Chloro-derivatives of Indazolo[2,3-*a*][3,1]benzoxazin-5-one and Indazolo-[2,1-*a*]indazole-6,12-dione

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Treatment of azobenzene-2,2'-dicarboxylic acid with phosphorus pentachloride (the Freundler reaction) has been shown to give four major products: 8-chloroindazolo[2,3-*a*][3,1]benzoxazin-5-one, 2-chloroindazolo-[2,1-*a*]indazole-6,12-dione, 10-chloroindazolo[2,3-*a*][3,1]benzoxazin-5-one (α and β modifications), and a minor product, indazolo[2,1-*a*]indazole-6,12-dione. The structures were assigned on the basis of independent syntheses, chemical behaviour, and spectroscopic examination.

THE structures of the chlorinated compounds obtained when azobenzene-2,2'-dicarboxylic acid is treated with phosphorus pentachloride have been in doubt for some time. Freundler [1] obtained two crystalline compounds, $C_{14}H_7ClN_2O_2$, both of m.p. 241°, which he considered to have structure (Ia). Mosby proposed [2] in the light of his earlier work [3] that these compounds had structure (II).

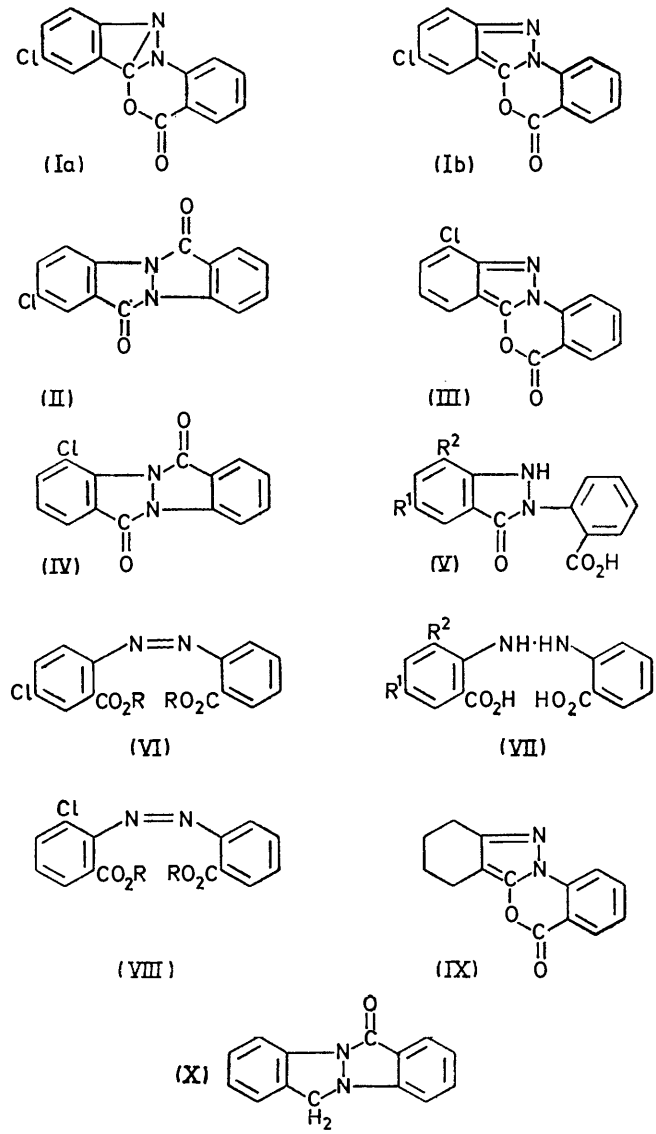
In continuation of earlier studies of the parent heterocyclic systems,[4] the products of the Freundler reaction [1] have been re-examined, and by fractional crystallization and chromatography one minor and four major products have been isolated. The structures now advanced for these compounds [5] have been established on the basis of independent syntheses, chemical transformations, and spectroscopic data.

All the major products possess the same empirical formula, $C_{14}H_7ClN_2O_2$, and are assigned structures as follows: (A) 8-chloroindazolo[2,3-*a*][3,1]benzoxazin-5-one, m.p. 210° (Ib); (B) 2-chloroindazolo[2,1-*a*]indazole-6,12-dione, m.p. 233° (II); (C) 10-chloroindazolo-[2,3-*a*][3,1]benzoxazin-5-one (III) α-modification, pale yellow prisms, m.p. 240°; (D) β-modification, colourless needles, m.p. 240°. A minor product was indazolo-[2,1-*a*]indazole-6,12-dione, m.p. 302°.[4]

Compound (A) was identified on the basis of its i.r. spectrum (Table 1), its ready hydrolysis to the monocarboxylic acid (V; $R^1 = Cl$, $R^2 = H$), its strong retention by chromatographic alumina, and its mass spectrum. On heating this compound (Ib) alone or with acetic anhydride the corresponding indazoloindazole-dione (II) was obtained, which was identical with compound (B). Reductive dechlorination [6] of (Ib) gave indazolo[2,1-*a*]indazole-6,12-dione.

Compound (II) was synthesised independently by condensing methyl 2-nitrosobenzoate with methyl 2-amino-5-chlorobenzoate to give the azo-derivative (VI; R = Me), which was hydrolysed to the diacid (VI; R = H). Reduction with zinc dust and acetic acid to the hydrazo-compound (VII; $R^1 = Cl$, $R^2 = H$) followed by heating with acetic anhydride gave compound (II).

The crystalline modifications of compound (III) clearly corresponded to those reported by Freundler. Their i.r. spectra were essentially identical except for some band splitting in the 700—900 cm^{-1} region (see Table 2). The substances differed strikingly in their solubility in benzene, ethyl acetate, and ethanol. On crystallisation from glacial acetic acid the α-modification



was converted into the β-form, whereas the β-form remained unchanged on crystallisation from this solvent.

[1] M. P. Freundler, *Bull. Soc. chim. France*, 1907, **1** [4] 206, 228.
[2] W. L. Mosby, 'Systems with Bridgehead Nitrogen,' Part 1, Interscience, New York, 1961, p. 228.
[3] W. L. Mosby, *Chem. and Ind.*, 1957, 17.
[4] G. K. J. Gibson, A. S. Lindsey, and H. M. Paisley, *J. Chem. Soc.*, 1967, 1792.
[5] A. S. Lindsey, report at the Second International Congress of Heterocyclic Chemistry, Montpellier, July 1969.
[6] W. L. Mosby, *Chem. and Ind.*, 1959, 1348.

The m.p. of a mixture of the two substances remained unchanged at 240°. The two modifications in ethanol had similar u.v. spectra with small intensity differences in the 220—230 nm band envelope, which may indicate variation in the conjugation pattern.

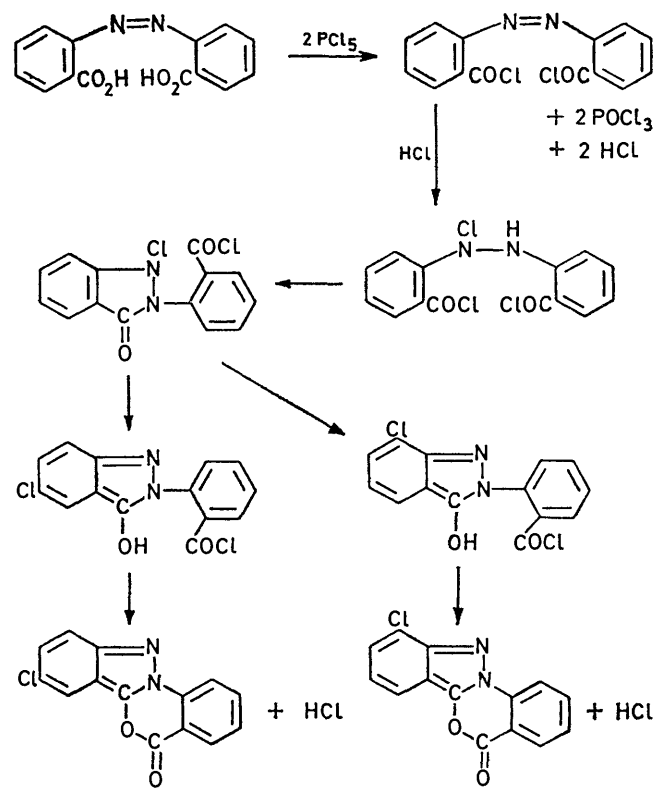
Dr. P. Clarke of these laboratories has made a preliminary *X*-ray crystallographic study of the two modifications.[7] He reports that both are triclinic (probably $P\bar{1}$ space group) and that the unit cell dimensions differ considerably for each modification. Both contain four molecules per unit cell, which means there are two crystallographically distinct types of molecule present, perhaps as two different conformations. Coupled with the abnormally high density (1·568 g cm^{-3}, whereas a value of about 1·2 g cm^{-1} would be expected) this suggests that the molecules are associated in pairs, or perhaps stacked in infinite columns with some form of polarisation or charge-transfer bonding between them. Such possibilities appear feasible on the basis of the ground structures proposed previously.[4]

Structure (III) was assigned to the α- and β-forms on the basis of the strong i.r. absorption at 1780 cm^{-1} (lactone) and other spectral similarities to the unsubstituted compound (see Table 1), and because of their ready hydrolysis to the monocarboxylic acid (V; $R^1 = H$, $R^2 = Cl$), which resulted in a strong absorption on to chromatographic alumina. Further confirmation was the conversion into 4-chloroindazolo[2,1-*a*]indazole-6,12-dione (IV) on heating alone or with boiling acetic anhydride. Reductive dechlorination of (III) caused rearrangement to the indazoloindazoledione (IV; H for Cl). As in the case of the unsubstituted compounds[4] the chloro-derivatives (III) and (IV) gave identical mass spectra, which is ascribed to the rapid conversion of (III) to (IV) on the heated probe under electron impact.

The proposed structure (III) was also confirmed by an independent synthesis of the derived compound (IV). Condensation of methyl 2-nitrosobenzoate and methyl 2-amino-3-chlorobenzoate gave the red azo-compound (VII; R = Me), which was hydrolysed to the dicarboxylic acid (VIII; R = H). The hydrolysis was invariably accompanied by partial replacement of the Cl by OH due to the lability of the former. Reduction, as before, to the hydrazo-compound (VII; $R^1 = H$, $R^2 = Cl$), and cyclisation with boiling acetic acid followed by chromatography on silica gave 4-chloroindazolo-[2,1-*a*]indazole-6,12-dione. The i.r. spectrum showed the product to contain a small amount of the corresponding 2-chloro-compound, which presumably arises through migration of the labile chlorine during the reaction sequence.

Evidence which supports the view that in compounds (Ib) and (III) the chlorine is a substituent on the indazole benzene ring was obtained by studying the reduction behaviour of these compounds, and of the unsubstituted series. On catalytic reduction of indazolo-[2,3-*a*][3,1]benzoxazin-5-one 2 mol. equiv. of hydrogen were rapidly absorbed to give 7,8,9,10-tetrahydroindazolo[2,3-*a*][2,1]benzoxazin-5-one (IX), identified on the basis of the sharp i.r. absorption bands near 2900 cm^{-1} (CH_2) and the disappearance of the dienoid bands[8,9] at 740 and 1570 cm^{-1}, and by the presence of the fragments *m/e* 56 (C_4H_8) and 184 ($C_{10}H_4N_2O_2$) in its mass spectrum. Under identical catalytic conditions indazolo-[2,1-*a*]indazole-6,12-dione did not absorb hydrogen. The dione was reduced with zinc dust and acetic acid, yielding the crystalline compound (X). These observations indicate that the dienoid system in these compounds is more readily reduced than the phenylene group under catalytic conditions, which is in line with other reports.[10,11] Under the same catalytic conditions both compounds (Ib) and (III) absorbed hydrogen with reluctance, yielding compound (IX). This supports the view that the chlorine is substituted on the indazole system.

The nuclear chlorination mechanism in the original treatment of azobenzene-2,2'-dicarboxylic acid with



SCHEME

phosphorus pentachloride may now be considered. A possible scheme is shown in which hydrogen chloride

[7] P. T. Clarke, *J. Appl. Cryst.*, in the press.
[8] S. M. Csicsery, *J. Org. Chem.*, 1960, **25**, 518.
[9] H. A. Szymanski, 'Interpreted Infrared Spectra,' Plenum Press, New York, 1964, vol. 1, p. 73.
[10] H. A. Smith and H. T. Merewether, *J. Amer. Chem. Soc.*, 1949, **71**, 413.
[11] K. Fries, K. Fabel, and H. Eckhardt, *Annalen*, 1941, **550**, 31.

generated in the first stage adds to the azo double bond to give *N*-chloro-hydrazo- or -indazolone derivatives, which, owing to the lability of the chlorine, are readily transformed into the *C*-substituted derivatives. This mechanism is supported by several observations in the literature. Thus addition of hydrogen chloride to an aromatic azo-linkage and subsequent rearrangement to give nuclear chloro-derivatives substituted *ortho* and *para* to the nitrogen atom is well established.[12] Such *N*-chloro-compounds are more readily labile under the influence of an adjoining carbonyl group.[13] The known preference for the enolic form of the pyrazol-5-ones [14] is likely to be enhanced by the nuclear-substituted chlorine and consequently the probability of reaction products with the lactone structure is increased.

The structural conclusions reported here have some bearing on the structures proposed for other chloro-derivatives of this series. Reich and Merki [15] found that reduction of 6,6′-dichloroazobenzene-2,2′-dicarboxylic acid with tin(II) chloride gave a product of m.p. 348° which they considered to be 1,7-dichloroindazolo[2,1-*a*]-indazole-6,12-dione. This compound was sublimable and its reported properties are similar to those of compounds (II) and (IV). On the other hand Cullen and L'Ecuyer [16] have described a product derived from the von Richter reaction with *p*-chloronitrobenzene which they thought to be 3,8-dichloroindazolo[2,3-*a*][3,1]-benzoxazin-5-one. However comparison of the quoted i.r. spectrum of this compound with those of compounds (Ib), (II), (III), and (IV) showed it to be similar to (II) but dissimilar to the others. This observation, together with the report that the compound sublimes unchanged, suggests that the compound is in fact 2,8-dichloro-indazolo[2,1-*a*]indazole-6,12-dione.

EXPERIMENTAL

U.v. spectra of compounds in ethanol were measured on an Optica CF4 double-beam recording spectrophotometer. I.r. spectra of solids dispersed in potassium bromide discs were measured on a Perkin-Elmer Infracord. Molecular weights were determined from mass measurements recorded on an A.E.I. MS9 instrument (direct insertion technique). All solvents used for crystallisation and chromatography were anhydrous.

Action of Phosphorus Pentachloride on Azobenzene-2,2′-dicarboxylic Acid.—The literature procedure [1] was modified. To phosphorus pentachloride (42 g) and anhydrous chloroform (200 ml) in a flask fitted with a condenser and immersed in an ice-bath finely powdered azobenzene-2,2′-dicarboxylic acid [17] (20 g) was added in portions with stirring. After 2 h at 0 °C the flask was heated on a steam-bath for 2 h. The cooled mixture was added to ice-cold water (400 ml) and the chloroform was distilled off. The solid deposited was filtered off, washed with cold distilled water and dried (yield 17·4 g). Fractional crystallisation from benzene and then from ethyl acetate gave 8-*chloro-indazolo*[2,3-a][3,1]*benzoxazin-5-one* (Ib) (*ca.* 5 g), which on chromatography from benzene on silica gel afforded needles, m.p. 210° (Found: C, 62·3; H, 2·5; Cl, 13·3; N, 10·3%; *M*, 270·0192. $C_{14}H_7ClN_2O_2$ requires C, 62·1; H, 2·6; Cl, 13·1; N, 10·4%; *M*, 270·0196), $\lambda_{max.}$ (EtOH) 232, 272, and 358 nm (log ε 4·61, 4·05, and 3·88); 10-*chloro-indazolo*[2,3-a][3,1]*benzoxazin-5-one* (III) α-modification (*ca.* 1 g), yellow prisms, m.p. 240—241° (Found: C, 62·2; H, 2·5; Cl, 13·1; N, 10·6%; *M*, 270·0192); β-modification (*ca.* 6 g), colourless needles, m.p. 239—240° (Found: C, 62·3; H, 2·5; Cl, 13·0; N, 10·5%; *M*, 270·0187); 2-*chloro-indazolo*[2,1-a]*indazole-6,12-dione* (II) (*ca.* 3 g), prisms, m.p. 232—233° (Found: C, 62·1; H, 2·6; Cl, 13·3; N, 10·4%; *M*, 270·0191), $\lambda_{max.}$ (EtOH) 239, 262, 273, and 357 nm (log ε 4·47, 4·05, 4·11, and 4·00); and indazolo[2,1-*a*]-indazole-6,12-dione (*ca.* 0·2 g), m.p. 302°. These compounds or their derivatives were identified by comparison with authentic samples (see later).

TABLE 1

I.r. absorption bands *

Structure	$\nu_{max.}$/cm^{-1}	Structure	$\nu_{max.}$/cm^{-1}
(Ib; H for Cl)	1780 (9·7)	(II; H for Cl)	1740 (8·7)
	1740 (6·7)		1720sh (9·6)
	1645 (10·0)		1690 (10·0)
	1620 (9·5)		1670sh (9·6)
	1600 (7·3)		1625 (10·0)
(I)	1770 (10·0)		1598 (9·2)
	1740 (5·5)	(II)	1730sh (4·7)
	1640 (8·5)		1715sh (7·6)
	1615 (8·9)		1685 (10·0)
	1595 (3·4)		1670sh (8·9)
(III)	1775 (10·0)		1610 (8·5)
	1750 (7·3)		1580 (6·7)
	1632 (8·3)	(IV)	1740 (7·7)
	1615 (8·7)		1712 (10·0)
	1590 (4·8)		1695sh (7·9)
(IX)	1770 (10·0)		1615 (6·2)
	1758 (10·0)		1597 (5·5)
	1740sh (6·0)	(X)	1735sh (6·0)
	1630 (10·0)		1700sh (9·1)
	1615 (10·0)		1685 (9·5)
	1590sh (3·8)		1670sh (9·1)
			1655 (10·0)
			1650 (9·4)

* Relative intensities with respect to the strongest band in the 6 μm region are shown in parentheses.

TABLE 2

Differences in the i.r. spectra ($\nu_{max.}$/cm^{-1}) of the α- and β-modifications of 10-chloroindazolo[2,3-*a*][3,1]benzoxazin-5-one

α-Modification	β-Modification
1321m	1330m, 1321m (doublet)
865m, 859m, 855m (triplet)	865m, 859s (doublet)
789m	789w,sh
778m, 771m (doublet)	780m, 771m (doublet)
756s, 743s, 738s (triplet)	749s, 740s (doublet)

2-Chloroindazolo[2,1-a]*indazole-6,12-dione* (II).—Methyl 2-nitrosobenzoate (656 mg) and methyl 2-amino-5-chloro-

[12] P. Jacobsen, *Annalen*, 1909, **367**, 304.
[13] A. Hantsch and M. Singer, *Ber.*, 1897, **30**, 320; K. J. P. Orton, F. G. Soper, and C. Williams, *J. Chem. Soc.*, 1928, 998; E. E. Slosson, *Ber.*, 1895, **28**, 3265.
[14] N. A. Evans, D. J. Whelan, and R. B. Johns, *Tetrahedron*, 1965, **21**, 3351.
[15] S. Reich and W. Merki, *Bull. Soc. chim. France*, 1917, **21**(4), 8.
[16] E. Cullen and Ph. L'Ecuyer, *Canad. J. Chem.*, 1961, **39**, 144, 155.
[17] J. Maier, *Ber.*, 1901, **34**, 4132.

benzoate (744 mg) in glacial acetic acid (5 ml) were kept at 40—45 °C for 7 days, after which all the nitroso-compound had dissolved. The cold solution was added to excess of aqueous ethanolic sodium hydroxide (20%; 50 ml) at 0 °C, and was then hydrolysed by heating on a steam-bath for 2 h. After cooling to 0 °C, acidification with concentrated hydrochloric acid gave an orange precipitate of *4-chloroazobenzene-2,2′-dicarboxylic acid* (760 mg), m.p. 220° (decomp.) (from acetone–water) (Found: C, 55·1; H, 2·9; Cl, 11·1; N, 9·0. $C_{14}H_9ClN_2O_4$ requires C, 55·0; H, 3·0; Cl, 11·6; N, 9·2%).

This compound (500 mg) in ethanol (30 ml) was treated with zinc dust (1 g) and glacial acetic acid (5 ml) at the b.p. for 15 min. The solution was immediately filtered into water (100 ml) to give a precipitate of 4-chlorohydrazobenzene-2,2′-dicarboxylic acid (280 mg), m.p. 180°. The dry product (250 mg) in acetic anhydride (15 ml) was refluxed for 2·5 h. Work-up in the usual manner gave 2-chloroindazolo[2,1-*a*]-indazole-6,12-dione (160 mg), m.p. 233° (Found: C, 62·1; H, 2·6; Cl, 13·3; N, 10·4. Calc. for $C_{14}H_7ClN_2O_2$: C, 62·1; H, 2·6; Cl, 13·1; N, 10·4%).

Conversion of 8-*Chloroindazolo*[2,3-a][3,1]*benzoxazin-5-one* (Ib) *into* 2-*Chloroindazolo*[2,1-a]*indazole-6,12-dione* (II).—(*a*) Compound (Ib) (45 mg) was heated at 300 ± 10 °C for 7 h. The melt was dissolved in warm benzene and filtered through a short column of chromatographic silica gel in benzene. The recovered solid (35 mg), m.p. 232°, possessed an i.r. spectrum identical with that of authentic 2-chloroindazolo[2,1-*a*]indazole-6,12-dione and with that of the chemically rearranged compound.

(*b*) Compound (Ib) (1·0 g) was refluxed with acetic anhydride (60 ml) for 72 h. The product, recovered in the usual way and crystallised from benzene–light petroleum (b.p. 60—80°), gave 2-chloroindazolo[2,1-*a*]indazole-6,12-dione as prisms, m.p. 232—233° (Found: C, 62·1; H, 2·65; Cl, 13·3; N, 10·3%), i.r. spectrum identical with an authentic spectrum.

Hydrolysis of 8-*Chloroindazolo*[2,3-a][3,1]*benzoxazin-5-one* (Ib).—Compound (Ib) (100 mg) in aqueous ethanol (2 : 8; 10 ml) containing sodium hydroxide (1 g) was kept at room temperature for 18 h, then filtered. The ethanol was removed under vacuum and water (25 ml) was added. The ice-cold solution was acidified with conc. hydrochloric acid to give a white solid. Crystallisation from aqueous ethanol gave 2-(2-*carboxyphenyl*)-5-*chloroindazol*-3(2H)-*one* (V; R^1 = Cl, R^2 = H) (300 mg) which was dimorphic (m.p. 198 and 206°) (Found: C, 58·1; H, 3·2; Cl, 12·7; N, 9·5. $C_{14}H_9ClN_2O_3$ requires C, 58·2; H, 3·1; Cl, 12·3; N, 9·7%).

Reductive Dechlorination of 8-*Chloroindazolo*[2,3-a][3,1]-*benzoxazin-5-one* (Ib).—Compound (Ib) (40 mg) was heated under reflux with hydrazine hydrate (0·4 ml), 5% palladium–charcoal (20 mg), and ethanol (15 ml) for 5 min. The catalyst was filtered off and the filtrate added to an equal volume of cold water, which was then made just acid with hydrochloric acid. On cooling, indazolo[2,1-*a*]indazole-6,12-dione separated as needles, m.p. 302° (from toluene) (yield 20 mg), identical with an authentic sample.[4]

Reductive Dechlorination of 10-*Chloroindazolo*[2,3-a][3,1]-*benzoxazin-5-one* (III).—By the same procedure compound (III) (70 mg) was converted into indazolo[2,1-*a*]indazole-6,12-dione (45 mg), identified by elemental analysis and i.r. spectrum.

4-*Chloroindazolo*[2,1-a]*indazole-6,12-dione* (IV).—Methyl 2-nitrosobenzoate (150 mg) and methyl 2-amino-3-chlorobenzoate (170 mg) in glacial acetic acid (6 ml) were kept at 40—45 °C for 10 days after which all the nitroso-compound had dissolved. The solution was cooled and added slowly to an excess of potassium hydroxide (1 g) in ethanol–water (20 ml; 1 : 1). The mixture was heated for 4 h on a water-bath and the ethanol was removed. Cooling (0 °C), acidification with concentrated hydrochloric acid, and concentration on a water-bath gave dark red crystals of the azo-compound, m.p. 220° (decomp.).

A solution of this in ethanol (30 ml) was treated at the b.p. with zinc dust and glacial acetic acid for 10—15 min, then filtered into water to precipitate the hydrazo-compound. The dried product was refluxed with acetic anhydride (20 ml) for 2 h; the acetic anhydride was evaporated off and the residue was taken up in a little dry benzene. The solution was filtered through chromatographic silica in benzene. The main fraction (60 mg), eluted with 20% ether–benzene, had m.p. 193—195° and was substantially 4-chloroindazolo[2,1-*a*]indazole-6,12-dione. The i.r. spectrum showed it to contain some 2-chloroindazolo[2,1-*a*]indazole-6,12-dione.

Conversion of 10-*Chloroindazolo*[2,3-a][3,1]*benzoxazin-5-one* (III) *into* 4-*Chloroindazolo*[2,1-a]*indazole-6,12-dione* (IV).—(*a*) Compound (III) (50 mg) was heated at 300 ± 10 °C for 7 h. The melt was dissolved in warm anhydrous benzene and filtered through a short column of chromatographic silica gel in benzene. The recovered solid (37 mg), m.p. 194—195°, was 4-chloroindazolo[2,1-*a*]indazole-6,12-dione (i.r. spectrum).

(*b*) Compound (III) (1·0 g) was refluxed with acetic anhydride (40 ml) for 72 h. The product (950 mg), recovered in the usual way, crystallised from benzene–light petroleum (b.p. 60—80°) to give 4-chloroindazolo[2,1-*a*]-indazole-6,12-dione, m.p. 195° (Found: C, 61·9; H, 2·6; Cl, 13·1; N, 10·2%) (i.r. spectrum).

Hydrolysis of 10-*Chloroindazolo*[2,3-a][3,1]*benzoxazin-5-one* (III).—Compound (III) (400 mg) was heated in ethanol (60 ml) and aqueous sodium hydroxide (20%; 15 ml) for 3 h. After the usual work-up, addition of hydrochloric acid at 0 °C precipitated 7-chloro-2-(2-carboxyphenyl)-indazol-3(2*H*)-one (300 mg), m.p. 234° (decomp.) (from ethanol) (Found: C, 58·1; H, 3·1; Cl, 12·0; N, 9·7. Calc. for $C_{14}H_9ClN_2O_3$: C, 58·2; H, 3·1; Cl, 12·3; N, 9·7%).

On heating this product with diethylaniline at 200 ± 10 °C for 2 h conversion into 4-chloroindazolo[2,1-*a*]indazole-6,12-dione (IV) occurred (confirmed by m.p. and i.r. spectrum).

Catalytic Reduction of Indazolo[2,3-a][3,1]*benzoxazin-5-one*.—The title compound (400 mg), dissolved in AnalaR ethyl acetate (100 ml) was shaken with 10% platinised charcoal (200 mg) under hydrogen (1 atm). After 4 h, absorption of hydrogen ceased (109 cm^3) and the catalyst was filtered off. Recovery of the product in the usual way and crystallisation from ether at −80° gave 7,8,9,10-tetrahydroindazolo[2,3-*a*][3,1]benzoxazin-5-one, m.p. 126—127° as feathery crystals (Found: C, 70·2; H, 5·2; N, 11·8%; *M*, 240·0913. Calc. for $C_{14}H_{12}N_2O_2$: C, 70·0; H, 5·05; N, 11·7%; *M*, 240·0899), $\nu_{max.}$ 2945, 2930, 2860 (CH_2), 1770, and 1760 (lactone or ester C=O) cm^{-1}.

Reduction of Indazolo[2,1-a]*indazole-6,12-dione*.—The title compound (500 mg) was suspended in concentrated hydrochloric acid (20 ml) and glacial acetic acid (20 ml), and zinc dust (5—10 g) was added in portions. The solution became hot and was filtered hot. The cool filtrate was added to twice its own volume of distilled water to give a

gelatinous white precipitate, which was filtered off and washed with water. The dried product was extracted (Soxhlet) with petroleum (b.p. 80—100°), from which, after concentration, pale yellow crystals, m.p. 142—143° (*ca.* 300 mg), of 6*H*-indazolo[2,1-*a*]indazol-12-one were obtained (Found: C, 75·6; H, 4·7; N, 12·7%; *M*, 222·0797. Calc. for $C_{14}H_{10}N_2O$: C, 75·65; H, 4·5; N, 12·6%; *M*, 222·0793).

Catalytic Reduction of 10-*Chloroindazolo*[2,3-a][3,1]*benzoxazin*-5-*one* (III).—Compound (III) (100 mg), dissolved in AnalaR ethyl acetate (80 ml), was shaken for 5 h under hydrogen (1 atm) over 10% platinised charcoal (100 mg) (uptake *ca.* 3 mol. equiv. 27·9 cm^3). Work-up as usual gave 7,8,9,10-tetrahydroindazolo[2,3-*a*][3,1]benzoxazin-5-one, m.p. 125° (i.r. spectra).

Catalytic Reduction of 8-*Chloroindazolo*[2,3-a][3,1]*benzoxazin*-5-*one* (Ib).—Compound (Ib) (30 mg) in AnalaR ethyl acetate (50 ml), was shaken for 5 h under hydrogen (1 atm) over 10% platinised charcoal (30 mg) (uptake *ca.* 3 mol. equiv., 11 cm^3). Work-up as usual gave 7,8,9,10-tetrahydroindazolo[2,3-*a*][3,1]benzoxazin-5-one, m.p. 125° (i.r. spectra).

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