LXXI.—*The Reactivity of Halogen Atoms in Compounds of the Pyridine Series. Part I. The Halides of 2-Stilbazole.*

By JOHN WALTER BLOOD and BRIAN DUNCAN SHAW.

BAURATH (*Ber.*, 1887, **20**, 2719 ; 1888, **21**, 818) found that 2-stilbazole (2-styrylpyridine) dibromide reacted with alcoholic potassium hydroxide, but was unable to isolate an acetylenic base analogous to tolane. Ladenburg (*Ber.*, 1903, **36**, 119), who reinvestigated the reaction at higher temperatures, described his product as deoxybenzazoin. Five years ago, one of us observed that the action of pyridine upon the dibromide regenerated 2-stilbazole. This evidence of the presence of a "positive" bromine atom led us to study the reaction of a variety of other reagents. Pyridine, phenol, aqueous-alcoholic potassium hydroxide, potassium iodide, and hydriodic acid yield 2-stilbazole even when the quantity of reagent is equivalent only to one bromine atom; indicating that after replacement of one bromine atom with hydrogen, loss of hydrogen bromide occurs spontaneously. This agrees with the known inability of 2-stilbazole to combine additively with hydrogen bromide at the ethylenic linking (compare Rath, *Ber.*, 1924, **57**, 841). On the other hand, with piperidine or sodium ethoxide a *monobromostilbazole* results, and alcoholic potassium hydroxide containing very little water yields a mixture of stilbazole and bromostilbazole. The position of the bromine atom in the latter compound, which is singularly unreactive, has not yet been determined; but as one of us has been obliged to abandon the work, the results so far obtained are now given. Similar results were obtained with 2-*stilbazole dichloride*. When stilbazole was the product, a small quantity of oil usually accompanied the solid base. This oil gradually yielded the solid base and treatment with bromine gave stilbazole dibromide. Similar oils accompanied the solid chloro- and bromo-stilbazoles; these also solidified on long standing. The investigation is being extended to the isomeric stilbazoles and their substitution products.

EXPERIMENTAL.

The 2-Stilbazole Chlorides.—A solution of chlorine (7·1 g.; 1 mol.) in carbon tetrachloride (50 c.c.) was added gradually to a solution of 2-stilbazole (18·1 g.; 1 mol.) in the same solvent. The mixture boiled, and was cooled in water; a gummy solid then separated. The clear solution deposited colourless needles of 2-*stilbazole dichloride*, m. p. 153—154° after recrystallisation from alcohol. The dichloride was readily soluble in acetone and sparingly soluble in cold alcohol, chloroform, or carbon tetrachloride (Found: Cl, 28·3. $C_{13}H_{11}NCl_2$ requires Cl, 28·2%). A little unchanged stilbazole was recovered from the mother-liquor.

The gummy solid was dissolved in hot alcohol; on cooling, small plates of 2-*stilbazole tetrachloride* were deposited, m. p. 180—181° after recrystallisation from alcohol (Found: Cl, 43·6. $C_{13}H_{11}NCl_4$ requires Cl, 43·96%). On treatment with cold aqueous sodium carbonate solution the compound readily gave the dichloride, indicating that half the chlorine was united to the nitrogen atom.

The 2-Stilbazole Bromides.—In the preparation of the dibromide by Baurath's method (*loc. cit.*) it was found better to employ less than the theoretical amount of bromine, as otherwise the product was contaminated with a yellow insoluble substance which appeared to be 2-stilbazole tetrabromide. The compound decomposed on being heated. Consistent analytical results could not be obtained, as it gradually lost bromine on exposure to the atmosphere, yielding the dibromide. The latter, crystallised from alcohol, had m. p. 172° (Baurath gives 166—167°).

Action of Reagents upon the Stilbazole Dihalides.—Except where otherwise stated, the results with the dichloride were exactly similar to those given for the dibromide.

Alcoholic potassium hydroxide. 2-Stilbazole dibromide (6·8 g.; 1 mol.) was boiled with a solution of potassium hydroxide (2·28 g.; 2 mols.) in 95% alcohol (50 c.c.). The solution rapidly became red, but was still alkaline after 6 hours. The alcohol was removed, water added to the residue, and the brown oil extracted with benzene. After removal of the solvent the oil was treated with successive small quantities of light petroleum (b. p. 50—60°). The first fractions deposited long, pale yellow prisms of *monobromostilbazole*, which were obtained colourless by recrystallisation from alcohol; m. p. 74—75° (Found: C, 60·15; H, 4·0; Br, 30·5. $C_{13}H_{10}NBr$ requires C, 60·2; H, 3·9; Br, 30·8%).

The later light petroleum fractions were coloured, and left a thick brown oil on removal of the solvent. The residue was distilled with steam; a colourless oil, which distilled very slowly, was separated with benzene. After removal of the solvent the pale brown oil partly crystallised. The solid, after crystallisation from light petroleum, had m. p. 91° alone or mixed with 2-stilbazole. A portion of the residual oil gave, with bromine, 2-stilbazole dibromide, m. p. 172.° The remainder, on exposure to the air, yielded the solid base. Yields: bromostilbazole 1·5 g., 2-stilbazole 2·1 g.; 30% and 60% of the theoretical respectively. Increase in the percentage of water raised the proportion of 2-stilbazole.

In a repetition experiment the mixture was not heated, but kept at room temperature for 2 days. Yields: bromostilbazole 2·5 g., 2-stilbazole 0·32 g.; 50% and 9% of the theoretical respectively. The residual oil slowly deposited more of the solid bromostilbazole.

Sodium ethoxide. Preparation of monobromostilbazole. A solution of sodium (0·35 g.; 1 atom) in anhydrous alcohol (7·0 c.c.) was added to stilbazole dibromide (5·1 g.; 1 mol.). A reaction commenced on warming and was complete after 5 minutes' boiling. Water (50 c.c.) precipitated an oil which solidified when rubbed; yield, 3·8 g. (85% of the theoretical). Crystallisation from light petroleum gave long colourless prisms, m. p. 75°. The mother-liquor, after evaporation, left an oil which gave solid monobromostilbazole on long standing. The length of the crystals obtained by slow crystallisation from light petroleum appears to be limited only by the size of the vessel. From alcohol, on the other hand, large compact prisms are obtained.

Pyridine. 2-Stilbazole dibromide (3·4 g.) was boiled with pyridine (6 g.) for 1 hour. The dark solution was poured into water, and the solid crystallised from alcohol; m. p. 90—91°, mixed m. p. (with 2-stilbazole) 90—91°. Yield, 1·35 g. (75% of the theoretical).

Piperidine. 2-Stilbazole dibromide (6·8 g.) was heated on the water-bath with piperidine (5 g.) during 10 minutes. The semi-solid product was treated with water (30 c.c.) and extracted with benzene. The solvent was removed and the residual oil crystallised from light petroleum; m.p. 74—75°; yield, 3·3 g. of monobromostilbazole (63% of the theoretical). A small quantity of oil was not examined.

Potassium iodide. 2-Stilbazole dibromide (0·2049 g.) was boiled with potassium iodide (4 g.) in alcoholic solution (100 c.c.). The reaction was followed by titration of aliquot portions of the liquid, largely diluted with water, with $N/10$-sodium thiosulphate solution. After 3 hours, the rate of liberation of iodine slackened and became constant; total, 0·1820 g. I_2. In a parallel experiment from which the dibromide was omitted, 0·025 g. I_2 was liberated; difference 0·1570 g. Theoretical, calculated from the equation $C_5NH_4{\cdot}CHBr{\cdot}CHBrPh + 2KI = C_5NH_4{\cdot}CH{:}CHPh + 2KBr + I_2$, 0·1527 g.

Hydriodic acid. 2-Stilbazole dibromide (0·110 g.) was heated on the water-bath with potassium iodide (0·10 g.) in acetic acid (10 g.). The iodine liberated was titrated with *N*/10-sodium thiosulphate solution. Found, 0·080 g. The equation C_5NH_4·CHBr·CHBrPh + 2HI = C_5NH_4·CH:CHPh + 2HBr + I_2 requires 0·0804 g.

A mixture of 2-stilbazole dibromide (3·4 g.; 1 mol.), acetic acid (10 c.c.), and potassium iodide (3·34 g.; 2 mols.) was heated to boiling and rapidly cooled to 15°. The brown crystalline mass which separated was removed, pressed, and treated with sulphurous acid to remove iodine. The yellow needles obtained softened at 96°, melted at 100°, resolidified at 116—120°, and again melted at 179—180°. A portion crystallised from hot water and dried at 100° had m. p. 182—184°, and mixed m. p. (with an authentic specimen of 2-stilbazole hydriodide) 182—184° (Found: I, 36·6; *M*, by titration with *N*/10-NaOH, 341. Calc. for $C_{13}H_{11}N,HI,2H_2O$: I, 36·8%; *M*, 345). A portion gave with sodium carbonate solution a white solid, m. p. 90—91°; mixed m. p. (with 2-stilbazole) 90—91°.

Phenol. 2-Stilbazole dibromide (2·5 g.) was heated with phenol (0·50 g.; excess) at the melting point of the mixture during 2 hours. The solid product was dissolved in hot alcohol; needles of hydrated 2-*stilbazole hydrobromide*, m. p. 187—189°, separated on cooling. Treatment with sodium carbonate gave 2-stilbazole, m. p. 90—91°. The alcoholic mother-liquor was poured into water; the red solid obtained, crystallised from hot water, had m. p. 94—95°, and mixed m. p. (with tribromophenol) 94—95°.

An authentic specimen of 2-stilbazole hydrobromide was prepared from the pure base in needles, readily soluble in hot water and sparingly soluble in alcohol; m. p. (anhydrous) 188—189° (Found: *M*, 280·5. $C_{13}H_{11}N,HBr,H_2O$ requires *M*, 280).

The experiment was repeated, sufficient phenol being used to remove only half the bromine as tribromophenol; the result was as before.

Action of Sodium Ethoxide upon 2-Stilbazole Dichloride.—To a solution of sodium (0·50 g.) in anhydrous alcohol (10 c.c.), 2-stilbazole dichloride (3 g.) was added, and the solution boiled during 10 minutes. The alcohol was removed, the residue treated with water and extracted with benzene, the solvent removed, and the oil dissolved in light petroleum; colourless prisms of *monochlorostilbazole*, m.p. 63°, readily soluble in alcohol and sparingly soluble in light petroleum, were obtained (Found: Cl, 16·5. $C_{13}H_{10}NCl$ requires Cl, 16·4%).

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, February 7th*, 1930.]
