426. *Synthesis of Plant-growth Regulators. Part II.* Dichloro-β-naphthyloxyacetic Acids.*

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1 : 6-Dichloro-2-naphthol (previously recorded m. p. 119·5°) has been synthesised by three routes and shown to have m. p. 99—100°. A mode of formation of 1 : *x*-dichloro-2-naphthols is described and new dichloro-2-naphthyloxyacetic acids, prepared as potential parthenocarpic or systemic fungicidal agents, are reported. Hydriodic acid, which demethylates chloromethoxynaphthalenes, causes elimination of α-chlorine atoms. Whilst hydrobromic acid demethylates normally in some cases, it converts 1 : 8-dichloro- into 8-bromo-1-chloro-2-naphthol.

The preparation of 1 : 6-dichloro-2-naphthol, claimed by Ruggli, Knapp, Merz, and Zimmermann (*Helv. Chim. Acta*, 1929, **12**, 1051), has already been discussed (James and

* Part I, *J.*, 1951, 3418.

Woodcock, *J.*, 1951, 1931). This naphthol was first mentioned in D.R.-P. 431,165 where reduction to 6-chloro-2-naphthol by ferrous sulphate is described, but there was no mention of the origin of the dichloro-compound or of its melting point.

Initial attempts were made to obtain 1 : 6-dichloro-2-naphthol from 1 : 6-disubstituted 2-naphthol or 2-naphthylamine derivatives. 1 : 6-Dichloro-2-naphthylamine, by diazotisation and hydrolysis, gave only a dark red alkali-insoluble material; the Sandmeyer reaction conditions, however, produced 1 : 2 : 6-trichloronaphthalene in high yield. Tetrazotisation of 1 : 6-diamino-2-naphthol or its methyl ether, followed by hydrolysis, gave only tars. Finally, the desired naphthol was produced in minute yield by the route : 6 : 2-$C_{10}H_8Cl{\cdot}OH$ $\longrightarrow$ 6 : 1 : 2-$C_{10}H_7Cl(NO_2){\cdot}OH$ $\longrightarrow$ 6 : 1 : 2-$C_{10}H_7Cl(NH_2){\cdot}OH$ $\longrightarrow$ 6 : 1 : 2-$C_{10}H_7Cl_2{\cdot}OH$. It was later obtained from 6-chloro-2-naphthol by treatment with sodium hypochlorite under certain conditions, and this method proved to be general for the formation of dichloro- from the remaining monochloro-2-naphthols. Entry of the second chlorine atom at position 1 was confirmed by the isolation of the known 1 : 3- and 1 : 4-dichloro-2-naphthols from the 3- and 4-chloro-2-naphthols respectively.

Nitration of 1-chloro-2-methoxynaphthalene gave two easily separable mononitro-derivatives, reduction of which, followed by diazotisation and Sandmeyer reactions, led to 1 : 6- and 1 : 8-dichloro-2-methoxynaphthalene. Attempts to demethylate these compounds led to similar treatment of other mono- and di-chloro-2-methoxynaphthalenes. Hydriodic acid eliminated chlorine from the α- but not from the β-position (cf. Franzen and Stäuble, *J. pr. Chem.*, 1921, **103**, 382), whilst hydrobromic acid generally only attacked the ether linkage. Hydrobromic–acetic acid converted 1 : 6-dichloro-2-methoxynaphthalene into 1 : 6-dichloro-2-naphthol, but with the 1 : 8-dichloro-ether yielded 8-bromo-1-chloro-2-naphthol. The identity of this compound was confirmed by synthesis from 8-chloro-7-methoxy-1-naphthylamine.

Whilst we were unable to produce 1-chloro-6-nitro-2-naphthol from the corresponding amine by diazotisation and subsequent hydrolysis, a Sandmeyer reaction gave 1 : 2-dichloro-6-nitronaphthalene in good yield. Reduction, diazotisation, and hydrolysis then gave the new 5 : 6-dichloro-2-naphthol.

Direct chlorination of 6-chloro-2-naphthol gave an alkali-insoluble product, probably a tetrachlorodihydroketonaphthalene, which on reduction with zinc dust was converted into, presumably, 1 : 3 : 6- or 1 : 4 : 6-trichloro-2-naphthol since oxidation with alkaline potassium permanganate yielded 4-chlorophthalic acid. Reduction with hydriodic acid gave a di- and not a mono-chloro-2-naphthol, however, showing that the trichloro-compound was 1 : 3 : 6-trichloro-2-naphthol. The reduction product, 3 : 6-dichloro-2-naphthol, may have been prepared by Claus and Schmidt (*Ber.*, 1886, **19**, 3172) and by Pollak (*Monatsh.*, 1929, **49**, 187) but in neither case was the orientation confirmed. In our hands, the former workers' method failed to give any phenolic material.

The results of the tests of both naphthols and naphthyloxyacetic acid as parthenocarpic and systemic fungicidal agents will be submitted for publication elsewhere.

Experimental

6-Chloro-2-naphthol.—The following procedure was more convenient and gave a better yield than that reported in Part I. 6-Nitro-2-naphthylamine (Saunders and Hamilton, *J. Amer. Chem. Soc.*, 1932, **54**, 638), diazotised in hydrochloric acid solution, gave, by a Sandmeyer reaction, 2-chloro-6-nitronaphthalene which, recrystallised once from dioxan, had m. p. 170—172°. Reduction in tetrahydrofuran in presence of Raney nickel gave 6-chloro-2-naphthylamine, m. p. 121—123°. The diazotised amine was hydrolysed by pouring it into boiling 20% sulphuric acid and a red product obtained. 6-Chloro-2-naphthol obtained by extraction of this product with 5% aqueous sodium hydroxide had m. p. 117—118° (yield based on nitro-amine, 37%). *6-Chloro-1-(6-chloro-2-naphthylazo)-2-naphthol* crystallised from dioxan in red needles, m. p. 234—236° (Found : C, 65·5; H, 3·4; Cl, 18·8. $C_{20}H_{12}ON_2Cl_2$ requires C, 65·4; H, 3·3; Cl, 19·3%). The m. p. was undepressed on admixture with the product obtained by coupling diazotised 6-chloro-2-naphthylamine and 6-chloro-2-naphthol.

6-Chloro-1-nitro-2-naphthol.—6-Chloro-2-naphthol (2 g.) in acetic acid (20 ml.) was added

slowly dropwise to a cooled mixture of fuming nitric acid (4 ml.) and acetic acid (15 ml.). After a further 1 hr.'s stirring at 0—5°, the mixture was poured on ice, and the product collected, washed with water and dried (1·6 g.; m. p. 129—131°). 6-*Chloro*-1-*nitro*-2-*naphthol* crystallised from aqueous methyl alcohol in dark yellow, rectangular prisms, m. p. 136—137° (Found : C, 53·7; H, 2·5; Cl, 15·8. $C_{10}H_6O_3NCl$ requires C, 53·7; H, 2·7; Cl, 15·9%). The *acetate* crystallised from acetic acid in colourless monoclinic prisms, m. p. 130—131° (Found : C, 54·2; H, 3·0; Cl, 13·0. $C_{12}H_8O_4NCl$ requires C, 54·2; H, 3·0; Cl, 13·4%). The *methyl ether*, which could only be prepared by refluxing the dry, finely powdered sodium salt of the naphthol with methyl sulphate, crystallised from dioxan in pale green rectangular prisms, m. p. 153—154° (Found : C, 55·8; H, 3·5; Cl, 14·4. $C_{11}H_8O_3NCl$ requires C, 55·6; H, 3·4; Cl, 14·9%).

1-*Amino*-6-*chloro*-2-*naphthol*.—6-Chloro-1-nitro-2-naphthol (3 g.) in tetrahydrofuran (20 ml.) was shaken in hydrogen in the presence of Raney nickel until no further gas was absorbed. Removal of the solvent from the filtered solution and crystallisation of the residue from aqueous methyl alcohol gave the *amino-naphthol* as colourless rhombs (2·2 g.), m. p. 177—178° (Found : C, 62·1; H, 4·3; Cl, 18·3. $C_{10}H_8ONCl$ requires C, 62·0; H, 4·1; Cl, 18·3%). The *diacetyl* derivative crystallised from aqueous methyl alcohol in rhombic prisms, m. p. 144—145° (Found : C, 60·8; H, 4·5; Cl, 13·0. $C_{14}H_{12}O_3NCl$ requires C, 60·5; H, 4·3; Cl, 12·8%).

1 : 6-*Dichloro*-2-*naphthol*.—(*a*) The above amino-naphthol (1·5 g.) was dissolved in glacial acetic acid (15 ml.) and concentrated sulphuric acid (4 ml.) and cooled to 0°. Sodium nitrite (0·5 g.) was added and stirring continued for 2 hr. The mixture was then added to cuprous chloride (5 g.) in concentrated hydrochloric acid (25 ml.) and stirred at room temperature for 15 min. The product, isolated with ether and re-extraction of the ethereal solution with alkali, was a dark solid. Further extraction with boiling light petroleum (b. p. 60—80°) gave rectangular prisms, m. p. 89—93°, raised to 97—99° by recrystallisation from the same solvent. This compound did not depress the m. p. of 1 : 6-dichloro-2-naphthol prepared as described below.

(*b*) 1 : 6-Dichloro-2-naphthylamine (Clemo and Legg, *J.*, 1947, 539) (1 g.) in concentrated hydrochloric acid (3 ml.) and water (10 ml.) was diazotised at 0° with sodium nitrite (0·5 g.). Addition of the filtered diazonium solution to boiling 20% sulphuric acid (300 ml.) caused no immediate effervescence but after several mintues the precipitation of a red solid was observed; no alkali-soluble material was isolated. When Sandmeyer conditions were used, the product was 1 : 2 : 6-trichloronaphthalene (0·9 g.), m. p. 91—92°, undepressed by admixture with an authentic specimen.

1 : 2-*Dichloro*-6-*nitronaphthalene*.—1-Chloro-6-nitro-2-naphthylamine (Clemo and Legg, *loc. cit.*) (5 g.), diazotised as already described, was added to a solution of cuprous chloride (5 g.) in concentrated hydrochloric acid (50 ml.), and the mixture warmed on a water-bath until the evolution of nitrogen had ceased. The *product*, washed with water and dried at 100° (5·1 g.), crystallised from aqueous dioxan in orange rectangular prisms, m. p. 170—171° (Found : C, 49·8; H, 2·1. $C_{10}H_5O_2NCl_2$ requires C, 49·6; H, 2·1%).

5 : 6-*Dichloro*-2-*naphthylamine*.—The preceding product (3·2 g.) in tetrahydrofuran (30 ml.) was shaken with Raney nickel until no further hydrogen was absorbed. The *amine*, on removal of the solvent from the filtered solution, crystallised from aqueous methyl alcohol in light brown, monoclinic prisms, m. p. 123—124° (Found : C, 56·8; H, 3·5; Cl, 33·1. $C_{10}H_7NCl_2$ requires C, 56·6; H, 3·3; Cl, 33·5%).

5 : 6-*Dichloro*-2-*naphthol*.—Diazotisation of 5 : 6-dichloro-2-naphthylamine and hydrolysis of the diazonium solution as described for 6-chloro-2-naphthol, gave 5 : 6-dichloro-2-naphthol (cf. below) in 40% yield.

Nitration of 1-*Chloro*-2-*methoxynaphthalene*.—A mixture of fuming nitric acid (*d* 1·5; 24 ml.) and acetic acid (120 ml.) was stirred at 5—10° for 45 min. during the addition of the methyl ether (15·5 g.) in acetic acid (120 ml.). Stirring was continued for a further 2·5 hr. at room temperature and then water (100 ml.) was added. The crystalline precipitate (A) which had gradually increased in amount was collected and washed with water. Further addition of water to the mother-liquors gave a second crop (B) which was treated similarly.

1-*Chloro*-2-*methoxy*-6-*nitronaphthalene* [product (A)] crystallised from acetone–ethyl alcohol in monoclinic prisms, m. p. 181—182° (Found : C, 55·4; H, 3·4; Cl, 14·6. $C_{11}H_8O_3NCl$ requires C, 55·6; H, 3·4; Cl, 14·9%). 1-*Chloro*-2-*methoxy*-8-*nitronaphthalene* [product (B)] crystallised from aqueous ethyl alcohol in rhombic prisms, m. p. 106—108° (Found : C, 55·6; H, 3·3; Cl, 15·2%).

5-*Chloro*-6-*methoxy*-2-*naphthylamine*.—This was obtained by shaking the appropriate nitro-compound in tetrahydrofuran in the presence of Raney nickel and hydrogen. When reduction

was complete, the catalyst was filtered off and the solvent removed. The ***amine*** crystallised from methyl alcohol in colourless stout rhombs, m. p. 117—118° (Found : C, 63·7; H, 5·0; Cl, 16·5. $C_{11}H_{10}ONCl$ requires C, 63·6; H, 4·8; Cl, 17·1%).

8-*Chloro*-7-*methoxy*-1-*naphthylamine*.—Prepared as was the isomer, this ***amine*** crystallised from methyl alcohol in colourless monoclinic prisms, m. p. 91—92° (Found : C, 63·6; H, 4·8; Cl, 17·0%).

1 : 6-*Dichloro*-2-*methoxynaphthalene*.—A solution of 5-chloro-6-methoxy-2-naphthylamine (1·6 g.) in water (10 ml.) and concentrated hydrochloric acid (10 ml.) was treated at 0° with sodium nitrite (0·7 g.). After 0·25 hr. the filtered solution was added to a solution of cuprous chloride (1·7 g.) in concentrated hydrochloric acid (20 ml.) and stirred at room temperature until the evolution of nitrogen ceased. The *dichloro*-compound, washed with water and dried, crystallised from light petroleum (b. p. 40—60°) (charcoal) in colourless monoclinic prisms, m. p. 70—71° (Found : C, 58·2; H, 3·7; Cl, 31·2. $C_{11}H_8OCl_2$ requires C, 58·1; H, 3·5; Cl, 31·2%). Admixture with the product obtained by methylating 1 : 6-dichloro-2-naphthol failed to depress the m. p. Oxidation in pyridine with potassium permanganate gave 4-chlorophthalic acid, m. p. 150° undepressed by admixture with an authentic specimen. Demethylation by refluxing hydriodic acid (*d* 1·7) and a trace of red phosphorus (4 hr.) gave 6-chloro-2-naphthol, m. p. and mixed m. p. 115—117°. Similar treatment in acetic acid with hydrobromic acid (*d* 1·7) gave 1 : 6-dichloro-2-naphthol, m. p. 98—99°, identical with the products previously described.

1 : 8-*Dichloro*-2-*methoxynaphthalene*.—Prepared as was the isomer, this *compound* crystallised from light petroleum (b. p. 40—60°) in rectangular prisms, m. p. 71—72° (Found : C, 58·1; H, 3·6; Cl, 30·8%). Admixture with the product obtained by methylating 1 : 8-dichloro-2-naphthol (described below) failed to depress the m. p. Oxidation with powdered potassium permanganate in pyridine gave 3-chlorophthalic acid, m. p. 179—181°, whilst demethylation with hydriodic acid (*d* 1·7) yielded β-naphthol, m. p. 120—121°, each undepressed by admixture with the appropriate authentic specimen.

8-*Bromo*-1-*chloro*-2-*methoxynaphthalene*.—A solution of 8-chloro-7-methoxy-1-naphthylamine (1·5 g.), diazotised in 33% sulphuric acid, was poured into a solution of cuprous bromide (1·5 g.) in hydrobromic acid (*d* 1·5; 15 ml.) and kept at ordinary temperature for 1 hr. Extraction with ether gave a red tar from which the *bromo*-compound was obtained by extraction with light petroleum (b. p. 60—80°). It crystallised from light petroleum (b. p. 40°) in rectangular prisms, m. p. 58—59° (Found : C, 48·5; H, 3·0. $C_{11}H_8OBrCl$ requires C, 48·6; H, 2·9%).

8-*Bromo*-1-*chloro*-2-*naphthol*.—(*a*) A solution of 1 : 8-dichloro-2-methoxynaphthalene (1·0 g.) in acetic acid (10 ml.) was refluxed with hydrobromic acid (*d* 1·7; 5 ml.) for 4 hr. The *product*, isolated with ether, crystallised from acetic acid in colourless rectangular prisms, m. p. 144—145° (Found : C, 46·4; H, 2·5; Br, 30·6; Cl, 13·6. $C_{10}H_6OBrCl$ requires C, 46·4; H, 2·3; Br, 31·0; Cl, 13·8%).

(*b*) Treatment of 8-bromo-1-chloro-2-methoxynaphthalene by the same procedure gave a product, m. p. 140—142°, which did not depress the m. p. of product (*a*). The ***acetate*** prepared from product (*a*) or (*b*) crystallised from aqueous methyl alcohol in rectangular prisms, m. p. 97—98° (Found : C, 48·0; H, 2·6. $C_{12}H_8O_2BrCl$ requires C, 48·1; H, 2·7%).

1 : 3-*Dichloro*-2-*methoxynaphthalene*.—This *compound* crystallised from aqueous methyl alcohol in prisms, m. p. 49—50° (Found : C, 58·0; H, 3·7; Cl, 31·4. $C_{11}H_8OCl_2$ requires C, 58·1; H, 3·5; Cl, 31·2%). Demethylation with (*a*) hydriodic acid (*d* 1·7) and (*b*) hydrobromic acid (*d* 1·7) in acetic acid, gave 3-chloro-2-naphthol, m. p. 92—93°, and 1 : 3-dichloro-2-naphthol, m. p. 71—73°, respectively. The identities of these products were confirmed by admixture with authentic specimens.

1 : 4-*Dichloro*-2-*methoxynaphthalene*.—This *compound* crystallised from ethyl alcohol in rectangular prisms, m. p. 84—85° (Found : C, 58·1; H, 3·5; Cl, 31·2. $C_{11}H_8OCl_2$ requires C, 58·1; H, 3·5; Cl, 31·2%). Demethylation with hydriodic acid (*d* 1·7) gave β-naphthol, m. p. and mixed m. p. 120—121°. Hydrobromic acid (*d* 1·7) in acetic acid gave 1 : 4-dichloro-2-naphthol, m. p. and mixed m. p. 121—122°.

1-*Chloro*-6-*nitro*-2-*naphthol*.—A solution of 1-chloro-2-naphthol (1·0 g.) in glacial acetic acid (10 ml.) was added dropwise during 0·25 hr. to a mixture of nitric acid (*d* 1·5) (2 ml.) and acetic acid (10 ml.) and stirred at room temperature for 1 hr. further. Water (*ca.* 10 ml.) was added and the crystalline precipitate which gradually formed was collected, washed with water, and dried (0·2 g.; m. p. 170—186°). The *nitronaphthol* crystallised from aqueous methyl alcohol in yellow rectangular prisms, m. p. 194—195° (Found : C, 53·5; H, 2·6; Cl, 15·7. $C_{10}H_6O_3NCl$ requires C, 53·7; H, 2·7; Cl, 15·9%). This result was only reproduced once; many other

attempts gave tars. The methyl ether had m. p. 180—181°, undepressed by admixture with 1-chloro-2-methoxy-6-nitronaphthalene described earlier.

2-Acetoxy-1 : 6-dinitronaphthalene.—The *acetyl* derivative prepared from 1 : 6-dinitro-2-naphthol (Bell, *J.*, 1930, 1932) crystallised from benzene (charcoal) in nacreous plates, m. p. 172—173° (Found : C, 52·1; H, 2·6. $C_{12}H_8O_6N_2$ requires C, 52·2; H, 2·8%).

Chlorination of 6-Chloro-2-naphthol.—The naphthol (0·5 g.) in tetrahydrofuran (5 ml.) was subjected to a slow stream of dry chlorine at 0°. After removal of the solvent the *substance* produced crystallised from methyl alcohol in brownish monoclinic prisms, m. p. 157—159° (Found : C, 42·6; H, 1·4; Cl, 49·8. $C_{10}H_4OCl_4$ requires C, 42·6; H, 1·4; Cl, 50·3%).

1 : 3 : 6-Trichloro-2-naphthol.—A solution of the preceding tetrachloro-product (1 g.) in glacial acetic acid (20 ml.) was refluxed with zinc dust (2 g.) for 1 hr. Addition of water to the hot filtered solution gave 1 : 3 : 6-trichloro-2-naphthol which crystallised from aqueous acetic acid in colourless needles, m. p. 98—99° (Found : C, 48·3; H, 2·0. $C_{10}H_5OCl_3$ requires C, 48·5; H, 2·0%). The *acetate* crystallised from aqueous methyl alcohol in colourless monoclinic prisms, m. p. 109—110° (Found : C, 49·8; H, 2·5. $C_{12}H_7O_2Cl_3$ requires C, 49·8; H, 2·4%).

3 : 6-Dichloro-2-naphthol.—Treatment of the above trichloronaphthol with boiling hydriodic acid (*d* 1·7) for 4 hr. gave an alkali-soluble *product* which crystallised from light petroleum (b. p. 60—80°) in colourless rectangular prisms, m. p. 124—125°. The *acetate* crystallised from aqueous methyl alcohol in nacreous plates, m. p. 98—99°. For analyses see the Table.

Chloro-substituents	M. p.	Solvent *	Found (%) : C	H	Chloro-substituents	M p	Solvent *	Found (%) : C	H
	Dichloro-2-naphthols.[1]					*Dichloro-2-naphthyl acetates.*[2]			
1 : 5-	143—144°	Aq. AcOH	56·5	2·9	1 : 5-	100—101°	MeOH	56·4	3·3
1 : 6-	99—100	Pet. (40—60°)	56·1	2·9	1 : 6-	98—99	Aq. AcOH	56·7	3·1
1 : 7-	121—122	Aq. AcOH	55·9	2·7	1 : 7-	111—112	Aq. MeOH	56·4	3·1
1 : 8-	126—127	Aq. MeOH	56·5	2·8	1 : 8-	87—88	,,	56·4	3·1
3 : 6-	124—125	Pet. (60—80°)	56·3	2·9	3 : 6-	98—99	,,	56·5	3·0
5 : 6-	151—152	,,	56·4	3·0	5 : 6-	92—93	,,	56·5	3·0
	Dichloro-2-naphthyloxyacetic acids.[3]								
1 : 5-	206—207°	MeOH	53·0	3·2					
1 : 6-	162—163	Aq. MeOH	53·4	3·0					
1 : 7-	176—177	,,	53·2	3·0					
1 : 8-	156—157	,,	53·15	3·2					
3 : 6-	179—180	,,	53·2	3·0					
5 : 6-	192—193	,,	53·4	2·8					

* Pet. = light petroleum (b. p. in parentheses).
[1] $C_{10}H_6OCl_2$ requires C, 56·35; H, 2·8%.
[2] $C_{12}H_8O_2Cl_2$ requires C, 56·5; H, 3·1%.
[3] $C_{12}H_8O_3Cl_2$ requires C, 53·15; H, 3·0%.

1 : x-Dichloro-2-naphthols.—The appropriate monochloronaphthol, dissolved in aqueous sodium hydroxide (1 equiv.), was stirred at 0—5° during the dropwise addition of aqueous sodium hypochlorite (4% w/v of available chlorine, 1 equiv.). Use of more concentrated hypochlorite solution gave tars but more dilute solutions have been successfully used. After 0·5 hr. the solution was acidified and the product collected, washed with water, dried, and recrystallised. For the products see the Table.

Dichloro-2-naphthyloxyacetic acids.—These were prepared as described in Part I; analytical details are tabulated.

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