Tetrahedron Letters No.9, pp. 513-519, 1965. Pergamon Press Ltd.
Printed in Great Britain.

SYNTHESIS OF 3,5,6-TRICHLORO-BENZENE-2-DIAZO-1-OXIDE

by

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(Received 12 January 1965)

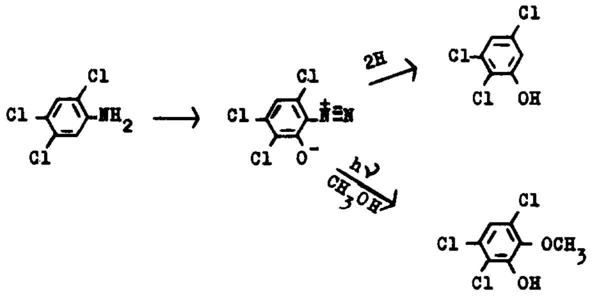
A convenient synthesis of 3,5,6-trichlorobenzene-2-diazo-1-oxide is found in the reaction of 2,4,5-trichlor-aniline with nitric acid.

Diazo-oxides have been known for years already. They are synthesized by diazotization of substituted 2-amino-phenols1). The diazo-oxides are interesting compounds, because some of them undergo a rearrangement2)3) and other derivatives are used in 1,3-dipolar reactions4)5)6).

Since the discovery of our synthesis, Brown et.al. have published an article on ortho diazo-oxide formation by the action of nitric acid on acetamido-benzothiophene or naphthalene derivatives[7].

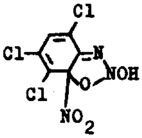
Surprisingly we discovered that the action of nitric acid on 2,4,5-trichlor-aniline gave a crystalline explosive compound, which decomposed in solution to 3,5,6-trichloro-benzene-2-diazo-1-oxide. The 2,4,5-trichloro-acetanilide was nitrated under these conditions to the 2-nitro-3,4,6-trichlor-aceetanilide[8]. The structure of the diazo-oxide was established on the basis of elementary analysis, U.V. and I.R. spectra and chemical properties. The I.R. spectrum has characteristic bands at 2140 cm^{-1} ($\overset{+}{N}\equiv N$), 1609 cm^{-1} (polarized $>C=O$)[9]. The U.V. spectrum has maxima at 285-290 mµ and 405-410 mµ[10]. The diazonium group was further demonstrated by the red dye formed by reation with naphthol-2.

In methanolic solution the 3,5,6-trichloro-benzene-2-diazo-1-oxide under the influence of light formed mainly 2-methoxy-3,5,6-trichloro-phenol[4] next to some carboxylic ester as a result of a rearrangement [2,3]. Huisgen et.al.[4] found for the photolysis of 3,4,5,6-tetrachloro-benzene-2-diazo-1-oxide only 3,4,5,6-tetrachloro-2-methoxyphenol as reaction product and no rearrangement. Reduction of the diazo-oxide with iron and hydro chloric acid yielded 2,3,5-trichloro-phenol.



The position of the substituents was confirmed by the reaction of 2-amino-3,4,6-trichloro-phenol with nitrous acid to 3,4,6-trichlorobenzene-2-diazo-1-oxide, different from the one described above.

The mechanism of the synthesis of the diazo-oxide from 2,4,5-trichloraniline is still unknown. We did not succeed in determining the structure of the intermediate. The I.R. spectrum showed a band which is ascribed to an acidic -OH of N-H (3200 cm^{-1}). Absorption at 1555, 1320 and 750 cm^{-1} may be attributed to a nitro group..There is no absorption at the position of the diazonium group. Thus a structure analogous to Brown's[7)]



may be possible.

The variables in the reaction conditions were the concentration and quantity of nitric acid, temperature, and reaction time. With fuming nitric acid at 0° the reaction was completed after 5 minutes. The yield was rather low. In eight experiments the yields varied between 25 and 32%, except in one, which gave 46%. The temperature was varied from -15 to 25°, the reaction time from 5 minutes to 18 hours, but neither variation had any influence on the yield. The concentration of the nitric acid must be higher than 73%, because almost no reaction occurred when nitric acid of 73% was used. Only a few percent of 2,4,5,2',4',5'-hexachlorodiazoaminobenzene was formed. Therefore this compound may also be an intermediate for the synthesis of the diazo-oxide. The scope and limitation of this synthesis of 2-diazo-1-oxides, the reaction mechanism and other reaction product(s) remain still to be investigated. We hope that this publication will lead to further research.

Experimental Part[*]

3,5,6-trichloro-benzene-2-diazo-1-oxide

18 g (0.091 mol) of 2,4,5-trichlor-aniline was added in 5 minutes to a mixture of 15 ml of concentrated nitric acid (d. 1.4) and 35 ml of fumine nitric acid (d. 1.52) at a temperature of 0-5°. The aniline slowly dissolved. The reaction mixture was kept one hour at 0° and 16 hours at room temperature. A red solution with white crystals was obtained.

A few crystals were filtered off. They decomposed very quickly in melting point determinations at the Kofler apparatus at a temperature of about 75°. The I.R. spectrum showed bands at 750, 1320 and 1555 cm^{-1}, which can be attributed to a nitro group, and a band at 3200 cm^{-1}, which belongs to an acidic OH or NH-group.

The reaction mixture was poured on ice. The yellow precipitate decomposed and partly liquefied. It was taken up in methylene chloride. A colourless gas evolved (N_2?). The solution in CH_2Cl_2 was dried and evaporated. The red residue (15.4 g) was extracted with 25 ml of methanol and crystallized from ca 200 ml of methanol. Yield 6.0 g (29%) orange-red needles of 3,5,6-trichloro-benzene-2-diazo-1-oxide with m.p. 159-161° (dec.).

U.V. spectrum: λ max. 285-290 and 405-410 mμ
ε resp. 7600 and 5400 (Values not reliable, because of decomposition by U.V. light.

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[*] The micro-analysis were carried out by Mr.W.M.Hazenberg, Laboratory for Org.Chemistry, State University of Groningen. The U.V. spectra were measured by Mr.H.Keuker of our Research Laboratories, the I.R. spectra by Mrs.F.v.Deursen, Research Laboratories, Weesp, and H.M.v.d.Bogaert of Philips Research Laboratories, Eindhoven.

I.R.-spectrum: $-\overset{+}{N}\equiv N$ group at 2140 cm^{-1}
polarized $>C=O$ group at 1609 cm^{-1}

Calc. for $C_6HCl_3N_2O$ (223.46): C 32.23; H 0.45; Cl 47.60; N 12.54
Found : " 32.1 ; " 0.7 ; " 46.9 ; " 12.6

We did not succeed in isolating pure substances from the mother liquor.

2,4,5,2',4',5'-hexachlorodiazoaminobenzene

9.0 g (0.045 mol) of 2,4,5-trichloroaniline was added to 25 ml of concentrated nitric acid (d. 1.40) and 10 ml of fuming nitric acid (d. 1.52) at a temperature of 10-15°. The reaction mixture was kept 17 hours at room temperature and then poured on ice. The precipitate was crystallized twice from 400 ml methanol. Yield 0.1 g of a yellow product, 2,4,5,2',4',5'-hexachlorodiazoaminobenzene with m.p. 161-163.

Calc. for $C_{12}H_5Cl_6N_3$(40391): C 35.68; H 1.24; Cl 52.67; N 10.39
Found : " 35.7 ; " 1.5 ; " 51.8 ; " 10.4

The I.R.-spectrum showed a band at 3262 cm^{-1}, which was attributed to a NH-group. From the mother liquor a considerable quantity of 2,4,5-trichlor-aniline with mp. 95° could be isolated.

2,3,5-trichloro-phenol

7.5 g (0.033 mol) 3,5,6-trichloro-benzene-2-diazo-1-oxide was partly dissolved in a mixture of 75 ml methanol and 60 ml concentrated hydrochloric acid. 5.0 g (0.09 mol) iron powder was slowly added. The diazo-oxide quickly dissolved, the red colour disappeared. After being poured on ice and extracted with methylene chloride, the solution in CH_2Cl_2 was dried and evaporated. The black oil (6.1 g) was crystallized from petroleum ether bp 40-60°. Yield 4.8 g (72%) of 2,3,5-trichlorophenol with mp. 56-57.5. Mixed m.p. with authentic sample (mp. 58-60): 56-58.

Calc. for $C_6H_3Cl_3O$ (197.46): C 36.48; H 1.54; Cl 53.86
Found : " 36.2 ; " 1.6 ; " 54.0

3,5,6-trichloro-2-methoxyphenol

1.0 g 3,5,6-trichloro-benzene-2-diazo-1-oxide was partly dissolved in 150 ml methanol in an open flat dish with a diameter of 15 cm and exposed to U.V.-light for two hours. After evaporation of the methanol, the I.R.-spectrum of the residue showed that it mainly consisted of 3,5,6-trichloro-2-methoxyphenol, next to a compound which contained a $COOCH_3$ group. The residue was crystallized from petroleum ether bp. 40-60. Yield 0.2 g (20%) 3,5,6-trichloro-2-methoxyphenol with mp. 100-102. Further crystallisation raised the mp. to 103-104°. (Brown et al[11]) described a trichloro-2-methoxy-phenol with mp. 102-104, synthesized by chlorination of 2-methoxy-3-chloro-phenol).

Calc. for $C_7H_5Cl_3O_2$ (227.49): C 36.97; H 2.21; Cl 46.76
Found : " 37.4 ; " 2.4 ; " 46.5

The I.R.-spectrum showed bands at 3340 cm^{-1} (aromatic OH); 2920 cm^{-1} (aromatic OH or OCH_3?); 1223 and 1251 cm^{-1} (aromatic OH or OCH_3?); 1310 cm^{-1} (C-H stretching).

In CH_2Cl_2 as solvent the diazo-oxide was decomposed by U.V.-light, but no pure substance could be isolated, although the I.R.-spectrum showed a considerable quantity of compound(s) with a COOH-group.

3,4,6-trichloro-benzene-2-diazo-1-oxide

1 g (0.005 mol) of 2-amino-3,4,6-trichloro-phenol suspended in 15 ml concentrated hydrochloric acid was diazotized with 0.5 g sodium nitrite in 5 ml of water. The amino-phenol dissolved. A new yellow precipitate was formed. The diazo-oxide was taken up in CH_2Cl_2. The solution was washed with water, dried and evaporated. Yield 0.9 g (80%) 3,4,6-trichloro-benzene-2-diazo-1-oxide with m.p. 112.5-114.5.

Calc. for $C_6HCl_3N_2O$ (223.46): C 32.23; H 0.45; Cl 47.60
Found : " 32.9 ; " 0.5 ; " 48.0

The I.R.-spectrum showed bands at 2150 cm^{-1} and 1620 cm^{-1}.

Acknowledgement:

Our thanks are due to Mr.C.J.Schoot of the Philips Research Laboratories, Eindhoven, for valuable discussion.

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