[Jour. Indian Chem. Soc., Vol. 43, No. 10, 1963]

Studies in Azides. Part II. Synthesis of Some Substituted 1,2,3-Triazoles

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A few phenylazides have been allowed to react with acetylene and phenylhydrazine to yield 1-aryl-1,2,3-triazoles and substituted 2-phenyl-1,2,3-benzotriazoles respectively.

Preparation of 4-chloro-2,6-dinitro-(I), 2-chloro-4,6-dinitro-(II), 4-bromo-2,6-dinitro-(III), 2,4,6-trinitro-3-methyl-(IV), 2-iodo-4-nitro-(V), and 4-iodo-2-nitro-(VI) phenylazides and their characteristics have been described previously[1]. During the present investigation their reactions with acetylene and phenylhydrazine have been studied.

When the nitrophenylazides (I-VI) are allowed to react with acetylene in acetone, the azido group adds to the triple bond of the hydrocarbon to yield 1-(4-chloro-2,6-dinitrophenyl)-, 1-(2-chloro-4,6-dinitrophenyl)-, 1-(4-bromo-2,6-dinitrophenyl)-, 1-(2,4,6-trinitro-3-methylphenyl)-, 1-(2-iodo-4-nitrophenyl)-, and 1-(4-iodo-2-nitrophenyl)-1,2,3-triazole respectively.

The reactions of the nitrophenylazides (I-IV) with phenylhydrazine, however, furnished 6-chloro-4-nitro-, 4-chloro-6-nitro-, 6-bromo-4-nitro-, and 4,6-dinitro-7-methyl-2-phenyl-1,2,3-benzotriazole, respectively, which were identical with authentic samples[2-4]. The reaction of phenylhydrazine with (V) and (VI), however, yields intractable gums.

EXPERIMENTAL

Reactions with Acetylene

1-(4-*Chloro*-2-6-*dinitrophenyl*)-1,2,3-*triazole*.—Pure acetylene was bubbled slowly into a refluxing solution of 4-chloro-2,6-dinitrophenylazide (2 g.) in acetone (50 ml). After ½ hour, the flow of acetylene was stopped and the mixture was refluxed for another hour. This was then diluted with water to form a precipitate which was crystallised from ethanol in light brown crystals, m.p. 136°. Analytical data and characteristics of 1,2,3-triazoles obtained from different phenylazides and acetylene by the above procedure are recorded in Table I.

1. Deorha *et al.*, this *Journal*, 1962, **39**, 534.
2. Deorha and Joshi, *ibid.*, 1961, **38**, 41.
3. Walter, Dissertation, Freiburg, i B, 1889, p. 11.
4. *Idem*, *ibid.*, p. 21.

TABLE I

Phenyl-azide used.	1,2,3-Triazole formed.	Yield.	Colour.	M.P.	Formula.	Found.	Reqd.
I	1-(4-Chloro-2,6-dinitrophenyl)-	70%	Light brown	136°	$C_8H_4O_4N_5Cl$	Cl : 13.22%	13.17%
II	1-(2-Chloro-4,6-dinitrophenyl)-	75	Yellowish brown	129°	$C_8H_4O_4N_5Cl$	Cl : 12.99	13.17
III	1-(4-Bromo-2,6-dinitrophenyl)-	68	Light brown	141°	$C_8H_4O_4N_5Br$	Br : 25.34	25.47
IV	1-(2,4,6-Trinitro-3-methylphenyl)-	65	Yellow	131°	$C_9H_6O_6N_6$	N : 28.46	28.57
V	1-(2-Iodo-4-nitrophenyl)-	80	Brownish yellow	93°	$C_8H_5O_2N_4I$	I : 40.28	40.19
VI	1-(4-Iodo-2-nitrophenyl)-	78	Do	77°	$C_8H_5O_2N_4I$	I : 40.32	40.19

Reactions with Phenylhydrazine

Polynitrophenylazides, dissolved in ethanol, and phenylhydrazine (1:2) were heated together on a water bath. Soon after shining crystals began to separate. After about 20 minutes, the mixture was cooled and filtered. The compounds separating were crystallised from toluene. Identical compounds were obtained when along with ethanolic solution of the polynitrophenylazide and phenylhydrazine (1:1), some sodium bicarbonate or sodium acetate was also taken.

Characteristics of 2-phenylbenzotriazoles, obtained by the above method, are recorded in Table II. The products from the azides (I-IV) were found to be identical with those obtained by the interaction of phenylhydrazine and 1,4-dichloro-2,6-dinitro-, 1,2-dichloro-4,6-dinitro-, 1,4-dibromo-2,6-dinitro-, and 1-chloro-2,4,6-trinitro-3-methyl-benzenes.

TABLE II

Phenylazide used.	2-Phenylbenzotriazole.	Yield.	M.P.	Colour.
I	6-Chloro-4-nitro- [3]	80%	199°	Yellow leaflets
II	4-Chloro-6-nitro- [2]	75	179°	Sepia needles
III	6-Bromo-4-nitro- [4]	85	212°	Yellow
IV	4,6-Dinitro-7-methyl- [2]	78	150°	Do

Thanks are due to Dr. R. C. Mehrotra, Professor and Head of the Chemistry Department, University of Rajasthan, and the Principal, Meerut College, for providing facilities.

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Jaipur
and
School of Chemistry,
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Received May 31, 1963.