556. *Studies in the Phenanthridine Series: Preparation of Some Methylphenanthridines and Amino-derivatives*

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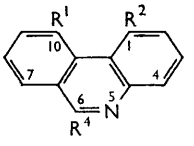
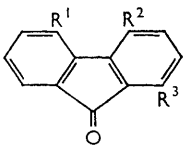
1- and 10-Methyl- and 1,10-dimethyl-phenanthridine have been synthesised. Amination of these bases, and 1,2- and 9,10-benzophenanthridine, gave the corresponding 6-amino-derivatives. A partial resolution of 6-amino-1,10-dimethylphenanthridine has been achieved.

During an investigation into the effects of nonplanarity (due to molecular overcrowding) on heteroaromatic reactivity we required 1- and 10-methyl-[1] and 1,10-dimethyl-phenanthridine (I; $R^1 = H$, $R^2 = Me$; $R^1 = Me$, $R^2 = H$; and $R^1 = R^2 = Me$, respectively) together with the corresponding 6-amino-derivatives (II) and those of the known 1,2- and 9,10-benzophenanthridine.



(I; $R^4 = H$) (II; $R^4 = NH_2$)



(III)

Molecular models indicate considerable overcrowding in 1,10-dimethylphenanthridine, and anomalous physical properties in derivatives of this compound have been ascribed to nonplanarity, although an attempt to resolve 6-(*p*-aminophenyl)-1,10-dimethylphenanthridine was abandoned.[2] Spectroscopic evidence for overcrowding in 9,10-benzophenanthridine derivatives has already been reported.[3]

Initially, we sought a convenient route to 4-methylfluorenone [4,5] (III; $R^1 = R^3 = H$, $R^2 = Me$) since this, or the corresponding fluorenol,[4] might provide both the required monomethylphenanthridines. Good yields of the fluorenone were obtained by cyclising 3-phenyl-4-methylphthalic anhydride [5] with aluminium chloride to 9-oxo-4-methylfluorene-1-carboxylic acid (III; $R^1 = H$, $R^2 = Me$, $R^3 = CO_2H$). Decarboxylation with either copper bronze in quinoline or basic copper carbonate gave 4-methylfluorenone. This compound was also obtained by the decarboxylation of 9-oxo-4-methylfluorene-5-carboxylic

[1] Whilst this work was in progress, M. S. Gibson (*J.*, 1961, 2249) described 10-methylphenanthridine picrate. The free base was not isolated.
[2] E. Ritchie, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 159.
[3] B. Mills and K. Schofield, *J.*, 1956, 4213.
[4] M. Orchin and E. O. Woolfolk, *J. Amer. Chem. Soc.*, 1945, **67**, 123.
[5] K. Alder, J. Haydn, K. Heinbach, and K. Neufang, *Annalen*, 1954, **586**, 110.

acid [6] (III; $R^1 = Me$, $R^2 = CO_2H$, $R^3 = H$), but this method consistently gave lower yields.

4-Methylfluorenone underwent the Schmidt ring expansion [7,8] to give a sharp-melting product which in fact comprised a mixture of the two possible phenanthridones. (The formation of a eutectic by isomeric phenanthridones has previously been reported.[9]) Reduction with lithium aluminium hydride followed by dehydrogenation yielded a mixture containing approximately equal amounts of the two methylphenanthridines. Oxidation of the crude dihydro-compounds by the method of Huppatz and Sasse [10] failed since more than the theoretical amount of permanganate was consumed and no methylphenanthridine was present in the resulting solution. Fractional crystallisation from light petroleum (or chromatography on alumina) yielded two fractions, the less soluble of which formed a picrate m. p. 205—207°; 10-methylphenanthridine picrate has been reported to have m. p. 204—206°.[1] The picrate of the isomeric base had m. p. 232°, and confirmation that this material was in fact 1-methylphenanthridine was obtained by comparison with a specimen synthesised by an unambiguous route. 2-Amino-6-methylbiphenyl [11] was obtained in good yield from 2-carboxy-6-methylbiphenyl [5] by a Curtius reaction; an attempt to carry out this conversion more directly with hydrazoic acid in the presence of sulphuric acid yielded the eutectic mixture of methylphenanthridones described above. 2-Formamido-6-methylbiphenyl (from the amine and formic acid) cyclised smoothly in polyphosphoric acid [12] to 1-methylphenanthridine, identical with the more soluble isomer described above. The reaction between *m*-toluidine, its hydrochloride, and diethylaminomethylcyclohexanone hydrochloride in the presence of stannic chloride has been shown to give either 1- or 3-methyl-7,8,9,10-tetrahydrophenanthridine.[13] Confirmation that the 3-isomer is formed as expected on steric grounds has now been obtained, since dehydrogenation with palladium–charcoal yielded a base which was clearly different from our 1-methylphenanthridine, but identical with a specimen of 3-methylphenanthridine obtained by the method of Arcus and Coombs.[13]

4-Methylfluorenol [4] was obtained in good yield by the action of aluminium isopropoxide on the corresponding fluorenone. With hydrazoic acid in the presence of sulphuric acid [14] the fluorenol formed a mixture of 1- and 10-methylphenanthridine in approximately equal amounts.

It was hoped that the Beckmann rearrangement of 4-methylfluorenone oxime might lead preferentially to one of the possible methylphenanthridones. Although the oxime appeared homogeneous, rearrangement in polyphosphoric acid [15] yielded the eutectic mixture of 1- and 10-methylphenanthridone.

1,10-Dimethylphenanthridone was obtained in satisfactory yield from 4,5-dimethylfluorenone [6,16] (III; $R^1 = R^2 = Me$, $R^3 = H$) by the Schmidt procedure. Identical material was obtained by the action of polyphosphoric acid on the corresponding oxime but this method offered no advantage. Reduction of the lactam followed by dehydrogenation in the usual way yielded 1,10-dimethylphenanthridine, m. p. 49°, picrate m. p. 207—209°. Walls [17] has suggested that the oily dimethylphenanthridine obtained by Hey and Jackson [18] (believed by these authors to be the 2,4-, 4,6-, or 2,6-dimethyl derivative) was in

[6] T. P. C. Mulholland and G. Ward, *J.*, 1956, 2415.
[7] P. A. S. Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 320.
[8] B. R. T. Keene and K. Schofield, *J.*, 1958, 2609.
[9] A. J. Nunn, K. Schofield, and R. S. Theobald, *J.*, 1952, 2797.
[10] J. L. Huppatz and W. H. F. Sasse, *Austral. J. Chem.*, 1963, 417.
[11] A. M. Sadler and G. Powell, *J. Amer. Chem. Soc.*, 1934, **56**, 2650.
[12] E. C. Taylor and N. W. Kalenda, *J. Amer. Chem. Soc.* 1954, **76**, 1699.
[13] B. L. Hollingsworth and V. Petrow, *J.*, 1948, 1537; 1960, 263.
[14] C. L. Arcus and M. M. Coombs, *J.*, 1954, 4319.
[15] " Organic Reactions," vol. XI, ed. Cope, Wiley and Sons, New York, 1960.
[16] S. Takahashi, *Agric. Biol. Chem.* (*Japan*), 1962, **26**, 323.
[17] L. P. Walls, " Heterocyclic Chemistry," vol. 4, ed. Elderfield, Wiley and Sons, New York, 1952.
[18] D. H. Hey and E. R. B. Jackson, *J.*, 1934, 645.

fact the 1,10-isomer. This compound formed a picrate with m. p. 241°, and thus clearly differs from our material.

The ultraviolet absorption spectra of 1- and 10-methyl- and 1,10-dimethyl-phenanthridine were determined between 220 and 390 mμ in absolute ethanol. In the monomethyl homologues the intensity of the α-band is less than in phenanthridine itself, and the effects of overcrowding are particularly marked in the spectrum of 1,10-dimethylphenanthridine in which only the *p* and β bands can be observed. Both bands show decreased intensities, and appear at longer wavelength than those of the parent compound.

The proton magnetic resonance spectra of phenanthridine and the 1- and 10-methyl and 1,10-dimethyl homologues have been determined in carbon tetrachloride containing tetramethylsilane as an internal standard, and details are in the Table.

	Chemical shift (τ)			
Compound	$C_{(9)}$ proton	$C_{(4),(5)}$ protons	Other aromatic protons	Methyl protons
Phenanthridine	0·88(s)	1·59(d)	2·2(m) *	—
1-Methylphenanthridine	0·94(s)	1·32(d)	2·3(m) *	6·99(s)
10-Methylphenanthridine	0·93(s)	1·29(d)	2·3(m) *	7·01(s)
1,10-Dimethylphenanthridine	1·08(s)	—	2·4(m) *	7·54(s)

* Width approximately 60 c.p.s.; relative area six.

s, singlet; d, doublet; m, multiplet.

Phenanthridine itself exhibits a doublet at low field equivalent to two protons, whilst in the 1- and 10-methyl homologues the intensity corresponds to one proton in each case. The value of the splitting constant ($J = 7$ c./sec.) is consistent with coupling to *ortho* protons.[19] Since this signal is absent from the spectrum of 1,10-dimethylphenanthridine the assignment of this doublet by Moore and Snyder[20] is thus confirmed. Aromatic protons adjacent to a hetero-atom are known to absorb at lower field than those at other positions.[19] All the bases show a singlet corresponding to one proton in this region and it is noteworthy that this signal moves to significantly higher field as the degree of overcrowding increases, possibly owing to increasing distortion of the hetero-ring. In 1,10-dimethylphenanthridine the methyl proton signal appears at an abnormally high value. The magnitude of this shift is interesting in view of the recent suggestion that where methyl groups are forced into close contact special shielding effects are operative,[21] although in 4',5-dimethyl-3,4-benzophenanthrene a similar shift has been attributed merely to out-of-plane deformation of the methyl groups.[22]

1,2- and 9,10-Benzophenanthridone, and hence the parent bases, are conveniently obtained from 3,4-benzofluorenone by the action of hydrazoic acid.[8] This method has been used in the present work but we have now shown that the action of polyphosphoric acid at 180° on the corresponding oxime forms only 9,10-benzophenanthridone. Oxime interconversion does not appear to occur at this temperature, since although traces of the original fluorenone were recovered from the reaction mixture, no 1,2-benzophenanthridone was detected.

Exploratory attempts to prepare naphthophenanthridine derivatives by similar methods failed, since naphtho[2,1-*c*]fluorenone[23] was recovered unchanged after treatment with hydrazoic acid under the usual conditions, and all attempts to form the oxime were unsuccessful.

All the bases described above reacted smoothly with sodamide in xylene[24] to give good

[19] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.
[20] H. W. Moore and H. R. Snyder, *J. Org. Chem.*, 1963, **28**, 535.
[21] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.
[22] M. S. Newman, R. G. Mentzer, and G. Slomp, *J. Amer. Chem. Soc.*, 1963, **85**, 4018.
[23] A. D. Campbell, *J.*, 1954, 3659.
[24] G. T. Morgan and L. P. Walls, *J.*, 1932, 2225.

yields of the corresponding 6-amino-derivatives. Theilacker and Baxman [25] were able to resolve 4,7-diamino-1,10-dimethylbenzo[*c*]cinnoline although previous attempts [26] to resolve the parent dimethylcinnoline had been unsuccessful. Accordingly, in re-examining the resolvability of the 1,10-dimethylphenanthridine system we sought to take advantage of the enhanced basic strength of the 6-amino-derivative (II; $R^1 = R^2 = Me$). A partial resolution was achieved with (+)-camphorsulphonic acid, although the (−)-amine obtained was of low optical stability. Attempts to insolate the (+)-isomer in crystalline form were unsuccessful.

Experimental

Ultraviolet absorption spectra were determined on a Unicam S.P. 500 spectrophotometer.

9-Oxo-4-methylfluorene-1-carboxylic Acid.—3-Phenyl-4-methylphthalic anhydride (13·8 g.) and aluminium chloride (16·8 g.) were heated together under reflux in benzene (80 ml.) for 2 hr. The cooled mixture was acidified with hydrochloric acid and steam-distilled. The residue of *9-oxo-4-methylfluorene-1-carboxylic acid* (13·1 g.) crystallised from xylene as orange needles, m. p. 229—230° (Found: C, 75·8; H, 4·4. $C_{15}H_{10}O_3$ requires C, 75·7; H, 4·2%). Decarboxylation of both 9-oxo-4-methylfluorene-1- and -5-carboxylic acid with basic copper carbonate gave 4-methylfluorenone, m. p. 86—88° (lit.,[4] 91°) from light petroleum (b. p. 100—120°). The *oxime*, prepared in pyridine–ethanol, formed yellow flakes, m. p. 195—196°, from ethanol (Found: C, 80·4; H, 5·3. $C_{14}H_{11}NO$ requires C, 80·3; H, 5·3%).

Ring Expansion of 4-Methylfluorenone.—(*a*) A mixture of 4-methylfluorenone (1·0 g.), sulphuric acid (1·0 ml.) and trichloroacetic acid (30 g.) was maintained at 55—65° and treated with sodium azide (0·3 g.). After 10 min. a further quantity of sodium azide (0·2 g.) was added. The mixture was kept at 55—65° for 1 hr., poured on ice, and extracted with chloroform. The extracts were washed with aqueous sodium carbonate, dried (Na_2SO_4), and evaporated. The residue (0·65 g.) afforded a eutectic mixture of 1- and 10-methylphenanthridone, m. p. 285—286°, as pale brown needles from ethanol.

(*b*) The same eutectic mixture, m. p. 286—288° (0·28 g.) was obtained by heating 4-methylfluorenone oxime (0·6 g.) in polyphosphoric acid at 180° for 30 min. and working up as above.

4-Methylfluorenol.—Reduction of 4-methylfluorenone with aluminium isopropoxide gave the fluorenol, which formed white needles, m. p. 159—160° (lit.,[4] 164°) from light petroleum (b. p. 60—80°) (Found: C, 85·4; H, 5·8. Calc. for $C_{14}H_{12}O$: C, 85·7; H, 6·15%).

1- and 10-Methylphenanthridine.—(*a*) Sulphuric acid (5 ml.) was added dropwise to an ice-cold suspension of sodium azide (1·25 g.) in chloroform (20 ml.). The mixture was stirred for 10 min. and then maintained at 25° whilst a suspension of 4-methylfluorenol (2·5 g.) in chloroform (50 ml.) was added during 1 hr. The mixture was stirred for a further hour, poured on ice, basified, and extracted with ether. Evaporation of the dried (Na_2SO_4) solution gave an oil which on treatment with ethanolic picric acid gave a bright yellow picrate (2·0 g.), m. p. 196—200°, from dioxan. Regeneration provided a mixture of bases (0·8 g.), m. p. 52—65°, which was fractionally crystallised from light petroleum (b. p. 40—60°).

The first two fractions (total 0·27 g.) melted in the range 85—100° and on further recrystallisation from the same solvent gave *10-methylphenanthridine*, m. p. 109—111° (Found: C, 86·7; H, 5·7. $C_{14}H_{11}N$ requires C, 87·0; H, 5·75%), $\lambda_{max.}$ 221, 246, 294, 304(infl.), 334, and 349 mμ ($\log_{10}\varepsilon$ 4·20, 4·69, 3·85, 3·78, 3·24, and 3·26). The picrate formed small yellow needles, m. p. 205—207° (lit.,[1] 204—206°) from dioxan.

The third fraction was oily; treatment of the mother-liquor with ethanolic picric acid gave a crude picrate (0·54 g.) which was repeatedly crystallised from dioxan. Regeneration gave *1-methylphenanthridine* as white needles from light petroleum (b. p. 40—60°), m. p. 64—65° (Found: C, 87·3; H, 6·2%), $\lambda_{max.}$ 220, 246, 295, 302, 334, and 348 mμ ($\log_{10}\varepsilon$ 4·26, 4·69, 3·85, 3·80, 3·14, and 3·07). The *picrate* crystallised from dioxan as fine, yellow needles, m. p. 229—230° (Found: C, 56·6; H, 3·7. $C_{14}H_{11}N,C_6H_3N_3O_7$ requires C, 56·85; H, 3·3).

(*b*) The mixture of 1- and 10-methylphenanthridone (1·3 g.) was extracted from a Soxhlet thimble into a suspension of lithium aluminium hydride (1·5 g.) in boiling tetrahydrofuran (100 ml.). After complete extraction, heating was continued for 1 hr. and then the excess of lithium aluminium hydride was decomposed by the addition of aqueous tetrahydrofuran to the cooled

[25] W. Theilacker and F. Baxmann, *Annalen*, 1953, **581**, 117.
[26] G. Wittig and H. Zimmermann, *Ber.*, 1953, **86**, 629.

mixture. Most of the solvent was distilled off and the residue was extracted with benzene and dried (Na_2SO_4). The green-yellow oil obtained by removal of the solvent was heated with palladium–charcoal (10%; 0·3 g.) at 280° in a stream of nitrogen for 3 hr. Extraction with ethanol followed by treatment with ethanolic picric acid gave the yellow, mixed picrates, m. p. 195—200° from dioxan. Regeneration gave a mixture of 1- and 10-methylphenanthridine (0·58 g.) which was separated as above.

2-*Amino*-6-*methylbiphenyl*.—2-Carboxy-6-methylbiphenyl (1·0 g.) was converted by a procedure similar to that described by Bachmann and Fornefeld [27] into the amine (0·62 g.), obtained as an oil which partially solidified at room temperature (lit.,[11] m. p. 43—44°).

2-*Formamido*-6-*methylbiphenyl*.—2-Amino-6-methylbiphenyl (0·60 g.) and 98% formic acid (30 ml.) were heated together under reflux for 4 hr. The excess of acid was removed under reduced pressure and the residue was dissolved in benzene and treated with charcoal. The residue obtained by evaporation of the filtrate was triturated with light petroleum (b. p. 60—80°) to give 2-*formamido*-6-*methylbiphenyl* (0·40 g.) which crystallised from light petroleum (b. p. 60—80°) as colourless plates, m. p. 83° (Found: C, 80·1; H, 6·1. $C_{14}H_{13}NO$ requires C, 79·6; H, 6·2%).

1-*Methylphenanthridine*.—2-Formamido-6-methylbiphenyl (0·15 g.) and polyphosphoric acid (12 ml.) were stirred together at 140—150° for 1 hr. The mixture was poured on ice, basified, and extracted with chloroform. Evaporation of the dried (Na_2SO_4) solution gave an oil which on treatment with ethanolic picric acid gave 1-*methylphenanthridine picrate*, m. p. 230°. The free *base* crystallised from light petroleum as colourless needles, m. p. 64—65°.

3-*Methylphenanthridine*.—3-Methyl-7,8,9,10-tetrahydrophenanthridine (1·5 g.) and palladium–charcoal (30%; 1·0 g.) were heated together at 260° in a stream of nitrogen for 4 hr. Extraction with hot ethanol followed by treatment with ethanolic picric acid gave 3-methylphenanthridine picrate (1·2 g.), which formed bright yellow needles, m. p. 250° (lit.,[28] 251°) from dioxan. The free base separated from light petroleum (b. p. 40—60°) as colourless needles, m. p. 78—79° alone or in an admixture with an authentic specimen [14] (lit.,[28] 81°).

1,10-*Dimethylphenanthridone*.—(*a*) A Schmidt reaction similar to that described in the case of 4-methylfluorenone converted 4,5-dimethylfluorenone into 1,10-*dimethylphenanthridone* (50% yield) as colourless plates, m. p. 220—221° from ethanol (Found: C, 80·2; H, 5·7. $C_{15}H_{13}NO$ requires C, 80·7; H, 5·9%).

(*b*) The rearrangement of 4,5-dimethylfluorenone oxime in polyphosphoric acid as above gave 1,10-*dimethylphenanthridone* in 30% yield.

1,10-*Dimethylphenanthridine*.—1,10-Dimethylphenanthridone was converted into 1,10-dimethylphenanthridine as described in the case of the monomethyl derivatives. Best yields (42—48%) were obtained when a dehydrogenation time of 45 min. was used. The crude product was converted into the *picrate* which crystallised from ethanol as yellow needles, m. p. 207—209° (Found: C, 57·9; H, 3·8; N, 12·3. $C_{15}H_{13}N,C_6H_3N_3O_7,\frac{1}{2}C_2H_5OH$ requires C, 57·5; H, 4·2; N, 12·2%). 1,10-*Dimethylphenanthridine*, regenerated from the picrate, was obtained as an oil which slowly formed a yellow solid, m. p. 49° (Found: C, 86·7; H, 6·3; N, 6·8. $C_{15}H_{13}N$ requires C, 86·9; H, 6·3; N, 6·8%), $\lambda_{max.}$ 250 and 312 mμ ($\log_{10}\varepsilon$ 4·58 and 3·67).

9,10-*Benzophenanthridone*.—3,4-Benzofluorenone oxime (10 g.) and polyphosphoric acid (250 ml.) were heated together at 180° for 6 hr. On working up in the usual way a dark oil was obtained which gave a brown solid (2·65 g.), m. p. 206—214°, on trituration with benzene. Crystallisation from xylene gave 9,10-benzophenanthridone (1·47 g.), m. p. 275—276° (lit.,[8] 275—276°).

6-*Amino*-1-*methylphenanthridine*.—1-Methylphenanthridine (0·35 g.) was heated with a suspension of sodamide (0·25 g.) in xylene (10 ml.) in nitrogen for 2 hr. The mixture was poured on ice, extracted with ether, and dried (Na_2SO_4). Removal of the solvents gave 6-*amino*-1-*methylphenanthridine* (0·18 g.) which crystallised from benzene–light petroleum (b. p. 60—80°) as colourless needles, m. p. 192—193° (Found: C, 80·8; H, 5·7. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8%), $\lambda_{max.}$ 240, 266, 286, 320, 338, and 354 mμ ($\log_{10}\varepsilon$ 4·61, 4·30, 3·81, 3·78, 3·74, and 3·70).

The following were obtained by the same method: 6-*amino*-10-*methylphenanthridine* (52%), colourless needles, m. p. 126—127° from benzene–light petroleum (b. p. 60—80°) (Found: C, 81·2; H, 5·9%), $\lambda_{max.}$ 240, 286, 310, 320, 338, and 354 mμ ($\log_{10}\varepsilon$ 4·64, 3·75, 3·77, 3·80, 3·77, and 3·75); 6-*amino*-1,10-*dimethylphenanthridine* (53%), pale brown needles, m. p. 197—198°, from

[27] W. E. Bachmann and E. J. Fornefeld, *J. Amer. Chem. Soc.*, 1951, **73**, 51.
[28] E. Ritchie, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 169.

benzene (Found: C, 81·4; H, 6·6. $C_{15}H_{14}N_2$ requires C, 81·05; H, 6·4%), $\lambda_{max.}$ 246, 262—264, 320—324, 346—350, and 370 mμ ($\log_{10}$ ε 4·51, 4·34, 3·80, 3·74, and 3·67); 6-*amino*-1,2-*benzophenanthridine* (50%), fawn needles, m. p. 250—252°, from benzene (Found: C, 83·0; H, 4·8. $C_{17}H_{12}N_2$ requires C, 83·6; H, 4·95%), $\lambda_{max.}$ 258, 274, 316, 345, 360, and 379 mμ ($\log_{10}$ ε 4·53, 4·50, 3·97, 3·62, 3·74, and 3·76); 6-*amino*-9,10-*benzophenanthridine* (42%), fawn needles, m. p. 190—192°, from benzene (Found: C, 83·75; H, 4·8%), $\lambda_{max.}$ 258, 275, 292, 322, 368, and 386 mμ ($\log_{10}$ ε 4·57, 4·36, 4·19, 3·95, 3·68, and 3·71).

The Partial Resolution of 6-*Amino*-1,10-*dimethylphenanthridine*.—A solution of 6-amino-1,10-dimethylphenanthridine (0·30 g.) in 0·1N-hydrochloric acid (80 ml.) was treated with (+)-camphorsulphonic acid (0·15 g.) and heated on a water-bath for 30 min. The salt (0·20 g.) which precipitated on cooling was washed with 0·1N-hydrochloric acid, dissolved in methanol (5 ml.) and added dropwise to cold 5% potassium hydroxide (80 ml.). The liberated base (0·087 g.) was washed with aqueous potassium hydroxide and dried under vacuum at room temperature; $[\alpha]_D^{20}$ −3·9° (*c* 0·538 in $CHCl_3$).

In an identical experiment a similar fraction, after standing overnight, had $[\alpha]_D^{20}$ −1·9° (*c* 1·53 in $CHCl_3$).

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