

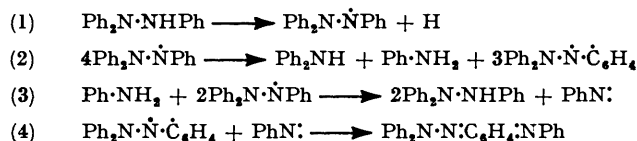
*The Thermal and Photochemical Decomposition of Triphenylhydrazine.*

By P. F. HOLT and B. P. HUGHES.

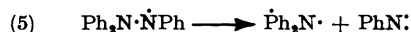
[Reprint Order No. 5867.]

[<sup>15</sup>N<sub>1</sub>]Triphenylhydrazine, when decomposed by heat, gives azobenzene in which the nitrogen atoms have a random distribution. The mechanism of this decomposition is discussed. Azobenzene is also formed when triphenylhydrazine is decomposed by light and when tetraphenylhydrazine and aniline are heated in benzene solution.

TRIPHENYLHYDRAZINE in inert solvents is decomposed by heat and by light. Wieland and Reverdy (*Ber.*, 1915, **48**, 1112) refluxed triphenylhydrazine in xylene under nitrogen, and isolated diphenylamine, azobenzene, and the highly coloured benzoquinone 1-anil 4-diphenylhydrazone, Ph<sub>2</sub>N·N:C<sub>6</sub>H<sub>4</sub>:NPh; aniline also was detected by a colour reaction. Goldschmidt (*Ber.*, 1920, **53**, 59) decomposed triphenylhydrazine in diethyl ether by irradiation "with August sunshine." After 24 hr., he isolated from the solution diphenylamine and quinone anil diphenylhydrazone but he detected neither azobenzene nor aniline. Goldschmidt found that triphenylhydrazyl, Ph<sub>2</sub>N·NPh, which he produced from triphenylhydrazine solutions by the action of oxidizing agents at -55°, also gave diphenylamine and quinone anil diphenylhydrazone when heated. He proposed, therefore, a reaction mechanism for the thermal decomposition of triphenylhydrazine which involved the formation and interaction of triphenylhydrazyl radicals:

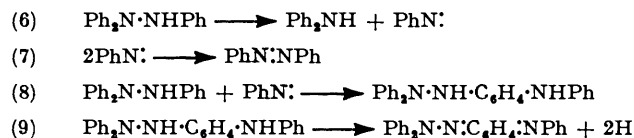


Goldschmidt rejected a sequence which was initiated by reaction (1) and followed by the fission of the triphenylhydrazyl radicals into diphenylamine and phenylimine radicals:

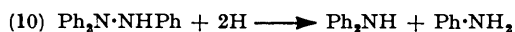


because he could not detect tetraphenylhydrazine among the products.

Wieland and Reverdy (*loc. cit.*) preferred a mechanism which was initiated by the transfer of a hydrogen atom and fission of the molecule to give diphenylamine and a phenylimine radical (6), the latter then dimerizing to give azobenzene (7) or reacting with triphenylhydrazine eventually to form quinone anil diphenylhydrazone (8) and (9):

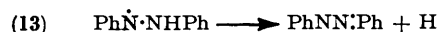
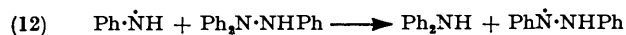
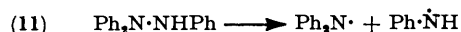


The hydrogen atoms reduce triphenylhydrazine to diphenylamine and aniline:



This mechanism is not, however, applicable to the oxidation of triphenylhydrazine in which the initial stage must involve the removal of hydrogen and the production of triphenylhydrazyl radicals.

Another mechanism can be postulated which is an extension of that proposed by Dewar (unpublished; reported by Swarc, *Chem. Rev.*, 1950, **47**, 151) for the thermal decomposition of hydrazobenzene, by assuming that the triphenylhydrazine first splits into a phenylamine radical and a diphenylamine radical (11). Azobenzene might then be formed by attack of a phenylamine radical on a molecule of triphenylhydrazine (12) and subsequent loss of hydrogen by the diphenylhydrazyl so formed (13):



We have sought fresh evidence concerning the mechanism of the decomposition of triphenylhydrazine by applying new methods for the separation of reaction products and by studying the azobenzene which is formed by the decomposition of isotopically labelled triphenylhydrazine.

Some information about the mechanism by which azobenzene is formed from triphenylhydrazine can be obtained by decomposing triphenylhydrazine which has been isotopically labelled at one nitrogen atom. This technique has been applied already to the decomposition of hydrazobenzene (Holt and Hughes, *J.*, 1953, 1666; 1955, 98). If the azo-group of a molecule of azobenzene is derived solely from one molecule of [ $^{15}\text{N}_1$ ]triphenylhydrazine, then the distribution of the nitrogen isotopes in the azobenzene will be non-random, but if the azobenzene is formed from fragments containing only one nitrogen atom, the distribution of the nitrogen isotopes in the azobenzene will be random.

The results of mass-spectrometric measurements on nitrogen samples derived from the azobenzene are expressed as the ratio of the masses ( $R$ ) ( $^{14}\text{N}\cdot^{15}\text{N}$ ) $^2$ / $(^{14}\text{N}\cdot^{14}\text{N})(^{15}\text{N}\cdot^{15}\text{N})$  which ratio, if random distribution exists, has the theoretical value 4. The results of two experiments gave values for  $R$  of 4.3 and 4.2, indicating random pairing. This result differs from that obtained when [ $^{15}\text{N}_1$ ]hydrazobenzene is decomposed photochemically or thermally to give azobenzene, as then random pairing does not occur. The mechanism which is denoted by equations (11)—(13) is not, therefore, applicable. The slight deviations from 4 of the experimental values of  $R$  are doubtless due to traces of hydrazobenzene which is also formed in the preparative reaction.

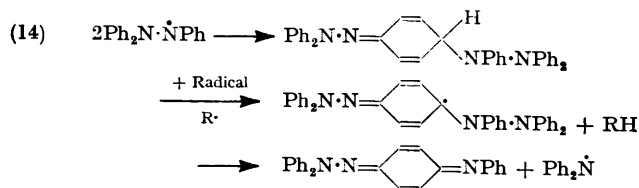
A repetition of Wieland and Reverdy's work (*loc. cit.*) confirmed that the main products of the thermal decomposition of triphenylhydrazine are azobenzene and diphenylamine. Aniline is also formed and can be detected by colour tests but in amount insufficient for isolation. The products are the same whether the decomposition is carried out in xylene, benzene, or ethanol.

Irradiation of an ethereal solution of triphenylhydrazine by ultraviolet light was found to produce diphenylhydrazine and quinone anil diphenylhydrazone, but no aniline. This result confirms Goldschmidt's report. However, contrary to Goldschmidt's findings, it was possible to isolate also a quantity of azobenzene by using chromatography. A known amount of triphenylamine was irradiated and the material was isolated and weighed so that the amount which had been decomposed could be deduced. It was apparent that thermal decomposition of triphenylhydrazine gives approximately twice as much azobenzene as does the photochemical reaction. Goldschmidt's observation that azobenzene is not formed when triphenylhydrazine is oxidized by lead dioxide was confirmed.

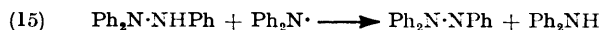
Goldschmidt considered that the thermal and the photochemical decomposition and the oxidation of triphenylhydrazine at normal temperatures were analogous, stating that the formation of azobenzene in the thermal reaction was due to the elevated temperature. His argument is no longer sound since azobenzene is also formed photochemically. Moreover, the ter- and the quadri-molecular reaction involved make the reaction mechanism proposed by Goldschmidt improbable.

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The decomposition of triphenylhydrazyl can be explained without recourse to quadri-molecular reactions by the following scheme : \*

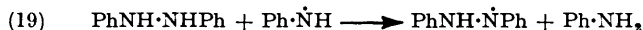
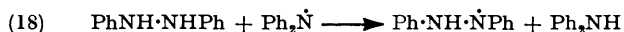
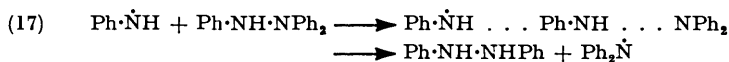


Initially the radical R· in this reaction will be triphenylhydrazyl but subsequently diphenylamine radicals also. The diphenylamine radical which is produced is removed according to equation (15) :

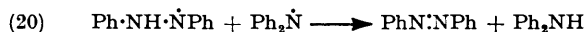


Goldschmidt's work leaves little doubt that the oxidation of triphenylhydrazine results initially in the production of triphenylhydrazyl but there is now no reason to retain this reaction as the initial stage of the photochemical and the thermal decomposition. By analogy with tetraphenylhydrazine, which readily dissociates into diphenylamine radicals (Wieland and Fressel, *Annalen*, 1912, **392**, 135), it is reasonable to assume that the initial reaction in the decomposition of triphenylhydrazine is a homolytic fission into the diphenylamine and phenylamine radicals, indicated by equation (11) above.

Both of these radicals will be stabilized by resonance. The combination of two phenylamine radicals (16) or the interaction of phenylamine radicals with triphenylhydrazine (17), would produce hydrazobenzene, which gives diphenylhydrazyl radicals with either diphenylamine radicals or phenylamine radicals.

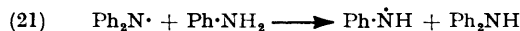


The diphenylhydrazyl radicals may react with diphenylamine radicals to give azobenzene (20) :



The diphenylamine and phenylamine radicals may in a similar way remove hydrogen atoms from triphenylhydrazine with the eventual formation of quinone anil diphenylhydrazone as described earlier in equation (14).

The absence of aniline in the photochemical reaction and the presence of only a trace in the thermal reaction may mean only that the aniline is removed by interaction with another free radical to give phenylamine radicals (21) which then take part in reaction (16) or (17) :



The feasibility of this mechanism was demonstrated by studying the action of diphenylamine radicals produced by the dissociation of tetraphenylhydrazine. When heated in benzene solution under nitrogen, tetraphenylhydrazine and aniline give azobenzene, a product which is most likely to be formed by the reaction (21) followed by reactions (16)—(20).

### EXPERIMENTAL

[<sup>15</sup>N<sub>1</sub>]Triphenylhydrazine.—The method described by Holt and Hughes (*J.*, 1954, 764) for the preparation of unlabelled material was used. [<sup>15</sup>N<sub>1</sub>]Azobenzene (500 mg.) (Holt and Hughes, *J.*, 1953, 1666) was dissolved in dry ether (20 ml.) under nitrogen and cooled to 0°. To

\* We thank a Referee for suggesting the alternative mechanism incorporated in equation (14).

this, a solution of phenyl-lithium (230 mg.) in dry ether (5 ml.) was added. The mixture was stirred for 5 min., then saturated ammonium chloride was added. The residue left on evaporation of the ethereal layer, when washed with light petroleum and recrystallized from ethanol, gave [ $^{15}\text{N}_1$ ]triphenylhydrazine, m. p. 141—142° (decomp.) (100 mg.).

*Thermal Decomposition of [ $^{15}\text{N}_1$ ]Triphenylhydrazine.*—[ $^{15}\text{N}_1$ ]Triphenylhydrazine (100 mg.) in benzene (5 ml.), in a Pyrex tube, was frozen in solid carbon dioxide and evacuated; the tube was sealed, heated for 2 hr. at 140°  $\pm$  1°, then cooled and opened. The contents were evaporated to dryness in a vacuum. The residue was dissolved in light petroleum (b. p. 40—60°), and the azobenzene (12—13 mg.) was separated by chromatography on alumina and eluted with light petroleum; it had m. p. 67—68°.

Nitrogen samples were derived from the  $^{15}\text{N}_1$ -azobenzene by the combustion procedure described by Holt and Hughes (*J.*, 1955, 95).

*Thermal Decomposition of Unlabelled Triphenylhydrazine.*—Unlabelled triphenylhydrazine (100 mg.) was similarly decomposed with a view to examining the other products of the reaction. By steam-distillation diphenylamine and the azobenzene were separated. The distillate was slightly acidified, then extracted with ether. Dry hydrogen chloride was passed through the dried ethereal solution, which contained the diphenylamine and azobenzene, and the precipitated diphenylamine hydrochloride was separated by filtration. Diphenylamine (m. p. 53—54°; 38 mg.) was obtained when the hydrochloride was washed with dilute ammonia. The quinone anil diphenylhydrazone is destroyed by steam-distillation and was not isolated.

*Photochemical Decomposition of Triphenylhydrazine.*—Triphenylhydrazine (100 mg.) in dry ether (25 ml.) under nitrogen was irradiated in a Pyrex tube with a low-pressure mercury-arc lamp (Thermal Syndicate Ltd., Type T/M5/564/0) for 24 hr. The reaction vessel and arc tube were housed in a Dewar flask. To cool the apparatus, the flask was filled with water which was constantly changed. Azobenzene (2—3 mg.; m. p. 67°) was separated as described above. The unchanged triphenylhydrazine (47 mg.) was also isolated by chromatography.

*Oxidation of Triphenylhydrazine.*—Triphenylhydrazine (100 mg.) in dry ether (10 ml.) was shaken with lead dioxide (1 g.) for 1 hr. The solution was filtered and the residue was washed with ether (10 ml.). The combined filtrate and washings were evaporated *in vacuo* and the residue was redissolved in light petroleum (b. p. 40—60°). The ethereal solution was adsorbed on alumina and eluted with more ether. No azobenzene was detected. Tests showed that 0.5 mg. of azobenzene could be detected by this procedure.

*Reaction of Aniline with Tetraphenylhydrazine.*—Tetraphenylhydrazine (1 g.) (Wieland and Gambarjan, *Ber.*, 1906, 39, 1500) was dissolved in benzene (30 ml.) under nitrogen, and freshly distilled aniline (0.2 g.) was added. The solution was refluxed for 2 hr. Azobenzene (m. p. and mixed m. p. 68°; lit., 68°) and diphenylamine (m. p. and mixed m. p. 54°; lit., 54°) were isolated by chromatography on alumina.

We are indebted to Dr. D. H. Tomlin who assayed our nitrogen samples, and to Imperial Chemical Industries Limited, Paints Division, for a grant to one of us (B. P. H.).

THE UNIVERSITY, READING.

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