731. *Some Derivatives of Biphenyl and of Phenanthridine.*

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Some 2-acylamino-4-chloro- and -4-methoxy-biphenyls have been cyclised to the corresponding phenanthridines. The nitrobiphenyls required as starting materials were synthesised by the Gomberg reaction.

During the preparation of αω-di(phenanthridin-6-yl)alkanes [1] we required some substituted 2-aminobiphenyls for conversion into the phenanthridines. 2-Amino-chloro-, -bromo-, and -nitro-biphenyls substituted in the 5-, 3,5-, and 5,4′-positions have been prepared by the reaction of nucleophilic reagents with 2-amino-,[2] 2-acetamido-,[2] and 2-toluene-*p*-sulphonamido-biphenyl,[3] but compounds substituted in the 4-position could not be prepared by this route. For these derivatives we turned to the Gomberg reaction.

Ritchie [4] and Petrow [5] prepared 4-methyl-2-nitrobiphenyl from 4-amino-3-nitrotoluene, by using the sodium acetate modification of the Gomberg reaction described by Elks, Haworth, and Hey.[6] This reaction has now been extended by the synthesis of 4-chloro-2-nitrobiphenyl in 51% yield from 4-chloro-2-nitroaniline, and of 4-methoxy-2-nitrobiphenyl in 20% yield from 4-amino-3-nitroanisole: the method described by Gomberg and his co-workers [7] gave 22% and 15% yield respectively. Reduction of the nitro-compounds with reduced iron in aqueous alcohol gave high yields of the 2-aminobiphenyls, from which the 2-acetamido-, 2-benzamido-, and 2-ethoxycarbonylamino-biphenyl were prepared.

Cyclisation of 2-acetamido-4-chloro-, 2-benzamido-4-chloro-, 2-acetamido-4-methoxy-, and 2-benzamido-4-methoxy-biphenyl with phosphorus oxychloride, a method previously employed by Morgan and Walls [8] for the preparation of 6-substituted phenanthridines, gave the respective phenanthridines smoothly. Attempts to cyclise the 2-ethoxycarbonyl-biphenyls with phosphorus oxychloride failed but by refluxing them with powdered zinc chloride in diethylene glycol ring closure was achieved. Prolonged refluxing of 2-ethoxy-carbonylamino-4-methylbiphenyl with phosphorus oxychloride and treatment of the product with ammonia gave *N*-(4-methyl-2-biphenylyl)urea.

Experimental

M. p.s in parentheses are as recorded elsewhere.

4-Methyl-2-nitrobiphenyl.—4-Amino-3-nitrotoluene (76 g., 0·5 mole) in concentrated hydrochloric acid (150 ml.; *d* 1·18) and water (100 ml.) was diazotised at 0—5°: during 1 hr. with sodium nitrite solution (38 g. in 50 ml.). The cold, filtered diazo-solution was added rapidly to stirred benzene (1 l.) at 5°, and sodium acetate (160 g., trihydrate in water, 400 ml.) was added at the same temperature during 1 hr. The mixture was stirred vigorously for a further 3 hr. at 3—5°, and for an additional 40 hr. at room temperature. The benzene layer was removed, washed, dried, and fractionally distilled under reduced pressure. The fraction boiling from 180° to 200° at 11 mm. was collected and redistilled under reduced pressure. *4-Methyl-2-nitrobiphenyl* separated from light petroleum (b. p. 40—60°) in very pale yellow cubes (50%), m. p. 49°, b. p. 188—190°/11 mm. (Found: C, 73·3; H, 5·3; N, 6·4. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·6%). Ritchie [4] gives b. p. 207—209°/28 mm., and Petrow [5] b. p. 208°/11 mm. Both describe it as an oil.

[1] Hollingsworth and Petrow, *J.*, 1961, 3664.
[2] Scarborough and Waters, *J.*, 1927, 89.
[3] Bell, *J.*, 1928, 2770.
[4] Ritchie, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 169.
[5] Petrow, *J.*, 1945, 21.
[6] Elks, Haworth, and Hey, *J.*, 1940, 1284.
[7] Gomberg, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372.
[8] Morgan and Walls, *J.*, 1931, 2447.

TABLE 1. *Substituted biphenyls.*

No.	Substituents	Form	Solvent for crystn.*	M. p.	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
1	2-Amino-4-methyl-	Oil	—	[a]	80	85·0	7·3	7·6	$C_{13}H_{13}N$	85·2	7·1	7·7
2	2-Acetamido-4-methyl-	Plates	EtOH–H_2O	151°	90	79·8	6·6	6·2	$C_{15}H_{15}NO$	80·0	6·7	6·2
3	2-Benzamido-4-methyl-	Needles	Pet(a)	94	85	83·3	5·9	5·1	$C_{20}H_{17}NO$	83·6	5·9	4·9
4	2-Ethoxycarbonylamino-4-methyl-	Cubes	Pet(a)	73—74	65	75·4	6·5	5·4	$C_{16}H_{17}NO_2$	75·3	6·7	5·5
5	4-Methoxy-2-nitro-	Yellow laths	Pet(a)	73—74 [b]	20	68·3	5·0	6·3	$C_{13}H_{11}NO_3$	68·1	4·8	6·1
6	2-Amino-4-methoxy-	Oil	—	[c]	77	78·4	6·5	6·9	$C_{13}H_{13}NO$	78·5	6·5	7·0
7	2-Acetamido-4-methoxy-	Needles	Pet(a)	96—97	85	74·5	6·1	6·0	$C_{15}H_{15}NO_2$	74·7	6·2	5·8
8	2-Benzamido-4-methoxy-	Needles	Pet(b)	148	80	79·2	5·6	4·5	$C_{20}H_{17}NO_2$	79·2	5·6	4·6
9	4-Chloro-2-nitro-	Yellow cubes	Pet(c)	53 [d]	51	61·7	3·7	5·9	$C_{12}H_8ClNO_2$	61·7	3·4	6·0
10	2-Amino-4-chloro-	Oil	—	[e]	88	70·5	4·8	7·1	$C_{12}H_{10}ClN$	70·8	4·9	6·9
11	2-Acetamido-4-chloro-	Prisms	MeOH–Pet(a)	129·5	75	68·7	5·1	5·6	$C_{14}H_{12}ClNO$	68·4	4·9	5·7
12	2-Benzamido-4-chloro-	Prisms	Pet(b)	104—105	75	74·3	4·8	4·6	$C_{19}H_{14}ClNO$	74·3	4·55	4·55
13	4-Chloro-2-ethoxycarbonylamino-	Cubes	Pet(a)	130—131	70	65·1	5·4	4·9	$C_{15}H_{14}ClNO_2$	65·4	5·1	5·1
14	2-Ethoxycarbonylamino-	Needles	EtOH–Pet(b)	186	70	74·5	6·2	5·7	$C_{15}H_{15}NO_2$	74·7	6·2	5·8
15	2-Amino-4′-ethoxycarbonylamino-	Plates	C_6H_6–Pet(b)	98	70	70·5	6·1	10·7	$C_{15}H_{16}N_2O_2$	70·4	6·35	10·9
16	2-Amino-4′-benzamido-	Needles	$COMe_2$–H_2O	180—181	80	78·8	5·8	9·7	$C_{19}H_{16}N_2O$	79·2	5·6	9·7
17	2-Acetamido-3,5-dibromo-	Rhombohedra	Pet(a)	134—135	78	45·7	3·2	3·6	$C_{14}H_{11}Br_2NO$	45·5	3·0	3·8

* Pet(a) = Light petroleum (b. p. 60—80°); Pet(b) = light petroleum (b. p. 80—100°); Pet(c) = light petroleum (b. p. 40—60°). [a] B. p. 170—171°/11 mm. [b] B. p. 207—208°/11 mm. [c] B. p. 212—213°/12 mm. [d] B. p. 191—193°/11 mm. [e] B. p. 185—186°/12 mm.

TABLE 2. *Substituted phenanthridines.*

No.	Substituents	Form	Solvent for crystn.*	M. p.	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
1	3-Methyl-6-phenyl-	Needles	Pet(a)	118·5°	80	89·3	5·7	5·2	$C_{20}H_{15}N$	89·2	5·6	5·2
	picrate	Yellow needles	EtOH	259 †				11·2	$C_{26}H_{18}N_4O_7$			11·2
2	3-Methoxy-6-methyl-	Prisms	Pet(c)	85	65	80·9	5·8	6·2	$C_{15}H_{13}NO$	80·7	5·8	6·3
	picrate	Yellow needles	EtOH	248 †				12·3	$C_{21}H_{16}N_4O_8$			12·4
3	3-Methoxy-6-phenyl-	Plates	EtOH	115·5	70	84·0	5·4	4·9	$C_{20}H_{15}NO$	84·2	5·3	4·9
	picrate	Yellow needles	EtOH	267 †				11·0	$C_{26}H_{18}N_4O_8$			10·9
4	3-Hydroxy-6-methyl-	Pale yellow needles	EtOH–Pet(b)	295—296 †	75	80·1	5·2	6·6	$C_{14}H_{11}NO$	80·4	5·2	6·6
5	3-Benzoyloxy-6-methyl-	Needles	EtOH–H_2O	148—149	85	80·3	4·7	4·4	$C_{21}H_{15}NO_2$	80·5	4·8	4·5
6	3-Hydroxy-6-phenyl-	Needles	EtOH–Pet(b)	297—298 †	85	83·7	4·6	5·1	$C_{19}H_{13}NO$	84·1	4·8	5·2
7	3-Benzoyloxy-6-phenyl-	Needles	EtOH–H_2O	191—192	80	83·3	4·5	3·6	$C_{26}H_{17}NO$	83·2	4·5	3·7
8	3-Chloro-6-methyl-	Plates	MeOH–Pet(a)	131·5—132	65	73·6	4·4	6·1	$C_{14}H_{10}ClN$	73·8	4·4	6·1
	picrate	Yellow needles	EtOH	233 †				12·5	$C_{20}H_{13}ClN_4O_7$			12·3
9	3-Chloro-6-phenyl-	Needles	EtOH–Pet(b)	142·5	70	78·8	4·2	4·9	$C_{19}H_{12}ClN$	78·7	4·1	4·8
	picrate	Yellow needles	EtOH	257 †				10·7	$C_{25}H_{15}ClN_4O_7$			10·8
10	2-Bromo-6-methyl-	Needles	Pet(b)	132	60	61·5	3·6	5·2	$C_{14}H_{10}BrN$	61·8	3·7	5·1
	picrate	Yellow needles	EtOH	245 †				11·1	$C_{20}H_{12}BrN_4O_7$			11·2
11	2,4-Dibromo-6-methyl-	Pale yellow needles	EtOH–Pet(b)	173—174	70	47·7	2·7	3·9	$C_{14}H_9Br_2N$	47·9	2·8	4·0
	picrate	Yellow needles	EtOH	201 †				9·5	$C_{20}H_{12}Br_2N_4O_7$			9·7
12	2,4-Dibromo-6-phenyl-	Needles	Pet(b)	208	60	55·2	2·8	3·4	$C_{19}H_{11}Br_2N$	55·2	2·7	3·4

* See Table 1. † With decomp.

The *compounds* in Table 1 were prepared similarly, or by standard methods. The following notes apply:

No. 1: Petrow [5] gives b. p. 183°/11 mm. This compound, and nos. 6 and 10, were prepared from the corresponding nitro-compounds by use of reduced iron in aqueous alcohol.

No. 2: Ritchie [4] gives m. p. 148°.

No. 3: Ritchie [4] gives m. p. 92°.

No. 14: Pictet and Hubert [9] give m. p. 186°.

No. 15: Prepared from 2-acetamido-4′-ethoxycarbonylaminobiphenyl [10] by hydrolysis in 10% alcoholic hydrochloric acid.

No. 16: Prepared from 2-acetamido-4′-benzamidobiphenyl [5] by hydrolysis in 10% alcoholic hydrochloric acid.

No. 17: Prepared from 2-amino-3,5-dibromobiphenyl [2] by means of acetic anhydride.

3,6-*Dimethylphenanthridine.*—2-Acetamido-4-methylbiphenyl (5 g.) and phosphorus oxychloride (15 ml.) were refluxed until evolution of hydrogen chloride had practically ceased (~2 hr.). The excess of phosphorus halide was removed under reduced pressure, and the cooled residue was poured on ice (200 g.) and neutralised with aqueous ammonia. The sticky solid so obtained was collected, dried, and crystallised from light petroleum (b. p. 40—60°). 3,6-Dimethylphenanthridine formed colourless octahedra (75%), m. p. 105° (104·5—105·5° [5]) (Found: C, 87·1; H, 6·3; N, 6·6. Calc. for $C_{15}H_{13}N$: C, 87·0; H, 6·3; N, 6·8%). The picrate separated from alcohol in very sparingly soluble yellow needles, m. p. 255° (decomp.) (240° [4]) (Found: N, 13·1. Calc. for $C_{15}H_{13}N,C_6H_3N_3O_7$: N, 12·9%).

The *compounds* in Table 2 were prepared similarly. The following notes apply:

No. 1: Ritchie [4] gives m. p. 120° and 243° (decomp.) respectively for the base and the picrate.

Nos. 4 and 6: Prepared from the corresponding methoxy-compounds by hydrolysis in constant-boiling hydrobromic acid.

2-Ethoxycarbonylamino-4-methylbiphenyl was refluxed with an excess of phosphorus oxychloride until the slow evolution of hydrogen chloride had ceased (4 hr.). The excess of phosphorus halide was removed under reduced pressure, and the oily residue poured into water and neutralised with aqueous ammonia. The precipitated N-(4-*methyl*-2-*biphenylyl*)*urea* crystallised from alcohol–light petroleum (b. p. 80—100°) in needles, m. p. 166° (Found: C, 74·2; H, 6·1; N, 12·3. $C_{14}H_{14}N_2O$ requires C, 74·4; H, 6·2; N, 12·4%). Yield 45%.

Phenanthridones.—2-Ethoxycarbonylaminobiphenyl (2 g.), powdered zinc chloride (5 g.), and diethylene glycol (10 ml.) were gently refluxed for 2 hr., then cooled and poured into warm 17% hydrochloric acid (200 ml.), precipitating a brownish powder. After being washed with boiling water and a little boiling alcohol, 5,6-dihydro-6-oxophenanthridine crystallised from aqueous acetic acid in needles (30%), m. p. 292—293° (289° [9]) (Found: C, 79·8; H, 4·5; N, 7·3. Calc. for $C_{13}H_9NO$: C, 80·0; H, 4·6; N, 7·2%).

The 3-methyl analogue, needles (from acetic acid), m. p. 250° (251° [4]) (Found: C, 80·1; H, 5·2; N, 6·6. Calc. for $C_{14}H_{11}NO$: C, 80·4; H, 5·3; N, 6·7%), was prepared (30%) by similar cyclisation of 2-ethoxycarbonylamino-4-methylbiphenyl.

3-Chloro-6-methylphenanthridine (2 g.) in glacial acetic acid (10 ml.) was treated with powdered potassium dichromate (5 g.) during 30 min. at 100° and refluxed for a further 2½ hr. The mixture was poured into warm dilute hydrochloric acid (150 ml.), precipitating a yellowish solid. This was collected, washed with boiling water and alcohol, and crystallised from acetic acid, giving 3-*chloro*-5,6-*dihydro*-6-*oxophenanthridine* as needles, m. p. 297—298° (75%) (Found: C, 68·0; H, 3·7; N, 6·1. $C_{13}H_8ClNO$ requires C, 67·7; H, 3·9; N, 6·1%).

The 2-*bromo*-, very pale yellow needles (from acetic acid) (60%), m. p. 337—338° (Found: C, 57·3; H, 2·8; N, 5·0. $C_{13}H_8BrNO$ requires C, 57·0; H, 2·9; N, 5·1%), and the 2,4-*dibromo*-*analogue*, light orange needles from nitrobenzene (55%), m. p. 356—357° (decomp.) (Found: C, 44·5; H, 1·9; N, 4·1. $C_{13}H_7Br_2NO$ requires C, 44·2; H, 2·0; N, 4·0%), were prepared similarly.

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[9] Pictet and Hubert, *Ber.*, 1896, **29**, 1188.
[10] Walls, *J.*, 1947, 70.