144. *Xylopic Acid. Part I.*

By Hussein A. Fahim and Ibrahim R. Shimi.

Xylopic acid, $C_{22}H_{32}O_4$ (Fahmy, El Deeb, and Karawya, *Proc. Pharm. Soc., Egypt*, 1951, **33**, 33) has been obtained in improved yield from the pericarp of *Xylopia æthiopica*, by the use of low-boiling light petroleum or aqueous pyridine. The acid gave a methyl ester, acid chloride, and amide. It exhibted no reducing properties, did not contain alkoxyl groups, and did not react with *p*-nitrophenylhydrazine, acetic anhydride, or benzoyl chloride. The absence of selective absorption between 200 and 400 mμ suggests that chromophoric groups are absent.

Experimental.—Xylopic acid. The acid formed small plates, m. p. 265—266°, $[\alpha]_D^{20\cdot5}$ −127° (in $CHCl_3$) [Found: C, 73·8, 74·0, 73·7; H, 8·9, 9·1, 9·3%; *M* (Rast), 368, 361; equiv. (by titration), 358·9, 357·4, 359·8, 360·3. $C_{22}H_{32}O_4$ requires C, 73·3; H, 8·9%; *M*, 360·5]. It was sparingly soluble in carbon disulphide, ether, and acetone, and sparingly soluble in light petroleum.

Derivatives. Treatment with diazomethane or methyl sulphate gave the *methyl* ester as plates, m. p. 124° (Found: C, 73·8; H, 9·1. $C_{23}H_{34}O_4$ requires C, 73·8; H, 9·1%). The acid chloride was prepared by refluxing the acid with excess of oxalyl chloride for 6 hours; treatment with ammonia then gave the *amide*, microscopic plates [from ethyl acetate–light petroleum (b. p. 40—60°)], m. p. 196—198° (decomp.) (Found: C, 73·4; H, 9·1; N, 3·4, 3·5, 3·6. $C_{22}H_{33}O_3N$ requires C, 73·5; H, 9·2; N, 3·9%).

Action of nitric acid. The acid was treated with a mixture of fuming and concentrated nitric acid (equal volumes) at 5—20° for 1 hour. The white product was purified by repeated treatment with benzene and light petroleum (b. p. 80—100°), giving a nitrogenous acid, m. p. 146° (decomp.) (Found: equiv., 301·3, 303·8).

The authors thank the Pharmacognosy Department for providing them with some xylopic acid extracts and the fruits, and Dr. M. H. Shaker, Biochemistry Dept., Fouad I Institute of Tropical Diseases, for providing the absorption spectrum data.

Fouad I University, Cairo, Egypt. [*Received, May 27th*, 1952.]

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145. *The Stereochemistry of Scopolamine.*

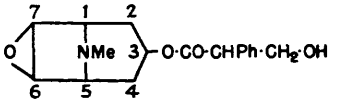
By Jerrold Meinwald.

Although no experiments designed to elucidate the stereochemistry of scopolamine (I) have been recorded, it is possible to assign unambiguously configurations to all five asymmetric centres in the bicyclic nucleus on the basis of facts already known (Henry, "The Plant Alkaloids," J. and A. Churchill, Ltd., London, 1949; Manske and Holmes, "The Alkaloids," Academic Press, New York, 1950, Vol. I).

The key is the structure of a hydrolysis product, scopoline, which requires the configuration (II). The oxide bridge of scopoline must be *trans* to the nitrogen bridge if the structure is to be sterically possible. The hydroxyl group at $C_{(7)}$ would be expected to be *trans* to the oxide bridge, since it must be formed by an internal nucleophilic opening of a *cis*-epoxide (Bartlett, *J. Amer. Chem. Soc.*, 1935, **57**, 224; Wilson and Lucas, *ibid.*, 1936, **58**, 2396). Thus, scopine, the immediate precursor of scopoline, must be (III) in order to satisfy the geometrical requirements for the internal displacement reaction. It would be difficult to envisage a path for the exceedingly ready rearrangement of scopine to scopoline if the displacing $C_{(3)}$-hydroxyl group were not *trans* to both the nitrogen bridge and the epoxide ring. Finally, since normal ester hydrolysis does not alter the configuration of the alcoholic component (cf. Alexander, "Principles of Ionic Organic Reaction Mechanisms," J. Wiley and Sons, New York, 1950), scopolamine itself must be represented by (IV).

Confirmatory evidence is provided by the novel transformations which occur when scopolamine is treated with hydrogen peroxide. Two epimeric *N*-oxides would normally

be expected. In fact, one such oxide (V) is the chief product. A secondary product, however, can be isolated as a crystalline, tetracyclic, quaternary bromide (VII), the formation of which is best represented as an internal displacement of tropate anion from the epimeric *N*-oxide (VI). This change emphasizes the necessity of a *trans*-relation



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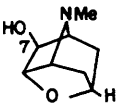

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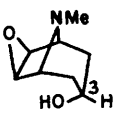

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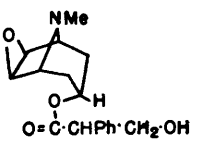

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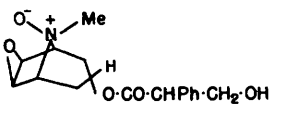

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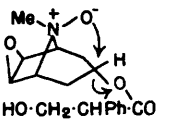

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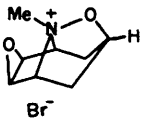

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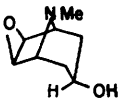

(VIII)

between the nitrogen bridge and the oxygen atom at $C_{(3)}$ in scopolamine itself. *pseudo*-Scopine, the product of chemical reduction of scopolinium bromide (VII), is then seen to have the $C_{(3)}$-hydroxyl group *cis* to the nitrogen bridge, as shown in (VIII). It is stable under the conditions which convert scopine into scopoline, as would be expected.

[Added, Oct. 1st, 1952.] Since the submission of this Note, a similar conclusion has been recorded independently by Fodor (*Nature*, 1952, **170**, 278).

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146. *Chloramines as a Source of Iodine Chloride. The Preparation of Iodo-phenols, -naphthols, and -aromatic Ethers by Means of a Chloramine and an Iodide.*

By BRYNMOR JONES and EILEEN N. RICHARDSON.

THE value of chloramines as chlorinating agents has long been established but, as Chattaway (*J.*, 1905, **87**, 145) and Orton (*Proc.*, 1909, **25**, 306) showed, the nature of the halogenating agent to which they give rise is determined by the nature of the halogen acid added, in accordance with the equation, $>NCl + HX = >NH + XCl$; *e.g.*, using dichloramine-T and hydrogen iodide, or, better, sodium iodide, Bradfield, Orton, and Roberts (*J.*, 1928, 782) readily prepared an acetic acid solution of iodine chloride suitable for use in the iodination of anilines. This reagent has now been applied to the iodination of phenols, hydroxybenzoic and hydroxynaphthoic acids, and aromatic ethers.

The range of such compounds which can conveniently be iodinated is limited by their susceptibility to oxidation and by the ease with which they undergo substitution. Highly reactive compounds, such as phenol, *p*-cresol, α- and β-naphthols, and even 4-chloro-1-naphthol undergo both iodination and oxidation, and give rather intractable tarry products. Less reactive hydroxy-compounds, such as the mono-halogeno- and -nitro-phenols, and the hydroxybenzoic acids, with one equivalent of the reagent, give mixtures of mono- and di-iodo-derivatives which are not easily separated: with two equivalents they give high yields of the di-iodo-compounds. On the other hand, 2 : 4-dihalogenophenols, 3-nitro-*p*-cresol and 3- and 6-hydroxy-2-naphthoic acids give excellent yields of the monoiodo-derivatives. Of the ethers examined, only those formed from the more reactive hydroxy-compounds undergo iodination smoothly. Others, such as *p*-bromoanisole, anisic acid, benzyl 4-chloro-1-naphthyl ether, and 4-ethoxy-1-naphthoic acid, do not react appreciably. The behaviour of the three isomeric dimethoxybenzenes shows that the *m*-isomer alone gives a high yield of a di-iodo-derivative. The yields of pure

products from the *m*-, *o*-, and *p*-isomers were 75, 30, and 20% respectively (cf. de la Mare and Vernon, *J.*, 1951, 1764).

The following table summarises the principal results obtained.

(M. p.s are uncorrected. Microanalyses were carried out by Drs. Weiler and Strauss, Oxford.)

Reactant	ICl, equiv.	Products	M. p.*	Yield, %	Formula	Found, % C	Found, % H	Reqd., % C	Reqd., % H
Anisole	1	*p*-Iodoanisole	52°	90	—	—	—	—	—
Phenetole	1	*p*-Iodophenetole	27	90	—	—	—	—	—
2-Naphthyl methyl ether	1	1-Iodo-2-naphthyl methyl ether	88	90	$C_{11}H_9OI$	47·0	3·3	46·5	3·2 [1]
2-Naphthyl ethyl ether	1	*Ethyl 1-iodo-2-naphthyl ether*	74	87	$C_{12}H_{11}OI$	48·3	4·1	48·3	3·7
1-Naphthyl ethyl ether	1	*Ethyl 4-iodo-1-naphthyl ether*	45	82	—	48·4	3·6	,,	,,
2 : 4-Dichlorophenol	1	2 : 4-Dichloro-6-iodophenol	62	80	—	—	—	—	— [2]
2 : 4-Dibromophenol	1	2 : 4-Dibromo-6-iodophenol	104	80	—	—	—	—	— [3]
3-Nitro-*p*-cresol	1	5-Iodo-3-nitro-*p*-cresol	83	90	$C_7H_6NO_3I$	30·2	2·0	30·1	2·2 [4]
2-Chloro-*m*-5-xylenol	1	2-Chloro-4-iodo-*m*-5-xylenol and 2-Chloro-4 : 6-di-iodo-*m*-5-xylenol	90 131	65	C_8H_8OClI	34·3	2·9	34·0	2·9 [5]
2-Chloro-*m*-5-xylenol	2	2-Chloro-4 : 6-di-iodo-*m*-xylenol	131	95	$C_8H_7OClI_2$	23·6	2·1	23·5	1·8
2 : 4-Dichloro-*m*-5-xylenol	1	2 : 4-*Dichloro*-6-*iodo*-m-5-*xylenol*	130	90	$C_8H_7OCl_2I$	30·2	2·2	30·3	2·2
Salicylic acid	2	3 : 5-Di-iodosalicylic acid	233	85	—	—	—	—	— [6]
p-Hydroxybenzoic acid	2	4-Hydroxy-3 : 5-di-iodobenzoic acid	262* (255°)	90	$C_7H_4O_3I_2$	22·0	1·2	21·5	1·0 [7]
3-Hydroxy-2-naphthoic acid	1	3-*Hydroxy*-4-*iodo*-2-*naphthoic acid*	d. (210°)	80	$C_{11}H_7O_3I$	42·1	2·3	42·0	2·2
6-Hydroxy-2-naphthoic acid	1	6-*Hydroxy*-5-*iodo*-2-*naphthoic acid*	234 (223°)	92	$C_{11}H_7O_3I$	42·1	2·1	42·0	2·2
6-Methoxy-2-naphthoic acid	1	5-*Iodo*-6-*methoxy*-2-*naphthoic acid*	d. (292°)	90	$C_{12}H_9O_3I$	44·0	2·7‡	43·9	2·7
6-*n*-Lauroyloxy-2-naphthoic acid	1	5-*Iodo*-6-n-*lauroyloxy*-2-*naphthoic acid*	†	90	$C_{23}H_{31}O_3I$	57·5	6·4	57·2	6·5 [8]
7-*n*-Octyloxy-2-naphthoic acid (m. p. 141°)	1	8-*Iodo*-7-n-*octyloxy*-2-*naphthoic acid*	148	90	$C_{19}H_{23}O_3I$	53·8	5·3	53·5	5·4
7-*n*-Cetyloxy-2-naphthoic acid (m. p. 137°)	1	7-n-*Cetyloxy*-8-*iodo*-2-*naphthoic acid*	123	90	$C_{27}H_{39}O_3I$	60·4	7·5	60·2	7·3
m-Dimethoxybenzene	2	4 : 6-*Di-iodo*-1 : 3-*dimethoxybenzene*	198—199	75	$C_8H_8O_2I_2$	24·9	2·0	24·7	2·1 [9]
o-Dimethoxybenzene	2	4 : 5-Di-iodo-1 : 2-dimethoxybenzene	134	30	—	24·9	2·3	,,	,, [10]
p-Dimethoxybenzene	2	2 : 5-Di-iodo-1 : 4-dimethoxybenzene	171	20	—	24·9	2·1	,,	,, [11]
Methyl *m*-5-xylyl ether	2	2 : 4-*Di-iodo*-3 : 5-*dimethylphenyl methyl ether*	125	50	$C_9H_{10}OI_2$	27·9	2·5	27·8	2·6

* Temperatures in parentheses are those at and above which iodine is evolved; d. = decomp.
† Mesomorphic: smectic phase 145—167°, nematic phase 167—170°.
‡ Found: I, 38·5. Calc. for $C_{12}H_9O_3I$: I, 38·7%.

[1] Ray and Moonaw (*J. Amer. Chem. Soc.*, 1933, **55**, 3833) record m. p. 88°. [2] Kohn and Sussman (*Monatsh.*, 1925, **46**, 594) give m. p. 63°. [3] Kohn and Sussman (*loc. cit.*) record m. p. 106°; Brenans and Girod (*Compt. rend.*, 1928, **186**, 1130) give m. p. 104°. [4] Datta and Prosad (*J. Amer. Chem. Soc.*, 1917, **39**, 446) give m. p. 83·5°. [5] Bordeianu (*Ann. Sci. Univ. Jassy*, 1937, **23**, 240; *Chem. Abs.*, 1938, 5802) gives m. p.s of 92—93° and 131—132°, respectively. [6] Woollett and Johnson (*Org. Synth.*, 1934, **14**, 52) give m. p. 235—236°. [7] Woollett and Johnson (*loc. cit.*) record m. p. 278—279° (corr.). [8] Cf. Gray and Brynmor Jones (*Nature*, 1951, **167**, 83; 1952, **170**, 451). [9] Cf. Meerwein, Hoffmann, and Schill (*J. prakt. Chem.*, 1940, **154**, 266). [10] G. M. Robinson (*J.*, 1916, **109**, 1086) gives m. p. 132°. [11] G. M. Robinson (*loc. cit.*) records m. p. 171°.

In the majority of cases the reagent was added cautiously to a well-stirred solution of the phenol or ether in acetic acid at room temperature, but, because of their low solubility, the

hydroxy- and alkoxy-naphthoic acids were iodinated at 60—75°. Occasionally some of the products were in part deposited from solution, but generally they were isolated by dilution to 50% acetic acid. At this dilution little toluenesulphonamide separated, and the iodo-derivatives were readily purified by crystallisation from alcohol or acetic acid.

Grateful acknowledgment is made to the Distillers Co. Ltd. and to Imperial Chemical Industries Limited for grants to the Department. The authors are also indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of them and to Mr. G. W. Gray, B.Sc., for samples of the alkoxynaphthoic acids.

UNIVERSITY COLLEGE, HULL. [*Received, September 16th*, 1952.]

147. *The Volatile Oil of* Metrosideros scandens.

By A. J. BIRCH.

GARDNER (*J. Soc. Chem. Ind.*, 1931, **50**, 141T) found the oil of *Metrosideros scandens* to contain a high proportion of a sesquiterpene hydrocarbon which by dehydrogenation gave cadalene and an unidentified azulene, and by the action of hydrogen chloride gave what appeared to be (+)-cadinene dihydrochloride. Its physical constants were in agreement with a tricyclic structure, and the formation of azulene and naphthalene derivatives from the same substance would make the structure of considerable interest. We find the reactions of this sesquiterpene to be explained by its containing (−)-aromadendrene and (−)-cadinene or a cadinene isomer.

Experimental.—A specimen of the oil (50 c.c.) was kindly given to the author by Dr. W. I. Taylor who had collected and distilled it near Auckland (N.Z.). Distillation, followed by fractionation over sodium, gave fractions (i) (21 c.c.) b. p. 96°/2 mm., $[\alpha]_D$ −22°, n_D^{18} 1·5010, d_{18}^{18} 0·9202 (Found: C, 88·3; H, 11·9. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%), and (ii) (6 c.c.) b. p. 100—102°/2 mm., $[\alpha]_D$ −80°.

Fraction (i) was principally (−)-aromadendrene. It had infra-red bands at 6·06 and 11·27 μ due to $C(CH_2)$, and was converted by ozonolysis into formaldehyde (2 : 4-dinitrophenylhydrazone, m. p. 177°) and α-*apo*aromadendrone, m. p. 71°, $[\alpha]_D$ −5·6° in EtOH, which gave rise on the steam-bath to *apo*aromadendrone, $[\alpha]_D$ +3·5° in EtOH, m. p. 83—84° undepressed by an authentic specimen kindly supplied by Professor F. N. Lahey (Brisbane). Dehydrogenation with sulphur at 280° (3 minutes) followed by chromatography in light petroleum (b. p. 40—60°) on alumina gave guaiazulene, identified as its trinitrobenzene complex, m. p. 150—151°, undepressed by an authentic specimen (m. p. 151—152°) kindly supplied by Dr. A. Fürst (Zurich); no cadalene could be detected. The action of hydrogen chloride in ether on the hydrocarbon gave no crystalline product.

Fraction (ii) on dehydrogenation and chromatography as above gave cadalene, identified as the trinitrobenzene complex, m. p. and mixed m. p. 113°. No azulene was formed. Dry hydrogen chloride gave (+)-cadinene dihydrochloride, m. p. 117°. The structure of this derivative was confirmed by refluxing it with sodium acetate in acetic acid and dehydrogenating the product as above to cadalene (trinitrobenzene complex, m. p. 113°).

M. p.s are corrected.

This work was carried out during the tenure of the Smithson Fellowship of the Royal Society.

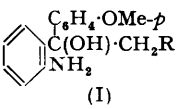
UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, October 20th*, 1952.]

148. *The Use of Sodamide in Preparation of 2- and 3-Pyridylmethylcarbinols.*

By A. J. Nunn and K. Schofield.

We have described the preparation of (I; R = 2-pyridyl) and related compounds from 2-pyridylmethyl-lithium and 2-amino-4'-methoxybenzophenone (Nunn and Schofield, *J.*, 1952, 589). The preparation by Brown and Murphey (*J. Amer. Chem. Soc.*, 1951, **73**, 3308) of 2-, 3-, and 4-ethylpyridine from methyl chloride and 2-, 3-, and 4-picoline in the presence of sodamide or potassamide in liquid ammonia suggested the use of similar methods for the synthesis of (I; R = 3- and 4-pyridyl). For comparison with the earlier experiments using 2-pyridylmethyl-lithium, 2-amino-4'-methoxybenzophenone was also treated with two equivalents of 2-picoline and sodamide in liquid ammonia. The yield of (I; R = 2-pyridyl) was approximately the same from both reactions (*ca.* 50%). Yields of (I; R = 3-pyridyl) from 3-picoline by the sodium method were lower, but were improved by using a larger excess of the reagent.

By treatment of 2-amino-4'-methoxybenzophenone with 4-picoline and sodamide in liquid ammonia a yellow compound $C_{14}H_{14}ON_2$ was obtained. This also resulted when the 4-picoline was omitted and was clearly 2-amino-4'-methoxybenzophenone imine (II). It was hydrolysed by hot dilute acid, or by passage in benzene over alumina, to the parent ketone, and on diazotisation provided the yellow 4-*p*-methoxyphenylbenzotriazine (III). The formation of ketimines by this method does not appear to have been observed previously, and the synthesis of a benzotriazine from an unmodified ketimine also appears to be new.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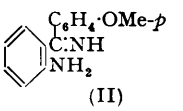
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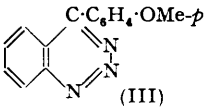
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Experimental.—1-o-*Aminophenyl*-1-p-*methoxyphenyl*-2-2'-*pyridylethanol.* To a suspension of sodamide [prepared according to Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120) from 2·5 g. of sodium] in liquid ammonia (150 c.c.), 2-picoline (9·3 g., 0·1 mole) was added during 5 minutes and the red solution was stirred for ¼ hour. 2-Amino-4'-methoxybenzophenone (11·4 g., 0·05 mole) in 2-picoline (5 c.c.) and dry ether (40 c.c.) was added during 10 minutes, the mixture was stirred for 4 hours, the ammonia allowed to evaporate, and the residue then decomposed with wet ether (100 c.c.) and water (30 c.c.). The yellow solid (10·8 g.; m. p. 128—150°) which separated crystallised from methanol (charcoal) as needles of 1-*o*-aminophenyl-1-*p*-methoxyphenyl-2-2'-pyridylethanol (8·0 g., 49·6%), m. p. 154—155°, identical with an authentic specimen (Schofield, *J.*, 1949, 2408).

1-o-*Aminophenyl*-1-p-*methoxyphenyl*-2-3'-*pyridylethanol.* 2-Amino-4'-methoxybenzophenone (7·6 g., 0·03 mole) in 3-picoline (4 c.c.) and dry ether (30 c.c.) was added to 3-pyridylmethylsodium [0·1 mole, formed by stirring 3-picoline (9·3 g.) for 3 hours with sodamide [from 2·5 g. of sodium) in liquid ammonia (150 c.c.)], the reaction mixture was worked up as described above, and the product was extracted with ether. The red gum remaining after removal of the dried (Na_2SO_4) solvent crystallised from benzene–ligroin (b. p. 60—80°) and the resulting yellow crystals were digested with hot benzene (20 c.c.). The residue remaining on cooling (2·1 g.; m. p. 135—145°) gave crystals (1·6 g., 14·5%; m. p. 161—163°) from aqueous alcohol. The *alcohol* separated from ethanol as needles, m. p. 169—170° (Found: C, 75·4; H, 6·1. $C_{20}H_{20}O_2N_2$ requires C, 75·0; H, 6·3%).

2-*Amino*-4'-*methoxybenzophenone imine.* (*a*) 4-Pyridylmethylsodium (0·1 mole, prepared from 4-picoline as described for the 3-isomer) was treated with 2-amino-4'-methoxybenzophenone (7·6 g.) in 4-picoline (4 c.c.) and ether (30 c.c.). The mixture was stirred for 4 hours, left overnight, and then decomposed with wet ether. The red gum, obtained from the ethereal extract, was dissolved in alcohol (8 c.c.) and the yellow *imine* (5·0 g.; m. p. 75—90°) which separated on cooling was recrystallised from benzene and then from alcohol as prisms (2·8 g., 26·1%), m. p. 91—92° (Found: C, 73·6; H, 6·2; N, 12·7. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2; N, 12·4%).

When the reaction time was doubled, a 29·4% yield resulted.

(*b*) 2-Amino-4′-methoxybenzophenone (7·6 g., 0·03 mole) in dry pyridine (4 c.c.) and ether (25 c.c.) was added during 5 minutes to a suspension of sodamide (from 2·5 g. of sodium) in liquid ammonia (200 c.c.). The mixture was stirred for 3 hours, left overnight, and decomposed with wet ether. The ethereal extract was washed with water and dried (Na_2SO_4). Removal of the solvent left a red gum which on dissolution in hot ethanol (8 c.c.) gave yellow crystals (3·6 g.), m. p. 85—87°. Yellow prisms (2·57 g.), m. p. 87—88°, separated from aqueous ethanol and gave a mixed m. p. of 88—90° with 2-amino-4′-methoxybenzophenone imine (m. p. 91—92°).

4-p-*Methoxyphenylbenzotriazine*. The imine (0·25 g.) in hydrochloric acid (10 c.c.; 2N) was treated at 0° with aqueous sodium nitrite (3 c.c.; 5%), whereupon a yellow solid (0·25 g.), m. p. 138—139°, separated immediately. Recrystallisation from benzene gave yellow plates of 4-p-*methoxyphenylbenzotriazine*, m. p. 138—139° (Found: C, 70·5; H, 4·6; N, 16·9. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·7; N, 17·7%).

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149. *An Improved Preparation of Phenanthridine.*

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SEVERAL methods of obtaining phenanthridine have been described (Theobald and Schofield, *Chem. Reviews*, 1950, **46**, 171; Badger, Seidler, and Thomson, *J.*, 1951, 3207), but the simplest, the cyclisation of 2-formamidodiphenyl, has hitherto yielded only 42% of the base [zinc chloride being the cyclising agent (Morgan and Walls, *J.*, 1932, 2225)], and involves a somewhat tedious purification. Recent demonstrations of the value of the combined action of stannic chloride and phosphorus oxychloride in cyclisations of this type (Barber *et al.*, *J. Soc. Chem. Ind.*, 1950, **69**, 82; Petrow and Wragg, *J.*, 1950, 3516; Nunn, Schofield, and Theobald, *J.*, 1952, 2797) suggested their application to 2-formamidodiphenyl. Several experiments indicated the advantage of using 2 mols. of stannic chloride, the yield of phenanthridine thus being raised to 90%.

Phenanthridine.—2-Formamidodiphenyl (Pictet and Hubert, *Ber.*, 1896, **29**, 1182) (10 g.), phosphorus oxychloride (50 c.c.), nitrobenzene (100 c.c.), and anhydrous stannic chloride (5·4 g.) were refluxed for 4 hours. The solvent was removed by steam-distillation, and the residual suspension was basified with ammonia solution. The product was crystallised from ligroin (b. p. 60—80°) giving phenanthridine (7·7 g.; 90%), m. p. 105—106° (Found: C, 87·0; H, 5·1. Calc. for $C_{13}H_9N$: C, 87·1; H, 5·1%).

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