CXVII.—*Diazo-derivatives of 4'-Amino-1-phenyl-5-methylbenzothiazole (Dehydrothio-p-toluidine).*

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THE stereochemical theory of diazo-compounds advocated by Hantzsch and accepted generally by workers in this field of organic chemistry is based on the existence in two isomeric forms of the aromatic diazo-cyanides, diazosulphonates, and diazo-oxides.

Of these two series, the more stable *anti*-diazo-compounds have frequently been prepared in a state of purity, so that their existence has been demonstrated by many analyses. The labile *syn*-diazo-compounds, on the other hand, are much less readily isolated, and analytical data in support of their existence as definite chemical entities are not always obtainable.

It should, however, be possible, by the selection of a base giving rise to exceptionally stable diazo-compounds, to obtain more decisive analytical evidence for or against the existence of the *syn*-diazo-series. 4'-Amino-1-phenyl-5-methylbenzothiazole (dehydrothio-*p*-toluidine) was shown by its discoverer to give rise to a diazo-chloride which is quite stable in solution at the ordinary temperature (A. G. Green, T., 1889, 55, 227). It therefore seemed likely that this thiazole base would furnish other stable diazo-derivatives.*

When suspended in absolute alcohol and diazotised with ethyl nitrite, 4'-amino-1-phenyl-5-methylbenzothiazole hydrochloride yields two isomeric compounds, an insoluble diazo-chloride and a soluble one precipitated on the addition of ether. These products have properties resembling those of the *syn*- and *anti*-diazocyanides derived from simpler aromatic amines.

The soluble *syn*-1-phenyl-5-methylbenzothiazole-4'-diazochloride, which decomposes at a much lower temperature than its isomeride, dissolves readily in water, couples immediately with alkaline β -naphthol, and evolves nitrogen on treatment with copper bronze, giving rise to 4'-chloro-1-phenyl-5-methylbenzothiazole.

The *anti*-1-phenyl-5-methylbenzothiazole-4'-diazochloride is insoluble in water or alcohol, does not couple with alkaline β -naphthol, and reacts very slowly with copper bronze.

Ice-cold solutions of the *syn*-diazo-chloride, when treated with alkaline sodium sulphite, yield *sodium syn*-1-phenyl-5-methylbenzothiazole-4'-diazosulphonate, a compound coupling with β -naphthol, whereas at the ordinary temperature (about 20°) the isomeric, non-coupling *sodium anti*-1-phenyl-5-methylbenzothiazole-4'-diazosulphonate is obtained.

Similar experimental conditions lead to the formation of *syn*- and *anti*-1-phenyl-5-methylbenzothiazole-4'-diazocyanides.

The three pairs of *syn*- and *anti*-diazo-compounds may be represented by the following stereochemical formulæ.

* The nomenclature and notation adopted in this communication are exemplified by the following numbered formula :

4'-Amino-1-phenyl-5-methylbenzothiazole.

Qualitative evidence was also obtained of the existence of the *syn*- and *anti*-sodium diazo-oxides, but in this case the products were not isolated in a state of purity.

The solubility in water of the *syn*-diazo-chloride and cyanide suggests that these compounds pass readily into the diazonium condition. If D is the aromatic complex, this equilibrium would be represented as follows :

On adding sodium azide to the aqueous solution of the *syn*-diazo-chloride, nitrogen is evolved in the cold with the formation of 4'-triazo-1-phenyl-5-methylbenzothiazole (III) :

When the insoluble *anti*-diazo-chloride is warmed with aqueous sodium azide, 4'-amino-1-phenyl-5-methylbenzothiazole is regenerated, while nitrogen and nitrous oxide are evolved :

4'-Amino-1-phenyl-5-methylbenzothiazole gives rise to a series of sparingly soluble, coloured diazo-salts, namely, the *diazo-nitrate*, *acid diazo-chromate*, *diazo-nitroprusside*, *diazo-ferrocyanide*, *acid diazo-carbonate*, *diazo-orthoborate* and *diazo-chlorate*.

With the exception of the last substance, which is extremely explosive at the ordinary temperature, the members of this series are stable in the solid condition at the ordinary temperature; they all couple readily with alkaline β -naphthol. These properties are consistent with the view that the foregoing diazo-derivatives belong to the *syn*-series.

EXPERIMENTAL.

4'-Amino-1-phenyl-5-methylbenzothiazole (dehydrothio-*p*-toluidine) was prepared by heating together at 180° for eight hours 100 grams of *p*-toluidine and 60 grams of sulphur, the fusion being heated subsequently at 250° for twenty hours. The product was worked up by Green's method (*loc. cit.*); the monothiazole base, after repeated crystallisation from amyl alcohol, melted at 191°.

syn- and anti-1-Phenyl-5-methylbenzothiazole-4'-diazochlorides
(Formulæ I and II).

4'-Amino-1-phenyl-5-methylbenzothiazole (15 grams) was converted into the hydrochloride by treatment with excess of alcoholic hydrochloric acid. The dry hydrochloride was suspended in about 50 c.c. of absolute alcohol and treated at 0° with 9 grams of ethyl nitrite in 50 c.c. of the same solvent. The sparingly soluble *anti*-diazochloride (2 grams) which separated was extracted successively with boiling chloroform, cold water, and again with chloroform, the extraction with the organic solvent being repeated fourteen times (Found: C=57.36; H=3.57; N=14.41; Cl=12.67; S=11.02. $C_{14}H_{10}N_3ClS$ requires C=58.51; H=3.50; N=14.58; Cl=12.30; S=11.12 per cent.). This *anti*-diazocompound, a brownish-yellow, amorphous powder, melted with decomposition at 270°; it was insoluble in water and did not couple with alkaline β -naphthol until after treatment with hydrochloric acid.

The soluble *syn*-diazochloride (9.5 grams), which was precipitated from the foregoing alcoholic solution by adding excess of ether, melted with decomposition at 139° (Found: C=56.94; H=3.88; N=14.31; Cl=12.13; S=10.75 per cent.).* The *syn*-diazocompound was very soluble in water and coupled readily with alkaline β -naphthol to a red azo-pigment, becoming violet with concentrated sulphuric acid.

1-Phenyl-5-methylbenzothiazole-4'-azo- β -naphthol,

crystallised from glacial acetic acid in intensely crimson needles melting at 214° and assuming a violet colour in concentrated sulphuric acid (Found: N=10.65; S=8.23. $C_{24}H_{17}ON_3S$ requires N=10.60; S=8.09 per cent.).

A repetition of the diazotisation with amyl nitrite, using ethyl alcohol, led to a smaller yield of the *syn*-diazocompound contaminated with a viscid by-product. In dilute hydrochloric acid, diazotisation led to the production of the soluble *syn*-diazocompound, but, on boiling, the solution lost its intense coupling power and yielded a reddish-brown solid melting at 255°, identified as 4'-hydroxy-1-phenyl-5-methylbenzothiazole (Jacobson, *Ber.*, 1889, 22, 334) (Found: N=5.66. Calc., N=5.79 per cent.). The aqueous solution of the *syn*-diazochloride, when treated in the cold with copper bronze, evolved nitrogen forthwith and in two hours the

* In the analyses of the isomeric diazochlorides, the carbon estimation, repeated several times, was consistently low, although the other constituents gave numbers agreeing very closely with the calculated values.

coupling power had disappeared. The chloro-derivative, when crystallised repeatedly from acetone, separated in pale yellow, granular nodules melting at 160° (Found: N=5.52; Cl=13.47; S=11.98. $C_{14}H_{10}NClS$ requires N=5.38; Cl=13.62; S=12.32 per cent.).

4'-Chloro-1-phenyl-5-methylbenzothiazole was insoluble in water and dissolved readily in the volatile organic media excepting ethyl alcohol, in which it was only sparingly soluble.

The anti-diazo-chloride (2 grams), when treated with copper bronze in dilute hydrochloric acid, remained unchanged for several hours, but after a week had yielded the above chloro-compound (m. p. 160°).

Potassium syn- and anti-1-Phenyl-5-methylbenzothiazole-4'-diazo-oxides.

A 15 per cent. solution of *syn*-1-phenyl-5-methylbenzothiazole-4'-diazo-chloride (2 grams) was added to 90 grams of potassium hydroxide in 60 c.c. of water at 5° , when a pink precipitate separated. This product, which was very soluble in cold water, coupled immediately with alkaline β -naphthol; it was not, however, obtained in a sufficiently pure state for analysis.

The foregoing alkaline solution was heated at 110° until the coupling power was lost. The *syn*-compound dissolved partly; the final residue of the *anti*-diazo-oxide, which was of a darker colour, no longer interacted with alkaline β -naphthol until it had first been acidified.

Action of Sodium Azide on the syn- and anti-1-Phenyl-5-methylbenzothiazole-4'-diazo-chlorides.

A slight excess of sodium azide was added to a cooled aqueous solution of the purified *syn*-diazo-chloride, nitrogen was evolved, and a pale pink precipitate of 4'-triazol-1-phenyl-5-methylbenzothiazole (III) was produced, which changed to a light brown on drying; it melted at 121° (Found: N=21.74. $C_{14}H_{10}N_4S$ requires N=21.00 per cent.).

A slight excess of sodium azide was gently warmed for half an hour with an aqueous suspension of the purified *anti*-diazo-chloride. The product melted at $182-184^{\circ}$ and after purification was identified as the original amine by its melting point (186°) by analysis (Found: N=11.44. Calc., N=11.63 per cent.), and by the formation of the acid diazo-chromate and the azo- β -naphthol.

The reactions with sodium azide were conducted in a gas-apparatus. The *syn*-diazo-chloride evolved nitrogen (Found:

N=9.33, 9.24). The *anti*-diazochloride evolved about twice as much gas, the amount varying with the age of the preparation (Found: $N_2O=16.24, 14.96$; $N=10.68, 9.54$. Calc., $N_2O=15.27$; $N=9.72$ per cent.).

Sodium syn- and anti-1-Phenyl-5-methylbenzothiazole-4'-diazosulphonates (Formulæ I and II).

An aqueous solution of the *syn*-diazochloride, prepared in the foregoing manner, was added slowly to a solution of sodium sulphite and sodium hydroxide cooled to 0° . After twenty minutes, the alkaline solution was filtered from an orange-brown, amorphous precipitate. This product, after five extractions with chloroform, melted with decomposition at 202° (Found: $N=11.66$; $S=18.07$; $Na=6.41$. $C_{14}H_{10}O_3N_3S_2Na$ requires $N=11.81$; $S=18.01$; $Na=6.46$ per cent.). This *syn*-diazosulphonate coupled readily with alkaline β -naphthol, yielding the foregoing azo-derivative.

The *anti*-diazosulphonate was obtained as in the foregoing preparation excepting that the alkaline sulphite solution was maintained at the ordinary temperature. The orange precipitate assumed almost instantly a brown colour and after four extractions with chloroform a yellow, amorphous product was left, melting with decomposition at 309° (Found: $N=11.08$; $S=17.12$; $Na=6.54$ per cent.). This *anti*-compound did not couple with alkaline β -naphthol unless it had first been treated with hydrochloric acid.

syn- and anti-1-Phenyl-5-methylbenzothiazole-4'-diazocyanides (Formulæ I and II).

The *syn*-diazocyanide was formed on adding 2 grams of potassium cyanide and 5 c.c. of water to 2 grams of the *syn*-diazochloride dissolved in 30 c.c. of water acidified with hydrochloric acid, and cooled below 0° . The bright brick-red product, which was very soluble in water, decomposed at 131° , coupled readily with alkaline β -naphthol, and quickly lost nitrogen with copper bronze (Found: $N=19.44$; $S=11.62$. $C_{15}H_{10}N_4S$ requires $N=20.09$; $S=11.49$ per cent.).

The *anti*-diazocyanide, obtained by adding 0.5 gram of potassium cyanide to 2 grams of the *syn*-diazochloride in 15 c.c. of water at 5° , separated as a deep orange precipitate insoluble in water; after crystallisation from moist acetone, it melted at 175° , and did not couple directly with alkaline β -naphthol. With copper bronze it evolved nitrogen, but much more slowly than in the case of the *syn*-compound (Found: $N=20.40$; $S=11.98$. $C_{15}H_{10}N_4S$ requires $N=20.09$; $S=11.49$ per cent.).

4'-Cyano-1-phenyl-5-methylbenzothiazole (Formula IV).

On adding copper bronze to an acid solution of the *syn*-diazocyanide, nitrogen was evolved immediately and a yellow solid separated, which on repeated crystallisation from acetone melted at 145° (Found: N=11.19; S=13.10. $C_{15}H_{10}N_2S$ requires N=11.17; S=12.78 per cent.). This cyano-derivative was rather yellower than the corresponding chloro-compound and had a similar solubility in the usual organic media.

syn-1-Phenyl-5-methylbenzothiazole-4'-diazio-salts.

The following sparingly soluble diazo-salts coupled readily with alkaline β -naphthol and belonged evidently to the *syn*-series.

1-Phenyl-5-methylbenzothiazole-4'-diazonitrate,

—Sodium nitrite was added to a solution of the aminothiazole (2 grams) in 20 c.c. of concentrated nitric acid, keeping the temperature at 0°. A yellowish-brown precipitate (1.5 grams) separated on adding water, which, when dry, exploded at 145° (Found: N=18.11; S=10.31. $C_{14}H_{10}O_3N_4S$ requires N=17.80; S=10.18 per cent.).

The *acid diazo-chromate*, $(C_{14}H_{10}NS \cdot N_2)HCrO_4$, obtained as a copious yellow precipitate on adding excess of potassium dichromate to an aqueous solution of the *syn*-diazio-salt, detonated at 120° (Found: N=11.44; Cr=14.25. $C_{14}H_{11}O_4N_3SCr$ requires N=11.36; Cr=14.10 per cent.).

The *diazo-nitroprusside*, $(C_{14}H_{10}NS \cdot N_2)_2FeNO(CN)_5$, prepared from the diazo-chloride by double decomposition with sodium nitroprusside, was a bright yellow, amorphous powder exploding at 140° (Found: N=22.48; Fe=7.90. $C_{33}H_{20}ON_{12}S_2Fe$ requires N=23.29; Fe=7.74 per cent.).

The *diazo-ferricyanide*, $(C_{14}H_{10}NS \cdot N_2)_3Fe(CN)_6$, was a greenish-yellow powder melting at 158° (Found: N=22.13; Fe=5.85. $C_{48}H_{30}N_{15}S_3Fe$ requires N=21.65; Fe=5.75 per cent.).

The *acid diazo-carbonate*, $(C_{14}H_{10}NS \cdot N_2)HCO_3$, prepared by double decomposition from the *syn*-diazio-chloride and sodium hydrogen carbonate, was a reddish-brown, amorphous powder melting at 128° with slight detonation; it effervesced with dilute sulphuric acid (Found: N=13.56; S=10.24. $C_{15}H_{11}O_3N_3S$ requires N=13.39; S=10.21 per cent.).

The *diazo-chlorate*, $(C_{14}H_{10}NS \cdot N_2)ClO_3$, a brilliant yellow, amorphous compound obtained by double decomposition, was slightly soluble in water. When dried, it was found to be extremely explo-

sive, detonating violently at 110° (Found: N=12.59. $C_{14}H_{10}O_3N_3ClS$ requires N=12.50 per cent.).

The *diazo-orthoborate*, $(C_{14}H_{10}NS \cdot N_2)_3BO_3$, was obtained as a bright brown powder by adding excess of concentrated borax solution (1 gram in 30 c.c.) to a solution of the *syn*-diazo-chloride; it melted at 154° with decomposition (Found: N=15.47; S=11.51. $C_{42}H_{30}O_3N_9S_3B$ requires N=15.42; S=11.76 per cent.). This orthoborate was soluble in chloroform and was precipitated therefrom by light petroleum.

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