

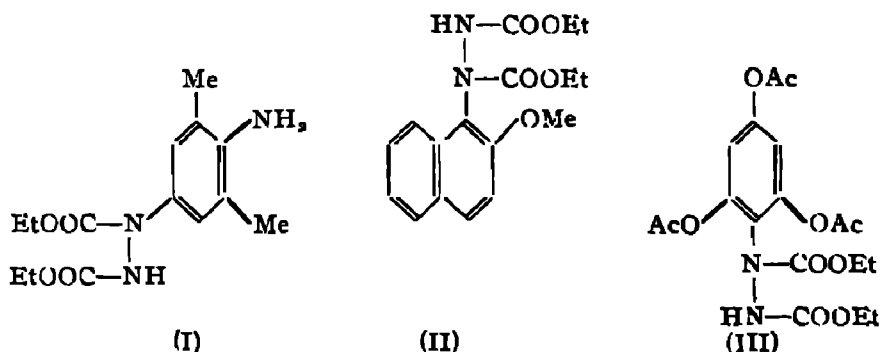
## SOME ADDITION REACTIONS OF AZODICARBONIC DIETHYL ESTER. PART I

BY G. S. MISRA AND S. B. SRIVASTAVA

The addition of azodicarbonic diethyl ester with a number of substituted anilines and phenylenediamines has been studied. The acid-catalysed and thermal addition of the azo-ester with several  $\beta$ -naphthylalkyl ethers have also been investigated. Phloroglucinol triacetate has been found to react with the azo-ester, yielding an adduct at the 4-position.

Azodicarbonic diethyl ester is a compound of great chemical activity, and as the works of Diels, Alder and Stollé show, it can react with various types of compounds in several different ways. The azo-ester is a proton acceptor and thus can oxidise hydroquinone to quinone and hydrogen iodide to iodine, the stable hydrazine dicarbonic diethyl ester being thereby obtained. It can be used as a dienophile in the diene synthesis, as has been shown by Alder and Niklas (*Annalen*, 1954, 585, 81, 97). The ability of the azo-ester to add on is best exhibited in its reaction with bases and nucleophilic agents; the azo-ester itself is electrophilic. As an example, the addition with aniline can be cited (Diels, *ibid.*, 1922, 429, 1).

In the present work, we have studied the influence of a large number of substituents in the benzene ring on the ease with which this nucleophilic addition on the azodicarbonic diethyl ester takes place. *p*-Anisidine, *p*-phenetidine, *m*-4-xylydine and phenylenediamines react to afford the expected products. *m*-2-Xylydine reacts abnormally. Here the addition occurs in 5-position (I) because nitrogen atom is flanked on both the sides by bulky methyl groups.



The composition of these adducts was determined by decomposition with hydroiodic and glacial acetic acids and the preparation of the dibenzoyl derivatives of the reaction products.

Of great interest was the study of the addition of azodicarbonic ester on the aromatic nucleus. According to Stollé *et al.* (*Ber.*, 1924, 57, 1061; *J. prakt. Chem.* 1925, 111, 167; 1929, 123, 74), under the influence of acid catalysts like hydrochloric acid or sulphuric acid, the azo-ester readily adds on to the aromatic nucleus.

$\beta$ -Methoxynaphthalene or nerolin undergoes a quantitative addition of the azo-ester in  $\alpha$ -position in presence of hydrochloric acid gas to yield the adduct (II) (Huisgen and Misra, unpublished work). The effect of increasing the length of the alkyl chain in the naphthyl ether on the ease of the formation of the adduct was examined. Table I records the yields and other relevant data.

TABLE I

*Reaction of  $\beta$ -naphthylalkyl ethers and azo-ester in presence of hydrochloric acid gas and on heating.*

(Yield in presence of HCl was 100%).

No.	Alkoxy group.	Yield on heating.	M.P.	Formula.	% Nitrogen.	
					Found.	Calc.
1.	OMe	10%	157°	$C_{17}H_{20}O_5N_2$	...	...
2.	OEt	10	115°	$C_{18}H_{22}O_5N_2$	8.94	8.88
3.	OPr <sup>n</sup>	8	112°	$C_{19}H_{24}O_5N_2$	8.02	8.43
4.	OPr <sup>i</sup>	8	91°	$C_{19}H_{24}O_5N_2$	8.82	8.43
5.	OBu <sup>n</sup>	5	97°	$C_{20}H_{26}O_5N_2$	7.78	8.09
6.	OBu <sup>i</sup>	Nil	90°	$C_{20}H_{26}O_5N_2$	7.69	8.09
7.	OAmyl <sup>n</sup>	Nil	92°	$C_{21}H_{28}O_5N_2$	7.38	7.77
8.	OAmyl <sup>i</sup>	Nil	83°	$C_{21}H_{28}O_5N_2$	7.37	7.77

The effect of heat alone on the formation of the adduct from the  $\beta$ -naphthylalkyl ethers was also investigated. Identical products, as obtained in the acid-catalysed reaction, were obtained in these cases also. The reaction may be considered to follow the following course :

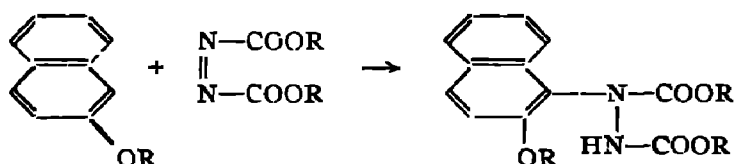


Table I shows that these products are obtained in poor yields and that the yield registers a decrease as the chain length of the alkyl group is increased. No reaction takes place in the case of butyl<sup>i</sup>, amyl<sup>n</sup> and amyl<sup>i</sup> ethers. The course of the reaction is not certain, but it takes place most probably by a polar mechanism, as the addition of small quantities of benzoyl peroxide and benzoquinone has no marked effect on the course of the reaction and the yields of the adducts remain unaltered.

Phloroglucinol triacetate reacts with the azo-ester in 4-position to furnish an adduct (III).

## EXPERIMENTAL

### *Reaction of Azodicarbonic Diethyl Ester with Substituted Anilines*

*p*-Methoxyphenyldicarboxydiethyltriazan.—Azo-ester (1 g.) and *p*-anisidine (1 g.) were taken in a small conical flask and kept for one day at room temperature.

The contents became viscous as the anisidine went into solution. The flask was kept in a refrigerator for 3 days when the adduct separated as a brown solid. Some ether was added to the mixture and the adduct filtered out and dried. It was crystallised three times from alcohol, m.p.  $190^{\circ}$ , yield 1 g. (50%).

*Constitution of the Adduct.*—The adduct (1 g.), HI (5 c.c.), glacial acetic acid (5 c.c.) and red phosphorus (1 g.) were heated together under reflux for 2 hours. The mixture was poured in 100 c.c. water and filtered. The filtrate was evaporated to dryness on a water-bath. A slightly yellow-coloured solid remained behind which was dissolved in excess of 10% NaOH solution and then benzoylated. The benzoylated product was recrystallised from alcohol, m.p.  $153^{\circ}$ . A mixed m.p. of this product with the benzoyl derivative of *p*-anisidine did not show any depression. The addition is thus on the  $\text{NH}_2$  group.

*p*-Phenetidine and *m*-4-xylylidine reacted similarly. The analytical data, m.p. and yields are summarised in Table II.

TABLE II

	Amines	Yield.	M P.	Formula.	% Carbon.		% Hydrogen.	
					Found.	Calc.	Found.	Calc.
1.	<i>p</i> -Anisidine	50%	$190^{\circ}$	$\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2$	52.50	52.52	6.20	6.39
2.	<i>p</i> -Phenetidine	50	$206^{\circ}$	$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$	54.54	54.71	6.73	6.75
3.	<i>m</i> -4-Xylylidine	25	$265^{\circ}$	$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$	56.56	56.94	7.41	7.11
4.	<i>o</i> -Phenylenediamine	50	$162^{\circ}$	$\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2$	46.91	47.36	6.26	6.24
5.	<i>m</i> - "	40	$238^{\circ}$	$\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$	46.88	47.36	5.55	6.14
6.	<i>p</i> - "	40	$245^{\circ}$	$\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$	47.16	47.36	6.42	6.14

*2-Amino-1-dicarboxydiethylhydrazino-1:3-dimethylbenzene* (II).—Azo-ester (1.6 g.) and *m*-2-xylylidine (1 g.) were taken in a small conical flask and allowed to remain in a refrigerator for 2 days, when the mixture became viscous. After addition of a little dry ether, the mass crystallised on rubbing and cooling. It was filtered, washed well with ether and crystallised several times from alcohol, m.p.  $119^{\circ}$ , yield 1.6 g. (61%). (Found: C, 56.53; H, 7.08; N, 13.98.  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$  requires C, 56.94; H, 7.11; N, 14.20%).

The constitution of the adduct was determined in the usual way, as already described above. The product obtained on benzoylation was found to be indistinguishable from the dibenzoyl derivative of 2:6-dimethyl-1:4-phenylenediamine as a mixed melting point determination showed no depression ( $279^{\circ}$ ).

#### Reactions of the Azo-ester with Phenylenediamines

*1:2-Dicarboxydiethyltriazanobenzene.*—To an ethereal solution of *o*-phenylenediamine (1 g.), taken in a small conical flask, the azo-ester (1.2 g.) was added under cooling. The mass became brown and viscous and after a few hours solidified. The adduct was filtered, washed well with ether and crystallised twice from alcohol, m.p.  $162^{\circ}$ , yield 1.1 g. (50%).

The constitution of the adduct<sup>1</sup> was determined in the usual way. The m.p. of the dibenzoyl derivative of the product showed no depression when mixed with the dibenzoyl derivative of *o*-phenylenediamine (301°).

Both *m*- and *p*-phenylenediamines reacted similarly. The relevant data are summarised in Table II.

*Reactions of the Azo-ester with  $\beta$ -Naphthylalkyl Ethers*

*Acid-catalysed Addition of the Azo-ester to  $\beta$ -Ethoxynaphthalene.*— $\beta$ -Ethoxynaphthalene or neonerolin (1 g.) and the azo-ester (1 g.) and a few c.c. of dry ether were taken in a small conical flask. A crystal of iodine was added and dry HCl gas was passed into it. In a few minutes the mass became viscous and, on cooling, solidified. Some ether was added to aid filtration. The crude product (m.p. 110°) was obtained in a quantitative yield. After two crystallisations from dilute acetic acid the product melted at 115°.

*Thermal Addition of the Azo-ester to  $\beta$ -Ethoxynaphthalene.*—Neonerolin (1 g.) and the azo-ester (1 g.) were heated under reflux in an oil-bath at 150° for 24 hours. The viscous product solidified when rubbed with a few drops of acetic acid, m.p. 110°, yield 0.2 g. (crude). After two more crystallisations the m.p. of the adduct rose to 115°.

The constitution of the adduct was determined in the usual way. A mixed melting point determination of the dibenzoyl derivative of the product, obtained thus, with that of the 1-amino-2-naphthol showed no depression (224°).

Other  $\beta$ -alkoxynaphthalenes reacted similarly. The data are summarised in Table I.

*Reaction of the Azo-ester with Phloroglucinol Triacetate*

Azo-ester (1 g.) and phloroglucinol triacetate (1 g.) were taken in a flask. A few drops of acetic acid were added to dissolve the triacetate. The contents were heated on a water-bath for 2 hours and then left at room temperature. After 24 hours a white solid separated. This was filtered and washed well with ether. The crude product melted at 210°. After two crystallisations from dilute acetic acid it melted at 216°, yield 0.37 g. (18.5%). (Found: C, 50.34; H, 5.40; N, 6.32.  $C_{18}H_{22}O_{10}N_2$  requires C, 50.70; H, 5.16; N, 6.57%).

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