Carcinogenic Nitrogen Compounds. Part LXXII.[1] The Möhlau–Bischler Reaction as a Preparative Route to 2-Arylindoles

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The Mohlau–Bischler cyclisation of ω-arylamino-ketones in the presence of arylamine hydrochlorides proved a convenient method for the preparation of diversely substituted 2-arylindoles, including polycyclic indoles; several are inducers of zoxazolamine hydroxylase.

2-ARYLINDOLES are of biochemical interest because of their structural relationship with carcinogenic indenoindoles [2] and carbazoles,[3] and because of the possibility of their being competitive substrates for the enzymes which metabolise physiological derivatives of indole (such as tryptophan). The classical method for their synthesis, *i.e.* the Fischer reaction, requires arylhydrazines, the preparation of which might present some inconveniences (especially in the case of polycyclic derivatives), as is seen later. Our need for a large number of 2-arylindoles, some of them polycyclic, prompted us to investigate an alternative route *via* the so-called Bischler reaction,[4] *i.e.* the cyclisation of ω-arylamino-ketones in the presence of the appropriate arylamine salts, or of ω-halogenated ketones with an arylamine in excess. Although the mechanism of this

[1] Part LXXI, N. P. Buu-Hoï, M. Dufour, P. Jacquignon, M. Renson, G. Maréchal, and A. Ruwet, *J. Chem. Soc.* (*C*), 1971, 2308.

[2] A. Lacassagne, N. P. Buu-Hoï, F. Zajdela, and N. D. Xuong, *Bull. Cancer*, 1955, **42**, 3.

[3] E. Boyland and A. M. Brues, *Proc. Roy. Soc.*, 1937, *B* **122**, 429; A. Lacassagne, N. P. Buu-Hoï, R. Royer, and F. Zajdela, *Compt. rend. Soc. biol.*, 1947, **141**, 635; A. H. M. Kirby and P. R. Peacock, *Brit. J. Exp. Path.*, 1946, **27**, 179.

[4] As Möhlau's discovery of this reaction (R. Möhlau, *Ber.*, 1881, **14**, 171; 1882, **15**, 2480) preceded Bischler's investigations by 11 years (A. Bischler, *Ber.*, 1892, **25**, 2860), it is only just to add Möhlau's name to the reaction.

reaction has been widely studied,[5] hitherto it has rarely been used for preparative purposes.[6] It has now proved most successful for the preparation of a wide range of 2-arylindoles substituted in the six-membered ring; overall yields of above 50% have been regularly obtained from substituted anilines and ω-bromoacetophenones when the intermediate ω-arylamino-ketones ArNH·CH_2·COAr′ were isolated and then cyclised. In particular this method is superior to the Fischer reaction for salts in the Möhlau–Bischler reaction when the ω-arylamino-ketone is particularly prone to cyclisation. (*b*) Cyclisation of *N*-(3,4-xylyl)aminoacetophenone occurred in both *o*- and *p*-positions, with the latter predominant.[7] Evidence that the higher-melting isomer obtained in this cyclisation was 5,6-dimethyl-2-phenylindole was furnished by its i.r. spectrum, which showed an intense band in 850—900 cm^{-1} region, similar to the one observed with pseudocumidine (at 850—880 cm^{-1})

TABLE 1

New indoles

Indole[a]	M.p.	Formula	Found (%) C	Found (%) H	Found (%) N	Requires (%) C	Requires (%) H	Requires (%) N
5,7-Dimethyl-2-phenyl	86°	$C_{16}H_{15}N$	86·6	6·9	6·2	86·8	6·8	6·4
picrate	164	$C_{22}H_{18}N_4O_7$	59·0	4·1	12·3	58·7	4·0	12·4
4,7-Dimethyl-2-phenyl	72	$C_{16}H_{15}N$	86·6	6·9	6·1	86·8	6·8	6·4
picrate	163	$C_{22}H_{18}N_4O_7$	58·4	4·0	12·2	58·7	4·0	12·4
4,6-Dimethyl-2-phenyl	105	$C_{16}H_{15}N$	86·8	6·9	6·3	86·8	6·8	6·4
picrate	150	$C_{22}H_{18}N_4O_7$	59·0	4·0	12·1	58·7	4·0	12·4
5,6-Dimethyl-2-phenyl[b]	226	$C_{16}H_{15}N$	86·5	6·8	6·1	86·8	6·8	6·4
picrate	163	$C_{22}H_{18}N_4O_7$	59·0	4·1	12·1	58·7	4·0	12·4
4,5-Dimethyl-2-phenyl	137	$C_{16}H_{15}N$	86·9	6·9	6·1	86·8	6·8	6·4
picrate	161	$C_{22}H_{18}N_4O_7$	58·7	4·0	12·1	58·7	4·0	12·4
6,7-Dimethyl-2-phenyl	134	$C_{16}H_{15}N$	86·7	6·8	6·2	86·8	6·8	6·4
picrate	161	$C_{22}H_{18}N_4O_7$	58·4	4·0	12·1	58·7	4·0	12·4
4,5,7-Trimethyl-2-phenyl	129	$C_{17}H_{17}N$	86·6	7·3	5·6	86·7	7·3	5·9
picrate	182	$C_{23}H_{20}N_4O_7$	59·5	4·3	12·5	59·5	4·3	12·1
3,4,5,7-Trimethyl-2-phenyl	151	$C_{18}H_{19}N$	86·6	7·7	5·4	86·7	7·7	5·6
picrate	143	$C_{24}H_{22}N_4O_7$	60·3	4·7	11·5	60·2	4·6	11·7
4,5,7-Trimethyl-2-(*o*-tolyl)	98	$C_{18}H_{19}N$	86·4	7·7	5·3	86·7	7·7	5·6
picrate	131	$C_{24}H_{22}N_4O_7$			11·7			11·7
4,5,7-Trimethyl-2-(*p*-tolyl)	158	$C_{18}H_{19}N$	86·6	7·7	5·5	86·7	7·7	5·6
picrate	171	$C_{24}H_{22}N_4O_7$			11·4			11·7
4,5,7-Trimethyl-2-(*p*-methoxyphenyl)	127	$C_{18}H_{19}NO$	81·2	6·9	5·0	81·5	7·2	5·3
picrate	176	$C_{22}H_{22}N_4O_8$			11·1			11·3
4,5,7-Trimethyl-2-(biphenyl-4-yl)[c]	215	$C_{23}H_{21}N$	88·5	6·9	4·2	88·7	6·8	4·5
4,5,7-Trimethyl-2-(2-thienyl)	140	$C_{15}H_{17}NOS$	69·4	6·6	5·2	69·3	6·6	5·4
picrate	174	$C_{21}H_{18}N_4O_7S$	53·5	3·8	11·8	53·6	3·9	11·9
4,5,7-Trimethyl-2-(2-pyridyl)	109	$C_{16}H_{16}N_2$	81·1	6·9	11·6	81·3	6·8	11·9
picrate[d]	246	$C_{22}H_{19}N_5O_7$	57·0	4·2	14·8	56·8	4·1	15·0
4,5,7-Trimethyl-2-(2-naphthyl)	181	$C_{21}H_{19}N$	88·1	6·8	4·7	88·4	6·7	4·9
dipicrate	181	$C_{33}H_{25}N_7O_{14}$	52·9	3·5	13·3	53·2	3·4	13·1
4,5,7-Trimethyl-2-(4-methoxy-1-naphthyl)	165	$C_{22}H_{21}NO$	83·6	6·7	4·2	83·8	6·7	4·4
dipicrate	152	$C_{34}H_{27}N_7O_{15}$	53·6	3·6	12·5	53·8	3·5	12·7

[a] Recrystallised from ethanol; aqueous ethanol, or hexane as colourless leaflets or prisms. The picrates or dipicrates crystallised from ethanol as brown needles, except for *d*. [b] Separated from the following isomer, which was a minor by-product, by fractional crystallisation from ethanol. [c] The brown picrate was unstable and dissociated in ethanol. [d] Deep yellow needles (ethanol).

preparing polymethylated aryl-indoles, since it avoids the risk of methyl displacements which occur in the presence of metal chlorides. Table 1 records a number of new 2-arylindoles bearing two or three methyl groups in the six-membered ring, and Table 2 lists the ω-arylamino-ketones used for their preparation. Two observations are pertinent: (*a*) 3,4,5,7-tetramethyl-2-phenylindole was obtained directly in an attempt to purify *N*-ω-pseudocumylaminopropiophenone by distillation *in vacuo*; this indicates the possibility of omitting arylamine and characteristic of tetrasubstituted benzene derivatives with the two free positions *para* to each other; the lower-melting 4,5-dimethyl-2-phenylindole and the 4,7-isomer both showed the strong absorption band in the 750—800 cm^{-1} region that is characteristic of the presence of tetrasubstituted benzenes having the two free positions in the *ortho* position.[8]

The use of polycyclic arylamines in the Möhlau–Bischler reaction necessitated a modification of the technique of cyclisation in order to avoid extensive thermal decomposition of the ω-amino-ketones. This consisted of performing the cyclisation in an inert liquid

[5] E. Fischer and T. Schmidt, *Ber.*, 1888, **21**, 1071; A. F. Crowther, F. G. Mann, and D. Purdie, *J. Chem. Soc.*, 1943, 58; P. E. Verkade and E. F. J. Janetzky, *Rec. Trav. chim.*, 1943, **62**, 763, 775; R. M. Cowper and T. S. Stevens, *J. Chem. Soc.*, 1947, 1041; F. Brown and F. G. Mann, *ibid.*, 1948, 847; K. L. Nelson and R. L. Seefeld, *J. Amer. Chem. Soc.*, 1958, **80**, 5957.

[6] *Cf.* N. P. Buu-Hoï, Ph. Mabille, and J. Brasch, *J. Chem. Soc.*, 1964, 3920; C. L. Kulkani, J. G. Hiriyakkanavar, and S. Siddapa, *J. Karnatak Univ.*, 1967, **12**, 61.

[7] For the orientation in similar reactions of derivatives of 3,4-xylidine, see N. P. Buu-Hoï, *J. Chem. Soc.*, 1949, 670.

[8] *Cf.* L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Ind. ed., Methuen, London, 1958; R. N. Jones and C. Sandorfy in 'Techniques of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 1956, vol. IX; D. G. O'Sullivan, *Spectrochim. Acta*, 1960, **16**, 762.

medium such as silicone oil, and, in this way, good yields of the expected polycyclic indoles were obtained. Thus, the two 9-aryl-5,6-dihydronaphtho[1,2-*f*]indoles (I) and (II) and the five 2-arylindeno[3,2-*f*]indoles [general formula (III)] were readily obtained; the structure assignment for these compounds (each of which was the compounds (III), are in line with the orientation postulated. The superiority of the Möhlau–Bischler method over that of Fischer for the synthesis of polycyclic indoles is shown in the poor yields recorded (37%) in the preparation of 2-phenanthrylhydrazine, which we used for obtaining 7*H*-naphtho[2,1-*c*]carbazole (IV).

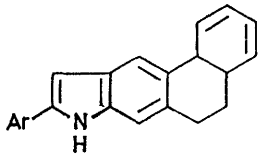
TABLE 2

ω-Arylamino-ketones [a] $ArNH{\cdot}CH_2{\cdot}COAr'$

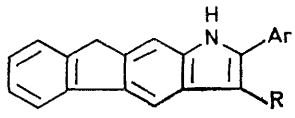
Substituents				Found (%)			Requires (%)		
Ar	Ar′	M.p.	Formula	C	H	N	C	H	N
2,4-Xylyl	Ph	100°	$C_{16}H_{17}NO$	80·1	7·2	5·5	80·3	7·2	5·8
2,5-Xylyl	Ph	106	$C_{16}H_{17}NO$	80·2	7·2	5·6	80·3	7·2	5·8
3,4-Xylyl	Ph	135	$C_{16}H_{17}NO$	80·0	7·1	5·5	80·3	7·2	5·8
3,5-Xylyl	Ph	134	$C_{16}H_{17}NO$	80·0	7·2	5·5	80·3	7·2	5·8
2,3-Xylyl	Ph	104	$C_{16}H_{17}NO$	80·4	7·2	5·6	80·3	7·2	5·8
2,4,5-Trimethylphenyl	Ph	126	$C_{17}H_{19}NO$	80·5	7·5	5·5	80·7	7·6	5·5
2,4,5-Trimethylphenyl	*o*-Tolyl	123	$C_{18}H_{21}NO$	80·6	7·9	5·0	80·6	7·9	5·2
2,4,5-Trimethylphenyl	*p*-Tolyl	170	$C_{18}H_{21}NO$	80·6	7·8	5·0	80·6	7·9	5·2
2,4,5-Trimethylphenyl	*p*-$MeOC_6H_4$	146	$C_{18}H_{21}NO_2$	76·2	7·2	5·1	76·3	7·5	4·9
2,4,5-Trimethylphenyl	*p*-$C_6H_5C_6H_4$	161	$C_{23}H_{23}NO$	83·6	7·0	3·9	83·9	7·0	4·2
2,4,5-Trimethylphenyl	2-Thienyl	140	$C_{15}H_{17}NOS$	69·4	6·6	5·2	69·3	6·6	5·4
2,4,5-Trimethylphenyl	2-Pyridyl	126	$C_{16}H_{18}N_2O$	—	—	11·0	—	—	11·0
2,4,5-Trimethylphenyl	2-Naphthyl	159	$C_{21}H_{21}NO$	82·9	7·0	4·3	83·2	7·0	4·6
2,4,5-Trimethylphenyl	4-Methoxy-2-naphthyl	161	$C_{22}H_{23}NO_2$	79·3	7·0	4·0	79·2	6·9	4·2
4-Methoxyphenylthio	Ph	114	$C_{15}H_{15}NO_2S$	69·7	6·0	5·1	70·0	5·9	5·4
1-Naphthyl	Ph	123	$C_{18}H_{15}NO$	82·6	5·6	5·1	82·7	5·8	5·4
2-Fluorenyl	Ph	189	$C_{21}H_{17}NO$	84·4	5·5	—	84·3	5·7	—
2-Fluorenyl	*p*-$C_6H_5C_6H_4$	218	$C_{27}H_{21}NO$	86·3	5·6	3·5	86·4	5·6	3·7
2-Fluorenyl	1-Naphthyl	211	$C_{25}H_{19}NO$	85·8	5·5	4·2	85·9	5·5	4·0
2-Fluorenyl	2-Naphthyl [b]	200	$C_{25}H_{19}NO$	86·0	5·6	3·9	85·5	5·5	4·0
2-Fluorenyl	3-Phenanthryl [b]	212	$C_{29}H_{21}NO$	87·3	5·2	3·3	87·2	5·3	3·5

[a] Pale yellow needles, from ethanol or ethanol–benzene. [b] Recrystallised from toluene.

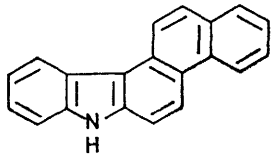
sole reaction-product) is consistent with the above observation on the behaviour of 3,4-xylidine, *i.e.* preferential cyclisation in position *para* to a methyl substituent (with the ethylene bridge in 2-amino-9,10-dihydrophenanthrene and the methylene one in 2-aminofluorene probably playing here the role of the methyl



(I) Ar=2,5-Xylyl
(II) Ar=2-Phenanthryl



(III)



(IV)

group). Further, the formation of fluorenisatin [9] from 2-aminofluorene, and the very high m.p.s (a constant feature of linear tetracyclic fluorenes [10]) recorded for

As the vast majority of polycyclic carcinogens are *in vivo* inducers of zoxazolamine hydroxylase in rats,[11] the properties of the indoles described in this respect were determined; the results (Table 3) show several of them to possess definite activity in this screening test.

EXPERIMENTAL

I.r. absorption spectra were determined in KBr discs with a Perkin-Elmer (model 457) spectrograph; we are grateful to Dr. Andrée Cheutin for some additional data.

Preparation of ω-Arylamino-ketones $ArNH{\cdot}CH_2{\cdot}COAr'$.—An ethanolic solution of equimolar amounts of the arylamine and the appropriate ω-brominated ketone was heated under reflux for 4 h with hydrogen sodium carbonate in slight excess; the precipitate which formed on cooling the solution was washed thoroughly with water and recrystallised from ethanol, ethanol–benzene, or benzene; the yields ranged from 60—85%.

Möhlau–Bischler Cyclisation.—An intimate mixture of the ω-arylamine-ketone (1 mol), the appropriate arylamine (2 mol), and its hydrobromide (0·05 mol) was heated at 200—250° for 5—15 min; after cooling the mixture was triturated with 10% aqueous hydrochloric acid. The indole was collected, washed with water, and recrystallised from hexane, ethanol, or aqueous ethanol, save for the polycyclic indoles which were recrystallised from benzene or toluene; yields 60—80%.

9-(2,5-*Xylyl*)-5,6-*dihydronaphtho*[1,2-f]*indole* (I).—A solution of 2-amino-9,10-dihydrophenanthrene [12] (3 g) and

[9] N. P. Buu-Hoï and Hiong-Ki-Wei, *Rev. Scientifique*, 1944, **82**, 306.
[10] See, for instance, O. Kruber, *Ber.*, 1937, **70**, 1556; N. P. Buu-Hoï, M. Mangane, and P. Jacquignon, *J. Het. Chem.*, 1970, **7**, 155.
[11] N. P. Buu-Hoï and D.-P. Hien, *Biochem. Pharmacol.*, 1969, **18**, 741.
[12] J. W. Krueger and E. Mosettig, *J. Org. Chem.*, 1939, **3**, 340.

ω-bromo-2,5-dimethylacetophenone (2·3 g) in toluene (50 ml) was heated under reflux for 2 h; the solvent was distilled off, and the residue was heated at 230—250° for 1 h in silicone oil (10 ml); the mixture was cooled and the solid formed was washed thoroughly with hexane and recrystallised from propanol to give the *indole* (I), as needles (1·5 g), m.p. 205° (Found: C, 89·3; H, 6·6; N, 4·4. $C_{24}H_{21}N$ requires C, 89·1; H, 6·6; N, 4·3%).

9-(2-*Phenanthryl*)-5,6-*dihydronaphtho*[1,2-f]*indole* (II) was similarly prepared, in 50% yield, from 2-ω-bromoacetylphenanthrene;[13] it formed needles, m.p. 176° (from propanol) (Found: C, 90·9; H, 5·7; N, 3·8. $C_{30}H_{21}N$ requires C, 91·1; H, 5·4; N, 3·6%).

2-*Phenylindeno*[3,2-f]*indole* (III; R = H, Ar = Ph).—A mixture of 2-aminofluorene (1·1 g), the *N*-2-(phenacyl)-aminofluorene (1 g), and 2-aminofluorene hydrobromide (0·1 g) in silicone oil (10 ml) was heated at 230—250° for 10 min; the mixture was cooled and the product was washed with hexane and recrystallised from toluene, to give the *indole* as sublimable needles (1 g), m.p. 330° (Found: C, 89·7; H, 5·3; N, 5·3. $C_{21}H_{15}N$ requires C, 89·7; H, 5·4; N, 5·0%). 2-*Biphenyl*-4-*ylindeno*[3,2-f]*indole* (III; R = H, Ar = *p*-PhC_6H_4), similarly prepared from *N*-ω-2-biphenyl-4-yl-aminofluorene, formed needles, m.p. 286° (from benzene) (Found: C, 90·7; H, 5·0; N, 3·6. $C_{27}H_{18}N$ requires C, 91·0; H, 5·1; N, 3·9%). 2-(2-*Naphthyl*)*indeno*[3,2-f]-*indole* (III; R = H, Ar = β-$C_{10}H_7$), prisms, m.p. 345° (from toluene) (Found: C, 90·8; H, 5·3; N, 4·2. $C_{25}H_{17}N$ requires C, 90·6; H, 5·2; N, 4·2%); it gave a dark brown *monopicrate*, m.p. >360° (from toluene) (Found: C, 66·6; H, 3·7; N, 10·2. $C_{31}H_{20}N_4O_7$ requires C, 66·6; H, 3·6; N, 10·0%). 2-(3-*Phenanthryl*)*indeno*[3,2-f]*indole* gave needles, m.p. 306° (from toluene) (Found: C, 91·1; H, 4·9; N, 3·7. $C_{29}H_{19}N$ requires C, 91·3; H, 5·0; N, 3·7%).

3-*Methyl*-2-*phenylindeno*[3,2-f]*indole* (III; R = Me, Ar = Ph).—1-*Phenyl*(*fluoren*-2-*ylamino*)*propan*-2-*ol*, prepared from 2-bromopropionylbenzene and 2-aminofluorene, crystallised from propanol as pale yellow prisms (80%), m.p. 139° (Found: C, 84·1; H, 6·1; N, 4·3. $C_{22}H_{15}NO$ requires C, 84·3; H, 6·1; N, 4·5%); cyclisation as above afforded in 75% yield the *indole* as prisms, m.p. 231° (from toluene) (Found: C, 89·1; H, 5·6. $C_{22}H_{17}N$ requires C, 89·4; H, 5·8%).

2-*Phenyl*-6,7-*benzindole*.—This indole, previously prepared by the Fischer method,[14] was obtained in 50% overall from α-naphthylamine and ω-bromoacetophenone as prisms, m.p. 167° (from hexane) (lit.,[14] m.p. 166—167°).

2-*Phenanthrylhydrazine*.—A solution of 2-aminophenanthrene[15] (10 g) in dioxan (20 ml) was treated with 10% hydrochloric acid (400 ml) and a solution of sodium nitrite (4·1 g) in water (18 ml) was then added dropwise with vigorous stirring at −2°. Stirring was continued for 1 h, after which stannous chloride (35·3 g in 75 ml hydrochloric acid) was added and, with continued stirring, the temperature was allowed to rise to 18°. After 12 h, the yellow solid which formed was collected and made basic with aqueous sodium hydroxide. The free base was taken up in ether and the solution was washed with water and dried (Na_2SO_4); the solvent was removed *in vacuo*, and the residue was recrystallised from heptane to give the *hydrazine* (37% yield) as yellow prisms, m.p. 128° (Found: C, 80·6; H, 5·8; N, 13·2. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·5%).

7H-*Naphtho*[2,1-c]*carbazole* (IV).—An ethanolic solution of 2-phenanthrylhydrazine (2 g) and cyclohexanone (1 g) was heated under reflux for 7 h; the crude, solid hydrazone formed from the cooling solution was treated with a boiling solution of hydrogen chloride in acetic acid (20 ml). The precipitate obtained on dilution with water was washed thoroughly with water, dried, and dehydrogenated by sublimation over 5% palladised charcoal. The *carbazole* (IV) crystallised as cream-coloured needles (0·6 g), m.p. 277° (from benzene) (Found: C, 89·8; H, 5·0; N, 4·9. $C_{20}H_{13}N$ requires C, 89·9; H, 4·9; N, 5·2%). N.m.r. spectrum in DMSO (Varian A60; internal reference, Me_4Si): singlet for the NH proton at 11·65 p.p.m.

TABLE 3

Zoxazolamine hydroxylase-inducing activity [a]

Indole	Duration of Paralysis (min) [b] Treated	Controls	*P*
4,6-Dimethyl-2-phenyl	98 ± 16 (6)	156 ± 27 (7)	<0·001
5,6-Dimethyl-2-phenyl	69 ± 13 (5)	156 ± 27 (7)	<0·001
6,7-Dimethyl-2-phenyl	103 ± 2 (6)	156 ± 27 (7)	<0·001
4,5,7-Trimethyl-2-phenyl	130 ± 18 (7)	176 ± 23 (7)	<0·01
4,5,7-Trimethyl-2-*o*-tolyl	125 ± 29 (6)	176 ± 23 (7)	<0·01
4,5,7-Trimethyl-2-*p*-tolyl	147 ± 15 (6)	176 ± 23 (7)	~0·02
4,5,7-Trimethyl-2-(4-methoxy-1-naphthyl)	137 ± 11 (7)	145 ± 29 (10)	>0·05
2-Phenyl-6,7-benzo	63 ± 25 (8)	176 ± 23 (7)	<0·001

[a] In 3-month-old Wistar male rats given 85 mg/kg zoxazolamine; treated animals received 20 mg/kg of the indole 18 h previously. Reduction of paralysis time parallels *in vivo* content of zoxazolamine hydroxylase. [b] Second figures in each column = standard deviation; figures in parentheses = number of rats; *P* calculated by variance analysis.

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