

472. A Study of Diazo-compounds by Use of Nitrogen Isotopes. Part I. The Structure of the Diazonium Ion.

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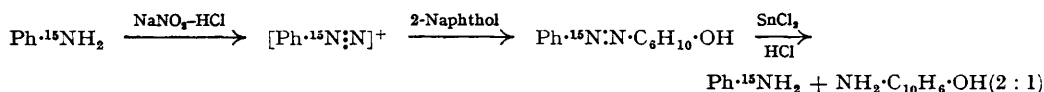
The non-equivalence of and absence of interchange between the nitrogen atoms of a diazonium ion has been demonstrated by diazotising isotopically labelled aniline, coupling the diazonium salt, and regenerating the aniline by reduction of the azo-compound.

THE diazonium ion is considered to have a structure similar to that of the ammonium ion but with an atom of nitrogen replacing three hydrogen atoms, a structure requiring the non-equivalence of the two nitrogen atoms. This non-equivalence has been demonstrated experimentally as a preliminary stage in the study of diazo-compounds in which one nitrogen atom is isotopically labelled.

A diazonium salt prepared from ^{15}N -labelled aniline and unlabelled sodium nitrite, was coupled with 2-naphthol. The amine hydrochlorides formed when the resulting azo-compound was reduced were separated, and a sample of nitrogen from each was prepared and analysed in the mass spectrograph. The complete synthesis was thrice repeated. In two of these later

Expt.	1 (preliminary run).	2.	3.	4.
Time between diazotisation and coupling (hrs.)	0	0	8	24
Aniline hydrochloride: ^{15}N atom-% excess	31.33	32.47	32.43	32.74
1-Amino-2-naphthol hydrochloride: ^{15}N atom-% excess ...	1.628	3.987	2.072	1.777
Atom-% ^{15}N in phthalimide: Found, 32.36.				

experiments the diazonium salt was stored for several hours at 0° before coupling so that any slow interchange between the nitrogen atoms might become apparent. The analyses (see Table) suggest that the reactions proceed according to the scheme shown and that interchange is absent or immeasurable.



Labelled aniline has been previously synthesised by Allen and Wilson (*J. Amer. Chem. Soc.*, 1943, 65, 611) and by Fones and White (*Arch. Biochem.*, 1949, 20, 118) from ammonia. The yield from phthalimide (92%) is similar to that obtained by Fones and White from ammonia, and the route described may be preferable because of its simplicity.

EXPERIMENTAL.

Labelled Anthranilic Acid.—Potassium phthalimide (1.00 g.; ^{15}N atom-% excess nominally 33), followed immediately by sodium hydroxide (1.07 g. in 3.3 ml. of water), was added to cold hypobromite solution (0.4 ml. of bromine added to 1.2 g. of sodium hydroxide in 5 ml. of water at 0°). The solution was heated for 2 minutes at 80° , cooled in ice, and neutralised by dropwise addition of hydrochloric acid (approx. 2.5 ml.). The anthranilic acid was precipitated by 1 ml. of glacial acetic acid, filtered off (filter-stick), washed with water, and vacuum-dried. It was not purified.

Labelled Aniline.—The anthranilic acid was transferred to a bulb-to-bulb distillation unit and kept at 210° in an electrically heated block. Aniline distilled into the cool bulb (yield, 0.46 g.).

Labelled 1-Benzeneazo-2-naphthol.—The aniline was dissolved in 2 ml. of diluted hydrochloric acid (1 : 1) and 40% sodium nitrite solution was added dropwise until free nitrous acid was detected. The solution was added to 0.6 g. of 2-naphthol in 3 ml. of 10% sodium hydroxide, and the precipitated azo-compound was filtered off, washed with water, and vacuum-dried (0.83 g., crude).

Reduction.—The 1-benzeneazo-2-naphthol, in alcohol (10 ml.), was boiled under reflux for 30 minutes with stannous chloride (2 g.) in concentrated hydrochloric acid (6 ml.) and the solution was decanted. On cooling, 1-amino-2-naphthol hydrochloride crystallised and was separated by aid of a filter-stick (0.45 g.). The filtrate was made alkaline and steam-distilled. From the acidified and concentrated distillate aniline hydrochloride crystallised (0.106 g.), m. p. 196—198°. Nitrogen samples for mass-spectrographic analysis were prepared from the amines (Rittenberg, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Michigan, 1948, p. 31).

DISCUSSION.

The synthesis of labelled compounds must necessarily be carried out on small quantities, and the final yields in the present series were small. From the reduction mixture of amines, separation of pure aniline is readily accomplished by steam-distillation, but complete purification of the amino-naphthol is impracticable on the small quantities involved. The values for the isotope ratios in the regenerated aniline were consistent; those for the aminonaphthol were less so, owing, presumably, to contamination of the aminonaphthol with aniline. The results in the table show that the nitrogen in the regenerated aniline had a similar isotope ratio to that of the starting material. This confirms the non-equivalence of the nitrogen atoms in the diazonium group, demonstrates the absence of interchange between them, and proves that the diazonium group is attached to the phenyl group throughout the synthesis.

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