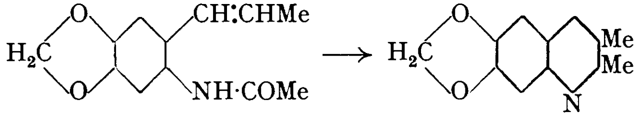
36. *Ring Closures of Derivatives of 2-Aminostyrene.*

By T. W. J. TAYLOR and (MISS) P. M. HOBSON.

FOULDS and ROBINSON (J., 1914, **105**, 1968) obtained methylenedioxydimethylquinoline (II) by boiling 2-acetamidosafrole (I) with phosphoryl chloride.

(I.)



(II.)

The purpose of the experiments recorded here was to see whether this type of quinoline synthesis could be extended to the acyl derivatives of 2-aminostyrene (V; R = H, R′ = acyl) and 2-aminostilbene (V; R = Ph, R′ = acyl). 2-Aminostyrene can be obtained from β-phenylethyl acetate (Sabetay, Bléger, and De Lestrange, *Bull. Soc. chim.*, 1931, **49**, 3), but the process is tedious and the yield small because the nitration gives mainly the 4-nitro-compound. Attempts to prepare the desired substance by other methods were unsuccessful. 2-Nitrocinnamic acid could not be decarboxylated to 2-nitrostyrene under any of the conditions or with any of the catalysts which were tried. β-2 : 4-Dinitrophenylethyl acetate, from which the 4-nitro-group might be eliminated, could not be obtained by the nitration of β-4-nitrophenylethyl acetate, only side-chain oxidation products being isolated. Blocking of the 4-position in phenylethyl acetate with a bromine atom did not prove a suitable method for increasing the amount of the 2-nitro-compound formed in nitration, since 4-bromophenylethyl acetate cannot be prepared by direct bromination.

It was found that the acyl derivatives of 2-aminostyrene can be converted into 2-substituted quinolines by heating with phosphoryl chloride, and in this way quinaldine was obtained from the acetyl compound, 2-*n*-amylquinoline from the *hexoic* derivative, and *αδ-di-(2-quinolyl)butane* (III) from *adipodi-2-vinylanilide*. This type of quinoline synthesis may prove useful for obtaining certain quinoline derivatives not accessible by other methods. 2-Aminostyrene can also be converted into indole; addition of bromine

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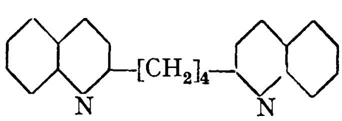
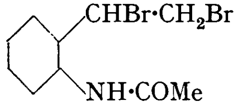
* An aqueous solution of calcium chloride kept at its freezing point by the occasional addition of commercial solid carbon dioxide.

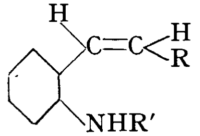
to the acetyl compound gives the dibromide (IV), from which indole is obtained with alcoholic potash (cf. Foulds and Robinson, *loc. cit.*).



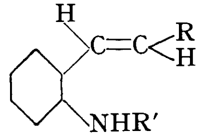
(III.)



(IV.)

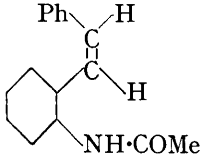


(V.)

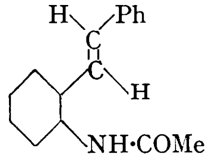


(VI.)

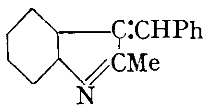
No quinoline derivatives could, however, be obtained from 2-acetamidostilbene. This compound should exist in two geometrically isomeric forms, of which only the *trans*-compound (VI; R = Ph, R′ = Ac) could give a quinoline, since in the *cis*-form (V) the hydrogen atom which would be involved in the ring closure is on the wrong side of the double bond.



(VII.)



(VIII.)



(IX.)

The two isomerides have been obtained and their configurations established, as is discussed below. With the *cis*-acetamido-compound, ring closure gives 3-benzylidene-2-methylindolenine (IX); this result would be expected, since, although a quinoline cannot be formed, the molecule can exist as in (VII) and a five-membered ring can be formed. The *trans*-compound undergoes the same ring closure as the *cis*-compound and gives no quinoline, in spite of the fact that its spatial configuration does not exclude that possibility. It is clearly reacting in the form (VIII) and the introduction of the phenyl group has upset the balance between quinoline and indole formation.

The aminostilbenes were prepared from *cis*-2-nitrostilbene, which has been obtained pure and in good yield. The behaviour of this compound is exceptional (cf. Stoermer and Prigge, *Annalen*, 1915, **409**, 34) in that it cannot be converted into the *trans*-isomeride by the methods which are effective for other *cis*-stilbenes. This behaviour seems to arise from the presence of the nitro-group, since it is also found in 2-nitro-α-phenylcinnamic acid. The stability of the *trans*-form, which is common to all stilbenes, is due to the mutual repulsion of the space-filling phenyl groups. The exceptional stability of the *cis*-form in the 2-nitro-compound must indicate that there is an attraction which can overcome this normal steric effect. This may well be an association between one phenyl group and the nitro-group attached to the other, which is of the same nature as the association which gives rise to stable complexes of nitro-compounds and aromatic hydrocarbons.

Reduction of *cis*-2-nitrostilbene gives a 2-aminostilbene not known hitherto, and this is converted by boiling hydrochloric acid into an isomeride which has been obtained previously by a different method (Sachs and Hilpert, *Ber.*, 1906, **39**, 1308; Stoermer and Prigge, *loc. cit.*). Hence the first reduction product is most probably the *cis*-compound, which undergoes the normal change into the more stable *trans*-isomeride. This conclusion is supported by the decomposition of the diazo-compounds derived from the two substances. By diazotising the less stable isomeride, phenanthrene can be obtained in good yield, but none is formed from the more stable isomeride. Hence it seems likely that in the former the two phenyl groups lie on the same side of the double bond, and this simple synthesis of phenanthrene can be taken as further evidence that the less stable compound has the *cis*-configuration (V; R = Ph, R′ = H) and the isomeride previously known the *trans*-configuration (VI; R = Ph, R′ = H). It also indicates that the success of Pschorr's synthesis of phenanthrene-9-carboxylic acid from 2-amino-α-phenylcinnamic acid depends on the carboxyl group. If this is present, the stable form has the two phenyl groups on the same side of the double bond; but if it is absent, the stable form has the *trans*-configuration, so the phenanthrene cannot be obtained from that form but only from the less stable isomeride.

EXPERIMENTAL.

Quinaldine.—2-Acetamidostyrene (Sabetay, Bléger, and De Lestrange, *loc. cit.*) was gently heated with 8 times its weight of phosphoryl chloride until reaction set in; after this had subsided, the mixture was boiled for 5 minutes and poured into water. From the filtered liquid, made alkaline, ether extracted quinaldine, identified by its b. p. and by the m. p. and mixed m. p. of its picrate.

Adipodi-2-vinylanilide.—1 G. of 2-aminostyrene in 10 c.c. of dry pyridine was treated with 0·8 g. of adipyl chloride drop by drop, and the mixture poured into water; the solid *product* crystallised from alcohol in colourless needles, m. p. 202° (Found : N, 8·3. $C_{22}H_{24}O_2N_2$ requires N, 8·1%).

αδ-Di-(2-quinolyl)butane (III).—The anilide was treated with phosphoryl chloride as above. The sticky solid resulting was purified by recrystallisation of its picrate from acetone in yellow needles, m. p. 224°. The picrate was decomposed with ammonia and ether, and the solid from the latter washed with light petroleum and recrystallised several times from aqueous alcohol. The *compound* formed colourless needles, m. p. 98°, soluble in all solvents except light petroleum (Found : N, 8·8. $C_{22}H_{20}N_2$ requires N, 8·9%).

2-n-*Hexamidostyrene.*—0·5 G. of 2-aminostyrene in 6 c.c. of acetone was treated with a few drops of concentrated aqueous potash and 0·6 g. of *n*-hexoyl chloride (prepared from synthetic hexoic acid; "Organic Syntheses," **4**, 11; **11**, 76) and boiled for 30 minutes. The acetone layer was poured into water; the precipitated oil solidified on standing; m. p. (from light petroleum) 61° (Found : N, 6·5. $C_{14}H_{19}ON$ requires N, 6·45%).

2-n-*Amylquinoline.*—The hexamido-compound was treated as above. A colourless basic oil was obtained, from which the picrate was prepared and crystallised repeatedly from alcohol (Found : N, 12·9. Calc. : N, 13·1%). The m. p. of the picrate was 104—105°, whereas Schopf and Lehmann (*Annalen*, 1932, **497**, 7) report 111—112°, but further recrystallisation failed to raise the m. p.

2-*Acetamidostyrene Dibromide* (IV).—0·8 G. of the styrene in chloroform was treated with 0·8 g. of bromine. The solution after concentration deposited white needles, which were recrystallised from chloroform; m. p. 125° (Found : Br, 49·75. Calc. : Br, 49·8%). A small quantity was heated with 50% alcoholic potash and diluted with water. The presence of indole was shown by colour tests with a pine shaving, with sodium nitroprusside, and with nitric and nitrous acids.

cis-2-*Nitrostilbene.*—10 G. of 2-nitro-α-phenylcinnamic acid (Pschorr, *Ber.*, 1897, **30**, 497) in 100 c.c. of quinoline were heated with 1 g. of copper chromite (Adkins and Connor, *J. Amer. Chem. Soc.*, 1931, **53**, 1092) at 200—210° until the evolution of carbon dioxide ceased (45 mins.). The mixture was then poured into 400 c.c. of 15% hydrochloric acid and extracted with ether. From the extract a brown oil was obtained, which solidified and formed yellow needles from alcohol, m. p. 62°. The compound was not transformed into an isomeride by boiling mineral acid or by exposure to sunlight in the presence of a little bromine or iodine.

cis-2-*Aminostilbene* (V; R = Ph, R′ = H).—The nitro-compound was reduced with ferrous sulphate and ammonia (Stoermer and Oehrlet, *Ber.*, 1922, **55**, 1239) or, better, by treating its solution in a mixture of equal parts of glacial acetic acid and concentrated hydrochloric acid with four times its weight of zinc dust. The amine is an oil; the m. p. of the sparingly soluble hydrochloride is 208—209°. The *acetyl* derivative, obtained with acetic anhydride, forms colourless needles (from alcohol), m. p. 112—113° (Found : N, 5·7. $C_{16}H_{15}ON$ requires N, 5·9%). When this derivative was treated with phosphoryl chloride, a brown solid of indefinite m. p. was formed. This was boiled with dilute sulphuric acid, benzaldehyde being expelled, and the solution was oxidised with acetic acid and ferric chloride; a bright red colour appeared and rosindole was slowly deposited as a red solid (cf. Freund and Le Bach, *Ber.*, 1905, **38**, 2640).

trans-2-Aminostilbene was prepared from the *cis*-compound by boiling with concentrated hydrochloric acid for 4 hours. The base obtained from the hydrochloride which separated on cooling had m. p. 101·5—102·5° (from alcohol). The acetyl derivative, m. p. 140° (cf. Sachs and Hilpert, *loc. cit.*), gave with phosphoryl chloride results similar to those obtained with the *cis*-compound.

Phenanthrene.—When *cis*-2-aminostilbene was diazotised, and the solution warmed after addition of excess of sodium carbonate, nitrogen was evolved and a brown tar separated, which solidified on cooling. Distillation under reduced pressure gave phenanthrene, recognised by the m. p. and mixed m. p. of the substance and of its picrate. Similar treatment of the *trans*-compound gave a tar, which decomposed profoundly on attempted distillation and gave no phenanthrene.

β-4-*Bromophenylethyl Alcohol*.—16 G. of 4-aminophenylethyl alcohol (Ferber, *Ber.*, 1929, **62**, 183) were diazotised in dilute hydrobromic acid and added to a boiling cuprous bromide solution. The resulting oil was washed with alkali and distilled; b. p. 147°/10 mm. It solidified to colourless needles, m. p. 36—38°; yield, 12 g. (50%). On oxidation with permanganate, 4-bromobenzoic acid was formed. The *phenylurethane*, prepared with phenyl *iso*cyanate, formed colourless plates, m. p. 126° (from alcohol) (Found: C, 56·1; H, 4·6. $C_{15}H_{14}O_2NBr$ requires C, 56·25; H, 4·4%).

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