·1 g). After the solution had been heated under reflux for 1 hr, 1 ml of acetic acid was added and the mixture was concentrated on a steam-bath. The orange coloured precipitate was collected and crystallised as a monohydrate from dilute ethanol (Found: N, 14·63. $C_{15}H_{11}N_3S{\cdot}H_2O$ requires N, 14·84 per cent).

Reaction between phosphorus pentachloride and 4-*nitroso*-3:5-*dimethylpyrazole* (XVI) 5-*Hydroxy*-3:6-*dimethyl*-as-*triazine* (XX). A solution of 4-nitroso-3:5-dimethylpyrazole (XVI) (11 g)[7] in anhydrous chloroform (70 ml) was slowly added to a stirred water-cooled supension of phosphorus pentachloride (28 g) in 150 ml of anhydrous chloroform while the temperature was kept-below 25°. When the addition had been completed, the chloroform solution was rapidly washed with ice-cold water, dried over calcium chloride and evaporated. The residue was dissolved in light petroleum, treated with Norit, filtered, evaporated under reduced pressure and then distilled under 0·5 mm of mercury. At 55–60°, a pale-yellow liquid (3 g) with a pungent odour was collected. It contained chlorine and had to be kept out of contact with air. In a moist atmosphere after 48 hr it slowly decomposed with evolution of hydrogen chloride to yield (XX), which was purified by crystallisation from water to give colourless plates, m.p. 139–140° (Found: C, 47·87; H, 5·84; N, 33·49. $C_5H_7ON_3$ requires C, 48·00; H = 5·60. N, 33·60 per cent).

The chlorinated substance (1 g) was dissolved in 15 ml of ethanol and treated with 1·1 ml of morpholine. A yellow basic solid was immediately precipitated, and it was recrystallised from water m.p. 115° (Found: N, 28·72. $C_9H_{14}ON_4$ requires N, 28·86 per cent).

Reaction between phosphorus pentachloride and 3-*methyl*-4-*nitroso*-5-*phenylpyrazole* (XXII): 1-*phenyl*-1-*chloro*-4-*methyl*-4-*cyano*-2:3-*diazabuta*-1:3-*diene* (XXIII). 3-Methyl-4-nitroso-5-phenylpyrazole (XXII) (18·7 g) in 200 ml of anhydrous chloroform was slowly added to a cold stirred suspension of 41·6 g phosphorus pentachloride in 300 ml of anhydrous chloroform. When the addition had been completed, the solution was left at room temperature for 2 hr and then washed with cold water and dried over calcium chloride. After evaporation of the chloroform, the residue was dissolved in light petroleum, and the solution was treated with Norit and filtered, the solvent was evaporated under reduced pressure and the residue was distilled *in vacuo*. The product boiling at 115–117°/5 mm was collected and recrystallised from light

[7] L. Wolff, *Liebigs Ann.* **325**, 193 (1902).

petroleum, m.p. 51°. The substance contained chlorine and had to be stored out of contact with air (Found: C, 58·43; H, 4·06, N, 20·12. $C_{10}H_8N_3Cl$ requires C, 58·53; H, 3·90; N, 20·48 per cent).

1-*Phenyl*-1-N-*morpholino*-4-*cyano*-4-*methyl*-2:3-*diazabuta*-1:3-*diene* (XXIV). When 1-phenyl-1-chloro-4-methyl-4-*cyano*-2:3-diazabuta-1:3-diene (XXIII) (1 g) was treated with morpholine (0·85 g), a pale-yellow solid was immediately formed, which after recrystallisation from ethanol had m.p. 115° (Found: N, 21·42. $C_{14}H_{16}ON_4$ requires N, 21·83 per cent). When 0·5 g of this product was heated under reflux for a short time in dilute hydrochloric acid (10 ml), colourless needles were obtained on cooling and were crystallised from water, m.p. 74°. The substance was identical with N-benzoylmorpholine (XXV)[8] with which it showed no depression on a mixed melting point determination.

1-*Phenyl*-1-N-*anilino*-4-*cyano*-4-*methyl*-2:3-*diazabuta*-1:3-*diene* (XXVII). To a solution of 1-phenyl-1-chloro-4-methyl-4-cyano-2:3-diazabuta-1:3-diene (XXIII) in anhydrous ether (15 ml) freshly distilled aniline (0·91 g) was added. In a short time the yellow solid that was precipitated was collected, washed thoroughly with water and crystallised from methanol to give yellow needles of a basic character, m.p. 138° (Found C, 72·99; H, 5·24. $C_{16}H_{14}N_4$ requires C, 73·28; H, 5·34 per cent).

1-*Phenyl*-1-*amino*-4-*cyano*-4-*methyl*-2:3-*diazabuta*-1:3-*diene* (XXVI). Dry ammonia was bubbled into a solution of 1-phenyl-1-chloro-4-methyl-4-cyano-2:3-diazabuta-1:3-diene (XXIII) (1 g) in anhydrous ether (15 ml) until ammonium chloride had completely separated. After the ammonium salt had been removed by filtration, evaporation of the solvent yielded a crystalline solid, m.p. 222°, after recrystallisation from water or dilute ethanol (Found: C, 64·77; H, 5·32. $C_{10}H_{10}N_4$ requires C, 64·51; H, 5·37 per cent).

3-*Phenyl*-5-*hydroxy*-6-*methyl*-as-*triazine* (XXVIII). When left in contact with air at room temperature, 1-phenyl-1-chloro-4-methyl-4-cyano-2:3-diazabuta-1:3-diene (XXIII) reacted slowly, absorbing moisture and evolving hydrogen chloride. The resulting product was crystallised twice from water. It can also be sublimed or distilled under reduced pressure (Found: C, 64·19; H, 4·99; N, 22·19. $C_{10}H_9ON_3$ requires C, 64·17; H, 4·81; N, 22·45 per cent).

3-*Phenyl*-4-*nitroso*-5-*carbomethoxypyrazole* (XXIX). Methylacetophenone oxalate (I; R = C_6H_5, R′ = $COOCH_3$) (20 g)[9] was dissolved into 100 ml of ice-cold glacial acetic acid and treated with a concentrated aqueous solution of sodium nitrite (7 g). To the stirred solution 12·5 ml of 85% hydrazine hydrate dissolved in 20 ml of acetic acid was slowly added. The temperature was kept between 10° and 15°. Addition of hydrazine must immediately follow that of sodium nitrite to obtain satisfactory yields in this preparation.* After addition of hydrazine the deep-green solution was kept in an ice-bath for 30 min and then diluted with 1 l. of ice-cold water. A crystalline colourless solid was precipitated and after 2 hr it was collected, washed with water and crystallised from 50% ethanol, to yield monohydrated prisms (yield 18 g) m.p. 104° (dec.) (Found: N, 16·62. $C_{11}H_9N_3O_3 \cdot H_2O$ requires N, 16·86 per cent).

3-*Phenyl*-4-*nitro*-5-*carbomethoxypyrazole* (XXXI). 3-Phenyl-4-nitroso-5-carbomethoxypyrazole (XXIX) (0·7 g) was dissolved in 80% nitric acid (8 ml) and heated on

* The intermediate methyl*iso*nitroso acetophenone oxalate (II; R = C_6H_5, R′ = $COOCH_3$) was rapidly hydrolysed to give hydrogen cyanide, oxalic acid and benzoic acid.

[8] L. Knorr, *Leibigs Ann.* **301**, 1 (1898).
[9] W. Wislicenus and W. Stoeber, *Ber. Dtsch. Chem. Ges.* **35**, 539 (1902).

a steam-bath until evolution of oxides of nitrogen subsided. The cool solution was diluted with 25 ml of water and extracted with ether, and the extracts in turn were treated with 5 ml of diluted sodium hydroxyde. On acidification 0·48 g of the pale yellow nitro compound were collected (yield 70 per cent), m.p. 193° after recrystallisation from water (Found: N, 17·22. $C_{11}H_9N_3O_4$ requires N, 17·00 per cent).

3-Phenyl-4-amino-5-carbomethoxypyrazole (XXX). 3-Phenyl-4-nitroso-5-carbomethoxypyrazole (XXIX) (0·5 g) was dissolved in 50% acetic acid (12 ml) and to the boiling solution iron dust (0·34 g) was added portionwise. Undissolved material was removed by filtration of the hot solution from which, on cooling, a solid colourless material separated (yield 0·28 g), m.p. 168–169°, after recrystallisation from water or benzene (Found: N, 19·08. $C_{11}H_{11}N_3O_2$ requires N, 19·35 per cent).

Reaction between phosphorus pentachloride and 3-phenyl-4-nitroso-5-carbomethoxypyrazole (XXIX): *1-cyano-1-phenyl-4-chloro-4-carbomethoxy-2:3-diazabuta-1:3-diene* (XXXII) *and 1-chloro-1-phenyl-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene* (XXXIII). To a stirred boiling suspension of phosphorus pentachloride (66 g) in dry chloroform (200 ml), a solution of 3-phenyl-4-nitroso-5-carbomethoxypyrazole (XXIX) (36 g) in chloroform (700 ml) was slowly added. Then 15 min after the addition had been completed heating was discontinued, the solution was cooled to 20° and 100 ml of water were added while temperature was kept below 25°. Stirring was continued for 10 min at room temperature, the water layer was decanted, and the chloroform layer was washed repeatedly with water, dried over calcium chloride and evaporated at reduced pressure. A yellow solid material that remained which was crystallised from ethanol (yield 27·5 g, 70 per cent). The mixture of isomers (XXXII) and (XXXIII) obtained melted between 98 and 110° (Found: C, 53·06; H, 3·30; N, 16·81. $C_{11}H_8O_2N_3Cl$ requires C, 53·01; H, 3·21; N, 16·86 per cent).

Separation of the two isomers was accomplished by fractional crystallisation from benzene. 1-Phenyl-1-cyano-4-chloro-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXII) was obtained in a pure state after three crystallisations as yellow needles melting at 110° (yield 10 g). When 1 g of this material was dissolved in ethanol (15 ml) and a concentrated ethanolic solution of thiourea (0·335 g) was added, after a brief heating on a steam-bath, thiazolinone (XXXIV) was obtained in theoretical yield as yellow needles, m.p. 221° (Found: N, 26·70. $C_{11}H_7ON_5S$ requires N, 27·23 per cent). From the benzene mother-liquors 16 g of a substance were obtained melting at 87–88°, which consisted chiefly of 1-phenyl-1-chloro-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXIII) and contained some of the higher-melting isomer (XXXII) (slightly positive thiourea test).

1-Cyano-1-phenyl-4-amino-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXV). 1-Phenyl-1-cyano-4-chloro-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXII) (8·2 g) was dissolved in dioxane (60 ml) and a saturated methanolic ammonia solution (9·5 ml) was added with cooling in ice. When the reaction was complete, a sample, after being washed with water, gave a negative Beilstein test for halogens. Then 500 ml of water was added, the precipitate was collected and crystallised from ethanol as pale-yellow flakes, very soluble in dioxan, ethanol and benzene, and sparingly in water (yield 6·75 g, 91 per cent), m.p. 132–133° (Found: N, 24·46; $C_{11}H_{10}N_4O_2$ requires N, 24·34 per cent). When the dioxan solution of the chloro ester (XXXII) was treated with dry ammonia gas for 15–20 min 1-phenyl-1-cyano-4-amino-4-carbamino-2:3-diazabuta-1:3-diene (XXXVI) was formed as pale-yellow needles, soluble in dioxan

and ethanol, and sparingly in water, m.p. 193°, after recrystallisation from ethanol (Found: N, 32·22. $C_{10}H_{10}N_5O$ requires N, 32·40 per cent).

3-*Carboxy*-5-*amino*-6-*phenyl*-as-*triazine* (XXXVII). 1-Phenyl-1-cyano-4-amino-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXV) (13 g) was suspended in water (250 ml), potassium carbonate (8 g) was added and the mixture was heated under reflux for 20 min. On cooling and acidification with acetic acid 12·4 g (96 per cent) of triazine was collected as colourless crystals after recrystallisation from water, m.p. 178° (dec.) (Found: N, 25·98. $C_{10}H_8N_4O_2$ requires N, 25·92 per cent).

5-*Amino*-6-*phenyl*-as-*triazine* (XXXVIII). 3-Carboxy-5-amino-6-phenyl-*as*-triazine (XXXVII)(5 g) was heated at 180° for 45 min in an oil-bath. After cooling the material was dissolved in hot water, treated with Norit and filtered. The product being monohydrated, the anhydrous 5-amino-6-phenyl-*as*-triazine was obtained by sublimation at 170° in a 2 Torr. vacuum (yield 2·1 g) m.p. 127° (Found N, 32·59. $C_9H_8N_4$ requires N, 32·55 per cent).

3-*Carboxy*-5-*hydroxy*-6-*phenyl*-as-*triazine* (XL). 1-Phenyl-1-cyano-4-amino-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXV) (1 g) was dissolved in boiling water (15 ml) and 30% sodium hydroxyde solution was added (0·8 ml). The solution was heated under reflux for 10 min, and then cooled and acidified with acetic acid to give monohydrated colourless crystals (yield 0·76 g) m.p. 265°, after recrystallisation from water (Found: N, 17·90. $C_{10}H_7N_3O_3 \cdot H_2O$ requires N, 17·87 per cent).

3-*Hydrazino*-5-*hydroxy*-6-*phenyl*-as-*triazine* (XLVI). 3-Mercapto-5-hydroxy-6-phenyl-*as*-triazine (XLV) (5 g) was dissolved in *n*-butanol (150 ml) and 85% hydrazine hydrate solution (10 ml) was slowly added. The hydrazine salt immediately separated and, when the solution was heated under reflux, it was slowly converted into the hydrazino derivative with evolution of hydrogen sulphide. After 3 hr the reaction was completed and the solid product that separated from the cold solution was collected and dissolved into hot water. Hydrochloric acid was added and the hydrochloride was obtained on cooling as colourless crystals (yield 2·5 g, m.p. 292–293° (Found: N, 29·37. $C_9H_9N_5O \cdot HCl$ requires N, 29·28 per cent).

5-*Hydroxy*-6-*phenyl*-as-*triazine* (XXXIX). (*i*) 5-Amino-6-phenyl-*as*-triazine (XXXVIII) (1 g) was dissolved in water (10 ml), 1 ml of 30% sodium hydroxide added and the solution was heated under reflux until evolution of ammonia ceased. On cooling and acidification with hydrochloric acid, colourless crystals were obtained (0·78 g), m.p. 208°, after recrystallisation (from water or ethanol) (Found: N, 24·25. $C_9H_7N_3O$ requires N, 24·27 per cent).

(*ii*) 3-Carboxy-5-hydroxy-6-phenyl-*as*-triazine (XL) (0·5 g) was heated in an oil-bath at 260–270° until evolution of carbon dioxide ceased. The residual material was dissolved into hot water, treated with Norit and filtered. Colourless crystals were obtained melting at 208° identical with the above described product.

(*iii*) 3-Hydrazino-5-hydroxy-6-phenyl-*as*-triazine (XLVI) hydrochloride (2g) was dissolved in a mixture of ethanol (80 ml) and water (10 ml). A concentrated aqueous solution of sodium hydroxide (0·52 g) was added and then in small portions 3·5 g of finely ground yellow mercuric oxide. The mixture was heated under reflux until the yellow colour disappeared, then filtered, acidified with hydrochloric acid, diluted with water (50 ml), treated with hydrogen sulphide, filtered and concentrated on a steam-bath. The collected solid material was crystallised from water (yield 0·63), m.p.

208°. The substance was identical with the hydroxy-*as*-triazine described above with which it showed no depression on a mixed melting point.

3-*Carbomethoxy*-5-*amino*-6-*phenyl*-as-*triazine* (XLI). To 1-Phenyl-1-cyano-4-amino-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXV) (5 g) in hot anhydrous methanol (100 ml) was added absolute methanol (10 ml) to which 0·2 g of sodium had previously been added. After being heated under reflux for 1 hr, the hot solution was filtered and, after cooling, colourless crystals were collected and recrystallised from ethanol (1 g), m.p. 229° (Found: N, 24·39. $C_{11}H_{10}N_4O_2$ requires N, 24·34 per cent).

3-*Carbohydrazino*-5-*amino*-6-*phenyl*-as-*triazine* (XLII). 3-Carbomethoxy-5-amino-6-phenyl-*as*-triazine (XLI) (0·13 g) was dissolved in hot ethanol (10 ml) and 0·5 ml of 85% hydrazine hydrate solution were added. The product was purified by being dissolved in dilute hydrochloric acid and reprecipitated with ammonia solution, and then washed with hot ethanol, m.p. 261–262° (Found: N, 36·51. $C_{10}H_{10}N_6O$ requires N, 36·52 per cent).

3-*Amino*-5-*hydroxy*-6-*phenyl*-as-*triazine* (XLIV). To a solution of 0·13 g of 3-carbohydrazino-5-amino-6-phenyl-*as*-triazine (XLII) (0·13 g) in cold dilute hydrochloric acid (15 ml). sodium nitrite (0·047 g) dissolved in a little water was added. The azide (LI) immediately separated as a green-yellow solid, which was filtered off and dried in a desiccator over phosphorus pentoxide under vacuum. The dry azide was heated under reflux in ethanol until evolution of nitrogen ceased, and the solvent was then distilled under reduced pressure and the residue was taken up with water (10 ml) to which 32% sodium hydroxide solution (0·5 ml) had been added. The mixture was heated under reflux for 1 hr, and after cooling it was neutralised with acetic acid, when the crude product that separated was collected and crystallised from water, m.p. 329° (Found: N, 29·47. $C_9H_8N_4O$ requires N, 29·78 per cent).

1-*Phenyl*-1-*amino*-4-*cyano*-4-*carbomethoxy*-2:3-*diazabuta*-1:3-*diene* (XLV). Crude 1-phenyl-1-chloro-4-cyano-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene (XXXII) (6 g) was dissolved in dioxan (50 ml) and a saturated solution of ammonia in methanol (6 ml) was added, the solution being cooled in ice; water (300 ml) was then added and the precipitate was collected and recrystallised from methanol as yellow needles, m.p. 159° (Found N, 24·27. $C_{11}H_{10}N_4O_2$ requires N, 24·34 per cent).

3-*Phenyl*-5-*amino*-6-*carboxy*-as-*triazine* (XLVI). 1-Phenyl-1-amino-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene (XLV) (3 g) was added to an aqueous potassium carbonate solution (1·8 g and 100 ml of water) and heated under reflux for about 15 min. When the yellow colour of the aminonitrile had completely disappeared, the solution was acidified with acetic acid and, on cooling, the crystalline precipitate was collected, and recrystallised from acetic acid, m.p. 184° (Found: N, 25·76. $C_{10}H_8N_4O_2$ requires N, 25·92 per cent).

3-*Phenyl*-5-*amino*-as-*triazine* (XLVII). 3-Phenyl-5-amino-6-carboxy-*as*-triazine (XLVI) (0·25 g) was heated at 190–200° for 1 hr in an oil-bath. After cooling, the material was dissolved in dilute acetic acid and the solution was treated with Norit, filtered and precipitated with ammonia solution to give colourless needles (yield 0·15 g), m.p. 249–250° after recrystallisation from water (Found: N, 32·36. $C_8H_8N_4$ requires N, 32·55 per cent).

3-*Phenyl*-5-*hydroxy*-as-*triazine* (XLVIII). 3-Phenyl-5-amino-*as*-triazine (XLVII) (0·2 g) was suspended in water (10 ml) containing 1 g of sodium hydroxide. The mixture

was heated under reflux until evolution of ammonia ceased, and it was then cooled, filtered and acidified with hydrochloric acid. The crude product was crystallised from water and from ethanol (yield 0·15 g), m.p. 245° (Found: N, 24·10. $C_9H_7N_3O$ requires N, 24·27 per cent).

3-*Phenyl*-5-*amino*-6-*carbomethoxy*-as-*triazine* (L). 1-Phenyl-1-amino-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene (XLV) (4 g) was dissolved in absolute methanol (60 ml) and a methanolic solution of sodium methoxide (0·2 g of sodium in 20 ml of methanol) was added. The mixture was heated under reflux for 10 min and the product was collected on cooling as straw-coloured crystals (yield 2·3 g), m.p. 232° (Found: N, 24·49. $C_{11}H_{10}N_4O_2$ requires N, 24·34 per cent).

3-*Phenyl*-5-*hydroxy*-6-*carboxy*-as-*triazine* (IL). 1-Phenyl-1-amino-4-cyano-4-carbomethoxy-2:3-diazabuta-1:3-diene (XLV) (1 g) was dissolved in hot water (15 ml) containing 0·3 g of sodium hydroxide. The solution was heated under reflux until evolution of ammonia ceased and it was then cooled, filtered and acidified with hydrochloric acid to give a product, m.p. 179–180° (Found: N, 19·60. $C_{10}H_7N_3O_3$ requires N, 19·35 per cent).

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