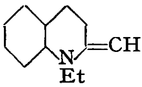
180. *Some Heterocyclic Methylene Bases and their Anilomethyl Derivatives.*

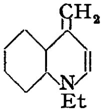
By Frances M. Hamer, Russell J. Rathbone, and Barbara S. Winton.

Some heterocyclic methylene bases, not hitherto described in the solid state, have been prepared by the action of alkali on quaternary salts at a low temperature, foregoing extraction. Some new anilomethyl derivatives of bases of this type were prepared by the action of alkali on quaternary salts having a 2-β-anilinovinyl group. They include anilomethyl derivatives of methylene bases derived from a benzoxazolium salt and a thiazolium salt, although the unsubstituted bases of these series are not precipitable. A practical method of preparation of ethyl*iso*formanilide is described. These compounds were made as starting materials for the synthesis of neocyanine and related dyes.

By treating quinaldine ethiodide with aqueous alkali, Vongerichten and Höfchen obtained an oil, which they regarded as the methylene base (I); they showed that it reacted with quinoline ethiodide to give a cyanine dye (*Ber.*, 1908, **41**, 3054). König expressed the opinion that bases such as (I) and (II) play an essential part in the formation of cyanines (*Ber.*, 1922, **55**, 3293).



(I.)



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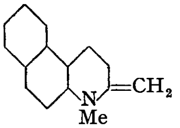
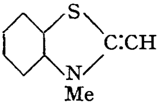


(III.)

Mills and Raper, considering that the oils formed by the action of alkali on quinaldine alkiodides could not be obtained analytically pure, examined the crystalline product (III) (*J.*, 1925, **127**, 2466); this led Rosenhauer (with Hoffmann and Unger) to record his preparation of the methyl analogue of (I) (*Ber.*, 1926, **59**, 946). From 2-methylbenzthiazole methoperchlorate König and Meier obtained (IV) (*J. pr. Chem.*, 1925, **109**, 324). Clark studied the conditions favouring formation of this base or of the thiophenol salt (V) and similarly, from 2-methylbenzselenazole methiodide, obtained two products, one of which was (VI) (*J.*, 1928, 2313).



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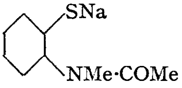

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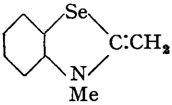
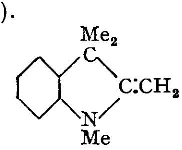
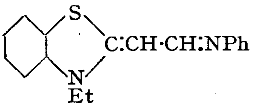


(VI.)

All these methylene bases were prepared from known quaternary salts but (VII), the first to be known, was made by direct synthesis (Fischer and Steche, *Annalen*, 1887, **242**, 348; Brunner, *Ber.*, 1898, **31**, 612).

(VII.)




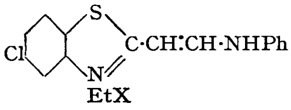
(VIII.)

In our work on the synthesis of neocyanines, the methylene bases are of interest as starting points. In the patent literature Brooker and White have described anilomethyl derivatives, *e.g.* (VIII), of some such bases (Kodak Ltd., B.P. 561,172/1940) and these also have the same interest. The present paper deals with methylene bases and their anilomethyl derivatives.

Success in preparing methylene bases, hitherto inaccessible in the solid state, was achieved by precipitating them at a low temperature, by the action of alkali on a solution of the quaternary salt, and foregoing extraction with a solvent. We began by making the *ethyl* analogue of (IV), choosing a readily soluble quaternary salt of 2-methylbenzthiazole; it was liable to manifest its instability by decomposing during drying but we succeeded in recrystallising both it and its 5-*chloro*-derivative. Its 6 : 7-*benz*-derivative showed a greater tendency to decompose and was not recrystallised; in preparing this and the *ethyl* analogue of (VI), aqueous suspensions of the quaternary salts were perforce used in place of concentrated solutions. From concentrated solutions of alko-*p*-toluenesulphonates, (I) and (II) were prepared. Colour changes, which indicate reactivity and tendency to cyanine dye formation on the part of the bases, occurred before they could be filtered off but did not proceed progressively after they had been dried.

Quaternary salts of certain other heterocyclic bases that are of interest in cyanine dye condensations do not give precipitates of methylene bases when their cold solutions are treated with alkali; such are salts of 2-methylbenzoxazole, 2 : 4-dimethylthiazole, 2-methylthiazoline, and α-picoline. In the different series of salts it appears that there is more than one cause for this. In the pyridine series, the base may possibly be too soluble and more complex methylene bases of this series have in fact been prepared (Mumm and Hingst, *Ber.*, 1923, **56**, 2301). In the benzoxazole series, it is due to fission of the ring, as recognised by König and Meier (*J. pr. Chem.*, 1925, **109**, 324).

In preparing the anilomethyl derivative (VIII) of the ethyl analogue of (IV) from 2-β-anilinovinylbenzthiazole ethiodide, the method of the patent (Kodak Ltd., B.P. 561,172/1940) was adopted with some modification. In preparing 5-*chloro*-2-β-*anilinovinylbenzthiazole ethiodide* (IX; X = I), in order to make the 5-chloro-analogue of (VIII), the salt was accompanied by so much *thiacarbocyanine* (X) as by-product that we were forced, in order to get rid of the dye, first to isolate the pure 5-*chloro*-analogue of (VIII), from which we prepared the pure *ethochloride* (IX; X = Cl), and ultimately from that the pure *ethiodide* (IX; X = I). We prepared the 6-*nitro*-derivative of (VIII), starting from the product of nitration of 2-methylbenzthiazole (Browning, Cohen, Ellingworth, and Gulbransen, *Proc. Roy. Soc.*, 1931, *B*, **108**, 119; for orientation of the nitration product see Brooker, Keyes, and Williams, *J. Amer. Chem. Soc.*, 1942, **64**, 199). The 6-nitro-2-methylbenzthiazole was converted into its *metho*-p-*toluenesulphonate*; this was condensed with ethyl*iso*formanilide (cf. Knott, *J.*, 1946, 120), and the resultant *salt* treated with alkali to give the desired *base*.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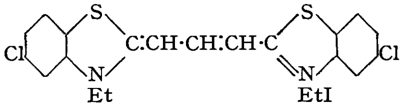
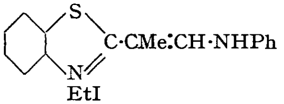
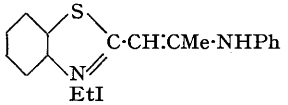
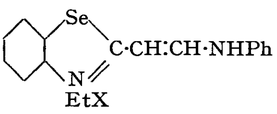

(X.)

To synthesise the α-*methyl* derivative of (VIII), 2-ethylbenzthiazole, prepared by two hitherto unpublished methods, was converted into its *etho*-p-*toluenesulphonate* and this was condensed with diphenylformamidine, or better with ethyl*iso*formanilide, and the product treated with potassium iodide to give (XI), whence the *base* was liberated by the action of alkali. We also prepared the β-*methyl* derivative of (VIII) by the action of alkali on the quaternary salt (XII).

(XI.)



(XII.)

In the preparation of the *selenium* analogue of (VIII), from the *quaternary salt* (XIII; X = I), the product refused to solidify, but after treatment with hydrochloric acid to give the *ethochloride* (XIII; X = Cl) it was possible to obtain the solid base by the action of alkali. In the quinoline series we prepared (XIV), the ethyl analogue of which has been described (Kodak Ltd., B.P. 561,172/1940). Particularly interesting is the record in the patent that the anilomethyl derivative of a methylene base of the thiazoline series was prepared, since the unsubstituted methylene base of this series is one of those not precipitable by the action of alkali on the quaternary salt. We were also able to prepare the corresponding *ethyl* analogue (XV), by applying different conditions, and the *anilomethyl* derivatives, (XVI) and (XVII), of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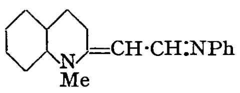
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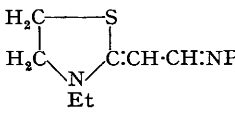
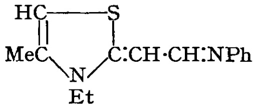
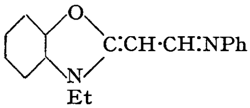

(XV.)

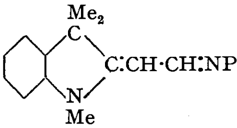
methylene bases of a thiazole series and of the benzoxazole series, respectively, where again the parent unsubstituted bases have not been described.



(XVI.)



(XVII.)



(XVIII.)

To obtain the *anilomethyl* derivative (XVIII) of the methylene base (VII), 2-β-anilinovinyl-3 : 3-dimethylindolenine methiodide was acted on, in benzene suspension, by aqueous alkali. The quaternary salt was originally prepared either by hydrolysing the corresponding acetanilidovinyl compound or else by heating 1 : 3 : 3-trimethylindolenine methiodide with diphenylformamidine (I.C.I. Ltd., Piggott, and Rodd, B.P. 344,409/1929), but we used ethyl*iso*formanilide instead of diphenylformamidine.

Ethyl*iso*formanilide was required for the present work and also for our synthesis of neocyanine, so that its large-scale production became a matter of interest. Claisen's methods for preparing it were to condense ethyl orthoformate (1) with aniline, (2) with diphenylformamidine, or (3) with formanilide in the presence of aniline hydrochloride (*Annalen*, 1895, **287**, 362). Monier-Williams (*J.*, 1906, **89**, 273) preferred to use the method of Comstock and Kleeburg (*Amer. Chem. J.*, 1890, **12**, 497) and treated dry silver *iso*formanilide with ethyl iodide in absolute ether. This last did not seem practicable on a large scale and we worked out a modification of Claisen's first method, including aniline hydrochloride in order to inhibit the formation of carbylamine.

EXPERIMENTAL.

3-*Ethyl*-2-*methylenebenzthiazoline*.—2-Methylbenzthiazole etho-*p*-toluenesulphonate (50 g.; 1 mol.) was dissolved in water (70 c.c.). The solution was cooled with ice and stirred during the addition of a cold solution of sodium hydroxide (6·3 g.; 1·1 mols.) in water (20 c.c.). The white solid was filtered off, and well washed with ice-cold water. It was dried in a vacuum desiccator and obtained in 83% yield (21 g.), being pale pink at this stage. Once dry, it kept for weeks without further deterioration but preparations on a larger scale were apt to decompose during drying. On recrystallisation from light petroleum (b. p. 80—100°; 20 c.c. per g.), the yield was 62%. After drying in a vacuum desiccator, it was analysed by the method of Carius, which method was used throughout this work (Found: S, 18·15. $C_{10}H_{11}NS$ requires S, 18·1%); m. p. 126—128° (decomp.).

5-*Chloro*-3-*ethyl*-2-*methylenebenzthiazoline*.—Similarly, 5-chloro-2-methylbenzthiazole etho-*p*-toluenesulphonate gave the *base* in 87% yield; on recrystallisation from light petroleum (b. p. 80—100°; 275 c.c. per g.), it fell to 57% (Found, after drying in a vacuum desiccator: Cl, 16·45; S, 15·1. $C_{10}H_{10}NClS$ requires Cl, 16·75; S, 15·15%). The chalky white solid had m. p. 178—180° (decomp.).

3-*Ethyl*-2-*methylene*-6 : 7-*benzbenzthiazoline*.—2-Methyl-6 : 7-benzbenzthiazole etho-*p*-toluenesulphonate (30 g.; 1 mol.) was ground to a paste with ice-cold water (30 c.c.), and an ice-cold solution of sodium hydroxide (3·3 g.; 1·1 mols.) in water (10 c.c.) was added. The sulphur-yellow solid was thoroughly washed with ice-cold water and was obtained in 68% yield (11·65 g.) (Found: S, 14·55. $C_{14}H_{13}NS$ requires S, 14·1%); it was liable to change overnight to a sticky mass at the early stages of drying but, once past those early stages, could be kept unchanged in a vacuum desiccator. When heated, shrinking and darkening began about 40° and it was brown and sticky by 50°; gradual melting and decomposition occurred, and by 90° it was a brown liquid.

3-*Ethyl*-2-*methylenebenzselenazoline*.—2-Methylbenzselenazole ethiodide when similarly treated gave a 76% yield of *base*. Selenium was determined as silver selenite (Becker and Meyer, *Ber.*, 1904, **37**, 2550) (Found: Se, 35·45. $C_{10}H_{11}NSe$ requires Se, 35·3%). The yellowish-brown powder softened from 70° and decomposed at about 120°. One specimen, which had been kept for several days in a vacuum desiccator without change, became sticky and dark overnight, although the vacuum had been maintained.

1-*Ethyl*-2-*methylene*-1 : 2-*dihydroquinoline* (I).—Quinaldine etho-*p*-toluenesulphonate (34·33 g.; 1 mol.), dissolved in ice-cold water (30 c.c.), was treated with ice-cold aqueous sodium hydroxide solution (4·4 g., 1·1 mols., in 11 c.c.). The buff precipitate was filtered off and thoroughly washed with ice-cold water. After drying in a vacuum desiccator, it was obtained in 78% yield (13·37 g.), and was then brick-red (Found: N, 7·95. $C_{12}H_{13}N$ requires N, 8·2%); m. p. 79° (decomp.) with previous softening. A sample which had been kept in a vacuum desiccator for a fortnight appeared to be unchanged.

1-*Ethyl*-4-*methylene*-1 : 4-*dihydroquinoline* (II).—Lepidine (14·31 g.; 1 mol.) and ethyl *p*-toluenesulphonate (20·02 g.; 1 mol.) were heated together in an oil-bath at 155—160° for 3 hours. A solution of the viscous salt in water (32 c.c.) was extracted with ether, then treated ice-cold with a solution of sodium hydroxide (4·4 g.; 1·1 mols.) in water (11 c.c.). The precipitate was filtered off and well washed with ice-cold water. The filtrate became deep blue. After drying in a vacuum desiccator, the yield of pale blue *solid* was 73% (12·55 g.) (Found: N, 8·2. $C_{12}H_{13}N$ requires N, 8·2%). It had no definite m. p. On heating, shrinking began at 59°; in one case, with slow heating, it was black and molten by 80°, whilst in another, violent frothing occurred between 95° and 108°.

3-*Ethyl*-2-*aniloëthylidenebenzthiazoline* (VIII).—The published method (Kodak Ltd., B.P. 561,172/1940) was varied in that the suspension of 2-β-anilinovinylbenzthiazole ethiodide (103 g.; 1 mol.) in acetone (940 c.c.) was shaken with a solution of sodium hydroxide (31 g.; 3 mols.) in water (75 c.c.), instead of being stirred mechanically. In one instance solution occurred, but in another, very much more acetone (11·4 l.) had to be added, this indicating the conversion of a less stable into a more stable form. The acetone extracts were filtered, with removal of bis-2-(3-ethylbenzthiazole)trimethincyanine iodide (5·81 g.), which was recrystallised from methyl alcohol (75 c.c. per g.; 2·7 g. obtained) and dried in a vacuum at 60—80°, which conditions of drying were used throughout this work, except where otherwise stated (Found: I, 25·95. Calc. for $C_{21}H_{21}N_2IS_2$: I, 25·8%). On pouring the acetone filtrate into its own volume of water, the base was precipitated in 70% yield (49 g.). Two recrystallisations from light petroleum (b. p. 80—100°; 100 c.c. per g.) reduced the yield to 43% (Found, after drying in a vacuum desiccator: S, 11·25. Calc. for $C_{17}H_{16}N_2S$: S, 11·45%). The yellow solid had m. p. 79°, whereas the m. p. quoted in the patent is 98—99° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 3935 A. and of one containing sulphuric acid at 4175 A.

5-*Chloro*-3-*ethyl*-2-*aniloethylidenebenzthiazoline*.—5-Chloro-2-methylbenzthiazole ethiodide (20 g.; 1 mol.) and ethyl*iso*formanilide (7 g.; 1 mol.) were heated together with stirring at 140—150° for 1 hour. The product was boiled with spirit (300 c.c.), and the crystals were filtered off after cooling (22 g. obtained). An attempt to separate the quaternary salt from the dye by-product by boiling out five times with spirit (2 × 100 c.c., 2 × 150 c.c., 250 c.c.) left a dye residue (5·69 g.), and a 36% yield (9·43 g.) of impure salt crystallised from the extracts. The dye was further boiled out twice with methyl alcohol (50 c.c., 100 c.c.) and the residue (4·96 g.) suspended in acetone (38 c.c.) and shaken with a solution of sodium hydroxide (1·35 g.) in water (5 c.c.), with the object of converting any contaminating salt into base. After two more acetone extractions, the residual dye was well washed with water (3·46 g. obtained) and recrystallised from methyl alcohol (1590 c.c.) (2·81 g. obtained) (Found: 2Cl + I, 35·45. $C_{21}H_{19}N_2Cl_2IS_2$ requires 2Cl + I, 35·25%). The blue needles of *bis*-2-(5-*chloro*-3-*ethylbenzthiazole*)*trimethincyanine iodide* (X) did not melt below 270°. The absorption maximum was at 5625 A. It sensitised a gelatino-bromide photographic emulsion from 5200 to 6200 A., with a maximum at 6000 A. The impure quaternary salt (9·43 g.; 1 mol.) was suspended in acetone (70 c.c.), and the ice-cold solution shaken with one of sodium hydroxide (2·56 g.; 3 mols.) in water (10 c.c.). The acetone extract was filtered and the aqueous part further extracted with acetone, dye by-product being left undissolved. The extracts were precipitated with thrice their volume of water and the resultant solid was obtained in 83% yield (5·57 g.). After recrystallisation from methyl alcohol (335 c.c.) the yield was 70% (Found: Cl, 11·45. $C_{17}H_{15}N_2ClS$ requires Cl, 11·3%). The yellowish-green powder had m. p. 138°. The absorption maximum of a methyl-alcoholic solution containing pyridine was at 4075 A. and of one containing sulphuric acid at 4205 A. The dye sensitised a chloride emulsion to 4900 A. with the maximum at 4600 A.

5-*Chloro*-2-β-*anilinovinylbenzthiazole Ethochloride* (IX; X = Cl).—5-Chloro-3-ethyl-2-aniloethylidenebenzthiazoline (6·64 g.) was warmed with spirit (13 c.c.), and the suspension treated with concentrated hydrochloric acid (7 c.c.). The crystals which separated on cooling (7·49 g.) were recrystallised from methyl alcohol (60 c.c.) and obtained in 86% yield (6·36 g.) (Found: Cl, 20·2. $C_{17}H_{16}N_2Cl_2S$ requires Cl, 20·2%). The bright yellow powder became orange at 100°, was brown by 200°, and melted at 214—215° (decomp.).

5-*Chloro*-2-β-*anilinovinylbenzthiazole Ethiodide* (IX; X = I).—The *ethochloride* (IX; X = Cl) (0·45 g.; 1 mol.) was dissolved in hot spirit (15 c.c.) and added to a hot solution of potassium iodide (16·6 g.; 10 mols.) in water (30 c.c.). The crude *salt* (0·47 g.) was recrystallised from methyl alcohol (47 c.c. per g.) and obtained in 58% yield (0·33 g.) (Found: Cl + I, 36·8. $C_{17}H_{16}N_2ClIS$ requires Cl + I, 36·7%). The dark orange crystals had m. p. 241—244° (decomp.).

6-*Nitro*-2-*methylbenzthiazole Metho*-p-*toluenesulphonate*.—6-Nitro-2-methylbenzthiazole (2·77 g.; 1 mol.) and methyl *p*-toluenesulponate (2·66 g.; 1 mol.) were heated together at 130° for 1 hour, and the product was ground with absolute ether (5·16 g. obtained; 95%). After recrystallisation from absolute ethyl alcohol (10 c.c.), the yield was 88% (4·77 g.) (Found: S, 16·8. $C_{16}H_{16}O_5N_2S_2$ requires S, 16·85%). The cream-coloured crystals had m. p. 194—195° (decomp.).

6-*Nitro*-2-β-*anilinovinylbenzthiazole Metho*-p-*toluenesulphonate*.—The foregoing *metho*-p-*toluenesulphonate* (19 g.; 1 mol.) and ethyl*iso*formanilide (9 g.; 1·2 mols.) were heated and stirred together at 130—140°. Fusion occurred, then vigorous reaction followed by solidification. Heating was continued for ½ hour. A suspension of the solid in spirit (50 c.c.) was poured into warm water. The *product*, after being washed with water and with acetone (18 g. obtained), was recrystallised from methyl alcohol (200 c.c. per g.), the yield falling from 75% to 23% (Found: S, 13·45. $C_{23}H_{21}O_5N_3S_2$ requires S, 13·25%). The green crystals had m. p. 255°.

6-*Nitro*-3-*methyl*-2-*aniloethylidenebenzthiazoline*.—The preceding compound (9·66 g.; 1 mol.), acetone (300 c.c.), and 20% sodium hydroxide solution (20 c.c.; 5 mols.) were warmed together on the steam-bath, then shaken vigorously for several minutes. The filtered acetone layer was concentrated to one-third, and poured into ice and water (500 c.c.), coagulation being assisted by addition of ammonium chloride. The washed *product* (4·83 g.; 78%) was purified by dissolving in benzene (10 c.c. per g.), filtering, and precipitating with an equal volume of light petroleum (b. p. 80—100°); yield, 63% (Found: S, 10·45. $C_{16}H_{13}O_2N_3S$ requires S, 10·3%). The brick-red crystals had m. p. 144° (decomp.) and desensitised strongly. The broad absorption curve of a methyl-alcoholic solution containing ammonia had its maximum at 3850 A.

2-*Ethylbenzthiazole*.—This was originally prepared by heating *o*-aminothiophenol in a sealed tube with propionyl chloride, being characterised as its platinichloride (Hofmann, *Ber.*, 1880, **13**, 8). According to our first method, *o*-aminothiophenol hydrochloride (80·6 g.; 1 mol.) was treated with propionic anhydride (69·5 c.c.; 1·1 mols.) and with zinc dust (11·2 g.). The reaction was started by warming; after it had subsided, the mixture was heated on the steam-bath for 2 hours, and then made alkaline with sodium hydroxide and steam-distilled; the oil was extracted with chloroform, and the extract dried (Na_2SO_4). After removal of the solvent, the residue was distilled in a vacuum and obtained in 52% yield, b. p. 127—131°/6 mm. (Found: S, 19·8. Calc. for C_9H_9NS: S, 19·65%). Our second method consisted in preparing *o*-aminothiophenol from *o*-chloronitrobenzene (cf. I.G. Farbenind. A.-G., F.P. 669,921/1929; Société Anonyme des Matières Colorantes et Produits Chimiques de Saint-

Denis, F.P. 714,682/1930) and effecting the ring closure to 2-ethylbenzthiazole by means of propionic anhydride. *o*-Chloronitrobenzene (100 g.; 1 mol.), crystalline sodium sulphide (400 g.; 2·63 mols.), and water (400 c.c.) were stirred together, being warmed to start the reaction; after its vigour had abated, heating on the steam-bath and stirring were continued for 4 hours. The mixture was steam-distilled to remove *o*-chloroaniline, formed as a by-product (26 g.; 32%), then it was cooled, treated with a solution of propionic anhydride (83 g.; 1 mol.) in propionic acid (156 g.; 3·3 mols.), and heated under reflux for an hour on the steam-bath. It was cooled, made alkaline and extracted with ether. The extract was dried (Na_2SO_4), the solvent removed, and the residue distilled under a vacuum. After a second vacuum distillation the yield was 34% (35 g.), b. p. 112—114°/5 mm. (Found: S, 19·9%). The preparation according to the first method was carried out by Miss E. M. Wilson, and that according to the second by Mr. J. Fraser.

2-*Ethylbenzthiazole Etho*-p-*toluenesulphonate*.—2-Ethylbenzthiazole (4·08 g.; 1 mol.) and ethyl *p*-toluenesulphonate (5 g.; 1 mol.) were heated together at 140—150° for 2½ hours. The solidified melt was ground and washed with acetone, being obtained in 84% yield (7·55 g.) (Found: S, 17·8. $C_{18}H_{21}O_3NS_2$ requires S, 17·65%). The pale pink *solid* melted at 138°.

2-(β-*Anilino-a-methylvinyl)benzthiazole Ethiodide* (XI).—The preceding compound (5 g.; 1 mol.) and ethyl*iso*formanilide (2·3 g.; 1·1 mols.) were heated together at 120—140°, vigorous reaction then occurring. Heating was continued for ½ hour, and the red liquid was dissolved in spirit (7 c.c.) and treated with a hot solution of potassium iodide (8·26 g.; 4 mols.) in water (7 c.c.). The *iodide* crystallised and, after being washed, was obtained in 72% yield (4·3 g.), decreased on recrystallisation from ethyl alcohol (50 c.c. per g.) to 50% (Found: I, 30·1. $C_{18}H_{19}N_2IS$ requires I, 30·05%). The dull red crystals melted at 212° (decomp.).

When a similar preparation was carried out with diphenylformamidine instead of ethyl*iso*formanilide, the yield of crude washed product was only 24%. Neither diphenylformamidine nor ethyl*iso*formanilide gave a positive result when the starting point was 2-ethylbenzthiazole ethiodide instead of the etho-*p*-toluenesulphonate.

3-*Ethyl*-2-*anilo*iso*propylidenebenzthiazoline*.—2-(β-Anilino-α-methylvinyl)benzthiazole ethiodide (5·44 g.; 1 mol.), 20% sodium hydroxide solution (12 c.c.; 5 mols.), and acetone (150 c.c.) were stirred together and warmed on the water-bath, then shaken in a separating funnel. The filtered acetone layer was poured into ice-water. The aqueous liquid was decanted from the sticky solid, which on crystallisation from light petroleum (b. p. 80—100°; 75 c.c.) gave a 41% yield (1·57 g.) of yellow crystals, m. p. 92° (decomp.) (Found after drying in a vacuum at 50—60°: S, 10·85. $C_{18}H_{18}N_2S$ requires S, 10·9%). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4005 A. The *compound* sensitised a chloride emulsion fairly strongly with its maximum at 4550 A., sensitisation extending to 4850 A.

2-(β-*Anilino*-β-*methylvinyl)benzthiazole Ethiodide* (XII).—The steps in the following synthesis of the salt required as starting point were carried out according to directions supplied by Dr. L. G. S. Brooker: 2-methylbenzthiazole etho-*p*-toluenesulphonate was converted successively into 3-ethyl-2-acetylmethylenebenzthiazoline (Kodak Ltd., B.P. 466,269/1935), 2-β-chloropropenylbenzthiazole ethochloride (*idem*, B.P. 533,425/1939), 3-ethyl-2-thioacetylethylbenzthiazoline (*idem*, B.P. 546,705/1941), and 2-(β-methylthiopropenyl)benzthiazole etho-*p*-toluenesulphonate (*idem*, B.P. 538,857/1941). This last salt (66·1 g.; 1 mol.), aniline (19·7 g.; 1·25 mols.), and absolute alcohol (170 c.c.) were boiled together under reflux for 30 minutes. The yellowish-brown solution was poured into a hot solution of potassium iodide (56 g.; 2 mols.) in water (100 c.c.). The *iodide* was obtained in 84% yield (60·0 g.). On recrystallising twice from spirit (15 c.c. per g.), the yield dropped to 69% (Found: I, 30·25. $C_{18}H_{19}N_2IS$ requires I, 30·05%). The bright yellow crystals had m. p. 208° (decomp.).

3-*Ethyl*-2-β-*anilopropylidenebenzthiazoline*.—2-(β-Anilino-β-methylvinyl)benzthiazole ethiodide (8·44 g.; 1 mol.), suspended in acetone (250 c.c.), was stirred and warmed for a few minutes on the steam-bath with 20% sodium hydroxide solution (20 c.c.; 5 mols.), and the mixture shaken. The filtered acetone layer was poured into ice-cold water (1000 c.c.). The *solid* (5·5 g.) was recrystallised from light petroleum (b. p. 80—100°; 25 c.c. per g.), the yield then being 65% (3·85 g.) (Found: S, 10·7. $C_{18}H_{18}N_2S$ requires S, 10·9%). The pale yellow crystals had m. p. 114° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 3670 A. The base was photographically inert.

2-β-*Anilinovinylbenzselenazole Ethiodide* (XIII; X = I).—2-Methylbenzselenazole ethiodide (28·2 g.; 1 mol.) and ethyl*iso*formanilide (13·2 g.; 1·1 mols.) were heated together at 150—160° for ½ hour. The *product* was ground with spirit (32·7 g. obtained); after recrystallisation from spirit (30 c.c. per g.) the yield was 59% (Found: I, 27·8. $C_{17}H_{17}N_2ISe$ requires I, 27·85%). The greenish-golden crystals had m. p. 222° (decomp.).

3-*Ethyl*-2-*aniloethylidenebenzselenazoline*.—The above ethiodide (32 g.; 1 mol.), ground to a paste with water, was treated with 40% sodium hydroxide solution (40 c.c.; 5 mols.) and acetone (500 c.c.). The mixture was slightly warmed, then well shaken. The filtered, concentrated acetone extract gave with dilute hydrochloric acid 2-β-*anilinovinylbenzselenazole ethochloride* (XIII; X = Cl), which, after recrystallisation from acetone–spirit (3 : 1, 30 c.c. per g.), was obtained in 55% yield (14·4 g.). Chlorine was determined by the method which has been found suitable for iodine in the presence of selenium (Hamer, *Analyst*, 1933, **58**, 26) (Found: Cl, 9·55. $C_{17}H_{17}N_2ClSe$ requires Cl, 9·75%). The bright yellow crystals had m. p. 205° (decomp.). They were dissolved in hot spirit, and the *base* precipitated by dilute ammonia (11·2 g.; 49%); it was recrystallised from light petroleum (b. p. 80—100°; 20 c.c. per g.) and the yield was 34% (7·8 g.) (Found: N, 8·55. $C_{17}H_{16}N_2Se$ requires N, 8·55%). The bright yellow crystals had m. p. 96°. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 3940 A. and of one containing sulphuric acid at 4235 A. For a chloride emulsion the base was a medium sensitiser, with the maximum at 4600 A., sensitisation extending to 5100 A.

1-*Methyl*-2-*aniloethylidenedihydroquinoline* (XIV).—2-β-Anilinovinylquinoline methiodide (7·76 g.; 1 mol.) was suspended in acetone (100 c.c.) and shaken for 12 minutes with a solution of sodium hydroxide (4 g.; 5 mols.) in water (50 c.c.). The filtered acetone layer with ice-cold water (600 c.c.) deposited the base in 97% yield (10·16 g.). On recrystallising from light petroleum (b. p. 80—100°)–benzene (1 : 1, 10 c.c. per g.), some tar was left undissolved and the yield fell to 62% (Found, after drying in a vacuum desiccator: N, 10·95. $C_{18}H_{16}N_2$ requires N, 10·75%). The bright orange crystals had m. p. 88° (decomp.). The absorption maximum of an alkaline methyl-alcoholic solution was at 4335 A. In a gelatino-chloride photographic emulsion, sensitisation extended to 5100 A., with a maximum at 4700 A.

3-*Methyl*-2-*aniloethylidenethiazolidine*.—This was prepared from 2-β-anilinovinylthiazoline methiodide and sodium hydroxide in aqueous acetone, followed by precipitation with water, as described (Kodak Ltd., B.P. 561,172/1940). The yield was 79%, dropping to 73% on recrystallisation from benzene (1 c.c. per g.) (Found, after drying to constant weight in a vacuum desiccator: S, 14·6. Calc. for $C_{12}H_{14}N_2S$: S, 14·7%). The m. p. was 79—80°, whereas that published is 99—100°.

3-*Ethyl*-2-*aniloethylidenethiazolidine* (XV).—2-β-Anilinovinylthiazoline ethiodide (36 g.; 1 mol.), benzene (800 c.c.), and 40% sodium hydroxide solution (80 c.c.; 8 mols.) were heated together under reflux on a steam-bath, with vigorous stirring, for 30 minutes. After the solvent had been distilled from the filtered benzene layer, the solid residue was recrystallised from light petroleum (b. p. 80—100°; 1000 c.c.) and obtained in 77% yield (18·0 g.) (Found, after drying in a vacuum desiccator: S, 13·75. $C_{13}H_{16}N_2S$ requires S, 13·8%). The cream-coloured *substance* had m. p. 65°. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 3585 A. with an inflexion to the curve at 3200 A.; one containing sulphuric acid had its maximum at 3660 A. On a gelatino-chloride photographic emulsion it conferred extra-sensitivity up to 4400 A.

4-*Methyl*-3-*ethyl*-2-*aniloethylidene*-Δ^4-*thiazoline* (XVI).—4-Methyl-2-β-anilinovinylthiazole ethiodide (18·6 g.; 1 mol.) was ground with 20% sodium hydroxide solution (50 c.c.; 4 mols.). The mixture was stirred and warmed with acetone (250 c.c.). The crude product (23 g.), obtained by precipitation of the acetone layer with ice-water (1000 c.c.), was recrystallised from light petroleum (b. p. 80—100°) and benzene (2 : 1, 20 c.c. per g.). A 74% yield of golden crystals (18·0 g.) was obtained (Found: S, 12·95. $C_{14}H_{16}N_2S$ requires S, 13·1%); m. p. 122° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 4090 A. and of one containing sulphuric acid at 4030 A. The *substance* sensitised a chloride emulsion fairly strongly, sensitisation extending to 4900 A., with the maximum at 4500 A.

3-*Ethyl*-2-*aniloethylidenebenzoxazoline* (XVII).—2-β-Anilinovinylbenzoxazole ethiodide (58·8 g.; 1 mol.), aqueous 40% sodium hydroxide solution (90 c.c.; 6 mols.), and benzene (1500 c.c.) were stirred together and warmed gently on a steam-bath, then shaken vigorously for several minutes. The benzene solution was filtered and distilled down to dryness: the resultant gum was taken up with acetone, and the *base* precipitated with water, being obtained in 58% yield (23 g.). Recrystallisation was difficult; benzene appeared to be the most suitable solvent (5 c.c. per g.) but the yield fell to 6% (Found, after drying in a vacuum desiccator: N, 10·5. $C_{17}H_{16}ON_2$ requires N, 10·6%). The pale yellow crystals had m. p. 65° (decomp.). The absorption maximum of a methyl-alcoholic solution containing ammonia was at 3660 A. and of one containing sulphuric acid at 3835 A. A gelatino-chloride photographic emulsion was weakly sensitised to 4400 A., with the maximum effect at 4200 A.

3 : 3-*Dimethyl*-2-β-*anilinovinylindolenine Methiodide*.—2 : 3 : 3-Trimethylindolenine methiodide (20 g.; 1 mol.) and ethyl*iso*formanilide (10 g.; 1 mol.) were heated together in an oil-bath at 140° for 40 minutes with continual breaking up of the lumpy solid. After dissolving in hot spirit (130 c.c.), the product crystallised in 75% yield (20 g.). It was boiled out with spirit (25 c.c.) and on recrystallising the residue from spirit (125 c.c.) the yield was 55% (Found: I, 31·35. Calc. for $C_{19}H_{21}N_2I$: I, 31·4%). The yellow crystals had m. p. 236—238° (decomp.).

1 : 3 : 3-*Trimethyl*-2-*aniloethylideneindoline* (XVIII).—The foregoing methiodide (3·91 g.; 1 mol.) was suspended in benzene (40 c.c.) and shaken with a solution of sodium hydroxide (1·16 g.; 3 mols.) in water (5 c.c.). Subsequently four more such benzene extractions were carried out. The benzene filtrate was taken to dryness and the residue twice recrystallised from light petroleum (b. p. 80—100°; 2 × 8 c.c.), the yields being 73% and 64% (1·70 g.) (Found, after drying in a vacuum desiccator: N, 10·0. $C_{19}H_{20}N_2$ requires N, 10·15%). The yellow powder had m. p. 89°. The absorption maximum of a methyl-alcoholic solution containing ammonia was at 3745 A. and of one containing snlphuric acid at 4120 A. It sensitised a gelatino-chloride photographic emulsion up to 4700 A.

*Ethyl*iso*formanilide*.—Ethyl orthoformate (1200 c.c.; 2 mols.), aniline (336 c.c.; 1 mol.), and aniline hydrochloride (36 g.) were boiled together in an oil-bath for 4 hours, in a flask fitted with fractionating column, condenser, and receiver to collect the alcohol eliminated. The temperature of the bath was kept at 120° until the first vigour of the reaction had subsided and was then raised to 140—150°. After cooling, any diphenylformamidine was filtered off, and the filtrate was fractionally distilled under a vacuum. After a forerun, b. p. 50—110°/20 mm., the ethyl*iso*formanilide was collected at 110—120°/20 mm. The foreruns from several batches were fractionated together, the fraction boiling up to 110°/20 mm. being used as ortho-ester for another preparation, and the fraction above 110°/20 mm. being refractionated with ethyl*iso*formanilide. As a result, the 85% yield from a second fractional distillation (504 g.) is slightly larger than that from the first fractionation (81% yield; 480 g.).

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