

DIRECT CHLORINATION OF INDANE UNDER THE CONDITIONS OF AROMATIC ELECTROPHILIC SUBSTITUTION

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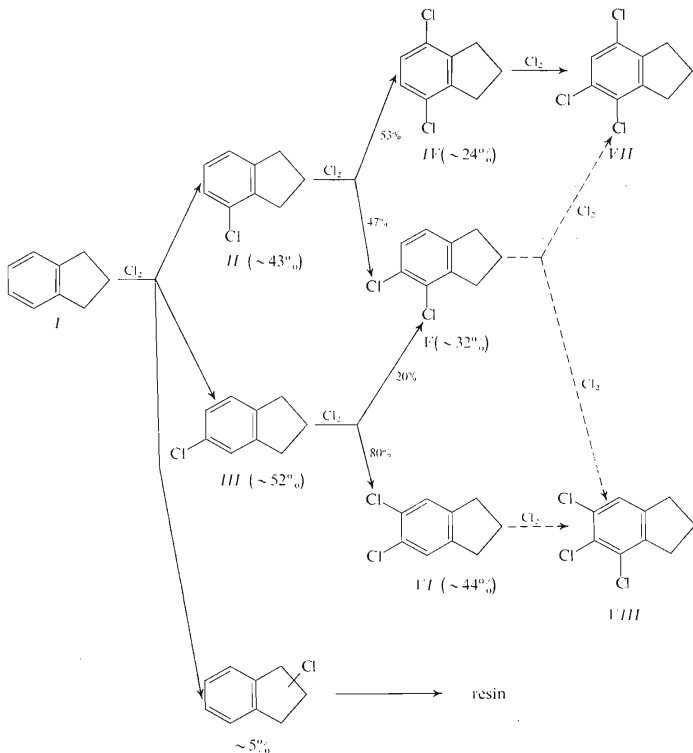
Received February 2nd, 1976

Chlorination of indane (*I*) has been carried out under the conditions of aromatic electrophilic substitution to give a mixture of 4-chloroindane (*II*) and 5-chloroindane (*III*). Further chlorination gave 4,5-dichloroindane (*V*), 4,7-dichloroindane (*IV*), 5,6-dichloroindane (*VI*) and not completely pure 4,5,6-trichloroindane (*VIII*) and 4,5,7-trichloroindane (*VII*). Individual monochloroindanes *II* and *III* were prepared by the Sandmeyer reaction.

Substitution chlorinations of indane can take place both in the aromatic and in the cycloaliphatic part of the molecule. The former ones are typical aromatic substitutions, the attacking reagent being a polarized chlorine molecule¹⁻³. Besides chlorine gas the reaction can be accomplished also with some metal halogenides as *e.g.* FeCl₃ (ref.⁴), SbCl₅ (ref.⁵) or (SCl₂)(AlCl₄) (ref.⁶) and a mixture HCl-HNO₃-H₂O-H₂SO₄ (ref.⁷). These chlorination reagents should attack predominantly the aromatic ring. The aim of the present work was to study the direct chlorination of indane and identify the reaction product.

Chlorination of the compound *I* under the conditions of aromatic electrophilic substitution is accompanied to a considerable extent by chlorination of the cycloaliphatic part of the molecule. The formed 1- and 2-chloroindanes are thermally unstable, being transformed easily into resinous products on heating⁸. If the chlorination of the compound *I* is carried out in polar solvents as *e.g.* acetic acid, FeCl₃ being the catalyst, the reaction follows Scheme 1. Under the conditions of monochlorination the ratio of the formed mixture of 4- and 5-monochloroindanes is 9 : 11. If two equivalents of chlorine are used in chlorination of the compound *I*, a mixture of all three expected dichloroindanes *IV-VI* is formed, their ratio being 24 : 32 : 44. The predominant isomer *VI* is formed mostly (80%) by chlorination of the monochloroindane *III*. The relative greater proportion of the isomer *V* as compared with *IV* is due to its formation from both *II* and *III*. Further chlorination produces trichloroindanes, too; the trichloroindane *VII* was obtained by further chlorination of *IV* and was relatively very pure, whereas the trichloroindane *VIII* could not be prepared in pure form, not even by the modified Sandmeyer reaction from 4-amino-5,6-di-

chloroindane (*X*). The chlorination of *VI* leads to almost no substitution of the aromatic part of the molecule, and preparation of *VIII* from *X* (substitution of diazo



group by chlorine) is accompanied by elimination of diazo group. From melting points of the obtained trichloroindanes it can be inferred that the isomer *VIII* represents the main portion of the product isolated from the distillation residues after isolation of dichloroindanes.

EXPERIMENTAL

Reagents

Indane (*I*): 3000 ml solvent naphtha *II* (Urxovy závody, Valašské Meziříčí) was rectified twice on 1000 × 30 mm column packed with constantan helices, using the reflux ratio 50 : 1, to give 1400 ml 96% indane b.p. 177.0–177.5°C (ref.⁹ b.p. 177.5°C). Composition of the indane fraction was checked by gas-liquid chromatography.

Purity and proportion of individual products were determined by gas-liquid chromatography using a Fractovap apparatus mod. GW (Carlo Erba). Structure of the compounds was inferred from IR spectral data (Spectrophotometer UR 20), electronic spectral data (Specord UV-VIS apparatus), and ¹H-NMR spectral data (Tesla BS 487 apparatus).

4-Chloroindane (*II*)

The 4-aminoindane prepared by catalytic reduction of 4-nitroindane was diazotised according to ref.¹⁰. The diazonium salt with ZnCl₂ was collected by suction, washed with ether, dried, and boiled in benzene for 2 h. From 0.25 mol (33 g) 4-aminoindane 13.1 g (30%) *II*, b.p. 221°C was obtained. For C₉H₉Cl (152.6) calculated: 70.83% C, 5.94% H, 23.23% Cl; found: 70.80% C, 6.00% H, 23.20% Cl.

5-Chloroindane (*III*)

5-Aminoindane was prepared according to ref.¹¹. Preparation and decomposition of the stabilized diazonium salt was the same as in the above preparation of *II*. 0.25 mol (33 g) 5-aminoindane gave 13.5 g (35.4%) *III*, b.p. 222°C. For C₉H₉Cl (152.6) calculated: 70.83% C, 5.94% H, 23.23% Cl; found: 70.80% C, 5.95% H, 23.20% Cl.

Chlorination of *I* in Acetic Acid Catalyzed with Ferric Chloride

1 mol (118 g) *I* was mixed with equal volume (131 ml) acetic acid 99% and 12 g FeCl₃, and chlorine gas was introduced into the mixture in the dark for 4 h until the final weight increase of 56.8 g (0.8 equiv. Cl₂). The reaction mixture was poured in 200 ml 10% HCl with stirring, the oil layer was separated and washed twice with 100 ml water. Distillation under the pressure 10 Torr gave two fractions: 20 ml, b.p. 65–80°C, containing 95% *I*, 3% indene and 2% *II* and *III*; 85 ml b.p. 95–98°C, containing 2% *I* and 98% mixture *II* and *III*. Rectification of the latter fraction on a 50 cm column packed with the Berl saddles gave 75 ml (93 g) fraction boiling 220–222°C (750 Torr) containing only *II* (45%) and *III* (55%). Yield 76.4% with respect to the reacted *I*. A similar result was obtained with the use of nitromethane as the solvent.

Chlorination of *I* with Cl₂ without Solvent, with Ferric Chloride and Antimonic Chloride

Chlorine was introduced into 1 mol (118 g) *I* under the same conditions as in the previous case with acetic acid; distillation of the organic portion resulted in considerable evolution of hydrogen chloride and resinification. Only 20 ml distillate was obtained containing 80.5% *I*, 9.5% indene and 10% mixture of *II* and *III*. Reaction of *I* with anhydrous ferric chloride at 40°C was accompanied by evolution of hydrogen chloride, and resinous products were formed; formation of *II* and *III* was not observed.

0.25 mol (75 g) Antimonic chloride was added drop by drop to 0.5 mol (65.5 ml) *I* with stirring during 20 minutes. The temperature increased spontaneously to 60°C. After 20 h the mixture was extracted with 100 ml chloroform. The extract was stirred with 150 ml 15% NaOH for 2 h.

The organic layer was washed twice with 100 ml water and distilled under normal pressure. The fraction boiling 217–222°C (25 g) contained 50% *II* and 50% *III*. Yield 65.6% with respect to the antimonite chloride used. Rectification of the mixture of isomeric monochloroindanes and attempt of selective sulfonation of one of the isomers were not successful. After treatment with sulphuric acid the mixture of monochloroindanes contained 42% *II* and 58% *III*.

Dichloroindanes *IV*–*VI*

Chlorination was carried out with 2 equivalents of chlorine in the presence of acetic acid in the same way as the preparation of monochloroindanes. The reaction mixture was washed with water, 10% Na₂SO₃ solution, again with water, and distilled to give 137 g (73%) fraction boiling 130 to 140°C/5 Torr. The precipitate formed on cooling to 20°C was collected by suction (73.5 g) and recrystallized from 130 ml mixture methanol–acetone 3 : 2. Yield 32.7 g (44.5%) needles, m.p. 59°C, b.p. 272°C. For C₉H₈Cl₂ (187.1) calculated: 57.80% C, 4.30% H, 37.9% Cl; found: 58.10% C, 4.40% H, 37.50% Cl. Analysis of ¹H-NMR spectra indicates that the product is the compound *VI*. After removing the crystalline portion the mother liquor was rectified on a 1000 × 30 mm column packed with constantan helices; using the reflux ratio 30 : 1 under the normal pressure, fractions were taken boiling within 1°C. The fractions with b.p. 220–228°C had equal composition 10% *II* and 90% *III*. The fractions with b.p. 260–263°C were rectified on the same column under reduced pressure (5 Torr) with the reflux ratio 55 : 1. Four portions were obtained, out of them that containing over 90% of one component was submitted to preparative GLC chromatography (column 3000 × 3 mm packed with chromosorb A with 20% SE-25, T col. 290°C, T inj. 310°C, T det. 330°C; 80–90 μl injections; flame-ionization detector). The obtained pure *IV*, b.p. 262°C was identified by ¹H-NMR spectroscopy. After distilling off the fractions boiling up to 263°C, the distillation residue solidified on cooling. It was distilled under the pressure 10 Torr. Pure isomer *VI* precipitated on cooling the distillate to 20°C, and further portion of the same compound precipitated on cooling to –30°C. The mother liquor was rectified under the pressure 172 Torr using the reflux ratio 55 : 1. The fraction (30.5 g, 22.3%) boiling at 207.5°C contained 99% *V* (b.p. 269°C; identified by ¹H-NMR spectrum) and 1% *VI*. The rectification residue was distilled under normal pressure. The fraction taken at 270–280°C gave a solid on cooling; its crystallization from CCl₄ gave needles (0.5 g, 38%) subliming within 185–190°C. For C₉H₇Cl₃ (221.5) calculated: 48.80% C, 3.18% H, 48.02% Cl; found: 49.00% C, 3.16% H, 47.84% Cl. The product represents a mixture 3 : 1 of the isomeric trichloroindanes *VIII* and *VII*.

Chlorination of the Compound *II*

The reaction was carried out as in the above cases using one equivalent of chlorine. From 0.1 mol (15.25 g) a fraction boiling within 261–269°C was obtained, yield 16 g (85%). According to GLC analysis¹² the product contains 52.6% *IV* and 47.4% *V*.

Chlorination of the Compound *III*

The procedure was the same as with *II*. The solidifying organic layer was extracted twice with 25 ml CCl₄. Distilling off of CCl₄ and distillation gave 15.8 g (84%) mixture of dichloroindanes (b.p. 126–130°C/10 Torr) containing 79.5% *VI* and 20.5% *V* (GLC analysis^{12,13}).

Chlorination of the Compound *IV*

The procedure was the same as above. From the chlorination product 1.3 g (0.6%) needles were isolated. After crystallization from CCl₄ and sublimation the product melted at 148–150°C.

For $C_9H_7Cl_3$ (221.5) calculated: 48.8% C, 3.18% H, 48.01% Cl; found: 48.9% C, 3.15% H, 47.45% Cl. According to GLC analysis the product consists of *VII* and traces *IV*.

The compound *VI* undergoes no substitution chlorination under the same conditions.

4-Nitro-5,6-dichloroindane (*IX*)

0.5 mol (94 g) *VI* was nitrated in analogy to preparation of 3-nitro-4,5-dichloro-1,2-dimethylbenzene^{14,15}. Crystallization from 99% acetic acid gave 70 g (60%) product melting at 94.5 to 95.5°C. For $C_9H_7Cl_2NO_2$ (232.1) calculated: 46.58% C, 3.04% H, 6.04% N, 30.5% Cl; found: 46.6% C, 3.00% H, 6.00% N, 30.40% Cl.

4-Amino-5,6-dichloroindane (*X*)

Reduction of *IX* was carried out in the same way as that with 4-nitroindane. The raw *X* was distilled, and the fraction boiling at 162–165°C/10 Torr was taken. The distillate was cooled to give the product m.p. 36–38°C, which was mixed with boiling 5M-HCl and filtered. The cooled filtrate was neutralized with 2.5M-NaOH, and the precipitate obtained was recrystallized from diluted ethanol, m.p. 53–54°C; purity of the product was checked by paper chromatography.

Preparation and decomposition of the stabilized diazonium salt from the amine *X* was carried out according to ref.¹⁰. After distilling off benzene the product was distilled, the fraction taken within 130–135°C/10 Torr being a mixture of *VIII* and *VI*. Isolation of pure *VIII* failed.

Elemental analyses and most GLC analyses were carried out in Department of Analytical Chemistry, Institute of Chemical Technology, Pardubice.

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Translated by J. Panchartek.