The Absence of Rearrangement in the Conversion of Benzene-n-*diazoate into the* iso*Diazoate, demonstrated by the Use of Isotopic Nitrogen.*

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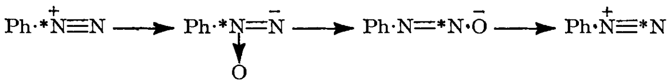
It has been shown by the tracer technique that in the *n*- and the *iso*-diazoate the same nitrogen atom is attached directly to the benzene nucleus.

For many decades the controversy as to whether the isomerism of the aromatic diazo-compounds is of a structural or a geometrical type remained unsettled. During the last few years, however, largely through the physical measurements made by Le Fèvre and his collaborators, Hantzsch's geometrical hypothesis has been upheld for the diazocyanides (see Campbell, *Ann. Reports*, 1947, **44**, 134) and the diazosulphonates (Freeman and Le Fèvre, *J.*, **1951**, 415); and hence, by analogy rather than through the accumulation of further experimental evidence, the geometrical isomerism of the *n*- and the *iso*-diazoates has become more widely accepted. So far as the structural isomerism of the latter is concerned, Bamberger's theory is unacceptable on present day views of valency, while Angeli's theory has received comparatively little attention, one of its chief drawbacks being that it involves postulating migration of an oxygen atom from one nitrogen atom to the other, for which neither analogy nor experimental support appears to have been brought forward. However, the work of Farrar and Gulland (*J.*, 1944, 368) suggested that the hydrolysis of azoxysulphones gives rise to an *n*-diazoate as primary product, which would imply oxygen transfer on either Hantzsch's or Angeli's theory, and merit further consideration of the latter.

There seems, however, to be an alternative possibility, namely, that it is the phenyl group, rather than the oxygen atom, which migrates, in which case one might have the scheme :



$$\mathrm{Ph{\cdot}{}^{*}\overset{+}{N}{\equiv}N} \longrightarrow \mathrm{Ph{\cdot}{}^{*}\underset{\substack{\downarrow\\ O}}{N}{=}\overset{-}{N}} \longrightarrow \mathrm{Ph{\cdot}N{=}{}^{*}N{\cdot}\overset{-}{O}} \longrightarrow \mathrm{Ph{\cdot}\overset{+}{N}{\equiv}{}^{*}N}$$

This has, however, been disproved by the tracer technique.

Holt and Bullock (*J.*, 1950, 2310) prepared a diazonium solution from [^{15}N]aniline and sodium [^{14}N]nitrite, coupled this with 2-naphthol, separated the two amines formed by reduction of the azo-compound, and showed that the aniline hydrochloride was enriched in ^{15}N, while the 1-amino-2-naphthol hydrochloride was enriched to a much lesser degree. (The fact that it was enriched at all was attributed to contamination with aniline hydrochloride.) This work has been repeated; and the conditions recorded in the Experimental section were found to give a much more satisfactory separation, as seen from the results in the Table.

The experiment was then repeated; but the diazonium salt was converted into potassium *iso*diazoate, which was isolated in the crystalline form, acidified to reconvert it into the diazonium chloride, and then coupled as before. In both experiments it was found that the aniline hydrochloride produced was enriched in ^{15}N to approximately the same extent as the starting aniline hydrochloride, and the 1-amino-2-naphthol was not appreciably enriched. These two experiments prove that in the *n*- and the *iso*-diazoate the same nitrogen atom is attached directly to the benzene nucleus, it being assumed that no rearrangement occurs in the transformation of *iso*diazoate into diazonium salt.

	^{15}N Excess (%)		
Compound	Original	Formed by coupling with *n*-diazoate	Formed by coupling with *iso*diazoate
Aniline hydrochloride	9·93	9·91	9·64
1-Amino-2-naphthol	—	0·06	0·02

EXPERIMENTAL

Isotope Analysis [by P. KELLY].—The isotopic enrichments were determined by the use of a Metropolitan Vickers Type M.S.2 mass spectrometer on nitrogen samples prepared from amines in the way described by Rittenberg, Keston, Rosebury, and Schoenheimer (*J. Biol. Chem.*, 1939, **127**, 291).

[^{15}N]*Aniline*.—In preference to the method of Holt and Bullock (*loc. cit.*), that of Fones and White (*Arch. Biochem.*, 1949, **20**, 118) was used, after modification so as to avoid the necessity for distilling the ammonia and of using an excess of the latter, which otherwise involves recovery. A solution of ammonium nitrate (0·8 g., containing approximately 10% excess of ^{15}N in the ammonium ion) in water was cooled in ice, treated with a solution of sodium hydroxide (0·84 g.) in water, and then shaken at room temperature for 1 hr. with a solution of benzoyl chloride (1·5 g.) in pure, dry chloroform (75 ml.). The chloroform layer was separated, and the aqueous layer extracted with several small portions of chloroform. The solvent was removed through a short fractionating column from the combined and dried (Na_2SO_4) extracts, and the residual solid was washed with a little light petroleum (b. p. 40—60°) to free it from a trace of benzoyl chloride. The yield of benzamide was 1·1 g. This was converted into aniline as described by Fones and White except that the product was isolated by steam-distillation; the acidified (hydrochloric acid) distillate was evaporated to dryness in a vacuum (water-bath), and yielded [^{15}N]aniline hydrochloride (1·05 g.).

Coupling Experiment with n-*Diazoate*.—[^{15}N]Aniline hydrochloride (0·1 g.) in water (1 ml.) containing concentrated hydrochloric acid (0·15 ml.) was diazotised by the dropwise addition of an aqueous solution of sodium nitrite until a permanent excess of nitrous acid was present. The resulting solution was poured into excess of 2-naphthol in sodium hydroxide solution; the precipitated azo-compound was collected, washed with water, and dried (0·16 g., m. p. 130°). This was heated under reflux on the water-bath with a solution of sodium dithionite (0·52 g.) in water (3 ml.) and ethanol (6 ml.), to which had been added sodium hydroxide (0·24 ml., 40% solution), until the red colour was discharged. A few drops of N-sodium hydroxide were then added to bring the pH of a mixture of a test portion of the solution with three volumes of water to approx. 8·5. The aniline was then removed by steam-distillation; approx. 30 ml. of distillate were collected, the distillation flask being heated to prevent the volume of liquid therein from increasing. After being cooled, the residue was filtered and the precipitate of 1-amino-2-naphthol (40 mg.) washed with water and dried in a vacuum. In one experiment, this base was purified by conversion into the hydrochloride; but no change in isotopic ratio was observed. The acidified (hydrochloric acid) steam-distillate was evaporated to dryness in a vacuum; the residue was dissolved in a small volume of methanol, and diluted with ether. Filtration of the cooled solution yielded aniline hydrochloride (65 mg.; m. p. 197—198°) which was washed with ether and dried.

Coupling Experiment with iso*Diazoate*.—A mixture of potassium hydroxide (1·5 g.) and water (0·5 ml.) was heated until homogeneous in a nickel crucible, then cooled in ice with stirring. To this was added, with stirring, a solution prepared by diazotisation of [^{15}N]aniline hydrochloride (0·26 g.) in water (0·5 ml.) and concentrated hydrochloric acid (0·35 ml.). When dissolution was complete, the crucible was plunged into an oil-bath at 140°, and the contents were stirred until they solidified. The crucible was then cooled to 100°, and the contents were dissolved in hot water (½ volume) and cooled. The resulting product was collected on a sintered-glass filter and extracted with a small volume of ethanol at 40°, and the filtered solution was diluted with ether and cooled to 0°. The resulting potassium benzene*iso*diazoate (0·13 g.) was collected, washed with ether, and dried in a vacuum. It was then dissolved in ice-cold water (0·2 ml.), and the resulting solution was added dropwise to stirred, ice-cold hydrochloric acid (1 ml.; 1 : 1). The resulting diazonium solution was then coupled with 2-naphthol as described above.

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