225. *Some Pyridyl Analogues of Triphenylmethane.*

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(*Note* by R. Wien and J. Harrison.)

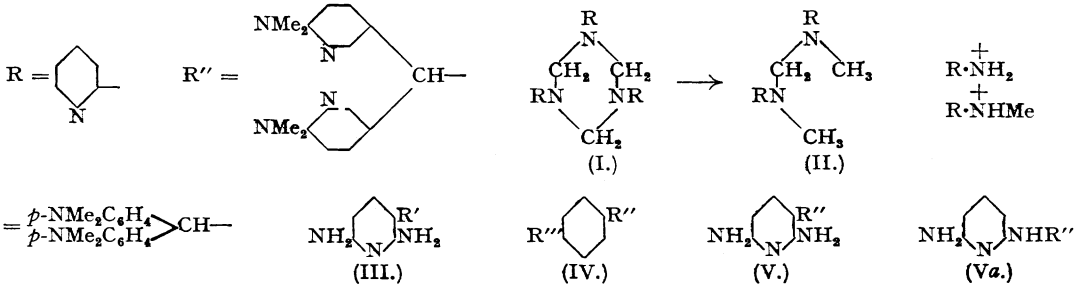
By an extension of Kern's method (G.P. 27032) for the synthesis of substituted triphenylmethanes from Michler's hydrol and arylamines, representative compounds of the *diphenylpyridyl-*, *phenyldipyridyl-*, and *tripyridyl-methane* series have been prepared. Biological examination of these new substances did not reveal any outstanding chemotherapeutic activity.

A new method is described for the preparation in quantity of di-(6-dimethylamino-3-pyridyl)thioketone.

The triphenylmethane dyestuffs were amongst the earliest effective chemotherapeutic agents against Gram-positive organisms, whilst certain members such as Malachite Green were also shown to be active in experimental trypanosomiasis. Although now largely displaced by the more effective sulphonamides, amidines, etc., such compounds as Gentian Violet still find limited application in the control of some infections (see Sutton, *J. Amer. Med. Assoc.*, 1938, **110**, 1733), and in the treatment of burns (Aldrich, *New England J. Med.*, 1937, **217**, 911). In addition Gentian Violet is the most effective anthelmintic against *Oxyuris vermicularis* (Wright and Brady, *J. Amer. Med. Assoc.*, 1940, **114**, 861) and is one of the few successful agents in *Strongyloides stercoralis* infestations.

The object of the present investigation was to determine whether the introduction of nuclear nitrogen into the benzenoid rings of the triphenylmethane dyestuffs would be accompanied by an increase in bactericidal activity, or by the appearance of novel pharmacological properties. Pyridyl analogues of triphenylmethane have previously been prepared (*a*) by condensation of pyridyl-2-aldehyde with dimethylaniline (Harries and Lenàrt, *Annalen*, 1915, **410**, 112), (*b*) from Michler's hydrol and 2-aminopyridine in sulphuric acid solution (Plazek and Sucharda, *Ber.*, 1928, **61**, 1811), (*c*) by the action of phenylmagnesium bromide on phenylpyridyl ketones (Tschitschibabin and Benewolenska, *Ber.*, 1928, **61**, 551), and (*d*) by condensation of 2-dimethylaminopyridine with benzaldehyde (Tschitschibabin and Knunjanz, *Ber.*, 1931, **64**, 2839).

On repeating the work of Plazek and Sucharda (*loc. cit.*) we found that we were unable to substantiate their claim that reaction (*b*) above leads to the formation of a tetramethyltriaminodiphenylpyridylmethane, m. p. 163° (uncorr.). In our hands condensation of 2-aminopyridine with Michler's hydrol in sulphuric acid solution gave a product, m. p. 173—175°, also obtained from 3- and 4-aminopyridines, which proved on analysis to be leuco-Crystal Violet. The formation of this compound from Michler's hydrol in acid solution has previously been demonstrated by Weil (*Ber.*, 1894, **27**, 3316).



The claim of Plazek and Sucharda (*loc. cit.*) that the reaction between 2-aminopyridine and Michler's hydrol leads to an atypical condensation in the 5-position of the pyridine nucleus has no other parallel in the literature. The only apparent analogy is the remarkable formation of di-(6-dimethylamino-3-pyridyl)-methane (R''H) from 2-aminopyridine by prolonged heating with formaldehyde–formic acid (Tschitschibabin and Knunjanz, *Ber.*, 1929, **62**, 3084). We have investigated this reaction as it represents the only authentic example of a condensation with an aldehyde involving the 5-position of 2-aminopyridine. The Russian authors had previously shown that 2-dimethylaminopyridine does not undergo reaction with formaldehyde–formic acid, and so cannot be an intermediate in the formation of R''H. When we submitted the complex reaction product of 2-aminopyridine with formaldehyde to vacuum distillation we obtained the *trimeride* of the hypothetical Schiff's base methylene-2-aminopyridine, $C_5H_4N{=}CH_2$, in a yield of approximately 20%. We have assigned the constitution of a 1 : 3 : 5-*tri*-(2'-*pyridyl*)-*trimethylenetriamine* (I) to this compound from analogy with the structure of the corresponding trimeride of methyleneaniline. Molecular weight micro-determinations (Rast), carried out by Drs. Weiler and Strauss (Oxford), gave values somewhat lower than required by (I), a behaviour exactly paralleled by the aniline analogue which, as shown by Miller and Wagner (*J. Amer. Chem. Soc.*, 1932, **54**, 3699), undergoes partial depolymerisation during molecular weight determinations in camphor. Reduction of (I) with formic acid at the boiling point gave a mixture from which 2-aminopyridine, 2-dimethylaminopyridine, and a *base*, $C_{13}H_{16}N_4$, were isolated. The last compound was recovered unchanged after treatment with dinitrobenzoyl chloride in pyridine, and so apparently has no free imino- or amino-groupings. We have therefore assigned it the constitution of a *methylene-di-*(*2-pyridylmethylamine*) (II), a structure agreeing well

with both its mode of formation and the behaviour on reduction of compounds of type (I) (cf., *e.g.*, Miller and Wagner, *ibid.*, p. 3700). Finally, Steinhäuser and Diepolder's benzylidene-2 : 2'-dipyridylamine (*J. pr. Chem.*, **1916, 93**, 392) gave, with formic acid, the known benzylaminopyridine (Tschitschibabin and Knunjanz, *ibid.*, p. 2893), there being no indication of the parallel formation of a dipyridylphenylmethane derivative. These observations led to the conclusion that the possibility of obtaining a triphenylmethane analogue from 2-aminopyridine is not very great, and threw doubt on the results of Plazek and Sucharda (*loc. cit.*).

We accordingly turned our attention to the reaction between Michler's hydrol and 2 : 6-diaminopyridine in sulphuric acid solution. Our reason for choosing the latter compound lay in the well-established reactivity of the 3-position in this base (cf., *e.g.*, Seide, *Ber.*, **1926, 59**, 2465). We succeeded thereby in preparing a monopyridyldiphenylmethane derivative in 40% yield. We have assigned it the constitution of a *di-(4-dimethylaminophenyl)-3'-(2' : 6'-diaminopyridyl)-methane* (III) on the basis of the analytical figures, the stability to acids (thus excluding a "leucauramine" type of structure), and the formation of a *dibenzoyl* derivative.

Di-(6-dimethylamino-3-pyridyl)-carbinol (R''OH), the dipyridyl analogue of Michler's hydrol, was obtained by Tschitschibabin and Knunjanz (*loc. cit.*) by the following series of reactions :

$$NH_2{\cdot}C_5H_4N \xrightarrow[H{\cdot}CHO]{H{\cdot}CO_2H} (NMe_2{\cdot}C_5H_3N)_2CH_2 \xrightarrow{S} (NMe_2{\cdot}C_5H_3N)_2CS$$

2-aminopyridine → di-(6-dimethylamino-3-pyridyl)methane → thioketone

$$\xrightarrow{HCl} (NMe_2{\cdot}C_5H_3N)_2CO \xrightarrow{NaHg} (NMe_2{\cdot}C_5H_3N)_2CHOH$$

di-(6-dimethylamino-3-pyridyl) ketone → di-(6-dimethylamino-3-pyridyl)-carbinol

When we attempted to prepare the thioketone by fusion of the methane base with sulphur at 190° under reduced pressure, we found that the scale of working specified by the Russian authors (3 g. methane base → 700 mg. thioketone) could not be increased without a drastic diminution in yield. We were, therefore, obliged to accumulate supplies of material by the tedious repetition of these small-scale preparations. It was only when the present investigation was practically completed that our continued attempts to evolve a suitable method for the preparation of the thioketone met with success. We observed that by carrying out the reaction in benzyl acetate, a solvent first used for sulphur reactions by Simpson (*J.*, 1939, 757), we occasionally obtained somewhat more encouraging results. We found ultimately that employment of technical ψ-cumene as a solvent led to yields of 40% thioketone, apparently independently of the scale of the experiment.

Condensation of di-(6-dimethylamino-3-pyridyl)-carbinol (R''OH) with aniline in sulphuric acid solution led to the formation of *4-aminophenyl-di-(6'-dimethylamino-3'-pyridyl)-methane* (IV; R''' = NH_2). The presence of one primary amino group in this compound was shown by the preparation of a *monobenzoyl* derivative which no longer gave a positive diazo-test. *4-Methylaminophenyl-di-(6'-dimethylamino-3'-pyridyl)-methane* (IV; R''' = NHMe), prepared in a similar way from monomethylaniline and R''OH, was characterised by a p-*toluenesulphonyl* derivative. Dimethylaniline gave *4-dimethylaminophenyl-di-(6'-dimethylamino-3'-pyridyl)-methane* (IV; R''' = NMe_2), although in only 17% yield. This compound resembled its aryl analogue, leuco-Crystal Violet, in the ease with which it underwent oxidation; thus, even picric acid converted it into a highly coloured dyestuff.

Condensation of R''OH with 2 : 6-diaminopyridine gave a 60% yield of a *compound*, $C_{20}H_{25}N_7$. We have assigned the constitution of a *di-(6'-dimethylamino-3'-pyridyl)-3-(2 : 6-diaminopyridyl)-methane* (V) to this product although, in contrast to (III), it formed only *monobenzoyl* and *mono*-p-*toluenesulphonyl* derivatives. Attempts to acetylate these compounds led to the formation of intractable gums. A "leucauramine" type of structure (V*a*) is not excluded by these observations. On the other hand such a formulation appears to be incorrect as we failed to obtain a leucauramine from R''OH and aniline by prolonged refluxing in various neutral solvents. Again, the reaction went equally smoothly in 30% sulphuric acid, a result that can hardly be reconciled with the well-established instability of leucauramines to acids.

We succeeded in oxidising some of the above pyridyl analogues of triphenylmethane to the dyestuffs with chloranil in alcoholic solution. In view of the small quantities of materials available, it did not prove feasible to isolate the carbinols in a state of purity. The crude oxidation products were directly converted into the highly coloured hydrochlorides, which were somewhat redder than the corresponding triaryl dyestuffs. These were used for biological examination without further purification.

Note.

*Therapeutic Activity.**

Antibacterial activity was tested by the serial dilutional method in nutrient broth against *Staphylococcus aureus*, *E. coli*, and *Pseudomonas pyocyanea*. The bacteriostatic activity (minimal effective concentration) was assessed by the turbidity of the broth after 18 hours' incubation at 37°. The toxicity was determined in mice by both intravenous and subcutaneous administration. The results are summarised below. All the above compounds were found to be inactive in *T. equiperdum* infections in mice.

* Work done in the Biological Division, May and Baker, Ltd., on behalf of the Therapeutic Research Corporation of Great Britain, Ltd.

Compound (hydrochloride).	L.D.$_{50}$ (mg./kg.). i/v.	s/c.	Antibacterial activity (minimal effective concentration). *Staph. aureus.*	*E. coli.*	*Ps. pyocyanea.*
Di-(6-dimethylamino-3-pyridyl) ketone	40	50	1 : 8,000	1 : 8,000	1 : 16,000
Di-(6-dimethylamino-3-pyridyl)carbinol	>40 (limit of solubility)	>50	1 : 8,000	1 : 8,000	1 : 16,000
4-Aminophenyl 2-pyridyl ketone	70	—	1 : 4,000	1 : 4,000	1 : 8,000
Di-(4-dimethylaminophenyl)-3′-(2′ : 6′-diaminopyridyl)-methane	20	—	1 : 8,000	1 : 2,000	1 : 2,000
Oxidation product	150	>400	1 : 32,000	1 : 2,000	1 : 2,000
4-Aminophenyl-di-(6-dimethylamino-3′-pyridyl)-methane	100	800	1 : 2,000	1 : 4,000	1 : 4,000
4-Methylaminophenyl-di-(6′-dimethylamino-3′-pyridyl)-methane	90	700	1 : 2,000	—	1 : 2,000
Oxidation product	150	220	1 : 256,000	—	1 : 2,000
4-Dimethylaminophenyl-di-(6′-dimethylamino-3′-pyridyl)-methane	—	—	1 : 2,000	1 : 2,000	1 : 4,000
Oxidation product	95	—	1 : 1,024,000	—	1 : 4,000
Di-(6-dimethylamino-3-pyridyl)-3′-(2′ : 6′-diaminopyridyl)-methane	240	750	1 : 1,000	—	1 : 2,000
Crystal violet	25	—	1 : 20,000,000	1 : 64,000	1 : 8,000
Gentian violet	—	—	1 : 20,000,000	—	—

Di-(6-dimethylamino-3-pyridyl)carbinol was tested against the following Gram-negative organisms, minimal effective concentrations being given :

B. coli-commune	1 : 2000	*S. paratyphi B* (2 vars.)	1 : 4000
B. coli-aerogenes	1 : 4000	*S. typhi-murium*	1 : 4000
B. dysenteriae (Flexner)	1 : 4000	*S. onteritidis*	1 : 4000
Salmonella typhi (2 vars.)	1 : 4000	*Proteus vulgaris*	1 : 4000
S. paratyphi A	1 : 4000		

It thus appears to have a specific effect against this type of organism, although not of a high order. It further appears that the leuco-compounds have approximately the same degree of activity against Gram negative organisms as against Gram positive organisms, whereas the oxidation products are many times more active against the latter than the former.

The oxidation product of 4-dimethylaminophenyl-di-(6′-dimethylamino-3′-pyridyl)-methane was also kindly tested by Dr. J. Ungar (Glaxo Laboratories, Ltd.) in tissue culture for toxicity to fibroblasts. Dilutions were made up in Tyrode solution and the tests performed on depression slides. In a dilution of 1 : 400,000 the outgrowth of cells in the control was greater than in the test slides, in which the cells began to degenerate.

Experimental.

M. p. s are corrected. Microanalyses are by Drs. Weiler and Strauss, Oxford, and The Wellcome Chemical Works, Dartford, Kent.

Condensation of Michler's Hydrol with the Aminopyridines.—To Michler's hydrol (2·7 g.) dissolved in water (20 ml.) and sulphuric acid (1·5 g.), the aminopyridine (1·0 g.) was added and the blue solution warmed for 4 hours on the water bath. The mixture was made alkaline, the greenish precipitate collected, dried, extracted with benzene, and crystallised from alcohol. The properties and results of analyses of the products isolated are given below, together with the data for leuco-Crystal Violet and the figures given by Plazek and Sucharda (*loc. cit.*) for their product.

	C, %.	H, %.	N, %.	M. p.
From 2-aminopyridine	80·1	8·2	11·7	173—175°
,, 3- ,,	80·4	8·3	11·4	173—175
,, 4- ,,	80·8	8·3	11·3	173—175
leuco-Crystal violet	80·4	8·3	11·3	172—173 (uncorr.)
Plazek and Sucharda	76·3	7·5	16·2	163 (uncorr.)

1 : 3 : 5-*Tri*-(2′-*pyridyl*)-*trimethylenetriamine* (I).—2-Aminopyridine (10 g.) was dissolved in formalin (30 ml.) and the solution evaporated to dryness on the water bath. The resinous solids were distilled and the fraction, b. p. 170—220°/15 mm., collected (5 g.). After dissolving in a little alcohol and standing for 12 hours at 0°, the crystalline product was collected and recrystallised from ligroin. 1 : 3 : 5-*Tri*-(2′-*pyridyl*)-*trimethylenetriamine* formed needles, m. p. 96° (Found : C, 67·9; H, 6·1; N, 26·5; *M*, 272. $C_{18}H_{18}N_6$ requires C, 67·9; H, 5·7; N, 26·4%; *M*, 318).

Methylene-di-(2-*pyridylmethylamine*) (II).—1 : 3 : 5-Tri-(2-pyridyl)-trimethylenetriamine (50 g.) was heated under reflux with formic acid (200 ml., *d* 1·2) for 12 hours. After removal of the volatile fraction by distillation on the water bath under reduced pressure, the residue was hydrolysed with conc. hydrochloric acid and the product distilled under reduced pressure. The fraction, b. p. 112—120°/20 mm. (15 g.), partly crystallised on standing at 0°, and was separated into a solid and a liquid fraction by decantation. The solid fraction, after crystallisation from ligroin, was identified as 2-aminopyridine by m. p. and by its dibenzoyl derivative, m. p. 167° (Found : N, 9·7. Calc. for $C_{19}H_{14}O_2N_2$: N, 9·3%) (Tschitschibabin and Bylinkin, *Ber.*, 1922, **55**, 1001). The liquid fraction was treated with benzoyl chloride in pyridine, the product distilled and the fraction, b. p. 200—205°/11 mm., collected; after further purification benzoyl-2-methylaminopyridine, m. p. 61—62°, was obtained (Found : N, 13·8. Calc. for $C_{13}H_{12}ON_2$: N, 13·2%) (Tschitschibabin and Knunjanz, *Ber.*, 1928, **61**, 2216, give m. p. 61—62° and b. p. 200°/11 mm.).

The fraction, b. p. 258—260°/20 mm., from the original distillation solidified on standing. After crystallisation from ligroin, it yielded *methylene-di-*(2-*pyridylmethylamine*) as white needles, m. p. 132—133° (Found : C, 68·0; H, 7·0; N, 25·0; *M*, 210. $C_{13}H_{16}N_4$ requires C, 68·4; H, 7·0; N, 24·6%; *M*, 228).

Di-(4-*dimethylaminophenyl*)-3′-(2′ : 6′-*diaminopyridyl*)-*methane* (III).—To Michler's hydrol (5·4 g.) dissolved in water

(40 ml.) and sulphuric acid (22 g., *d* 1·84), 2 : 6-diaminopyridine (2·2 g.) was added and the intense blue solution warmed on the water bath for 2 hours; on making the solution alkaline, a greenish gummy precipitate was produced and this eventually crystallised. It was collected, dried under reduced pressure, extracted with a little benzene, and crystallised twice from benzene–ligroin (1 : 1). *Di*-(4-*dimethylaminophenyl*)-3′-(2′ : 6′-*diaminopyridyl*)-*methane* formed colourless prisms, m. p. 181—182° (Found : C, 73·1; H, 7·5; N, 19·4. $C_{22}H_{27}N_5$ requires C, 73·1; H, 7·5; N, 19·4%). *Di*-(4-*dimethylaminophenyl*)-3′-(2′ : 6′-*dibenzamidopyridyl*)-*methane*, prepared by treating the base (1·5 g.) in dry pyridine (20 ml.) with benzoyl chloride (1·4 g.) for 12 hours at room temperature, followed by precipitation with alkali, formed silky needles from methanol, m. p. 143—144° (Found : C, 75·4; H, 6·3. $C_{36}H_{35}O_2N_5$ requires C, 75·6; H, 6·4%).

Improved Method for the Preparation of Di-(6-*dimethylamino*-3-*pyridyl*) *Thioketone.*—To di-(6-dimethylamino-3-pyridyl)-methane (54 g.) dissolved in ψ-cumene (60 ml.), finely powdered sulphur (15 g.) was added and the mixture heated under reflux for 4½ hours. After standing overnight at 0°, the deep purple crystalline mass of thioketone was collected, washed with a little methyl alcohol, and dried on the water bath; yield 25 g. Hydrolysis was accomplished essentially by the method of Tschitschibabin and Knunjanz (*loc. cit.*) : the thioketone (55 g.) was dissolved in 10% hydrochloric acid (700 ml.) and the deep violet solution heated under reflux until the colour had changed to pale brown (*ca.* 1 hour). The mixture was filtered, made alkaline with sodium hydroxide, and the pale yellow precipitate collected and crystallised from alcohol. Di-(6-dimethylamino-3-pyridyl) ketone separated in yellow plates, m. p. 169° (43 g., 34% calc. on the methane base).

4-*Aminophenyl-di*-(6′-*dimethylamino*-3′-*pyridyl*)-*methane* (IV; R‴ = NH_2).—To di-(6-dimethylamino-3-pyridyl)-carbinol (6 g.) dissolved in water (70 ml.) and sulphuric acid (15 g.), freshly redistilled aniline (2·5 g.) was added and the solution warmed for 7 hours on the water-bath. After making the solution alkaline, the solid product (8 g.) was collected, dried, dissolved in pyridine (40 ml.) and treated at 0° with excess of benzoyl chloride. After 12 hours at room temperature, excess of dilute ammonia was added and the precipitated material collected and crystallised from aqueous alcohol (4·2 g., 41%). 4-*Benzamidophenyl-di*-(6′-*dimethylamino*-3′-*pyridyl*)-*methane* formed nacreous white plates, m. p. 200° (Found : C, 74·1; H, 6·4; N, 15·8. $C_{28}H_{29}ON_5$ requires C, 74·5; H, 6·6; N, 15·5%). The benzamido-compound (3 g.) was hydrolysed by heating with syrupy phosphoric acid (9 ml.) for 1 hour at 200°, and the base (2·2 g., 96%) precipitated by addition of ammonia. 4-*Aminophenyl-di*-(6′-*dimethylamino*-3′-*pyridyl*)-*methane* was obtained in needles from aqueous alcohol, m. p. 146·5° (Found : C, 72·2; H, 7·1; N, 20·4. $C_{21}H_{25}N_5$ requires C, 72·6; H, 7·2; N, 20·2%).

4-*Methylaminophenyl-di*-(6′-*dimethylamino*-3′-*pyridyl*)-*methane* (IV; R‴ = NHMe).—This was prepared by heating the carbinol (6·0 g.), water (50 ml.), conc. sulphuric acid (10 g.) and monomethylaniline (2·8 g.) together for 7 hours on the water-bath. After basification, excess monomethylaniline was removed in steam, the product collected (2·8 g., 40%) and crystallised from aqueous alcohol and finally from ligroin. 4-*Methylaminophenyl-di*-(6′-*dimethylamino*-3′-*pyridyl*)-*methane* formed needles, m. p. 156—157° (Found : C, 73·1; H, 7·5; N, 19·4. $C_{22}H_{27}N_5$ requires C, 73·1; H, 7·5; N, 19·5%). The p-*toluenesulphonyl* derivative was prepared by heating the violet solution of the base (1·8 g.) in pyridine (10 ml.) and *p*-toluenesulphonyl chloride (1·0 g.) for 1½ hours on the water-bath, followed by precipitation with water; it formed needles from ligroin, m. p. 133° (Found : S, 6·0. $C_{29}H_{33}O_2N_5S$ requires S, 6·3%).

4-*Dimethylaminophenyl-di*-(6′-*dimethylamino*-3′-*pyridyl*)-*methane* (IV; R‴ = NMe_2).—This was prepared by heating the carbinol (3 g.), water (25 ml.), sulphuric acid (4 g.), and dimethylaniline (1·5 g.) for 10 hours on the water-bath. The product was extracted with benzene and crystallised from ligroin (780 mg., 17%). 4-*Dimethylaminophenyl-di*-(6′-*dimethylamino*-3′-*pyridyl*)-*methane* formed needles, m. p. 137° (Found : C, 73·6; H, 7·7; N, 18·8. $C_{23}H_{29}N_5$ requires C, 73·6; H, 7·7; N, 18·7%).

Di-(6′-*dimethylamino*-3′-*pyridyl*)-3-(2 : 6-*diaminopyridyl*)-*methane* (V) was prepared by heating together the carbinol (1·5 g.), water (12 ml.), sulphuric acid (2 g.), and 2 : 6-diaminopyridine (0·7 g.) for 7 hours on the water-bath. The product (7·3 g., 62%) was extracted with a little benzene and crystallised from ligroin–methanol. *Di*-(6′-*dimethylamino*-3′-*pyridyl*)-3-(2 : 6-*diaminopyridyl*)-*methane* formed cubic crystals, m. p. 233° (Found : C, 66·0; H, 6·9; N, 27·0. $C_{20}H_{25}N_7$ requires C, 66·1; H, 6·9; N, 27·0%). The *monobenzoyl* derivative formed needles from alcohol, m. p. 210° (Found : C, 69·0; H, 6·2. $C_{27}H_{29}ON_7$ requires C, 69·4; H, 6·2%). The *mono*-p-*toluenesulphonyl* derivative formed yellow flat prisms from aqueous pyridine, m. p. 234—235° (Found : S, 6·2. $C_{27}H_{31}O_2N_7S$ requires S, 6·2%).

Chloranil Oxidations.—The base (1·0 g.), dissolved in alcohol (20 ml.), was heated under reflux with chloranil (600 mg.) for 1 hour. The mixture was evaporated to dryness on the water bath, the residue dissolved in a little water and made alkaline with 5% sodium hydroxide solution. The gummy precipitate was extracted with benzene or ether, the filtered solution extracted with conc. hydrochloric acid and the intensely coloured acid liquors evaporated to dryness. The residue, dissolved in methanol, was saturated with hydrogen chloride, and the solution evaporated to dryness; this residue was washed with dry ether and dried under reduced pressure. The hydrochlorides formed crystalline hygroscopic powders. The colours of the dilute solutions were as follows : Oxidation product from : (III), blue–blue green; (IV) (R‴ = NHMe), magenta; (IV) (R‴ = NMe_2), mauve. Dyestuffs could not be obtained from (IV) (R‴ = NH_2) or from (V).

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