# Nucleophilic Substitution on Perchloroindane; Reactions and Structural Reassignments

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Nucleophilic substitution on perchloroindane (1) with ethoxide ion gives nonachloro-5-ethoxyindane (6), heptachloro-1,1,5-triethoxyindane (7), and 3,5,6-trichloro-4-ethoxy-2-trichlorovinylbenzoic acid (8). The results show that in perchloroindane (1) aromatic chlorines are more susceptible to substitution than aliphatic chlorines. Since this has not previously been realised, structures of the products (6), (7), and (8) given in the literature are incorrect. From these products the following new compounds have been synthesized: pentachloro-5-hydroxy-indane-1,3-dione (9), pentachloro-5-ethoxyindane-1,3-dione (10), heptachloro-5-ethoxyindan-1-one (11), heptachloro-5-hydroxyindan-1-one (12) and its sodium salt (13), 2-bromohexachloro-5-hydroxystyrene (14), 2-bromohexachloro-5-methoxystyrene (15), 3,5,6-trichloro-4-hydroxy-2-trichlorovinylbenzoic acid (16), penta-chloro-5-hydroxy-1H-inden-1-one (17), pentachloro-5-methoxy-1H-inden-1-one (18), 5,7,8-trichloro-6-ethoxyisochroman-1,4-dione (19), 5,6,8-trichloro-7-ethoxyisochroman-1,4-dione (20), trichloro-4-ethoxy-phthalic acid (21) and its anhydride (22), 2,4,5-trichloro-3-hydroxybenzoic acid (25), 2,4,5-trichloro-3-methoxy-benzoic acid (27) and its methyl ester (26), 3-bromo-2,5,6-trichloroanisole (28), and 2,4,5-trichloro-3-methoxy-benzoyl chloride (29). An unexpected, abnormally easy hydrolysis of a dichloromethylene group in the salt (13) is reported. Some remarkable decarboxylations and ether cleavages in KBr–dimethyl sulphoxide are also described.

WHILE nucleophilic substitutions of perchlorobenzene,[1a] perchlorobiphenyl,[1b] and perchlorostyrene [2] have been studied reasonably well, those of the perchloroaryl-alkanes have not. (i) Before the use of spectroscopy became general, perchloroindane (1) was assumed to give nonachloro-2-ethoxyindane (2) and tetrachloro-2-(1,2-dichloro-2-ethoxyvinyl) benzoic acid (4) when treated with ethanolic KOH, or heptachloro-1,2,3-triethoxyin-dane (3) with ethanolic sodium ethoxide.[3] Pentachloro-2-ethoxyindane-1,3-dione (5) was assumed, therefore, to
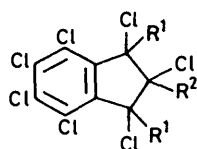
(1) R¹ = R² = Cl
(2) R¹ = Cl, R² = OEt
(3) R¹ = R² = OEt
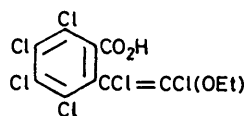
(4)
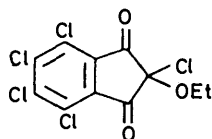
(5)

result from the acidic hydrolysis of compounds (2) or (3).[3] (ii) It was reported that treatment of perchloro-benzocyclobutene with methanolic NaOH gives a mixture of heptachloro-1-methoxybenzocyclobutene and pentachloro-1,1,2-trimethoxybenzocyclobutene.[4]

Since the initial nucleophilic attack by the alkoxide ion on αH-heptachlorotoluene [5] and on 2H-heptachloro-toluene [6] presumably occurs in the ring,† it was reasoned that the structures (2)—(5), as well as those derived from perchlorobenzocyclobutene, could have been incor-rectly assigned; the structures of compounds (2)—(5) are revised herein. Also, in this paper we give the correct assignments for these compounds and report the synthe-sis of several new, highly chlorinated phenols and phenol ethers. Some unusual results have been found.

RESULTS AND DISCUSSION

Perchloroindane (1) gives a mixture of nonachloro-5-ethoxyindane (6), heptachloro-1,1,5-triethoxyindane (7), and 3,5,6-trichloro-2-trichlorovinyl-4-ethoxybenzoic acid (8) when treated with ethanolic KOH (Scheme 1) and only the indane (7) when perchloroindane (1) is treated with a great excess of ethanolic sodium ethoxide.‡ The monoethoxy-indane (6) is an inter-mediate in the formation of the triethoxy-indane (7) since (i) compound (6) affords the indane (7) when treated with ethanolic sodium ethoxide under similar reaction conditions and (ii) perchloroindane (1) gives a mixture of compounds (6) and (7) when treated with an equimole-cular amount of ethanolic sodium ethoxide. The relevant diethoxy-compound could not be isolated, which suggests that it is highly reactive under the condi-tions used.

The evidence reported herein indicates that nucleo-philic substitution first occurs at C-5 of the benzene ring. This is attributed to the powerful, accumulated electron-attracting effect of the chlorines.[7] The struc-ture of the indane (7) has been recently and unequivocally established by X-ray analysis,[8] in collaboration with the authors. Thus, the 5-ethoxy-group of the indane (6)

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† This has been fully established in the nucleophilic sub-stitution of perchlorostyrene (ref. 2).

‡ Products (6), (7), and (8) have previously been assigned the incorrect structures (2), (3), and (4), respectively.

assists preferentially, *via* its positive tautomeric effects, the substitution of the geminal chlorines at C-1 with respect to those at C-3. A similar mechanism favours the immediate substitution of the second geminal chlorine.

The evidence concerning the position of the ethoxy-
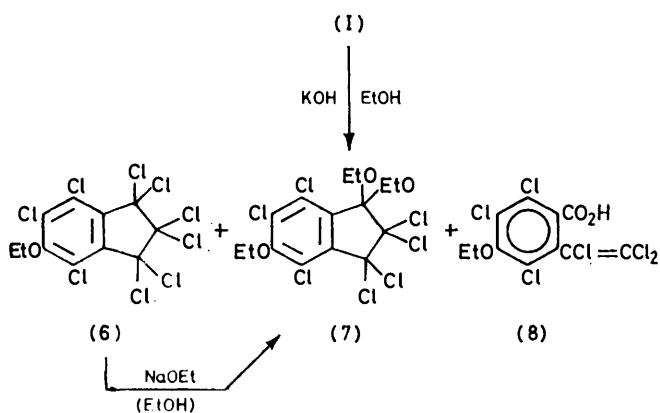
SCHEME 1

group in the monoethoxy-indane (6) is its conversion, when treated with fuming sulphuric acid, into penta-chloro-5-hydroxyindane-1,3-dione (9). The structure of the dione (9) has been ascertained by independent, stepwise hydrolysis of the indane (7) with fuming HNO_3, giving pentachloro-5-ethoxyindane-1,3-dione (10),* and subsequent treatment of the latter with fuming sulphuric acid to give the required dione (Scheme 2).
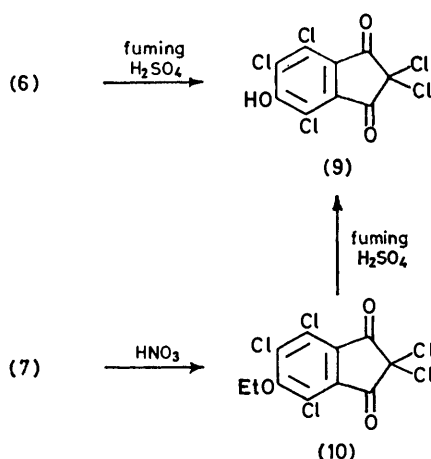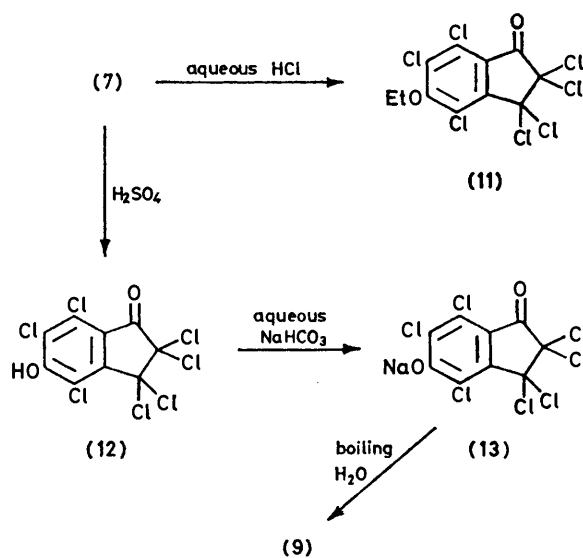

SCHEME 2

The triethoxy-indane (7) displays other interesting hydrolyses. With HCl (dioxan–water) it gives hepta-chloro-5-ethoxyindan-1-one   (11). However, under stronger acidic conditions (concentrated H_2SO_4), total hydrolysis of the ethoxy-substituents occurs, affording heptachloro-5-hydroxyindan-1-one   (12). The   latter compound, with aqueous $NaHCO_3$, gives first its sodium

* Compound (10) has previously been incorrectly assigned structure (5) (ref. 3).

salt (13), which hydrolyses further, in boiling water, to give compound (9) (Scheme 3).
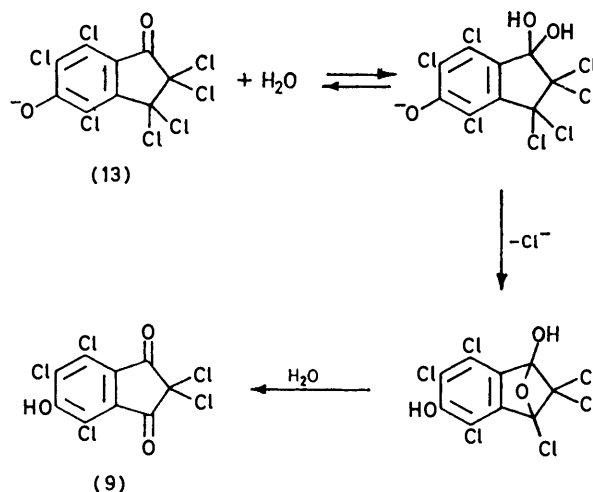
This is an abnormal result, since the geminal C-3 chlorines of (13) were expected to be inert under such mild nucleophilic conditions. Thus, it is emphasized

SCHEME 3

again that under strong nucleophilic conditions (ethoxide ion) the geminal chlorines at C-1 of perchloroindane (1) are remarkably resistent. Furthermore, the mesomeric effect of the 5-ethoxy-group in the indane (6) explains the geminal chlorine substitution. It seems likely that steric shielding of C-1 in the perchloroindane (1), or C-3 in the indan-1-ones, is important in hindering such nucleophilic substitutions. Moreover, no tautomeric assistance in the substitution of the chlorines on C-3 in compounds (12) or (13) is possible.

Consequently, it is suggested that in the hydrolysis of the sodium salt (13) the process shown in Scheme 4, involving an anchimeric effect, might occur. It has not

SCHEME 4

(11)   KOH / aqueous dioxan

(9)   fuming H$_2$SO$_4$ (8)   KBr DMSO

(15)   CH$_2$N$_2$ / fuming H$_2$SO$_4$ (14)
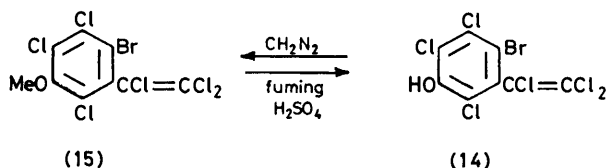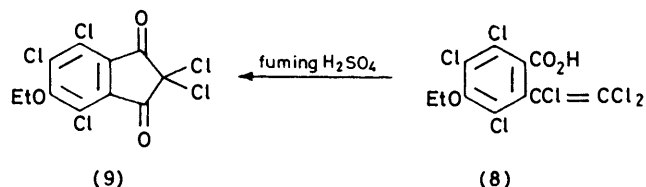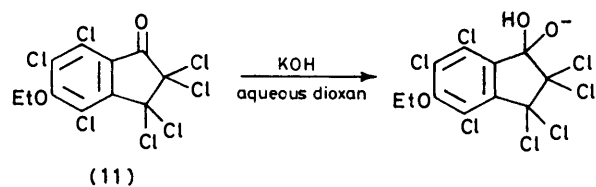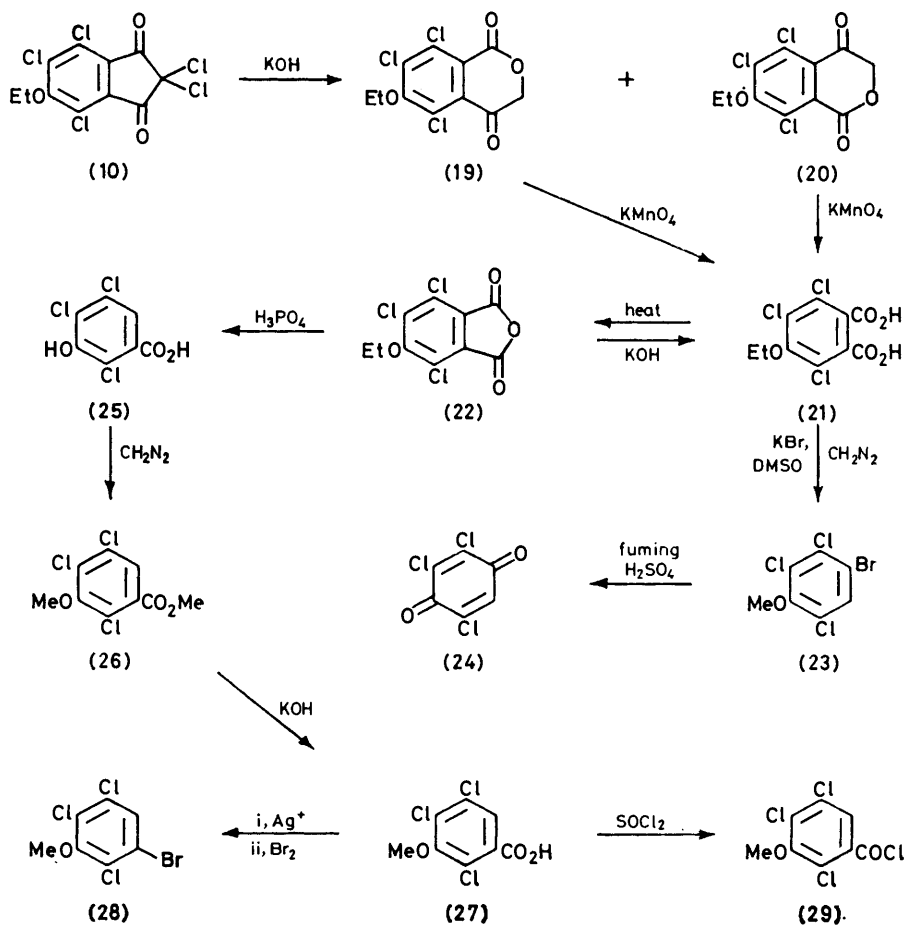
SCHEME 5

been possible to establish firmly, on a chemical basis, the full structure of the indane (7), and consequently the structures of compounds (8), (11), (12), and (13). For this purpose, the following reactions were carried out, some giving unexpected results.

(12)   KOH / aqueous dioxan   (16)

SnCl$_2$

(17)   CH$_2$N$_2$ (18)
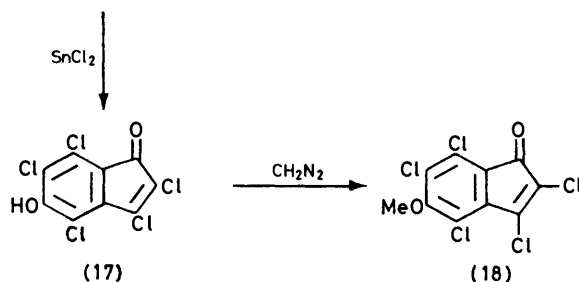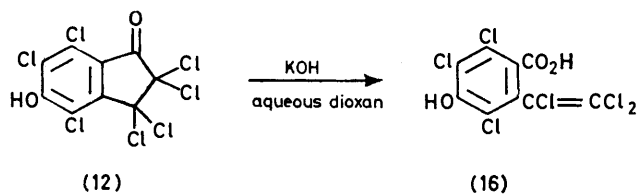
SCHEME 6

The reactions shown in Scheme 5 emphasize that the indanone (11) reacts under strong basic conditions (KOH in aqueous dioxan) to give the acid (8), according to a haloform-type ring-opening reaction. Cyclization of the acid (8) into the indanone (9) by treatment with fuming

(10)   KOH   (19)   +   (20)

KMnO$_4$ KMnO$_4$

(25)   H$_3$PO$_4$ (22)   heat / KOH   (21)

CH$_2$N$_2$ KBr, DMSO | CH$_2$N$_2$

(26)   (24)   fuming H$_2$SO$_4$ (23)

KOH

(28)   i, Ag$^+$ ii, Br$_2$ (27)   SOCl$_2$ (29).

SCHEME 7

sulphuric acid at room temperature occurs, surprisingly, in an almost quantitative yield. This can be accounted for by assuming the formation of a carbonium ion from the carbonyl group by proton addition.

Decarboxylation of the acid (8) (using the method of Chen et al.[9]) by heat treatment (ca. 190 °C) with KBr in dimethyl sulphoxide (DMSO) gives, unexpectedly, styrene (14) and its methyl ether (15) (with CH_2N_2).

Since it is well known that DMSO favours nucleophilic substitution by halide ions, formation of the styrene (14) can be interpreted as a replacement of the CO_2H group by a bromide ion. The DMSO conversion of the phenyl ether (8) into phenol is also of interest since it appears to be the first example of such a cleavage effected under these conditions.

Scheme 6 shows parallel reactions to those in Scheme 5. Note that the indenone (17) *cannot* be obtained by

(10)

(31)

(30)

(19),(20)
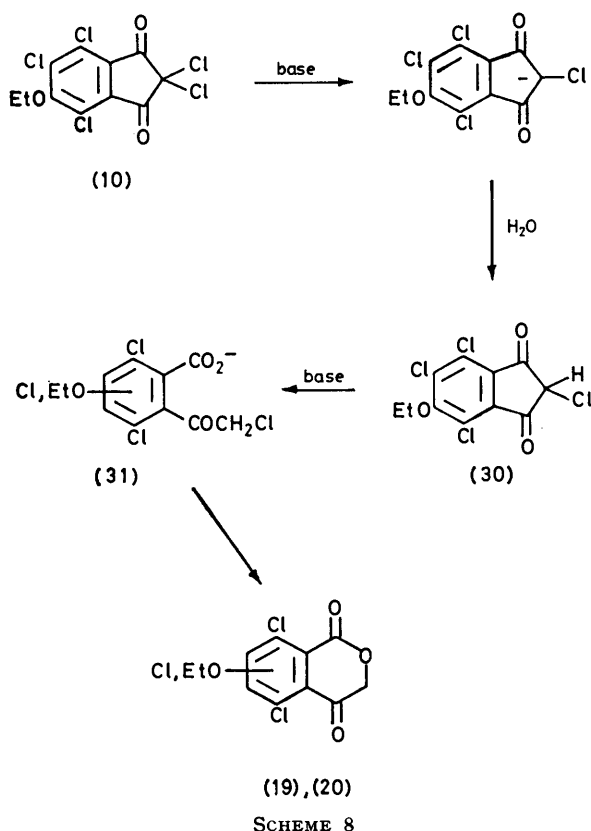
SCHEME 8

nucleophilic substitution of perchloroindenone (with KOH in MeOH), since substitution takes place at C-3 and proceeds no further.[10]

Treatment of the indanone (10) with KOH in aqueous dioxan gives a mixture of the diones (19) and (20); structural assignment between these isomers is uncertain. Oxidation of either isomer with $KMnO_4$ and base, in boiling water, gives the acid (21), which can be easily converted into its anhydride (22), and *vice versa* (Scheme 7). Decarboxylation of the acid (21) with KBr in DMSO, as in Scheme 5, gives 4-bromo-2,3,6-trichlorophenol,

which was identified *via* bromoanisole (23) (CH_2N_2) and by conversion into the *p*-benzoquinone (24) (Scheme 7); the last two compounds are known.[11-13]

Phthalic anhydride (22) undergoes both decarboxylation and hydrolysis to give the acid (25) with H_3PO_4. The structure of compound (25) was established by the reaction sequence shown in Scheme 7, compound (28) being characterised on the basis of i.r., n.m.r., and mass spectroscopic evidence. The melting point and i.r. spectrum of compound (28) differ from those of bromoanisole (23). 2,4,5-Trichloro-3-methoxybenzoyl chloride (29) has been prepared from the acid (27) with $SOCl_2$.

The remarkable conversion of the indanone (10) into the isochromans (19) and (20) is accounted for by the reaction sequence shown in Scheme 8 [for the reaction of (10) to give (30), see ref. 14].

EXPERIMENTAL

The n.m.r. spectra were recorded with a Perkin-Elmer R12B spectrometer, tetramethylsilane being used as an internal standard. The i.r. and u.v. spectra were recorded with Perkin-Elmer 457 and Perkin-Elmer 350 spectrometers, respectively.

Reactions of Perchloroindane (1) *with Ethanolic Sodium Ethoxide.*—(a) A mixture of the perchloroindane (1) (5.00 g, 11 mmol), sodium ethoxide (from 1.51 g Na, 66 mmol), and ethanol (35 ml) was refluxed (4 h). The solvent was distilled off under reduced pressure and the residue was treated with a water–ether mixture. Evaporation of the ethereal layer, followed by recrystallization, gave hepta-chloro-1,1,5-triethoxyindane (7) (3.20 g), m.p. 99.5—101.5 °C (from ethanol) (Found: C, 36.7; H, 3.1; Cl, 50.4. $C_{15}H_{15}Cl_7O_3$ requires C, 36.7; H, 3.1; Cl, 50.5%); τ (CCl_4) 8.47 [3 H, t, J 7.2 Hz, MeCH$_2$O (arom.)], 8.73 [6 H, t, J 7.2 Hz, MeCH$_2$O (aliph.)], 5.6—6.6 (6 H, complex, MeCH_2O); $\lambda_{max.}$ (C_6H_{12}) 224 (ε 47 700), 242sh (11 000), 289 (820), and 299 nm (830). The mother-liquors gave a residue which, after t.l.c. (silica, hexane), afforded more heptachloro-1,1,5-triethoxyindane (7) (0.740 g). The overall yield was 74.2%.

(b) A solution of sodium ethoxide [from 0.022 g Na (0.96 mmol) in ethanol (8 ml)] was added in drops (2.5 h) to a stirred, refluxing solution of perchloroindane (1) (0.432 g, 0.93 mmol) in dioxan (6 ml), and then stirred and refluxed further (22 h). The resulting mixture was poured into water–ether, the ethereal solution was evaporated, and the residue was purified on silica (t.l.c., hexane) giving (i) the initial indane (1) (0.20 g, 46.5%); (ii) *nonachloro-5-ethoxy-indane* (6) (0.091 g, 38%), m.p. 116—118 °C (from hexane) (Found: C, 27.9; H, 1.0; Cl, 67.5. $C_{11}H_5Cl_9O$ requires C, 28.0; H, 1.1; Cl, 67.6%); τ (CCl_4) 5.83 (c, J 7.2 Hz, CH$_2$) and 8.43 (t, J 7.2 Hz, Me); $\lambda_{max.}$ (C_6H_{12}) 232 (ε 43 500), 255sh (8 000), 282sh (525), 293 (672), and 305sh nm (480); and (iii) heptachloro-1,1,5-triethoxyindane (7) (0.014 g, 2.8%).

Reaction of Perchloroindane (1) *with Ethanolic Potassium Hydroxide.*—A solution of ethanolic KOH (1N, 8 ml) was added in drops (10 min) to a stirred, refluxing solution of perchloroindane (1) (2.00 g) in ethanol (80 ml), and the resulting mixture was kept under the same conditions (20 min). The solvent was distilled off under reduced pressure, and the resulting solid residue was treated with water–ether. The ethereal solution was washed with water, dried

and evaporated to give a residue which was purified on silica (t.l.c., hexane) yielding the initial indane (1) (0.294 g, 14.7%), nonachloro-5-ethoxyindane (6) (0.533 g, 26.1%), and heptachloro-1,1,5-triethoxyindane (7) (0.219 g, 10.4%). The aqueous solution was acidified with concentrated HCl to give 3,5,6-*trichloro-4-ethoxy-2-trichlorovinylbenzoic acid* (8) (0.056 g, 3.5%), m.p. 147—150 °C (from ether–hexane) (Found: C, 32.8; H, 1.6; Cl, 53.1. $C_{11}H_6Cl_6O_3$ requires C, 33.1; H, 1.5; Cl, 53.3%); $\nu_{max.}$ (KBr) 3 500—2 220 (OH), 1 705 (C=O), and 1 600 cm⁻¹ (C=C); τ (CDCl₃) 1.35 (1 H, s, OH), 5.82 (2 H, c, *J* 6.6 Hz, CH_2Me), and 8.50 (3 H, t, *J* 6.6 Hz, CH₂*Me*); $\lambda_{max.}$ (C_6H_{12}) 221 (ε 20 100) and 293 nm (500).

Reaction of Nonachloro-5-ethoxyindane (6) *with Ethanolic Sodium Ethoxide.*—A mixture of the ethoxy-indane (6) (0.024 g, 0.05 mmol), sodium ethoxide (from 0.006 g Na, 0.26 mmol), and ethanol (2 ml) was refluxed (4 h). The resulting mixture was poured into water–ether and evaporation of the etheral layer gave a residue which was purified through a silica column (hexane) to give heptachloro-1,1,5-triethoxy-indane (7) (0.014 g, 56.0%), identified by its mixed m.p. and i.r. spectrum.

Oxidation of Heptachloro-1,1,5-triethoxyindane (7) *with Fuming Nitric Acid.*—A mixture of the triethoxy-indane (7) (1.00 g) and fuming nitric acid (49 ° Bé, 5 ml) was heated (100 °C, 8 h). The resulting mixture was cooled, poured into water, made alkaline (Na₂CO₃), and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give a residue of *pentachloro-5-ethoxy-indane-1,3-dione* (10) (0.525 g, 71.4%), m.p. 117.5—119.0 °C (from hexane) (Found: C, 36.6; H, 1.4; Cl, 48.7. $C_{11}H_5$-Cl_5O_3 requires C, 36.5; H, 1.4; Cl, 48.9%); $\nu_{max.}$ (KBr) 1 762 and 1 735 cm⁻¹ (C=O); τ (CDCl₃) 5.67 (c, *J* 7.2 Hz, CH₂) and 8.43 (t, *J* 7.2 Hz, Me); $\lambda_{max.}$ (C_6H_{12}) 260 (ε 49 600), 310 (1 300), 326 (1 510), and 339 nm (1 740).

Heptachloro-5-ethoxyindan-1-one (11).—A mixture of the indane (7) (0.505 g), dioxan (10 ml), and concentrated HCl (2 ml) was refluxed, with stirring, for 65 h during which time additions of concentrated HCl (8 ml) were made. The resulting mixture was poured into water and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give a residue which was purified on silica (t.l.c., hexane) to afford the *indanone* (11) (0.253 g, 59.0%), m.p. 111.0—113.5 °C (from hexane) (Found: C, 31.5; H, 1.2; Cl, 59.6. $C_{11}H_5Cl_7O_2$ requires C, 31.6; H, 1.2; Cl, 59.5%); $\nu_{max.}$ (KBr) 1 760 cm⁻¹ (C=O); τ (CDCl₃) 5.72 (2 H, c, *J* 7.2 Hz, CH_2Me), 8.40 (3 H, t, *J* 7.2 Hz, CH₂*Me*); $\lambda_{max.}$ (C_6H_{12}) 240 (ε 36 000), 279 (9 830), 310 (1 640), and 323 nm (1 320).

Heptachloro-5-hydroxyindan-1-one (12).—A mixture of the indane (7) (0.800 g) and concentrated H_2SO_4 (200 ml) was stirred at room temperature (8.5 h). The resulting mixture was poured into water and the precipitate was extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give the *indanone* (12) (0.482 g, 76.0%), m.p. 147—152 °C (from hexane) (Found: C, 27.5; H, 0.4; Cl, 63.6. $C_9HCl_7O_2$ requires C, 27.8; H, 0.3; Cl, 63.7%); $\nu_{max.}$ (KBr) 3 400 (OH) and 1 745 cm⁻¹ (C=O); τ (C₃D₆O) 4.51 (1 H, s); $\lambda_{max.}$ (C_6H_{12}) 243 (ε 33 200), 285 (9 850), and 340 nm (200).

Sodium Salt (13) *of the Indanone* (12).—A solution of the indanone (12) (1.076 g) in ether (25 ml) was shaken twice in the dark * with aqueous NaHCO₃ (total 50 ml). The ethereal solution was dried and evaporated to give a solid (1.057 g) which was then digested in refluxing hexane (35 ml,

* Light turned the yellow solution brown.

1.5 h).† The resulting residue was the required *sodium salt* (13) (1.030 g, 86.8%), a yellow powder, m.p. 221—224 °C (decomp.) (Found: C, 25.2; H, 0.4; Cl, 57.9. $C_9Cl_7O_2$-Na·H₂O requires C, 25.2; H, 0.5; Cl, 57.8%); $\nu_{max.}$ (KBr) 3 680—2 900 (OH) and 1 706 cm⁻¹ (C=O). From the hexane extract and the NaHCO₃ solution (treated separately) was recovered some of the initial indanone (12) (0.052 g, 4.8% overall recovery).

Hydrolysis of the Sodium Salt (13).—A solution of the sodium salt (13) (0.037 g) in water (2 ml) was strongly acidified with concentrated HCl and then extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give the indanone (12) (0.030 g, 89.4%), identified by its m.p. and i.r. spectrum.

3,5,6-Trichloro-4-ethoxy-2-trichlorovinylbenzoic Acid (8).— A solution of the indanone (11) (0.102 g), KOH (0.056 g) in dioxan–water (3 : 1 v/v) was refluxed (24 h). The mixture was poured into water and acidified with concentrated HCl; the precipitate which formed was extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give the benzoic acid (8) (0.062 g, 63.9%), identified by its mixed m.p. and i.r. spectrum.

Decarboxylation of Benzoic Acid (8).—A mixture of the benzoic acid (8) (0.302 g), KBr (1.180 g), and DMSO (8 ml) was heated (189 °C, 6.5 h), poured into water, and extracted with ether. The ethereal solution was washed with aqueous NaHCO₃ and water, dried, and excess of CH₂N₂ in ether was then added. . Evaporation of the solvent gave a residue which was purified on silica (t.l.c., hexane) to give 2-*bromohexa-chloro-5-methoxystyrene* (15) (0.124 g, 41.2%), m.p. 89.0—93.5 °C (Found: C, 25.8; H, 0.6; Br, 19.2; Cl, 50.5. $C_9H_3BrCl_6O$ requires C, 25.8; H, 0.7; Br, 19.0; Cl, 50.7%); $\nu_{max.}$ (KBr) 1 605 cm⁻¹ (C=C): τ (CCl₄) 6.08 (3 H, s); $\lambda_{max.}$ (C_6H_{12}) 218 (ε 59 400), 293 (1 320), and 302 nm (1 530).

2-*Bromohexachloro-5-hydroxystyrene* (14).—A mixture of the styrene (15) (0.041 g) and 20% fuming sulphuric acid (10 ml) was stirred (70 °C; 1 h). The resulting mixture was poured into ice–water and extracted with ether. The ethereal solution was washed with water, dried, and evaporated, giving a residue which was purified on silica (t.l.c., CHCl₃) to give the *styrene* (14) (0.034 g, 85.0%), m.p. 78.5—82.5 °C (Found: C, 23.8; H, 0.3; Br, 19.6; Cl, 52.2. C_8H-$BrCl_6O$ requires C, 23.7; H, 0.3; Br, 19.7; Cl, 52.4%); $\nu_{max.}$ (KBr) 3 508 (OH) and 1 608 cm⁻¹ (C=C); $\lambda_{max.}$ (C_6H_{12}) 215 (ε 52 100), 300sh (3 000), and 309 nm (3 520).

3,5,6-*Trichloro-4-hydroxy-2-trichlorovinylbenzoic Acid* (16). —A mixture of the indanone (12) (2.241 g), KOH (2.00 g), dioxan (25 ml), and water (25 ml) was refluxed (1.5 h). The mixture was poured into water, acidified with concentrated HCl, and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give the *benzoic acid* (16) (1.248 g, 58.4%), m.p. 166—169 °C (Found: C, 29.1; H, 0.6; Cl, 57.4. $C_9H_2Cl_6O_3$ requires C, 29.1; H, 0.5; Cl, 57.4%); $\nu_{max.}$ (KBr) 3 600—2 300 (OH), 1 715 (C=O), and 1 600 cm⁻¹ (C=C); $\lambda_{max.}$ (methanol) 214 (ε 34 400) and 303 (2 840); m/e 368 (M^+), 351 (M^+ − OH), and 333 (M^+ − Cl).

Pentachloro-5-hydroxyinden-1-one (17).—A mixture of the indanone (12) (0.902 g, 2.32 mmol), SnCl₂·2H₂O (0.579 g, 2.57 mmol), and dioxan (40 ml) was refluxed (5.5 h) under a dry atmosphere and with stirring. The resulting mixture was poured into dilute HCl (150 ml) and extracted with ether. The ethereal layer was washed with water, dried, and evaporated. Recrystallization of the residue (0.820 g)

† The solubility of this salt is greater in ether than in water.

from hexane gave two fractions: (i) the *indenone* (17) (0.469 g, 63.6%) as orange crystals, m.p. 213.5—217.5 °C (Found: C, 34.2; H, 0.5; Cl, 55.8. $C_9HCl_5O_2$ requires C, 34.0; H, 0.3; Cl, 55.7%); $v_{max.}$ (KBr) 3 380 (OH), 1 721 (C=O), and 1 575 cm^{-1} (C=C); $\lambda_{max.}$ (CHCl₃) 270 (ε 29 300) and 363 nm (2 600); and (ii) the initial indanone (12) (0.217 g, 24.0%).

Pentachloro-5-methoxyinden-1-one (18).—An excess of diazomethane in ether was added to a solution of the indenone (17) (0.060 g) in the same solvent (2 ml). Evaporation gave a solid (0.060 g), which was recrystallized from hexane to give the *indenone* (18) (0.044 g, 70.2%) as yellow crystals, m.p. 195.5—198.0 °C (Found: C, 36.1; H, 1.0; Cl, 53.1. $C_{10}H_3Cl_5O$ requires C, 36.1; H, 0.9; Cl, 53.3%); $v_{max.}$ (KBr) 1 727 (C=O) and 1 576 cm^{-1} (C=C); $\lambda_{max.}$ (C_6H_{12}) 258 (ε 31 000), 266 (39 800), 353 (1 920), 370 (1 940), and 410 nm (1 030).

Pentachloro-5-hydroxyindane-1,3-dione (9).—(a) *From the indane* (7). A mixture of the indane (7) (0.261 g) and 20% fuming sulphuric acid (15 ml) was stirred at room temperature (24 h). The mixture was poured into ice–water and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give the *dione* (9) (0.136 g, 76.8%), m.p. 220—224 °C (from hexane) (Found: C, 32.2; H, 0.1; Cl, 53.0. $C_9HCl_5O_3$ requires C, 32.3; H, 0.3; Cl, 53.0%); $v_{max.}$ (KBr) 3 330 (OH), 1 762 and 1 738 cm^{-1} (C=O); τ (C_3D_6O) 3.65 (1 H, s); $\lambda_{max.}$ (C_6H_{12}) 263 (ε 42 400), 287 (8 650), 312 (1 540), 326 (1 940), and 340 nm (1 850).

(b) *From the benzoic acid* (8). A mixture of the acid (8) (0.616 g) and 20% fuming sulphuric acid (10 ml) was stirred at room temperature (4 h). The resulting mixture was worked-up as before to give the dione (9) (0.505 g, 97.9%).

(c) *From the dione* (10). A mixture of the ketone (10) (0.064 g) and 20% fuming sulphuric acid (5 ml) was stirred at room temperature (4 h). The mixture was worked-up as before to give the dione (9) (0.039 g, 66.1%).

(d) *From the indane* (6). A mixture of the indane (6) (0.054 g) and 20% fuming sulphuric acid (8 ml) was stirred at room temperature (28 h). The mixture was worked-up as before to give the dione (9) (0.035 g, 92.1%).

(e) *From the sodium salt* (13). A solution of the sodium salt (13) (0.350 g) in water–dioxan (1 : 1, 2 ml) was refluxed (9 h) under argon in the dark. The resulting mixture was acidified with dilute HCl and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give a solid (0.272 g) which was digested in refluxing hexane (25 ml, 0.5 h) to afford the dione (9) (0.172 g, 63.1%). The hexane extract, after evaporation, gave the indanone (12) (0.092 g, 27.7%).

5,7,8-*Trichloro-6-ethoxyisochroman-1,4-dione* (19) *and* 5,6,8-*Trichloro-7-ethoxyisochroman-1,4-dione* (20).—A solution of KOH (1.99 g) in water (25 ml) was added to a solution of the dione (10) (3.016 g) in dioxan (50 ml). The mixture was refluxed (24 h), cooled, poured into water, and acidified with concentrated HCl. The precipitate was separated, filtered through silica (CHCl₃), and recrystallized from ether–hexane to give the *dione* (19) or (20) (0.477 g, 18.5%), m.p. 138.5—141.0 °C (Found: C, 42.7; H, 2.6; Cl, 34.4. $C_{11}H_7Cl_3O_4$ requires C, 42.7; H, 2.3; Cl, 34.4%); $v_{max.}$ (KBr) 1 762 cm^{-1} (C=O); τ (CDCl₃) 4.84 (2 H, s, CH_2CO), 5.86 (2 H, c, J 7.2 Hz, MeCH_2O), and 8.50 (3 H, t, J 7.2 Hz, $MeCH_2$O); $\lambda_{max.}$ (C_6H_{12}) 220 (ε 54 500), 240 (10 000), 246 (11 050), 254 (10 650), 294 (2 810), and 304 nm (3 450). The residue from the mother-liquors was recrystallized

from hexane to give the dione (20) or (19) (0.246 g, 9.5%), m.p. 116—119 °C (Found: C, 42.4; H, 2.6; Cl, 34.5. $C_{11}H_7Cl_3O_4$ requires: C, 42.7; H, 2.3; Cl, 34.4%); $v_{max.}$ (KBr) 1 772 cm^{-1} (C=O); τ (CDCl₃) 4.86 (2 H, s, CH_2CO), 5.80 (2 H, c, J 7.2 Hz, MeCH_2O), and 8.50 (3 H, t, J 7.2 Hz, $MeCH_2$O); $\lambda_{max.}$ (C_6H_{12}) 222 (ε 55 400), 253 (8 700), 290 (1 325), and 300 nm (1 550).

Trichloro-4-ethoxyphthalic Acid (21) *and its Anhydride* (22). —(a) *Oxidation of the chromandione of m.p.* 138.5—41.0 °C. A solution of the chromandione of m.p. 138.5—141.0 °C (0.349 g), KOH (1.30 g), and KMnO₄ (0.59 g) in water (65 ml) was refluxed (5 h). The mixture was cooled and an excess of ethanol was added. The filtered solution was acidified with concentrated HCl and the precipitate which formed was extracted with ether. The ethereal solution was washed with water, dried, and evaporated to afford a residue which was recrystallized from ether–hexane to give the *phthalic acid* (21) (0.121 g, 34.3%), m.p. 118—128 °C (decomp.) (Found: C, 38.3; H, 2.2; Cl, 33.9. $C_{10}H_7Cl_3O_5$ requires C, 38.3; H, 2.2; Cl, 33.9%); $v_{max.}$ (KBr) 3 300— 2 300 (OH), 1 735, and 1 718 cm^{-1} (C=O); τ (C_3D_6O) 0.39 (2 H, s, acid), 5.80 (2 H, c, J 7.2 Hz, CH_2) and, 8.53 (3 H, t, J 7.2 Hz, Me); $\lambda_{max.}$ (C_6H_{12}) 215 (ε 31 800) and 289 nm (630). The mother-liquors were evaporated and the residue was heated (185 °C, 0.5 h) to give the *anhydride* (22) (0.126 g, 37.8%), m.p. 111—113 °C (from hexane) (Found: C, 40.5; H, 1.6; Cl, 35.9. $C_{10}H_5Cl_3O_4$ requires C, 40.6; H, 1.7; Cl, 36.0%); $v_{max.}$ (KBr) 1 860 and 1 775 cm^{-1} (C=O); τ (CDCl₃) 5.72 (2 H, c, J 7.2 Hz, CH_2) and 8.47 (3 H, t, J 7.2 Hz, Me).

(b) *Oxidation of the chromandione of m.p.* 116—119 °C. A solution of the chromandione of m.p. 116—119 °C (0.188 g), KOH (0.69 g), and KMnO₄ (0.32 g) in water (40 ml) was refluxed (5 h). The mixture was worked-up as before to give the phthalic acid (21) (0.119 g, 62.6%) and the anhydride (22) (0.048 g, 27.8%).

(c) *The anhydride* (22) *of the acid* (21). The phthalic acid (21) (0.108 g) was heated (175 °C; 1.5 h) to give the corresponding anhydride (22) (0.098 g, 96.1%).

(d) *Hydration of the anhydride* (22). A mixture of the phthalic anhydride (22) (0.054 g) and aqueous 0.3N KOH (20 ml) was heated (90 °C, 1.25 h) and then acidified with concentrated HCl and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give the phthalic acid (21) (0.053 g, 93.0%).

Decarboxylation of the Phthalic Acid (21).—A mixture of the phthalic acid (21) (1.014 g), KBr (5.8 g), and DMSO (16 ml) was heated (189 °C; 6.5 h) and then worked up as in the decarboxylation of the benzoic acid (8), to give pure 4-bromo-2,3,6-trichloroanisole (23) (0.210 g, 22.4%); $v_{max.}$ (KBr) 1 530w, 1 452s, 1 408s, 1 348s, 1 250m, and 1 000s cm^{-1}, identified by its m.p. (68—70 °C; lit.,[11] m.p. 69—70 °C), elemental analyses, and oxidation to the *p*-benzoquinone (24) (see below).

Oxidation of the Anisole (23).—A solution of the anisole (23) (0.160 g) in 20% fuming sulphuric acid (5 ml) was heated (90 °C; 3 h) and then cooled, poured into ice–water, and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give a residue which was purified through silica (CHCl₃). Fuming nitric acid (49 °Bé) was added to the resulting phenolic ($v_{max.}$ 3 480 cm^{-1}) residue (0.132 g), and the solution was left at room temperature (7 h). It was then poured into water and extracted with ether. The ethereal solution gave a residue which was purified on silica (t.l.c., CHCl₃) to give trichloro-*p*-benzoquinone (24) (0.048 g, 41.4%), identified

by its m.p. [170 °C (decomp.); lit.,[12] 168 °C], elemental analyses, and i.r. spectrum.[13]

Decarboxylation of the Anhydride (22) *with Phosphoric Acid.*—A solution of the phthalic anhydride (22) (0.331 g) in H_3PO_4 (85%; 35 ml) was refluxed (65 h) and then poured into water and extracted with ether. The ethereal solution was washed with water and dried to give 2,4,5-*trichloro-3-hydroxybenzoic acid* (25) (0.231 g, 85.5%), m.p. 206.5—210.5 °C (subl.) (Found: C, 34.8; H, 1.3; Cl, 44.0. $C_7H_3Cl_3O_3$ requires C, 34.8; H, 1.3; Cl, 44.0%); $\nu_{max.}$ (KBr) 3 260—3 400 (OH) and 1 708 cm^{-1} (C=O); τ (C_3D_6O) -0.08 (2 H, s, OH) and 2.42 (1 H, s, arom.); $\lambda_{max.}$ (methanol) 210 (ε 34 850) and 301 nm (2 520).

Methyl 2,4,5-Trichloro-3-methoxybenzoate (26).—An excess of diazomethane in ether was added to a solution of the benzoic acid (25) (0.438 g) in ether (15 ml). The solvent was evaporated to give the *methyl benzoate* (26) (0.432 g, 88.3%), m.p. 71—74 °C (Found: C, 39.9; H, 2.4; Cl, 39.7. C_9H_7-Cl_3O_3 requires C, 40.1; H, 2.6; Cl, 39.5%); $\nu_{max.}$ (KBr) 1 728 cm^{-1} (C=O); τ (CCl$_4$) 2.32 (1 H, s, arom.), 6.10 (6 H, s, Me); $\lambda_{max.}$ (C_6H_{12}) 219 (ε 32 800) and 297 nm (1 200).

2,4,5-Trichloro-3-methoxybenzoic Acid (27).—A mixture of the ester (26) (0.300 g), KOH (0.661 g), and water (50 ml) was refluxed (2 h) and then acidified with concentrated HCl and extracted with ether. The ethereal solution was washed with water, dried, and evaporated to give the *benzoic acid* (27) (0.256 g, 90.1%), m.p. 174.0—177.5 °C (Found: C, 37.7; H, 1.9; Cl, 41.4. $C_8H_5Cl_3O_3$ requires C, 37.6; H, 2.0; Cl, 41.6%); $\nu_{max.}$ (KBr) 3 300—2 220 (OH), 1 710, and 1 685 cm^{-1} (C=O); τ (C_3D_6O) 2.15 (1 H, s, arom.), 3.47 (1 H, s, OH), and 6.01 (3 H, s, Me); $\lambda_{max.}$ (methanol) 210 (ε 36 200) and 294 nm (1 170).

2,4,5-Trichloro-3-methoxybenzoyl Chloride (29).—A solution of the benzoic acid (27) (1.048 g) in SOCl$_2$ (4 ml) was refluxed (30 min) and then evaporated to give the *benzoyl chloride* (29) (1.054 g, 93.8%), m.p. 59.5—62.5 °C (Found: C, 35.2; H, 1.4; Cl, 51.7. $C_8H_4Cl_4O_2$ requires C, 35.1; H, 1.5; Cl, 51.8%); $\nu_{max.}$ (KBr) 1 782 cm^{-1} (C=O); τ (CCl$_4$) 2.15 (1 H, s, arom.) and 6.07 (3 H, s, Me).

Bromodecarboxylation of the Silver Salt of the Benzoic Acid (27).—A solution of AgNO$_3$ (0.134 g) in water (1 ml) was added to the benzoic acid (27) (0.184 g) in aqueous NaOH (1%, 2.8 ml) and the mixture was stirred at room temperature (15 min). The precipitate was separated, washed with water, and dried to give *silver 2,4,5-trichloro-3-methoxy-benzoate* (0.160 g, 61.5%), m.p. 170 °C (decomp.); $\nu_{max.}$ (KBr) 1 590s, 1 535s, 1 448w, 1 420w, 1 390s, 1 365s, and 1028s cm^{-1}.

A solution of Br$_2$ (0.565 g) in CCl$_4$ (5 ml) was added, in drops during 0.5 h, to the silver salt (0.944 g) in the same solvent, and the mixture was then refluxed (3 h). The solid was filtered off and the solution was washed successively with aqueous NaHSO$_3$ (40%), aqueous NaHCO$_3$, and water, and then evaporated. The residue was purified on silica (t.l.c., pentane) giving a solid (0.307 g) which was treated with 20% fuming sulphuric acid (35 ml) at room temperature (35 min). The mixture was then poured into ice–water and extracted with ether. The ethereal solution was washed with water, dried, and evaporated, and the residue was purified on silica (t.l.c., CHCl$_3$) to give two fractions. The first-eluted one was treated with diazomethane in ether and gave 3-*bromo-2,5,6-trichloroanisole* (28) (0.055 g, 7.7%), m.p. 93—96 °C; $\nu_{max.}$ (KBr) 1 545m, 1 448w, 1 402s, 1 370s, and 1 010s cm^{-1}; τ (CCl$_4$) 2.47 (1 H, s, arom.), 6.13 (3 H, s, Me); *m/e* 288 (M^+; 3 Cl, Br), 273 ($M^+ -$ Me), and 345 ($M^+ -$ Me $-$ CO). The second fraction gave, similarly, 3,4-dibromo-2,5,6-trichloroanisole (0.036 g, 3.9%);[11] τ (CCl$_4$) 6.11 (3 H, s, Me); *m/e* 366 (M^+; 3 Cl, 2 Br), 351 ($M^+ -$ Me), and 323 ($M^+ -$ Me $-$ CO).

REFERENCES

[1] (*a*) M. Ballester and S. Olivella, ' Polychloroaromatic Compounds,' ed. H. Suschitzky, Plenum, 1974, p. 26; (*b*) *ibid.*, p. 30.
[2] M. Ballester, J. Riera, L. Juliá, J. Castañer, and F. Ros, *An. Quim.*, 1980, **76C**, 255.
[3] A. Roedig, *Chem. Ber.*, 1947, **80**, 206.
[4] A. Roedig, G. Bonse, R. Helm, and R. Kohlhaupt, *Chem. Ber.*, 1971, **104**, 3378.
[5] S. D. Ross and M. Markarian, *J. Am. Chem. Soc.*, 1949, **71**, 2756.
[6] P. G. Harvey, F. Smith, M. Stacey, and J. C. Tatlow, *J. Appl. Chem.*, 1954, **4**, 325.
[7] A. L. Rocklin, *J. Org. Chem.*, 1956, **21**, 1478.
[8] X. Solans and C. Miravitlles, *Acta Crystallogr., Sect. B*, 1979, **35**, 757.
[9] C. T. Chen, S. J. Yan, and C. H. Wang, *Chem. Ind. (London)*, 1970, **27**, 895.
[10] F. Ros, Ph.D. Thesis, University of Barcelona, 1978.
[11] M. Kohn and S. Fink, *Monatsh. Chem.*, 1930, **56**, 137.
[12] H. Biltz and W. Giese, *Chem. Ber.*, 1904, **37**, 4016.
[13] P. Tates, M. I. Ardao, and F. L. Fieser, *J. Am. Chem. Soc.*, 1956, **78**, 650.
[14] M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, 1959, **6**, 109.