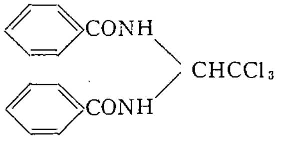
SYNTHESIS OF 1,1,1-TRICHLORO-2,2-*BIS*-(*p*-CYANOPHENYL)-ETHANE[1]

By Yvon Perron and Roger Barré

ABSTRACT

The synthesis of 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane was carried out with the condensation product of chloral and toluene as starting material. This product was converted, through the corresponding tetraacetate, to 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane which in turn reacted with hydroxylamine to give the dioxime. The subsequent dehydration of the latter gave rise to the desired dinitrile. The corresponding dichloro derivatives of the oxime and nitrile were also prepared.

The first attempt to prepare 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane was made by Hepp and Spiess (2). According to their procedure, the condensation of chloral with benzonitrile was made, using sulphuric acid as condensing agent; a compound having Structure I was obtained.



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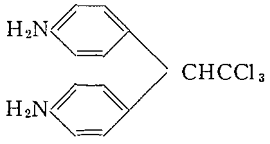
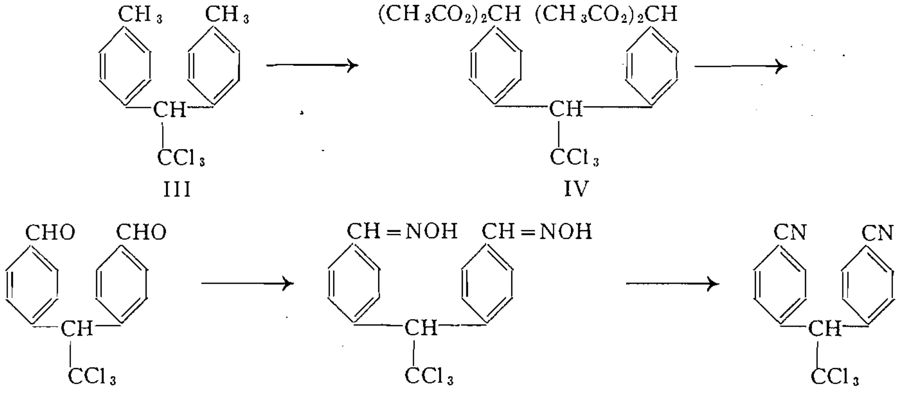


II

Later, Weizmann and co-workers (3) started with 1,1,1-trichloro-2,2-*bis*-(*p*-aminophenyl)-ethane (II) which was diazotized and the resulting diazo compound was treated with cuprous cyanide; an oil was obtained which could not be crystallized. Similarly, unsuccessful results were obtained in our laboratory when we followed the same procedure.

The synthesis of 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane was successfully carried out, when the condensation product of chloral and toluene was used as starting material. This condensation product (III) was submitted to the treatments outlined in the following scheme of equations:



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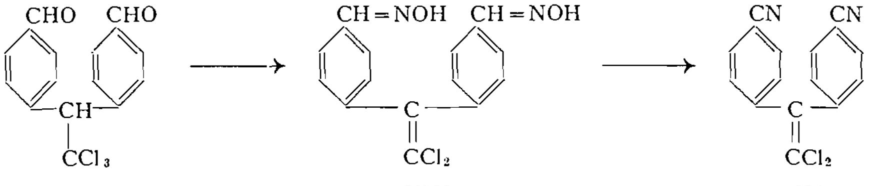
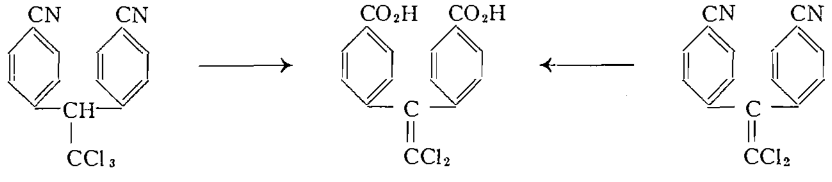
1,1,1-Trichloro-2,2-*bis*-(*p*-tolyl)-ethane (III), dissolved in a mixture of acetic acid and acetic anhydride, was oxidized with the aid of chromium trioxide to the tetraacetate (IV). This last compound, upon acid hydrolysis, gave rise to 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (V). This aldehyde reacted with hydroxylamine to give the corresponding dioxime (VI) which, on elimination of two molecules of water by treatment with acetic anhydride or thionyl chloride, formed the expected dinitrile (VII).

When the Compound V was treated with hydroxylamine, in an alkaline medium, one molecule of hydrogen chloride was eliminated and 1,1-dichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethylene (VIII) was obtained. Dehydration of this ethylenic dioxime, by treatment with thionyl chloride or acetic anhydride, gave rise to 1,1-dichloro-2,2-*bis*-(*p*-cyanophenyl)-ethylene (IX).



V VIII IX

Both the dinitrile, VII, and the ethylenic dinitrile, IX, upon alkaline hydrolysis, produced 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene (X).



VII X IX

EXPERIMENTAL

Tetraacetate of 1,1,1-*Trichloro*-2,2-*bis*-(*p*-*aldehydophenyl*)-*ethane*

A 1000 ml. three-necked flask was equipped with a mechanical stirrer and thermometer, while the third neck was closed with a stopper and used for the addition of reagents. The reaction flask was immersed in an ice-salt bath and 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane (25 gm.), prepared according to the procedure outlined by Fischer (1), was introduced together with acetic anhydride (300 cc.) and glacial acetic acid (100 cc.). The resulting solution was cooled to 0°C. and concentrated sulphuric acid (40 cc.) was added slowly, from a dropping funnel, with cooling and stirring. After completion of the addition, the solution was cooled again to 0°C. and then chromic anhydride (50 gm.) was added, in small portions, at such a rate that the temperature did not rise above 5°C. The stirring was continued for 10 min. after all the chromium trioxide had been added. The contents of the reaction flask was poured on crushed ice contained in a large beaker. The precipitate was filtered off and washed with cold water until the washings were colorless. The solid was suspended in a solution

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of cold 2% sodium hydroxide (200 cc.) and the suspension was mechanically stirred for 10 min. The product was filtered off, washed several times with small quantities of cold water, and recrystallized from water–dioxane. After two recrystallizations, the crystals consisted of colorless elongated plates containing a molecule of dioxane of crystallization. On heating, *in vacuo* at the temperature of boiling water, the solvent of crystallization was eliminated and the dried product melted at 122°C. Yield, 70%. Calc. for $C_{24}H_{23}O_8Cl_3 . C_4H_8O_2$: C, 53.03; H, 4.90; Cl, 16.81; dioxane, 13.89%. Found: C, 53.01; H, 4.95; Cl, 16.80; dioxane, 13.77%.

1,1,1-*Trichloro*-2,2-*bis*-(*p-aldehydophenyl*)-*ethane*

The tetraacetate (15 gm.) was dissolved in a boiling 50% water–ethanol mixture (250 cc.), and concentrated sulphuric acid (10 cc.) was added cautiously. The resulting solution was refluxed for 30 min. The hot solution was then filtered and allowed to cool slowly; crystals of the aldehyde deposited. The filtered crystalline product was recrystallized from boiling ethanol–water from which it separated as an almost white crystalline solid, melting at 148°C. (dec.). Yield, 98%. Calc. for $C_{16}H_{11}O_2Cl_3$: C, 56.22; H, 3.22; Cl, 31.18%. Found: C, 56.28; H, 3.30; Cl, 31.20%.

1,1,1-*Trichloro*-2,2-*bis*-(*p-aldoximinophenyl*)-*ethane*

To a solution of 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (10 gm.) in ethanol (100 cc.), hydroxylamine hydrochloride (6.1 gm.) and anhydrous sodium acetate (7.2 gm.) were added. The resulting mixture was refluxed gently for one hour. After cooling, the sodium chloride formed during the reaction was filtered off. The alcoholic filtrate was diluted with water to the point of incipient turbidity. The solution, while standing overnight in the cold, deposited a crop of crystals. These were recrystallized from ethanol–water from which were obtained colorless rods, containing water of crystallization, m.p. 126°C. On heating *in vacuo*, at the temperature of boiling water, the molecule of water was eliminated; the dried product melted at 139°C. Yield, 60%. Calc. for $C_{16}H_{13}O_2N_2Cl_3 . H_2O$: C, 49.30; H, 3.85; Cl, 27.36; N, 7.18; H_2O, 4.62%. Found: C, 49.24; H, 3.90; Cl, 27.32; N, 7.21; H_2O, 4.30%.

1,1,1-*Trichloro*-2,2-*bis*-(*p-cyanophenyl*)-*ethane*

Thionyl chloride was added slowly from a dropping funnel to anhydrous 1,1,1-trichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethane (5 gm.), until evolution of sulphur dioxide and hydrogen chloride had ceased. Water was then added cautiously to destroy the excess thionyl chloride. A yellow gum separated from which the supernatant liquor was decanted. The gummy residue was washed several times with cold water and subsequently dissolved in 70% acetic acid. The resulting solution was decolorized with charcoal, filtered, and the filtrate was allowed to cool. The nitrile which separated, after recrystallizations from 70% acetic acid, consisted of colorless plates, melting at 149°C. Yield, 80%. Calc. for $C_{16}H_9N_2Cl_3$: C, 57.22; H, 2.68; N, 8.34; Cl, 31.74%. Found: C, 57.15; H, 2.74; N, 8.36; Cl, 31.70%.

Alternatively, acetic anhydride instead of thionyl chloride could be used as dehydrating agent, according to the following procedure.

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1,1,1-Trichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethane (4.2 gm.) was dissolved in acetic anhydride (50 cc.) and the resulting solution refluxed for two hours. It was then filtered to remove a small quantity of insoluble impurities, and the filtrate concentrated to half-volume by distillation. The excess acetic anhydride was hydrolyzed by adding water dropwise to the boiling solution. The yellow solution so obtained was boiled with a little charcoal to remove the colorizing material, filtered, and allowed to cool. The crystalline product thus obtained was recrystallized from 70% acetic acid from which it separated as colorless plates, melting at 149°C. Yield, 70%.

1,1-*Dichloro-2,2-bis-(p-aldoximinophenyl)-ethylene*

To a solution of 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (1 gm.) in 95% ethyl alcohol (50 cc.), hydroxylamine hydrochloride (1 gm.) and potassium hydroxide (1.5 gm.) were added. The resulting mixture was refluxed gently for 30 min., after which it was filtered from the potassium chloride formed during the reaction. The filtrate was acidified with concentrated hydrochloric acid and subsequently diluted with an equal volume of water. On cooling, crystals of the ethylenic dioxime deposited. After recrystallization from 50% ethanol, the crystalline product consisted of slightly yellow plates, melting at 187-188°C. Yield, 80%. Calc. for $C_{16}H_{12}O_2N_2Cl_2$: C, 57.28; H, 3.58; Cl, 21.19; N, 8.35%. Found: C, 57.21; H, 3.63; Cl, 21.12; N, 8.40%.

1,1-*Dichloro-2,2-bis-(p-cyanophenyl)-ethylene*

1,1-Dichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethylene (1 gm.) was treated dropwise with thionyl chloride, until the evolution of sulphur dioxide and hydrogen chloride had ceased. The unreacted thionyl chloride was decomposed by the cautious addition of water from a dropping funnel. This caused the separation of a yellow gum from which the supernatant liquor was decanted. The residual gum was washed several times with cold water and finally dissolved in boiling 70% acetic acid. The resulting solution was refluxed with charcoal, filtered, and allowed to cool. On cooling, a crystalline product separated which, after recrystallization from 70% acetic acid, was obtained as colorless rectangular plates, melting at 139°C. Yield, 85%. Calc. for $C_{16}H_8N_2Cl_2$: C, 64.21; H, 2.67; Cl, 23.74; N, 9.36%. Found: C, 64.16; H, 2.75; Cl, 23.67; N, 9.30%.

1,1-*Dichloro-2,2-bis-(p-carboxyphenyl)-ethylene*

A mixture of 1,1-dichloro-2,2-*bis*-(*p*-cyanophenyl)-ethylene (1 gm.), 10% sodium hydroxide solution (40 cc.), and 95% ethyl alcohol (10 cc.) was refluxed for three hours or until a clear solution was obtained. The alcohol was then distilled off and the residual aqueous solution acidified with a 10% sulphuric acid solution to liberate the free acid. The precipitated carboxylic acid was filtered off and washed with small portions of cold water. It was then dissolved in boiling 50% ethanol and the resulting solution was decolorized with charcoal. On cooling, 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene crystallized out as colorless needles, melting at 278°C. Yield, 60%. Calc. for $C_{16}H_{10}O_4Cl_2$: C, 56.97; H, 2.96; Cl, 21.06%; mol. wt., 337. Found: C, 56.85; H, 2.99; Cl, 21.15%; mol. wt., 339.

Similarly, this ethylenic carboxylic acid was prepared by alkaline hydrolysis of 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane, from which a molecule of hydrogen chloride was eliminated during the reaction of hydrolysis. The procedure employed was the same as the one described above for the alkaline hydrolysis of the corresponding dichloroethylenic dinitrile.

ACKNOWLEDGMENT

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REFERENCES

1. Fischer, E. Ber. 7: 1191. 1874.
2. Hepp, E. and Spiess, G. Ber. 9: 1428. 1876.
3. Weizmann, M., Israelashvili, S., and Papo, R. J. Am. Chem. Soc. 70: 4263. 1948.

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