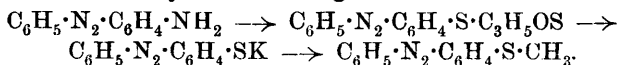


CLXI.—*Substituted Thiolazo-derivatives of Benzene.*

By JOHN JACOB FOX and FRANK GEORGE POPE.

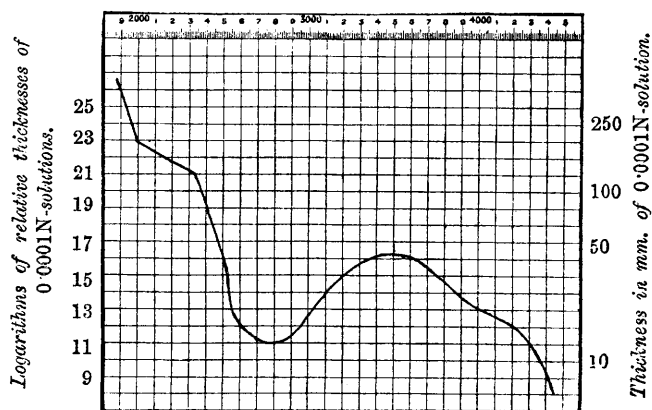
ALTHOUGH phenyl mercaptan resembles phenol in its general characters, it has hitherto not been found possible to couple it directly with diazonium salts so as to yield thiol derivatives corresponding with benzeneazophenol. Hantzsch and Freese (*Ber.*, 1895, **28**, 3241) found that benzenediazonium chloride and an alkaline solution of phenyl mercaptan yielded an unworkable oil, whilst with other diazonium salts diazothiophenyl ethers resulted, having the constitution $R \cdot N:N \cdot SPh$. These substances are readily decomposed with hydrochloric and sulphuric acids, have low melting points, and are more nearly related to diazoamino-compounds than to benzeneazophenol. It seemed possible that thiolazo-derivatives might be obtained through the xanthic esters by the method described by Leuckart (*J. pr. Chem.*, 1890, [ii], **42**, 187). Aminoazobenzene was used by Leuckart, but he finally obtained a disulphide, $(C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot S)_2$, after hydrolysis of the xanthic ester by alcoholic potassium hydroxide. Whilst it was not found possible to isolate benzeneazophenyl mercaptan in a pure state by acidification of the alkaline solution resulting from this hydrolysis, we were able to obtain the methyl and ethyl ethers of benzeneazophenyl mercaptan by treatment of the potassium salt with the corresponding alkyl iodides. The methyl and ethyl ethers of benzeneazophenyl mercaptan are stable solids resembling the ethers of benzeneazo-

phenol. The course of the reaction whereby these substances are obtained is shown by the following scheme:



They are in all respects strictly analogous to the latter substances, that is, they give hydrochlorides, platinum salts, and combine with water, giving substances of the type $(\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{R})_2\cdot\text{H}_2\text{O}$. The curve for the absorption spectrum is of the same type as was found by Tuck for benzeneazophenetole (Trans., 1907, **91**, 449) and by Hewitt and Thomas for aminoazobenzene (Trans., 1909, **95**, 1295). It is noteworthy that the curve occupies an intermediate position

Oscillation frequencies.



Benzeneazothioanisole in alcohol.

between that of benzeneazophenetole and of aminoazobenzene. The positions of the heads of the bands are as follows:

$\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$	about $1/\lambda$ 2900
$\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$	„ „ 2740
$\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	„ „ 2600

The solutions of the thiolazo-compounds in strong mineral acids are purple as compared with yellowish-brown of benzeneazophenol and yellow of aminoazobenzene.

p-Nitrobenzeneazophenylmethylmercaptole was prepared in small amount by the coupling of *p*-nitrobenzenediazonium chloride with an alkaline solution of phenyl mercaptan and treatment of the potassium salt of the resulting *p*-nitrobenzeneazophenyl mercaptan with methyl iodide, the main product of the reaction, however, consisting of *p*-nitrodiazobenzenethiophenyl ether.

EXPERIMENTAL.

Benzeneazophenylmethylmercaptole.—19.7 Grams of aminoazobenzene were made into a paste with 22 grams of hydrochloric acid (D 1.17: or the equivalent proportion of sulphuric acid) and 100 c.c. of water. The salt was diazotised with 6.9 grams of sodium nitrite, and allowed to remain in ice-water until practically all the original suspended matter was dissolved. The resulting diazonium solution was filtered, and added a little at a time to a moderately strong solution of 17 grams of potassium xanthate in water at a temperature of about 75°. Each addition of diazonium salt was followed by a violent evolution of gas and the separation of a red oil. When all the diazonium solution had been added, the vessel was warmed on a water-bath for half an hour and then cooled. The aqueous liquid was decanted from the xanthic ester, which was dissolved in benzene and treated successively with a little hydrochloric acid and aqueous sodium hydroxide to remove any aminoazobenzene or benzeneazophenol. The benzene was removed by evaporation, leaving the xanthic ester practically pure, as described by Leuckart (*loc. cit.*). Without further purification the xanthic ester was dissolved in an excess of 8 per cent. alcoholic potassium hydroxide, and boiled for twenty hours under a reflux condenser. The deep magenta-coloured liquid was then decanted from a little tarry matter and mixed with excess of methyl iodide, and heated under a reflux condenser until the liquid was almost neutral. The alcoholic solution was diluted with water, the precipitated yellow solid collected, washed with water, and recrystallised from 60 per cent alcohol or 90 per cent. acetic acid. From both these solvents benzeneazophenylmethylmercaptole crystallises in hard, orange-coloured needles, melting at 83—84°. The yield of pure product is from 4 to 5 grams from 20 grams of aminoazobenzene.

Benzeneazophenylmethylmercaptole dissolves readily in the usual organic solvents, and is best crystallised from dilute acetic acid. It is insoluble in alkali hydroxides, and dissolves in concentrated sulphuric acid with a deep purple colour:

0.1606 gave 0.4022 CO₂ and 0.0774 H₂O. C=68.3; H=5.4.

0.1478 „ 15.6 c.c. N₂ at 17° and 756 mm. N=12.3.

0.2744 „ 0.2772 BaSO₄. S=13.9.

C₁₃H₁₂N₂S requires C=68.4; H=5.3; N=12.3; S=14.0 per cent.

Attempts to obtain benzeneazophenyl mercaptan in the free state were not altogether successful. If the alkaline solution obtained after hydrolysis of the xanthic ester is acidified, an orange-coloured precipitate of the thiolazo-derivative results, but this is oxidised to

disulphide on removal from the liquid. Operating in an atmosphere of carbon dioxide was more successful, but the dry product after crystallisation from alcohol was only partly soluble in aqueous sodium hydroxide, owing to rapid oxidation, and did not possess a sharp melting point, although the portion which actually dissolved in the sodium hydroxide yielded a deep magenta-coloured solution.

The absorption spectrum of benzeneazophenylmethylmercaptole is of particular interest, inasmuch as the type of curve obtained is similar in character to that of benzeneazophenol, including the "step-out," obtained with solutions of the latter, using the nickel-iron spark. The head of the band for benzeneazophenylmethylmercaptole is nearer the red end of the spectrum than the band of benzeneazophenol (or benzeneazophenetole), and the curve slopes towards the red rather rapidly with increasing concentration of the solution.

Benzeneazophenylmethylmercaptole Hydrochloride.—Through a solution of benzeneazophenylmethylmercaptole in benzene dry hydrogen chloride is passed so long as any precipitate forms. The flocculent precipitate is collected, and rapidly dried on a porous tile. The hydrochloride so obtained is a reddish-brown powder with a metallic glance, and is unstable in moist air. It decomposes on heating a little above 100° :

0.1886 gave 0.1072 AgCl. Cl=14.0.

$C_{13}H_{12}N_2S.HCl$ requires Cl=13.4 per cent.

On exposure to moist air the hydrogen chloride is replaced by water, and at the same time the substance becomes paler in colour. The hydrate so formed has the composition $(C_{13}H_{12}N_2S)_2.H_2O$, and retains the water somewhat persistently on drying:

0.1192 gave 0.2868 CO_2 and 0.0616 H_2O . C=65.6; H=5.7.

$C_{13}H_{12}N_2S, \frac{1}{2}H_2O$ requires C=65.8; H=5.5 per cent.

Additive products with methyl iodide were not obtained, a large proportion of the original substance being recovered on heating benzeneazophenylmethylmercaptole under pressure with methyl iodide and methyl alcohol.

Benzeneazophenylmethylmercaptole Platinichloride.—This substance was prepared by dissolving benzeneazophenylmethylmercaptole in glacial acetic acid, adding platinic chloride, and passing dry hydrogen chloride into the solution. It separates as a violet powder:

0.2262 gave 0.0334 Pt. Pt=14.8.

$(C_{13}H_{12}N_2S)_4.H_2PtCl_6$ requires Pt=14.8 per cent.

When obtained by evaporation of a strongly acid alcoholic solu-

1502 SUBSTITUTED THIOLAZO-DERIVATIVES OF BENZENE.

tion, the salt approximates in composition to $(C_{13}H_{12}N_2S)_2, H_2PtCl_6$. (Found, Pt=19.9. Calc., Pt=22.7 per cent.)

Benzeneazophenylethylmercaptole.—This substance was prepared in a similar manner to the methyl derivative described above, except that ethyl iodide was used in the place of methyl iodide. The product was yellower than the methyl derivative, but behaved similarly and melted at 72° :

0.1240 gave 0.3172 CO_2 and 0.0676 H_2O . C=69.8; H=6.1.

0.1446 „ 14.7 c.c. N_2 at 18° and 747 mm. N=11.8.

0.2336 „ 0.2214 $BaSO_4$. S=13.0.

$C_{14}H_{14}N_2S$ requires C=69.4; H=5.8; N=11.6; S=13.2 per cent.

Benzeneazophenylethylmercaptole Hydrochloride.—This was prepared from a solution of benzeneazophenylmethylmercaptole in benzene; it decomposed below 100° . (Found, Cl=12.9. $C_{14}H_{14}N_2S, HCl$ requires Cl=12.7 per cent.)

The *hydrate* obtained from the hydrochloride by means of moist air corresponded in composition with $C_{14}H_{14}N_2S, \frac{1}{2}H_2O$. (Found, H_2O =3.4. Calc., H_2O =3.6 per cent.)

It has been shown by Hantzsch and Freese (*Ber.*, 1895, **28**, 3241) that the coupling of diazonium solutions with phenyl mercaptan does not produce substances analogous to benzeneazophenol. Working, however, with larger quantities of materials we were able to obtain the methyl ether of *p*-nitrobenzeneazophenyl mercaptan. 13.8 Grams of *p*-nitroaniline were diazotised, and the solution was poured into an alkaline solution of 11 grams of phenyl mercaptan kept near 0° . An immediate separation of a dark yellow solid resulted, and this increased on keeping. After twenty-four hours the yellow solid was collected, washed, and recrystallised from alcohol. This substance, which is the main product of the reaction, was *p*-nitrodiazobenzenethiophenyl ether, melting at 96° , and agreed in properties with the compound described by Hantzsch and Freese. The clear alkaline filtrate from this substance was of greenish colour, and was saturated with carbon dioxide and boiled in an atmosphere of carbon dioxide to remove unchanged phenyl mercaptan. A brown solid separated, which was collected and washed in carbon dioxide. This solid is probably *p*-nitrobenzeneazophenyl mercaptan. It was dissolved in alcoholic potassium hydroxide, and boiled under a reflux condenser with an excess of methyl iodide, as in the preparation of benzeneazophenylmethylmercaptole. The alcoholic solution was treated as in the latter case, and the brown solid was crystallised from 85 per cent. acetic acid. It crystallised in small needles melting at 137° :

0.1548 gave 20.5 c.c. N_2 at 20° and 750 mm. $N=15.2$.

0.3038 „ 0.2532 $BaSO_4$. $S=11.5$.

$C_{13}H_{11}O_2N_3S$ requires $N=15.4$; $S=11.7$ per cent.

p-Nitrobenzeneazophenylmethylmercaptole is moderately soluble in alcohol, benzene, or chloroform, and readily so in glacial acetic acid. It yields a reddish-brown solution in concentrated sulphuric acid, and does not decompose with strong acid, as in the case of *p*-nitrodiazobenzenethiophenyl ether.

We desire to express our thanks to the Research Fund Committee of the East London College for a grant towards the cost of this investigation.

EAST LONDON COLLEGE.
