

LXXIV.—*Iodination in the Carbazole Series.*

By STANLEY HORWOOD TUCKER.

OXIDATION of carbazole brought about the formation of the two dicarbazyls described by Perkin and Tucker (J., 1921, **119**, 216). Attempts to synthesise these compounds and their possible isomerides have led to the preparation of iodo-derivatives of carbazole and of its alkyl and acyl compounds. Except the iodo-compounds described by Stevens and Tucker (J., 1923, **123**, 2146) and Tucker (J., 1924, **125**, 1144), the only one prepared was di-iodocarbazole (Classen, D.R.-P. 81929, 1894). Classen's description of it is inaccurate.

3-Iodocarbazole has been synthesised from 3-aminocarbazole (Tucker, *loc. cit.*). It has now been obtained directly from carbazole by the action of potassium iodide and iodate in glacial acetic acid solution, working according to the equation $3C_{12}H_9N + 2KI + KIO_3 + 3CH_3 \cdot CO_2H = 3C_{12}H_8NI + 3H_2O + 3CH_3 \cdot CO_2K$, except that potassium iodate and acetic acid are used in excess. The iodine at first liberated is gradually used up and the solution finally becomes colourless. The 3-iodocarbazole so obtained is mixed with considerable quantities of di-iodocarbazole. Much of the 3-iodocarbazole can be separated by crystallisation, but to obtain the di-iodocarbazole it is necessary to utilise the acetyl or benzoyl derivative.

The di-iodocarbazole described by Classen, and prepared by a different method from the above, was alleged to be yellow, and to melt at 184° ; repetition of his work gave only colourless di-iodocarbazole, m. p. $202-204^\circ$. The di-iodocarbazole is almost cer-

tainly 3 : 6-di-iodocarbazole by analogy with other disubstitution products of carbazole.

Iodination of 9-methyl and 9-ethylcarbazole by the above method likewise gives the respective 3-iodo- and di-iodo-compounds.

Like carbazole and the 9-alkylcarbazoles, 9-benzoylcarbazole may be iodinated by means of potassium iodide and iodate in glacial acetic acid to give a corresponding yield of its 3-iodo-derivative, but the discharge of the iodine coloration is much less rapid, *viz.*, 10 minutes for carbazole (less for the 9-alkylcarbazoles) and 75 minutes for 9-benzoylcarbazole. Incomplete iodination of 9-toluene-*p*-sulphonylcarbazole took place under similar conditions in 2 hours. Iodination of 9-acetylcarbazole did not proceed to any appreciable extent. Judged, therefore, by this process of iodination, resistance to replacement of hydrogen in the carbazole nucleus increases in the order 9-alkylcarbazoles, carbazole, 9-benzoyl-, 9-toluene-*p*-sulphonyl-, and 9-acetyl-carbazole. All may be iodinated by the action of the more vigorous iodinating reagent, iodine and nitric acid in glacial acetic acid (Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 292). The 9-alkylcarbazoles and carbazole give at once idonitro-compounds.

There is no evidence of the formation of any 1-iodo-derivatives.

EXPERIMENTAL.

Iodination of Carbazole.—(i) *Using potassium iodide and potassium iodate in glacial acetic acid.* Pure * carbazole (16.7 g.) was dissolved in boiling glacial acetic acid (250 c.c.), and potassium iodide (11 g.) added. The solution was cooled somewhat, finely-powdered potassium iodate (16 g., *i.e.*, approximately twice the amount theoretically required) added, and the mixture then boiled until it acquired a clear straw-coloured tint (10 minutes). The hot solution was decanted from the undissolved potassium iodate and allowed to cool slowly to 45°. The faintly brown, nacreous plates which separated were rapidly filtered off and recrystallised from glacial acetic acid (or alcohol), the solution being allowed to cool to 45° and filtered as before from the white, nacreous plates (10—12 g.) of 3-iodocarbazole, m. p. 192—194°. From the united filtrates, on standing, there separated 3 : 6(?)*-di-iodocarbazole*, m. p. 202—204° (Found : I, 60.6. C₁₂H₇NI₂ requires I, 60.6%), but since the

* The yield of 3-iodocarbazole is considerably diminished if the carbazole used is impure. Pure carbazole exhibits a faint violet fluorescence, and melts at 238° when the melting point is taken in the usual way with a long emergent stem; when taken with a short Anschütz thermometer having the stem immersed, the m. p. is 245° (compare Graebe and Glaser, *Ber.*, 1872, **5**, 12; Täuber, *ibid.*, 1891, **24**, 2597; Kirby, *J. Soc. Chem. Ind.*, 1921, **40**, 274*t*; Senseman and Nelson, *Ind. Eng. Chem.*, 1923, **15**, 382).

quantity was very small it was found better to proceed thus : The united filtrates were poured into water and the white precipitate was dried (16.5 g.). Crystallisation of this product from various solvents did not raise the melting point above 160°. Accordingly, the material was boiled with acetic anhydride and a trace of concentrated sulphuric acid. After a short time, a white, crystalline precipitate suddenly separated. It was washed with boiling glacial acetic acid and recrystallised several times from benzene. 3 : 6(?) -*Di-iodo-9-acetylcarbazole* was thus obtained in long, colourless needles, grouped in porcupine-like tufts, m. p. 224—225° (Found : I, 55.4. $C_{14}H_9ON_2$ requires I, 55.1%). The acetic anhydride filtrate was poured into water, and the precipitate produced was crystallised from glacial acetic acid. Colourless needles separated in rosettes very like those of 3-iodo-9-acetylcarbazole (m. p. 145—147°), but repeated crystallisation from glacial acetic acid, alcohol, and benzene—light petroleum failed to raise the melting point above 133—137°. However, by boiling this material with alcoholic potassium hydroxide solution for a few minutes, pouring into water, and recrystallising the precipitate from glacial acetic acid as described under the isolation of 3-iodocarbazole, a good yield of pure 3-iodocarbazole was obtained.

The separation of 3-iodocarbazole and 3 : 6-di-iodocarbazole can also be effected by benzylation.* The product (16.5 g., obtained after removal of 3-iodocarbazole by preliminary crystallisation) was dissolved in acetone (100 c.c.), and powdered potassium hydroxide (12 g.) added. The mixture was boiled, allowed to cool slightly, and benzoyl chloride (10 c.c.) added slowly; a vigorous reaction took place. The liquid was swirled round after each addition of benzoyl chloride, but not shaken vigorously until the end; it was then poured into water. The pale brown oil at first precipitated, which solidified to a pasty, white solid, was dissolved in acetone. The crystals which separated were much less soluble in acetone than the crude material, and were best recrystallised

* The method of benzylation of carbazole (Stevens and Tucker, *loc. cit.*, p. 2146) proceeds as given for the quantities used, but with larger quantities of carbazole (16.7 g., *e.g.*) vigorous shaking must be avoided; the liquid, after addition of benzoyl chloride, should be gently swirled, and only shaken finally. (The author is indebted to Mr. A. Kent, M.A., B.Sc., of this Department, for this observation.) To separate 9-benzoylcarbazole from unchanged carbazole, the mixture is dissolved in benzene and allowed to cool; carbazole then separates, and more is obtained by concentrating the filtrate to half-bulk. The benzene (in which 9-benzoylcarbazole is very soluble) is evaporated and the residue crystallised from much alcohol. Pure 9-benzoylcarbazole, m. p. 98°, is obtained. If carbazole is not thus removed, the m. p. of the product does not rise above 90° even after repeated crystallisation. The above applies generally to all benzoylations described in this paper.

from pyridine to which a drop of water was added, or from carbon tetrachloride, giving 3 : 6-di-iodo-9-benzoylcarbazole, m. p. 204—205° (Found : I, 48.9. $C_{19}H_{11}ONI_2$ requires I, 48.6%). Concentration of the acetone filtrate gave a further crop, the total yield of pure material being 3.2 g. The very concentrated acetone filtrate deposited 3-iodo-9-benzoylcarbazole (0.8 g.), m. p. 145—146° (Found : I, 31.9. $C_{19}H_{12}ONI$ requires I, 32.0%). A thick, brown oil was left. When macerated with cold glacial acetic acid, much dissolved ; but a yellow powder remained insoluble. After several crystallisations from carbon tetrachloride or light petroleum, it melted at 184—186°, but appears to be 3-iodocarbazole (0.2 g.).

(ii) *Using iodine and yellow mercuric oxide in alcohol* (Classen, *loc. cit.*). Classen's procedure was followed as described, then the product was recrystallised three times from carbon tetrachloride, and red crystals were obtained, m. p. 201—204°. These were boiled in glacial acetic acid with animal charcoal, and recrystallised from alcohol in colourless, long, rectangular laminæ of 3 : 6-di-iodocarbazole, m. p. 202—204°.

3-Iodo-9-acetylcarbazole.—The best method of preparing this compound is acetylation of 3-iodocarbazole (Tucker, *loc. cit.*); but it is readily prepared from 9-acetylcarbazole thus : 9-Acetylcarbazole (2 g.) and iodine (1 g.) were dissolved in glacial acetic acid (40—50 c.c.), the solution cooled to about 60°, and a solution of 2 c.c. of concentrated nitric acid in 8 c.c. of glacial acetic acid added drop by drop. When 1 c.c. of the solution had been added, the mixture was boiled and the addition of the nitric acid solution continued at intervals during the boiling until the iodine coloration had just vanished. Yellow crystals separated on cooling. They recrystallised from glacial acetic acid, and from alcohol, in colourless crystals, slightly soluble in light petroleum. Attempts to iodinate 9-acetylcarbazole by means of iodide and iodate, as for the iodination of carbazole, showed that after several hours' boiling some iodine had been used up, but no iodo-compounds could be isolated.

3 : 6(?)*-Di-iodo-9-acetylcarbazole* was prepared from 3 : 6(?)*-di-iodocarbazole* by boiling with acetic anhydride containing a trace of concentrated sulphuric acid. The solution set at once to a pure white solid, which crystallised from benzene, much glacial acetic acid, or alcohol in clusters of long needles, m. p. 224—225°. It was readily hydrolysed by boiling alcoholic potassium hydroxide solution to 3 : 6-di-iodocarbazole.

3-Iodo-9-benzoylcarbazole was prepared (a) from 3-iodocarbazole by the method described under the separation of 3-iodocarbazole and 3 : 6-di-iodocarbazole. Using theoretical quantities (2.9 g. of 3-iodocarbazole, 1.4 g. of benzoyl chloride, and 0.6 g. of solid

potassium hydroxide in 20 c.c. of acetone), the yield was practically as good. Twenty-five per cent. of the 3-iodocarbazole was recovered ; (b) from 9-benzoylcarbazole—(i) 9-Benzoylcarbazole (4 g.), potassium iodide (1.6 g.) and potassium iodate (excess) in glacial acetic acid (40 c.c.) were boiled until the solution became colourless (1¼ hours). It was then decanted from unchanged iodate into water, and the salmon-pink, powdery solid recrystallised from acetone. The yield of pure 3-iodo-9-benzoylcarbazole was 2.2 g. A small amount, m. p. 201°, was obtained from the residues by crystallisation from pyridine. It is therefore probably 3 : 6-di-iodo-9-benzoylcarbazole : (ii) 9-Benzoylcarbazole (5.4 g.) and iodine (2.5 g.) were dissolved in glacial acetic acid (100 c.c.), and a solution of nitric acid in acetic acid was added as in the preparation of 3-iodo-9-acetylcarbazole. The solution became clear in about 20 minutes, was poured into water, and the precipitated yellow solid crystallised from pyridine with addition of a drop of water. The crystals so obtained dissolved in alcohol except a small amount of insoluble, white substance, which, after recrystallisation from pyridine, melted at 204—205° and was 3 : 6-di-iodo-9-benzoylcarbazole. The alcoholic filtrate therefrom deposited 3-iodo-9-benzoylcarbazole. It crystallised well from alcohol, but the crystals were ill-defined and resembled seaweed in shape and arrangement. On certain occasions when the alcoholic solutions were left standing, the crystals assumed a plate shape, but this could not be repeated at will. The acetone solution of 3-iodo-9-benzoylcarbazole deposited clusters of very long needles, which could be removed and were stable out of the solution, whereas the crystals remaining in solution, if scratched, immediately changed into thick, six-sided plates. The acetone solution usually deposited a mixture of needles and plates. Pyridine, in which it is very soluble, and light petroleum, in which it is soluble with difficulty, also gave plate crystals. It is sparingly soluble in glacial acetic acid, but crystallisation therefrom does not purify the substance. Benzene and carbon tetrachloride solutions gave small, colourless crystals. The two crystalline forms mentioned above melted at 145—146°, and a mixed m. p. was unchanged. The substance is therefore dimorphic. Exposure to light turns it faintly brown ; a property possessed also by 9-benzoylcarbazole. It is readily hydrolysed to 3-iodocarbazole by alcoholic potassium hydroxide solution.

3 : 6-Di-iodo-9-benzoylcarbazole.—3 : 6-Di-iodocarbazole (1 g.) was treated with benzoyl chloride (0.6 g.) and potassium hydroxide (0.5 g.) in acetone (20 c.c.) in the usual way. 3 : 6-Di-iodo-9-benzoylcarbazole was precipitated, and after washing with hot acetone, in which 3 : 6-di-iodocarbazole is very soluble, was obtained

pure (0.8 g.), m. p. 204—205°. A mixed m. p. with 3 : 6-di-iodo-carbazole (m. p. 202—204°) was much lower. It crystallises best from a dilute solution in pyridine, to which a few drops of water are subsequently added, in long rods. It is much less soluble in carbon tetrachloride, and soluble with difficulty in acetone, from which microcrystals are obtained. It is readily hydrolysed by alcoholic potassium hydroxide solution to 3 : 6-di-iodocarbazole.

3-Iodo-9-toluene-*p*-sulphonylcarbazole was prepared thus : (i) 3-Iodocarbazole (1.5 g.), toluene-*p*-sulphonyl chloride (1.0 g.), and potassium hydroxide (0.3 g.) in acetone (10 c.c.) were boiled together for 10 minutes, and poured into water. The precipitated solid crystallised from alcohol, in which it was sparingly soluble, in colourless, diamond-shaped rhombs (1.3 g.), m. p. 170—171° (Found : I, 28.5. $C_{19}H_{14}O_2NIS$ requires I, 28.4%). 3-Iodocarbazole (0.3 g.) was recovered from the alcoholic filtrate. 3-Iodo-9-toluene-*p*-sulphonylcarbazole is easily soluble in cold pyridine, hot acetone, benzene, glacial acetic acid, ethyl acetate, aniline, or carbon tetrachloride, and less soluble in light petroleum, from all of which it crystallises, but best from acetone, benzene, alcohol-acetone, or alcohol-pyridine. (ii) 9-Toluene-*p*-sulphonylcarbazole* (2.6 g.) and iodine (0.8 g.) were dissolved in glacial acetic acid (50 c.c.), and a solution of nitric acid in glacial acetic acid (usual strength) was slowly added to the boiling solution. In 10 minutes, about 3 c.c. of the nitric acid solution had been added, and the solution was free from iodine coloration. The pale yellow solution poured into water gave a canary-yellow solid, which was extracted with alcohol. A white, insoluble portion crystallised from much glacial acetic acid in colourless needles, m. p. 257°. It is 3 : 6-di-iodo-9-toluene-*p*-sulphonylcarbazole (Found : I, 43.7. $C_{19}H_{13}O_2NI_2S$ requires I, 44.3%). The alcoholic extract deposited impure 3-iodo-9-toluene-*p*-sulphonylcarbazole, a substance melting at 175°, and colourless rods melting at 118—121° (Found : I, 11.4; *M*, by Rast's method, 334. A mixture of 9-toluene-*p*-sulphonylcarbazole and 3-iodo-9-toluene-*p*-sulphonylcarbazole, $C_{19}H_{15}O_2NS + C_{19}H_{14}O_2NIS$, requires I, 16.5%; *M*, 384).

(iii) 9-Toluene-*p*-sulphonylcarbazole (1 g.) was boiled with potassium iodide (0.34 g.) and excess of potassium iodate in glacial acetic acid (10 c.c.) for several hours, but the iodine coloration did not disappear. In another experiment, using half the quantity of

* Compare footnote on benzylation of carbazole. Application of the same method of removal of carbazole after preparation of 9-toluene-*p*-sulphonylcarbazole produced the latter in large, colourless, prismatic crystals, softening at 128°, and giving a clear melt at 133° (compare Cassella, D.R.-P. 224951, 1909; Herz, A.P. 966092, 1910).

potassium iodide, the colour was discharged in $2\frac{1}{4}$ hours and a nearly theoretical yield of the substance (m. p. 118—121°) mentioned under (ii) was obtained.

3 : 6 - *Di - iodo - 9 - toluene - p - sulphonylcarbazole*.—9-Toluene-*p*-sulphonylcarbazole (2.5 g.), iodine (2.0 g.), and glacial acetic acid (50 c.c.) were boiled together during addition of nitric acid in acetic acid (usual strength) until the iodine colour disappeared (45—60 minutes). Before the colour had vanished, needle-shaped crystals began to separate. The mixture was allowed to cool; the separated crystals crystallised from glacial acetic acid and then from benzene in tetrahedral prisms, m. p. 257°. It is only slightly soluble in glacial acetic acid, carbon tetrachloride or acetone, but readily soluble in hot benzene.

Iodination of 9-Methylcarbazole.—The methylation of 3-iodo-carbazole has been described (Stevens and Tucker, *loc. cit.*, 2146). Iodination of 9-methylcarbazole was effected as follows: 9-Methylcarbazole (0.8 g.), potassium iodide (0.47 g.), and excess of potassium iodate were boiled in glacial acetic acid (10 c.c.) for 2 minutes, in which time a green solution was obtained. By the usual treatment there were separated in small quantity by means of alcohol 3-iodo-9-methylcarbazole and a product, m. p. 181°. The latter is 3 : 6-*di-iodo-9-methylcarbazole* (Found: I, 58.6. $C_{13}H_9NI_2$ requires I, 58.7%). It was also prepared by the action of methyl sulphate on 3 : 6-di-iodocarbazole in presence of acetone and solid potassium hydroxide. It is readily soluble in glacial acetic acid, very sparingly soluble in alcohol, and, although sparingly soluble, crystallises from acetone in long, thin rods, m. p. 181—182°.

Iodination of 9-Ethylcarbazole.—9-Ethylcarbazole (19.5 g.) and potassium iodide (11.0 g.) were dissolved in glacial acetic acid (200 c.c.), and potassium iodate (16 g.) was added in portions to the hot solution. A gentle reaction set in, and the colour soon gave place to green. The solution was poured into water, and a pasty solid possessing a silky sheen was deposited. This was dissolved in excess of glacial acetic acid. In sufficiently dilute solution, no oil separated, but impure green crystals (11 g.), m. p. 71°. The filtrate from these on concentration deposited colourless crystals, m. p. 80° (3.5 g.). By further concentration, a final crop (5.5 g.) of green crystals, m. p. 140—144°, was obtained. The crystals, m. p. 80°, were purified by recrystallisation from glacial acetic acid or alcohol, and separated in long needles, m. p. 83—84°, identical with 3-iodo-9-ethylcarbazole (Stevens and Tucker, *loc. cit.*). The green crystals, m. p. 140—144°, crystallised from much glacial acetic acid and finally from alcohol in colourless needles, m. p. 152—153°, and were shown to be 3 : 6-*di-iodo-9-ethylcarbazole* (Found :

I, 56.9. $C_{14}H_{11}NI_2$ requires I, 56.8%). It is only slightly soluble in alcohol or in glacial acetic acid.

3-Iodo-9-isopropylcarbazole was prepared by Mr. W. H. Chalmers, B.Sc., A.I.C., by boiling a mixture of 3-iodocarbazole (2 g.), isopropyl iodide (4 g.), and potassium hydroxide (2 g. in 1 c.c. of water) in acetone (6 c.c.) for 6 hours. The usual procedure, and crystallisation of the product from glacial acetic acid, gave white, silvery leaflets, m. p. 95—97° (Found: I, 38.2. $C_{15}H_{14}NI$ requires I, 37.9%).

3-Iodocarbazole could not be obtained from carbazole by the action of iodine and nitric acid in glacial acetic acid. It crystallises well from light petroleum, and is very soluble in benzene, pyridine, or acetone. As already stated, it is best crystallised from carbon tetrachloride or glacial acetic acid.

3:6-Di-iodocarbazole, isolated in small yield in the iodination of carbazole, was prepared from carbazole by method (i), using twice the quantity of potassium iodide used to obtain monoiodocarbazole, and proceeding as before. Purification of the pink product was difficult, but it was effected as given under the mercuric oxide experiment, method (ii). It was found best, in order to obtain pure 3:6-di-iodocarbazole, to acetylate or benzoilate the material (as described above), and hydrolyse the product with alcoholic potassium hydroxide solution. 3:6-Di-iodocarbazole is very soluble in acetone. It crystallises best from glacial acetic acid or alcohol, in long laminæ.

UNIVERSITY OF GLASGOW.

[Received, November 13th, 1925.]
