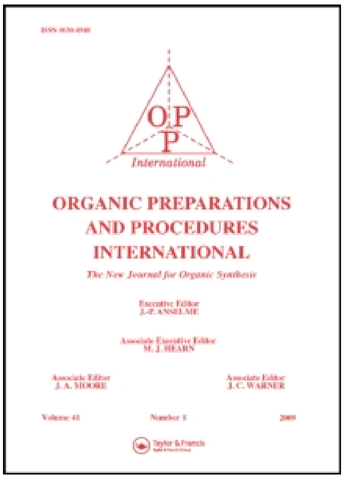

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PREPARATION OF MONO, BIS, TRIS AND TETRAKIS(CHLOROMETHYL) DERIVATIVES BY PHOTOCHLORINATION OF HEXAMETHYLBENZENE

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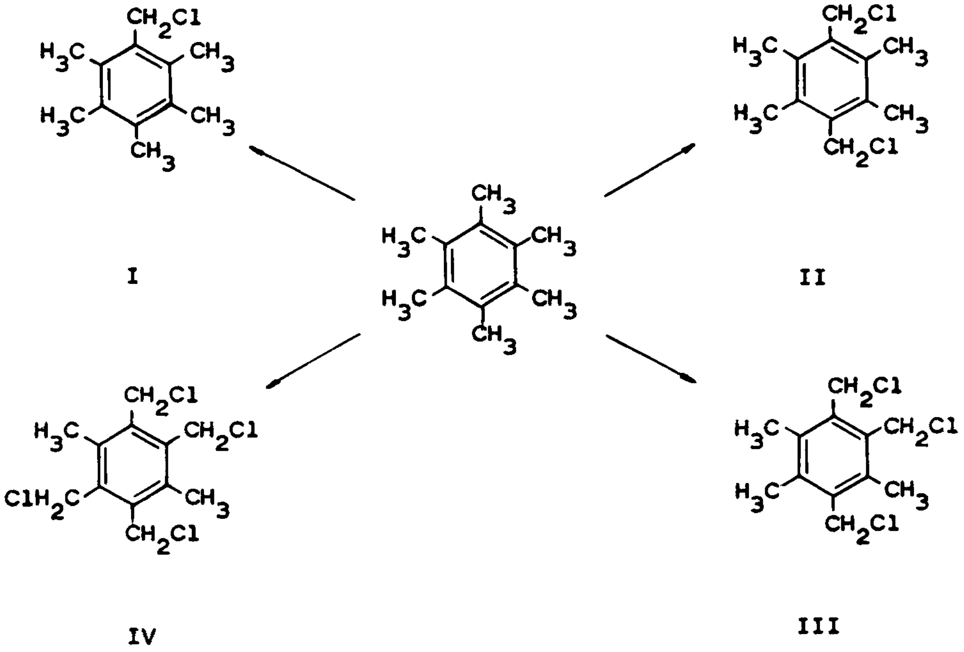

Chloromethyl derivatives of polymethylbenzenes are useful intermediates for the preparation of substances which find application in coatings, fibers, plastics, etc.[2]

Although chloromethylation is a good method for obtaining these products, some difficulties arise in trying to introduce more than two chloromethyl groups in a given polymethylbenzene.

During the course of our work it became necessary to prepare large amounts of chloromethyl derivatives and we have studied the side-chain photochlorination of the hexamethylbenzene as a method for preparing the mentioned substances.

Reactions were performed by bubbling a stream of chlorine through a boiling solution of hexamethylbenzene under illumination with an incandescent lamp. Using a 40-W lamp and chloroform as solvent, chloromethylpentamethylbenzene (I) was obtained after 4 hr treatment (yield 78 %); if the reaction time was extended to 6 hr, the bis(chloromethyl) derivative II was formed in 70 % yield, together with a small amount of 1,2-bis-(chloromethyl)-3,4,5,6-tetramethylbenzene (II′).

When the side-chain photochlorination of hexamethylbenzene was carried out in chloroform solution employing a 100-W incandescent lamp, a tris(chloromethyl)-trimethylbenzene, namely the 1,2,4-tris(chloromethyl)-3,5,6-trimethylbenzene (III) was formed (yield 52 %). The same product could be obtained when the bis(chloromethyl) derivative II was submitted to photochlorination under similar conditions for 2 hr.

To introduce more than three chlorine atoms, a higher b.p. solvent (dichloroethane) was used, and the photochlorinations were performed with a 40-W lamp. Thus, from hexamethylbenzene (31 hr reflux, yield 54 %) and from compound III (6 hr reflux, yield 73 %), the tetrakis(chloromethyl) derivative IV was obtained.

The structures of compounds II′, III and IV were determined by correlation of NMR data, taking into account the deshielding effect of the chloromethyl groups on vicinal methyl and methylene groups.

EXPERIMENTAL

Chloromethylpentamethylbenzene (I). A stream of dry chlorine (flow rate: 250 ml/hr) was bubbled through a stirred, boiling solution of hexamethylbenzene (190 g) in chloroform (500 ml).

The solution was illuminated with a 40-W incandescent lamp placed at 5 cm from the reaction vessel. The reaction (followed by TLC, silica-gel, ligroin) was stopped after 4 hr and the solvent evaporated. The residue was distilled (b.p. 170-180º, 18 mm, yield 78 %) giving after recrystallization from ligroin, colorless needles, m.p. 83-84º (lit.[3] m.p. 81-82º).

NMR (CCl_4) 3-, 4- and 5-CH_3 δ 2.20 (9 H); 2- and 6-CH_3 δ 2.31 (6 H); CH_2 δ 4.65 (2 H).

1,4-Bis(chloromethyl)-2,3,5,6-tetramethylbenzene (II). Hexamethylbenzene (322 g) was chlorinated in a boiling solution of chloroform (1 l) using as luminous source a 40-W lamp. The reaction progress was followed by TLC (silica-gel, ligroin) and after 6 hr all the hexamethylbenzene had been transformed.

The mixture was then cooled and the solid was filtered.

Colorless prisms from acetone (yield 70 %), m.p. 191-193º (lit.[4] m.p. 193-194º).

NMR ($CDCl_3$) CH_3 δ 2.38 (12 H); CH_2 δ 4.78 (4 H).

The chloroform filtrate contained 1,2-bis(chloromethyl)-3,4,5,6-tetramethylbenzene (II′) as the major component (TLC).

This compound was isolated by distillation of the liquors mother residue (180-200º/ 18 mm) and then chromatographed on a silica-gel column using ligroin as eluent. The product obtained from the first eluted fraction was recrystallized from ligroin giving colorless needles, m.p. 128-129º.

Anal. Calcd. for $C_{12}H_{16}Cl_2$, C, 62.34; H, 6.98; Cl, 30.68.
Found, C, 62.21; H, 6.89; Cl, 30.58.

NMR ($CDCl_3$) 3- and 6-CH_3 δ 2.35 (6 H); 4- and 5-CH_3 δ 2.25 (6 H); 1- and 2-CH_2 δ 4.81 (4 H).

1,2,4-Tris(chloromethyl)-3,5,6-trimethylbenzene (III). It was obtained from hexamethylbenzene (500 g) in a similar manner to that described for compound II, using a 100-W incandescent lamp.

Colorless needles from acetone (yield 52 %), m.p. 153-154º.

Anal. Calcd. for $C_{12}H_{15}Cl_3$, C, 54.25; H, 5.70; Cl, 40.04.
Found, C, 54.14; H, 5.80; Cl, 40.14.

NMR ($CDCl_3$) 5- and 6-CH_3 δ 2.35 (6 H); 3-CH_3 δ 2.46 (3 H);
4-CH_2 δ 4.63 (2 H); 1- and 2-CH_2 δ 4.73 (4 H).

Compound III was also obtained by photochlorination of II in chloroform solution with a 100-W lamp for 2 hr (yield 58 %).

1,2,4,5-Tetrakis(chloromethyl)-3,6-dimethylbenzene (IV). Hexamethylbenzene (600 g) dissolved in dichloroethane (2.5 l) was chlorinated for 31 hr using a 40-W lamp. The voluminous precipitate formed during the reaction, was filtered and recrystallized from dioxane (yield 54 %), giving colorless prisms, m.p. 239-241º.

Anal. Calcd. for $C_{12}H_{14}Cl_4$, C, 48.04; H, 4.70; Cl, 47.28.
Found, C, 47.80; H, 4.67; Cl, 47.60.

NMR ($AsCl_3$) CH_3 δ 2.46 (6 H); CH_2 δ 4.73 (8 H).

Compound IV was also prepared by photochlorination of III in dichloroethane solution with a 40-W lamp for 6 hr (yield 73 %).

REFERENCES

1. Research Member of the Consejo Nacional de Investigaciones Científicas y Técnicas.
2. H.W. Earhart, "Polymethylbenzenes", p. 24, Noyes Development Corporation, Park Ridge, New Jersey, 1969.
3. R.R. Aitken, G.M. Badger and J.W. Cook, J.Chem.Soc., 331 (1950).
4. M.J. Rhoad and P.J. Flory, J.Am.Chem.Soc., 72, 2216 (1950).

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