## CHLORO DERIVATIVES OF 1,2,4-TRIAZOLE

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5-Substituted 3-chloro-1,2,4-triazoles were synthesized by diazotization of 5-substituted 3amino-1,2,4-triazoles in hydrochloric acid. In addition to replacement of the amino group by a chloro group, diazotization of 5-aryl-3-aminotriazoles at high temperatures leads to chlorination of the aromatic ring.

According to patent data [1], halo derivatives of 1,2,4-triazole are good heat and light stabilizers for chlorinated polyolefins, particularly polyvinyl chloride; 3-chloro-1,2,4-triazole has better properties than the analogous bromo derivatives. In order to ascertain the effect of the nature of the substituents in the triazole ring on the stabilizing activity of the compound, we synthesized a number of chloro derivatives of 1,2,4-triazole.

Inasmuch as the direct chlorination of 5-phenyl-substituted 1,2,4-triazoles is always accompanied by N-halogenation [2], to prepare 5-aryl-substituted 3-chloro-1,2,4-triazoles we chose replacement of the amino group by chlorine in readily accessible amino derivatives of the general formula



It is known [3] that the amino group is replaced by bromine when sodium nitrite is added to a refluxing solution of 5-aryl-3-amino-1,2,4-triazole in hydrobromic acid. When this reaction is carried out in hydro-chloric acid, in addition to replacement of the resulting diazo group by chlorine, one also observes chlorination of the aryl residue.



According to the IR and PMR spectroscopic data, the ortho position of the phenyl ring is chlorinated in the diazotization of 5-phenyl-3-amino-1,2,4-triazole (Ia). Electron-donor substituents in the aromatic ring promote chlorination. Thus 5-(2'-chloro-4'-methylphenyl)-3-chloro-1,2,4-triazole (90%) and 5-(3'-chloro-4'-methylphenyl)-3-chloro-1,2,4-triazole (10%) are formed in the diazotization of 5-(4'-methylphenyl)-3-amino-1,2,4-triazole (Ig). A more complex mixture of isomeric derivatives is obtained in the diazotization of 5-(3'-methylphenyl)-3-amino-1,2,4-triazole (Ig). A more complex mixture of isomeric derivatives is obtained in the diazotization of 5-(3'-methylphenyl)-3-amino-1,2,4-triazole (If). In this case 5-(3'-methyl-6'-chlorophenyl)-3-chloro-1,2,4-triazole (50-60%) and a mixture (40-50%) of 5-(3'-methyl-2'-chlorophenyl)-3-chloro-1,2,4-triazole and 5-(3'-methyl-4'-chlorophenyl)-3-chloro-1,2,4-triazole are formed. Chlorination of the aromatic ring of 5-(2'-methylphenyl)-3-amino-1,2,4-triazole (Ie) was not observed. The presence of electron-acceptor substituents (NO<sub>2</sub>, Br) in the aromatic ring prevents its chlorination.

Chlorination can be excluded if the diazotization of aryl-substituted aminotriazoles is carried out in the cold.

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TABLE 1. 5-Substituted 3-Amino-1,2,4-triazoles

| Com-                        | mn °Ca                                      | Empirical<br>formula  | Found, %                             |                                 |                                      | Calcu                | Yield,            |                      |                            |
|-----------------------------|---|---|--------------------------------------|---------------------------------|--------------------------------------|----------------------|-------------------|----------------------|----------------------------|
| pound                       | mp, C-                                      |   | с                                    | н                               | N                                    | С                    | н                 | N                    | %                          |
| ld<br>Ie<br>If<br>Ig<br>I h | 158<br>191—193<br>179—180<br>186<br>205—207 | $\begin{array}{c} C_8H_7N_5O_2{}^b\\ C_9H_7N_4\\ C_8H_7B_7N_4{}^c\end{array}$ | 46,6<br>61,9<br>62,0<br>61,8<br>40,5 | 3,2<br>5,5<br>5,9<br>6,0<br>2,8 | 34,3<br>32,2<br>32,0<br>31.9<br>23,2 | 46.8<br>62,1<br>40.2 | 3,4<br>5,8<br>3,0 | 34,1<br>32,1<br>23,4 | 83<br>72<br>78<br>66<br>73 |

a All of the compounds were purified by recrystallization from water. Found: O 15.9%. Calculated: O 15.7%. Found: Br 33.1%. Calculated: Br 33.4%.

| N-   | -c/CI |  |
|------|-------|--|
| , с́ | Ň     |  |
| - N  | · · · |  |
| +    |       |  |

R

| TABLE 2. | 5-Substituted | 3-Chloro-1 2 4-triazoles |
|----------|---------------|--------------------------|
|          | o Susseiluteu | 0.0m010.1,4,1.0100       |

|   | mp <b>, °C</b>  |  | Found, %   |   |  | Calculated, %  |  |   |  | 1. %   |  |
|---|---|--|--|---|--|--|--|---|--|--|--|
| R   |   | Empirical formula  | с  | н   | Cl   | N  | с  | н   | Cl   | N  | Yiel   |
| $\begin{array}{c} C_{6}H_{5} \\ m\text{-}NO_{2}C_{6}H_{4} \\ p\text{-}NO_{2}C_{6}H_{4} \\ o\text{-}OO_{2}C_{6}H_{4} \\ o\text{-}CH_{3}C_{6}H_{4} \\ m\text{-}CH_{3}C_{6}H_{4} \\ p\text{-}CH_{3}C_{6}H_{4} \\ o\text{-}BrC_{6}H_{4} \\ O\text{-}BrC_{6}H_{4} \\ OC \\ H_{2}NCO \\ CN \end{array}$ | $\begin{array}{c} 176-177^a\\ 163-164 \\ 233^b\\ 157-158 \\ 191-193 \\ 179-180 \\ 186 \\ 191 \\ 191 \\ 121 \\ 190-192 \\ 160^e \end{array}$ | $\left. \begin{array}{c} C_8H_6CIN_3 \\ C_8H_5CIN_4O_2 \\ \end{array} \right\} \left. \begin{array}{c} C_9H_5CIN_3 \\ C_9H_5CIN_3 \\ C_8H_6B_7CIN_3^C \\ C_4H_4CIN_3O_2 \\ C_3H_5CIN_4O \\ C_9HCIN_4 \end{array} \right. $ | 53,5<br>42,9<br>43,1<br>43,0<br>56,0<br>55,6<br>55,6<br>36,8<br>29,3<br>24,9<br>27,6 | 3,4<br>2,2<br>2,1<br>2,2<br>4,0<br>4,1<br>4,0<br>2,1<br>2,6<br>2,1<br>1,0 | 19,6<br>15,7<br>16,0<br>15,7<br>18,2<br>18,1<br>18,3<br>13,6<br>22,1<br>24,0<br>27,4 | 23,6<br>25,2<br>24,6<br>25,2<br>21,7<br>22,0<br>22,0<br>16,1<br>26,1<br>38,4<br>43,8 | 53,6<br>42,8<br>55,8<br>37,2<br>29,7<br>24,6<br>28,0 | 3,3<br>2,2<br>4,1<br>1,9<br>2,5<br>2,1<br>0,8 | 19,8<br>15,8<br>18,4<br>13,7<br>22,0<br>24,2<br>27,6 | 23,4<br>24,9<br>21,7<br>16,3<br>26,0<br>38,2<br>43,6 | 69<br>53<br>47<br>73<br>49<br>68<br>79<br>58<br>80<br>44<br>50 |
| a<br>From aqu<br>From wat<br>Found: E   | ieous alcoho<br>ter.<br>3r 30.6%. C   | ol.<br>alculated: Br   | 30.9   | %.  |  |  |  |   |  |  |  |

e From methanol. From toluene.

The amino group is similarly replaced by chlorine in the diazotization of 3-amino-5-methoxycarbonyl-1,2,4-triazole. On treatment with ammonia the resulting chloro-substituted ester II is converted to an amide, from which the nitrile was obtained by means of phosphorous oxychloride.



The ability of the synthesized compounds to stabilize chlorinated polyolefins is under investigation.

## EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectrum of 10% solutions of the compounds in alcohol or dioxane were recorded with a Tesla BS 4873 spectrometer.\*

5-Aryl-3-amino-1,2,4-triazoles (Ia-h). These compounds were obtained by the methods in [4, 5]. The physical constants of Ia-c are in agreement with the literature values [6, 7], and the physical constants of Id-h, synthesized for the first time in this research, are presented in Table 1.

Diazotization of Aryl-Substituted Aminotriazoles. A) A solution of 0.02 mole of 5-aryl-3-amino-1.2.4-triazole in a mixture of 200 ml of concentrated hydrochloric acid and 100 ml of water was heated to the boiling point, and a solution of 0.5 mole of sodium nitrite in 50 ml of water was added dropwise to it with vigorous stirring. The mixture was then allowed to stand at room temperature for 16 h, after which it was refluxed until it was colorless and poured into ice water. The resulting precipitate of 5-chloroaryl-substituted 3chloro-1,2,4-triazole was removed by filtration and purified by recrystallization.

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B) A 0.02-mole sample of 5-aryl-3-amino-1,2,4-triazole was heated in a mixture of 200 ml of concentrated hydrochloric acid and 100 ml of water until it dissolved completely. The solution was then cooled to 0°, and a solution of 0.5 mole of sodium nitrite in 50 ml of water was added dropwise. The mixture was then allowed to stand at room temperature for 16 h and at 50-70° for 3 h, after which it was poured into ice water. The resulting precipitate of 5-aryl-3-chloro-1,2,4-triazole was removed by filtration and purified by recrystallization.

<u>5-Methoxycarbonyl-3-chloro-1,2,4- triazole (II)</u>. A solution of 2.4 g (0.03 mole) of sodium nitrite in 20 ml of water was added dropwise at  $0-3^{\circ}$  to a suspension prepared from 5 g (0.35 mole) of methyl 3-amino-1,2,4-triazole-5-carboxylate [5] in 40 ml of water and 12 ml (0.14 mole) of hydrochloric acid (sp. gr. 1.18), after which the mixture was stirred at this temperature for ~1 h. The precipitated methyl diazotriazolocarboxylate was removed by filtration. Inasmuch as the diazo ester in dry form was sensitive to mechanical action, it was used in crude form for the subsequent syntheses.

Hydrochloric acid (15 ml) was added to a suspension of the diazo compound in 10 ml of water, and the mixture was heated at 30-40° for 4 h. It was then cooled, diluted with 100 ml of water, and extracted with ether. Evaporation of the ether gave II.

5-Carbamoyl-3-chloro-1,2,4-triazole. A 1-g (7 mmole) sample of ester II was refluxed with 50 ml of ammonium hydroxide (sp. gr. 0.91) for 3 h, after which it was cooled, and the precipitated amide was removed by filtration.

5-Cyano-3-chloro-1,2,4-triazole. A solution of 11.2 g (7.6 mmole) of the amide was refluxed in 100 ml of phosphorus oxychloride for 3 h, after which the excess phosphorus oxychloride was removed by vacuum distillation and the residue was dissolved in 30 ml of ice water. The aqueous solution was extracted with ether, the ether was removed by evaporation, and the residual nitrile was purified by recrystallization.

The results of elementary analysis, the melting points, and the yields of the 5-substituted 3-chloro-1,2,4-triazoles are presented in Table 2.

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