38. *Heterocyclic Compounds from Urea Derivatives. Part V.* Synthesis and Cyclisation of* N-o-*Hydroxyphenyl*-N′N″-*diarylguanidines.*

By Frederick Kurzer and Phyllis M. Sanderson.

Diarylcarbodi-imides react additively with *o*-aminophenol, forming *N*-*o*-hydroxyphenyl-*N*′*N*″-diarylguanidines rapidly in good yield. The products are cyclised to 2-arylaminobenzoxazoles under a variety of conditions.

The results confirm that, in addition reactions with carbodi-imides, aromatic groups exhibit decreasing reactivity in the order: SH > NH_2 > OH.

A previous paper [1] in this series outlined addition reactions between *o*-aminothiophenol and diarylcarbodi-imides. A single example of the parallel reaction involving *o*-aminophenol had originally been given by Busch, Blume, and Pungs.[2] Since we were unable to confirm their experimental result, we have re-examined this reaction.

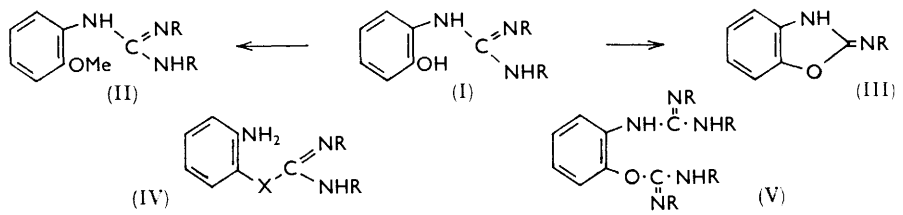
Equimolar quantities of *o*-aminophenol and diarylcarbodi-imides reacted additively in acetone to form *N*-*o*-hydroxyphenyl-*N*′*N*″-diarylguanidines (I; R = Ar) in good yield. This formulation, presupposing preferential addition at the amino-group of

* Part IV, Godfrey and Kurzer, *J.*, 1962, 3561.

[1] Kurzer and Sanderson, *J.*, 1962, 230.

[2] Busch, Blume, and Pungs, *J. prakt. Chem.*, 1909, **79**, 513.

o-aminophenol, agrees with the known low reactivity of the phenolic hydroxyl [2] (except in the presence of hydrogen chloride [3]) towards carbodi-imides. The assigned structure was confirmed by alkylation of (I; R = Ph) using dimethyl sulphate in alkali; the resulting *N*-*o*-methoxyphenyl-*N'N''*-diphenylguanidine (II; R = Ph) was identical with the product obtained from *o*-anisidine and diphenylcarbodi-imide.



N-*o*-Hydroxyphenyl-*N'N''*-diphenylguanidine (I; R = Ph) was amphoteric. Its pronounced stability in both dilute mineral acids and alkalis is typical of a guanidine, but incompatible with the alternative isourea structure (IV; X = O). Under suitable conditions, *N*-*o*-hydroxyphenyl-*N'N''*-diarylguanidines were readily cyclised, with loss of amines, to 2-anilinobenzoxazoles (III; R = Ar). This reaction occurred almost quantitatively on fusion, in phosphoric acid at 140°, or in boiling acetic anhydride, resulting in the last case in the acetyl derivative of (III). The remarkable power of dilute acetic acid to effect this cyclisation contrasts with the inability of hydrochloric acid to do so; the difference is ascribed to the stabilising effect, by salt formation, of the strong acid on the substituted guanidine (I).

Unlike *o*-aminothiophenol, which is capable of combining with two moles of diarylcarbodi-imide,[1] *o*-aminophenol did not form di-addition products (V). Treatment of *N*-*o*-hydroxyphenyl-*N'N''*-diphenylguanidine (I; R = Ph) with an additional mole of carbodi-imide gave merely 2-anilinobenzoxazole (III; R = Ph) and *NN'N''*-triphenylguanidine. The carbodi-imide thus appears to promote strongly the cyclisation (I ⟶ III), simultaneously converting the eliminated amine into triarylguanidine. Essentially the same observations were made when *o*-aminophenol reacted directly with two moles of carbodi-imide. 2-Anilinobenzoxazole and *NN'N''*-triphenylguanidine, both basic and of similar solubility in the usual solvents, were separated reasonably satisfactorily by the differential solubility of their picrates.

Busch, Blume, and Pungs,[2] when adding diphenylcarbodi-imide to *o*-aminophenol in boiling benzene, obtained a product, m. p. 132—133° (" silky needles from ethanol "), which they formulated as *N*-*o*-hydroxyphenyl-*N'N''*-diphenylguanidine. The authentic compound, m. p. 164—166° (prisms from ethanol), was invariably produced when the solvent was acetone, or a sufficiently large volume of benzene, so that complete solution of the *o*-aminophenol was assured before the addition of the carbodi-imide. In smaller volumes of benzene, the reaction did indeed give products of approximate m. p. 130—135°, but these were mixtures, separable by alkali, of the desired guanidine (I) and its cyclisation product (III). *NN'N''*-Triphenylguanidine was also isolated as the most soluble fraction. It is suggested that, under these conditions, owing to the incomplete initial dissolution of the *o*-aminophenol, diphenylcarbodi-imide is temporarily present in excess in the dissolved phase and promotes cyclisation (to III) as demonstrated above. Support for this view is provided by the observation that the time of subsequent refluxing was without influence on the proportion of products formed, and that cyclisation was greatly reduced, when the carbodi-imide was added gradually, even if the volume of solvent was small. Busch's erroneous result thus finds a reasonable explanation, the more so because the guanidine and benzoxazole (I and III; R = Ph) differ only little in ultimate composition.

The ultraviolet absorption curves of *N*-*o*-hydroxyphenyl-*N'N''*-diarylguanidines (I),

[3] Short and Smith, *J.*, 1922, **121**, 1803.

in outline not unlike those of *S*-*o*-aminophenyl-*N'N''*-diarylisothioureas [1] (IV; X = S), contained a shallow wide maximum in the 260—280 mμ range. The spectra of 2-anilinobenzoxazoles (III) agreed with those previously recorded (for III; R = Ph, *p*-C_6H_4·Me) by Passerini,[4] featuring maxima in the 260 mμ and 290 mμ region. Contributions to the latter may again [1] be ascribed to conjugation involving the oxazole and either of the benzene nuclei, persisting in both tautomeric 2-arylaminobenzoxazole and 2-aryliminobenzoxazoline forms. The presence of substituents in the 2-anilino-group caused the expected [5] small bathochromic shifts.

Our previous parallel experiments [1] with *o*-aminothiophenol demonstrated the greater reactivity of the mercapto- over that of the amino-group towards carbodi-imides. This observation agrees with the experience that C–S bonds are generally more rapidly formed than C–N bonds, as illustrated, for example, by the preferential *S*-alkylation and -acylation of thioureas. The exclusive formation of guanidines (I) from *o*-aminophenol in the present reaction thus confirms the decreasing order of reactivity of aromatic mercapto-, amino-, and hydroxyl groups [1] towards diarylcarbodi-imides. The subsequent stage (I ⟶ III) provides an additional example of the well-known versatile benzoxazole synthesis [6] by ring-closure of suitable *o*-aminophenol derivatives. It particularly resembles the synthesis of 2-anilinobenzoxazole by fusion of *o*-aminophenol and *NN'*-diphenyl-*S*-methylisothiourea,[7] which is likely to proceed by the same mechanism, and the cyclisation of *N*-*o*-hydroxyphenyl-*N'*-phenylurea to benzoxazol-2-one,[8] which occurs also with elimination of aniline.

Experimental

Acetone was dried over calcium sulphate hemihydrate. Light petroleum had b. p. 60—80°. Ultraviolet spectra were measured with a Unicam S.P. 500 spectrophotometer for 0·00005M-ethanolic solutions.

Reaction of o-*Aminophenol with Diphenylcarbodi-imide.*—(a) *In acetone.* A solution of *o*-aminophenol (5·45 g., 0·05 mole) in acetone (120 ml.) at 45° was treated with diphenylcarbodi-imide (9·7 g., 0·05 mole) during 3 min., the yellow liquid was refluxed for 5 min., and the solvent was removed under reduced pressure during 15—20 min. The viscous syrup, dissolved in boiling ethanol (80 ml.), filtered (pump), and gradually diluted with half its volume of light petroleum slowly deposited massive prisms (total, including material from mother-liquors, 9·85—10·6 g., 65—70%). Further crystallisation from ethanol (10—12 ml. per g., recovery approx. 80%) gave glass-like prisms of N-*o*-*hydroxyphenyl*-N'N''-*diphenylguanidine*, m. p. 162—164° [Found: C, 75·45; H, 5·6; N, 13·8%; *M* (cryoscopically, in thymol), 290. $C_{19}H_{17}N_3O$ requires C, 75·25; H, 5·6; N, 13·9%; *M*, 303], $\lambda_{min.}$ (shallow) 243 mμ (log ε 4·18), $\lambda_{max.}$ (shallow) 265 mμ (log ε, 4·26). The final mother-liquors from the crude crops were nearly black and contained only intractable oils.

The compound separated from benzene (20 ml. per g., recovery 90%) as a white crystalline powder, m. p. and mixed m. p. 162—163°. It was unaffected by being refluxed for 2 hr. in benzene or ethanol. It was soluble in cold N-hydrochloric acid, less so in 3N-acid, and was very sparingly soluble in cold and hot ammonia. Though sparingly soluble in 3N-sodium hydroxide, it was soluble in hot N-alkali, from which it was reprecipitated by successive acidification with 3N-hydrochloric acid and basification with ammonia.

The *picrate* formed microprisms (70%), m. p. 180—181° (decomp.) (from acetone–ethanol) (Found: C, 56·8; H, 4·3; N, 15·9. $C_{19}H_{17}N_3O,C_6H_3N_3O_7$ requires C, 56·4; H, 3·8; N, 15·8%).

(b) *In benzene.* *o*-Aminophenol (2·18 g., 0·02 mole) in boiling anhydrous benzene (250 ml., *i.e.*, sufficient for complete solution) was treated with diphenylcarbodi-imide (3·88 g., 0·02 mole),

[4] Passerini, *J.*, 1954, 2256.
[5] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York and London, 1951.
[6] Cornforth, in Elderfield, "Heterocyclic Compounds," Vol. V, Wiley, New York, 1957, p. 418 *et seq.*
[7] Deck and Dains, *J. Amer. Chem. Soc.*, 1933, **55**, 4986.
[8] Leuckart, *J. prakt. Chem.*, 1890, **41**, 327.

and the yellow liquid immediately distilled in a vacuum to remove all the solvent (20—30 min.). The residual syrup, crystallised as before, gave *N-o*-hydroxyphenyl-*N'N''*-diphenylguanidine (4·55 g., 75%), m. p. and mixed m. p. 162—163°.

(c) *In small volumes of benzene.* A suspension of *o*-aminophenol (5·45 g., 0·05 mole) in hot dry benzene (80 ml.), treated with diphenylcarbodi-imide (9·70 g., 0·05 mole), was refluxed for 10 min., solution occurring within 3—5 min. The liquid was diluted with light petroleum (40 ml.) and the separated crystals were collected after storage for 12 hr. at 0° (product A, m. p. 132—135°, after sintering at 120°, but occasionally higher, 10—11·5 g.). The filtrate was distilled in a vacuum successively to half, and then very small bulk, giving product B (m. p. as A; 1—2 g.) and product C (large prisms, m. p. 134—140°; 1·5—2 g.).

The finely-powdered combined products A and B were stirred at room temperature with 1·5N-sodium hydroxide (90 ml.) and ethanol (45 ml.), the undissolved product M filtered off at the pump, and the filtrate adjusted to pH 8 with 3N-hydrochloric acid and successive addition of 3N-ammonia. The resulting precipitate N was collected. Product M, crystallised from ethanol, was 2-anilinobenzoxazole (2·6—3·7 g., 25—35%), m. p. and mixed m. p. 172—173° (Found: C, 74·2; H, 4·9. Calc. for $C_{13}H_{10}N_2O$: C, 74·3; H, 4·8%). Precipitate N consisted, after crystallisation from ethanol, of prisms of *N-o*-hydroxyphenyl-*N'N''*-diphenylguanidine (6·8—8·3 g., 45—55%), m. p. and mixed m. p. 162—164°. Product C, crystallised from a little ethanol, gave prisms of *NN'N''*-triphenylguanidine (1—1·5 g.), m. p. and mixed m. p. 142—144°.

Alternatively, crystallisation of product A (provided it consisted mostly of the guanidine) from ethanol (10 ml. per g.) gave the substituted guanidine (48—55%), m. p. and mixed m. p. 162—164°, directly.

Product A was not changed appreciably in m. p. or composition after crystallisation from benzene (Found: C, 74·9; H, 5·0; N, 13·7%), benzene–light petroleum, chloroform–light petroleum, or after refluxing for 1 hr. in benzene and recovery by addition of light petroleum.

Essentially the same results were obtained when the time of reaction was 30 min. In experiments in which the carbodi-imide was added dropwise during 8—10 min. the guanidine predominated (50%) regardless of the time of refluxing (15—45 min. total).

Reactions of N-o-*Hydroxyphenyl*-N'N''-*diphenylguanidine.*—(a) *Pyrolysis.* The melted reactant (1·0 g., 0·0033 mole) was kept at 200° during 1 hr., aniline being evolved. The solidified melt, crystallised from ethanol, gave 2-anilinobenzoxazole (0·62 g., 90%), m. p. and mixed m. p. 172—173°, $\lambda_{min.}$ 234 mμ (log ε 3·58), $\lambda_{max.}$ 261 (4·32), $\lambda_{min.}$ 272 (4·13), $\lambda_{max.}$ 288, 295 (twinned) (4·42, 4·42).

(b) *Stability in mineral acid and alkali.* The compound was recovered (85%) after being refluxed in 1·5N-ethanolic hydrochloric acid for 30—45 min., or in 0·5N-ethanolic sodium hydroxide for 1 hr. (80%), or in 3N-aqueous sodium hydroxide for 30 min. (60%).

(c) *Action of acetic acid.* A solution of the guanidine (1·52 g., 0·005 mole) in ethanol (10 ml.) and 3N-acetic acid (5 ml.) was refluxed for 30 min., stirred into ice–water (60 ml.), and basified with 3N-ammonia. The precipitate (1 g.) was 2-anilinobenzoxazole (0·9 g., 86%), m. p. 172—173°, (from ethanol).

(d) *Action of phosphoric acid.* A solution of the reactant (1·52 g., 0·005 mole) in 100% orthophosphoric acid (8 ml.) was kept at 140° for 2 hr., stirred into ice (100 g.), and basified with concentrated ammonia (*d* 0·88), and the precipitate collected at once. The dried product was boiled with ethanol (12 ml.), and a little undissolved inorganic material removed at the pump. The filtrate gave 2-anilinobenzoxazole (0·84 g., 80%), m. p. and mixed m. p. 172—173° (from ethanol). One hour's treatment at 120° gave the same material (40%).

(e) *Action of acetic anhydride.* A solution of the guanidine (0·76 g., 0·0025 mole) in acetic anhydride (6 ml.) was refluxed for 1 hr., and then added to water. The resulting precipitate (92%), crystallised from 50% ethanol, was 3-acetyl-2-phenyliminobenzoxazole, m. p. and mixed m. p.[9] 91—93° (Found: C, 71·6; H, 4·9; N, 10·8. Calc. for $C_{15}H_{12}N_2O_2$: C, 71·4; H, 4·8; N, 11·1%).

(f) *Action of diphenylcarbodi-imide.* A solution of the reactant (3·03 g., 0·01 mole) in acetone (100 ml.), treated with diphenylcarbodi-imide (1·94 g., 0·01 mole), was refluxed during 30 min. The solvent was removed in a vacuum, the yellow residual oil dissolved in ethanol (75 ml.) and the filtered liquid treated with picric acid (4·6 g., 0·02 mole) in hot ethanol (30 ml.). The resulting copious crystalline precipitate P (3·75 g., 85%) was collected at 30—35° (filtrate

[9] Young and Dunstan, *J.*, 1908, **93**, 1055.

H) and rinsed with a little ethanol; it was 2-anilinobenzoxazole picrate, m. p. and mixed m. p. 190—192° (decomp.) (from 95% ethanol) (lit.,[10] m. p. 188°) (Found: C, 52·0; H, 3·05. $C_{19}H_{13}N_5O_8$ requires C, 51·9; H, 3·0%).

Filtrate H was evaporated to small volume in a vacuum, and more solid P (0·2—0·3 g.) removed while hot. The picrate which separated on cooling (4·3 g.) gave, after two crystallisations from ethanol, *NN'N''*-triphenylguanidine picrate (3·2 g., 62%), m. p. and mixed m. p.[11] 181—183° (decomp.).

Interaction of o-*Aminophenol with Two Moles of Diphenylcarbodi-imide.*—The reactants (0·01 and 0·02 mole, respectively) were refluxed in acetone (50 ml.) during 30 min. and the mixture worked up as described in (f). There resulted 2-anilinobenzoxazole picrate (3·05 g., 70%), m. p. and mixed m. p. 190—192° (decomp.), and *NN'N''*-triphenylguanidine picrate (1·80 g., 35%), m. p. and mixed m. p. 181—183° (decomp.).

Both in this and the foregoing experiment, direct separation of the bases by fractional crystallisation from ethanol did give pure specimens of the benzoxazole and the (more soluble) guanidine, but in much diminished yields.

N-o-*Methoxyphenyl*-N'N''-*diphenylguanidine.*—(*a*) *o*-Anisidine (3·08 g., 0·025 mole) and diphenylcarbodi-imide (4·85 g., 0·025 mole) in acetone (30 ml.) were refluxed for 30 min., the solvent removed in a vacuum, and the syrupy brown residue redissolved in methanol (10 ml.). On prolonged storage, the very viscid solution deposited three successive crops of solid (4·8 g.) which gave, on crystallisation from methanol (10 ml. per g.), lustrous prisms (2·75 g., 35%) of N-o-*methoxyphenyl*-N'N''-*diphenylguanidine*, m. p. 125—127° (Found: C, 75·6; H, 6·1; N, 13·0. $C_{20}H_{19}N_3O$ requires C, 75·7; H, 6·0; N, 13·25%), $\lambda_{min.}$ 238 mμ (shallow) (log ε 4·15), $\lambda_{max.}$ 265 mμ (shallow) (4·31), $\lambda_{infl.}$ 280 mμ (4·27). No further crystalline material was obtainable from the viscid filtrate.

The *picrate* (0·49 g., 90%) separated slowly when a solution of equimolar quantities (0·001 mole) of the components in methanol (6 ml.) was gradually treated with light petroleum. It formed an opaque powdery yellow solid, m. p. 107—108° (decomp.) (from methanol–light petroleum) (Found: C, 56·4; H, 4·5. $C_{26}H_{22}N_6O_8,CH_3{\cdot}OH$ requires C, 56·05; H, 4·5%.

(*b*) Finely powdered *N-o*-hydroxyphenyl-*N'N''*-diphenylguanidine (3·03 g., 0·01 mole) was dissolved in 3N-sodium hydroxide (20 ml., 0·06 mole) and methanol (10 ml.). The cooled stirred liquid was treated during 5—8 min. with dimethyl sulphate (6·3 g., 0·05 mole), and stirring continued during 1 hr. Half-way through the addition of the methylating agent, oily globules separated and were deposited as a resinous film on the walls of the vessel. Dilution with water (120 ml.), and continued stirring, gradually converted the resin into a pale yellow powder. This was collected, air-dried, (2·5—3·0 g.), and dissolved in methanol (10 ml.). The filtered solution slowly deposited prisms (1·6 g., 50%) of the *o*-methoxy-homologue, m. p. and mixed m. p. 127—129° (from methanol) (Found: C, 75·3; H, 6·0; N, 13·2%). Its ultraviolet absorption curve was identical with that of the product in (*a*).

Reaction of o-*Aminophenol with Di-*p*-tolylcarbodi-imide.*—(a) *In acetone.* A solution of *o*-aminophenol (4·35 g., 0·04 mole) in acetone (100 ml.), treated with di-*p*-tolylcarbodi-imide [12] (8·9 g., 0·04 mole), was refluxed during 10 min., the solvent removed in a vacuum (during 10 min.), and the residual oil dissolved in ethanol. The successive crops of white solid (9·25 g., 70%), crystallised from ethanol (10 ml. per g.), consisted of felted needles of N-o-*hydroxyphenyl*-N'N''-*di*-p-*tolylguanidine* (60%), m. p. 141—142° (Found: C, 76·35; H, 6·4; N, 12·4. $C_{21}H_{21}N_3O$ requires C, 76·1; H, 6·3; N, 12·7%), $\lambda_{min.}$ (shallow) 246 mμ (log ε 4·22), $\lambda_{max.}$ (shallow) 265 mμ (log ε 4·27).

(b) *In benzene.* *o*-Aminophenol (0·04 mole) in anhydrous benzene (80 ml.) was treated with di-*p*-tolylcarbodi-imide (0·04 mole) and refluxed for 30 min. The product (A) which separated on cooling was collected after 12 hr., and two successive crops (B and C) isolated by evaporation of the benzene filtrates. Product A (7—8 g.) gave, on crystallisation from ethanol, felted needles (4·6 g., 35%) of *N-o*-hydroxyphenyl-*N'N''*-di-*p*-tolylguanidine, m. p. and mixed m. p.141—142°. Product B (2·7 g., 30%) was 2-*p*-toluidinobenzoxazole, prismatic needles, m. p. 179—180° (from ethanol) (lit.,[7,10] m. p. 178°) (Found: C, 74·9; H, 5·0; N, 12·9. Calc. for $C_{14}H_{12}N_2O$: C, 75·0; H, 5·35; N, 12·5%), $\lambda_{min.}$ 235 mμ (log ε 3·62), $\lambda_{max.}$ 263 (4·34) $\lambda_{min.}$ 272 (4·14), $\lambda_{max.}$ 290 (4·42). Product C, which separated slowly as large glass-like prisms (2·3 g., 35%)

[10] Desai, Hunter, and Khalidi, *J.*, 1934, 1186.
[11] Dains, *J. Amer. Chem. Soc.*, 1900, **22**, 184.
[12] Hünig, Lehmann, and Grimmer, *Annalen*, 1953, **579**, 77.

was *NN'N''*-tri-*p*-tolylguanidine, m. p. 117—119° (from ethanol) (lit.,[13] m. p. 123°) (Found: C, 80·2; H, 7·2. Calc. for $C_{22}H_{23}N_3$: C, 80·2; H, 7·0%).

Reaction of o-*Aminophenol with Di*-p-*bromophenylcarbodi-imide.*—*o*-Aminophenol (2·18 g., 0·02 mole) in benzene (40 ml.) was treated with the carbodi-imide [12] (7·05 g., 0·02 mole) and refluxed for 30 min. The crystalline solid, which had separated already during the refluxing, was collected at 0°; it crystallised from acetone–ethanol (5 and 15 ml. per g.) as felted needles (3·75 g., 65%) of 2-p-*bromoanilinobenzoxazole*, m. p. 222—224° (Found: C, 53·85; H, 3·1; Br, 27·9; N, 9·5. $C_{13}H_9BrN_2O$ requires C, 54·0; H, 3·1; Br, 27·8; N, 9·7%), $\lambda_{min.}$ 237 mμ (log ε 3·59), $\lambda_{max.}$ 267 (4·34), $\lambda_{min.}$ 274 (4·19), $\lambda_{max.}$ (plateau) 291 (4·50).

Interaction of the above reactants in boiling acetone (75 ml.) during 5 min., removal of the solvent, and dissolution of the residual oil in ethanol, (30 ml.) deposited, after several days' storage, needles of the same product (1·85 g., 32%), m. p. 221—223° (from acetone–ethanol).

N-o-*Hydroxyphenyl*-N'N''-*di*-p-*methoxyphenylguanidine.*—*o*-Aminophenol (2·18 g., 0·02 mole) and di-*p*-methoxyphenylcarbodi-imide (5·08 g., 0·02 mole) in acetone (100 ml.) were refluxed for 15 min., the solvent removed in a vacuum, and the residual oil dissolved in methanol (25 ml.). On prolonged storage the liquid deposited a granular solid which gave microprisms (2·32 g., 32%) of the *guanidine*, m. p. 106—108° (from ethanol) (Found: C, 68·8; H, 6·2; N, 11·7. $C_{21}H_{21}N_3O_3$ requires C, 69·4; H, 5·8; N, 11·6%), $\lambda_{max.}$ (wide plateau) 250—280 mμ (log ε 4·22), with a slight shallow $\lambda_{max.}$ 260 mμ (log ε 4·24).

2-p-*Methoxyanilinobenzoxazole.*—The residual oily crude guanidine obtained as in the foregoing paragraph was redissolved in ethanol (25 ml.) and treated with 3N-acetic acid (10 ml.). The liquid was refluxed for 30 min., heated on the steam bath for 15 min., stirred into ice–water (120 ml.), and basified with 3N-ammonia. The precipitate, crystallised successively from methanol (10 ml. per g.) and chloroform, gave lustrous prisms of the *benzoxazole* (3·45 g., 72%), m. p. 134—135° (Found: C, 69·9; H, 4·8; N, 11·6. $C_{14}H_{12}N_2O_2$ requires C, 70·0; H, 5·0; N, 11·7%), $\lambda_{min.}$ 235 mμ (log ε 3·67), $\lambda_{max.}$ 264 (4·32), $\lambda_{min.}$ 273 (4·14), $\lambda_{max.}$ 289 (4·42).

ROYAL FREE HOSPITAL SCHOOL OF MEDICINE (UNIVERSITY OF LONDON),
8 HUNTER STREET, LONDON, W.C.1. [*Received, April 6th*, 1962.]

[13] Merz and Weit, *Z. Chem.*, 1868, 610.