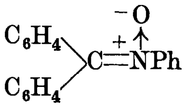
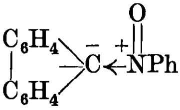
NOTES.

A Reaction of Fluorene. By ANTHONY JAMES HAILWOOD and ROBERT ROBINSON.

FLUORENE condenses with nitrobenzene in the presence of metallic sodium with the formation of an azoxymethine (I or II) which may be termed *fluorenylideneaniline oxide.*


(I.)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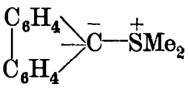

(III.)

We prefer formula (I) as being the more natural and the more closely related to the azoxy-compounds and the nitro-compounds themselves, but (II) is not quite out of the question in view of the analogous substance (III) obtained by Ingold and Jessop (J., 1930, 713).

In any case it is evident that sodiofluorene does not react with nitrobenzene in analogous fashion to potassiocarbazole, which furnishes *p*-nitrophenylcarbazole (G. and M. de Montmollin, *Helv. Chim. Acta*, 1923, **6**, 94).

Hydrolysis of the azoxymethine by means of boiling 40% sulphuric acid affords fluorenone and, probably, *p*-aminophenol. Reduction gives fluorenylaniline (Staudinger and Gaule, *Ber.*, 1916, **49**, 1951), which we have also prepared from fluorenyl chloride.

Fluorenylideneaniline Oxide (I).—Fluorene (16·6 g.) was added to a suspension of finely granulated sodium (2·3 g.) in xylene (50 c.c.) and, after the introduction of nitrobenzene (100 c.c.), the mixture was heated on the steam-bath for 8 hours. It was then cooled and poured into water (1200 c.c.), the liquid filtered, and the xylene and nitrobenzene removed by distillation in steam. The aqueous solution was decanted from the plastic residue, which was extracted with boiling alcohol (600 c.c.) and the extract concentrated to 150 c.c., cooled, and filtered. The filtrate was added to an equal volume of water, and the red spongy precipitate was collected and triturated with ether, which dissolved the red impurity. The crude *azoxymethine* crystallised from alcohol in transparent yellow needles (3·5 g.), m. p. 193° (Found : C, 84·1; H, 5·0; N, 5·2; *M*, in camphor, 279, 280. $C_{19}H_{13}ON$ requires C, 84·2; H, 4·8; N, 5·2%; *M*, 271). It was devoid of basic or acidic properties, and when 1 g. was refluxed for ½ hour with 40% sulphuric acid (25 c.c.), fluorenone was produced; it was isolated by means of benzene and recognised by its m. p. and properties. The aqueous acid solution exhibited the reactions of a solution of *p*-aminophenol, but this substance was not isolated.

Fluorenylaniline.—(A) Solutions of fluorenylideneaniline oxide (1 g.) in alcohol (60 c.c.) and of sodium hydrosulphite (6 g.) in water (40 c.c.) were mixed and refluxed for 10 hours. On cooling, fluorenylaniline separated in colourless needles, m. p. 122—123°.

(B) A mixture of fluorenyl chloride (3·2 g.), anhydrous sodium acetate (2·5 g.), aniline (10 c.c.), and *iso*amyl alcohol (50 c.c.) was refluxed for 6 hours. The residue after steam distillation crystallised from alcohol in long colourless needles, m. p. 121—123° (Found : N, 5·5. Calc. for $C_{19}H_{15}N$: N, 5·5%).

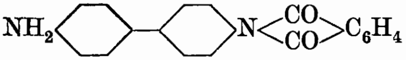
The *acetyl* derivative crystallised from alcohol in lozenge-shaped plates, m. p. 177° (Found : N, 4·9. $C_{21}H_{17}ON$ requires N, 4·7%). The *nitroso*-derivative crystallised in buff needles, m. p. 104° (Found : N, 9·6. $C_{19}H_{14}ON_2$ requires N, 9·8%).

The authors wish to thank Imperial Chemical Industries Limited for permission to publish these results.—BRITISH DYESTUFFS CORPORATION, LIMITED, BLACKLEY, MANCHESTER. [*Received, February 17th*, 1932.]

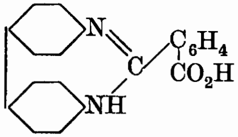
The Configuration of Phthalylbenzidine. By Eustace Ebenezer Turner.

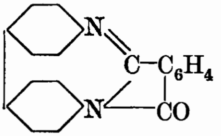
Le Fèvre and Turner (J., 1926, 2476) showed that monophthalylbenzidine, obtained by Koller (*Ber.*, 1904, **37**, 2880) by boiling an aqueous suspension of benzidine and phthalic anhydride, was *N*-4(4′-aminodiphenylyl)phthalimide (I), but Guglialmelli, Chanussot, and Ruiz (*Anal. Asoc. Quim. Argentina*, 1930, **18**, 257) conclude that the primary product of the above condensation is (II), this substance being very readily converted into (III), *e.g.*, by mere crystallisation from *cyclo*hexanol, their main point being that the crude condensation product dissolves slowly in 1% aqueous sodium hydroxide at 60—80°, the solution on acidification giving a precipitate of the substance they regard as (II). They stated that this substance could not be diazotised in dilute hydrochloric acid solution, which corresponds with (II).

(I.)



(II.)





(III.)

The present author finds that the condensation product does dissolve in warm stirred 1% sodium hydroxide solution, either before or after being crystallised from *cyclo*hexanol, provided it is finely ground. Acidification of the solution obtained gives a gelatinous white precipitate, corresponding to the iminazole acid of Guglialmelli, Chanussot, and Ruiz. These authors attempted the diazotisation of their product in dilute hydrochloric acid, but their test would fail if applied to most weak bases. If sodium nitrite is added to a solution of the sodium salt, and the mixture is poured into dilute hydrochloric acid, diazotisation proceeds rapidly, and the suspension obtained couples excellently with β-naphthol in alkaline solution. The alkaline solution therefore contains the sodium salt of the phthalamic acid,

$$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

produced by scission of the imide ring in (I), and the gelatinous precipitate is the corresponding acid.

Preparation of Phthalylbenzidine from Benzidine Phthalate.—Benzidine phthalate was prepared by dissolution of benzidine (1 mol.) in a boiling aqueous solution of 1 mol. of phthalic acid, filtration, and cooling. After being dried at 100°, it contained acid and base in molecular proportion.

(1) The salt (20 g.) was added during 5 minutes to 100 c.c. of *cyclo*hexanol, kept gently boiling. The solution was boiled for a further 5 minutes; then it suddenly became a paste. Alcohol was rapidly added, and the suspension was cooled. Filtration, followed by washing with alcohol and drying of the solid at 100°, gave 11 g. of phthalylbenzidine, m. p. 303°. This was identified by conversion into the benzylidene and salicylidene derivatives, these being identified in turn by hydrolysis with boiling 75% sulphuric acid.

(2) Benzidine phthalate was heated until water was no longer given off. The greenish-brown liquid set to a crystalline mass of phthalylbenzidine on cooling.

The materials used in this work were purchased with a grant for which the author is indebted to the Royal Society.—BEDFORD COLLEGE, UNIVERSITY OF LONDON. [*Received, February 3rd*, 1932.]