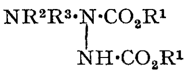
388. *The Compounds of Alkylamines with Esters of Azodicarboxylic Acid.*

By G. W. Kenner and R. J. Stedman.

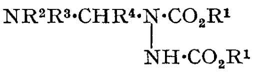
The adducts of dimethylamine and benzylmethylamine with diethyl and dibenzyl azodicarboxylate are rather unstable substances, to which structures of type (I) are assigned. In contrast the compounds formed from trimethylamine and diethyl azodicarboxylate, and from benzyldimethylamine and dibenzyl azodicarboxylate, are relatively stable and are formulated as (II; $R^1 = Et$, $R^2 = R^3 = Me$, $R^4 = H$) and (II; $R^1 = R^2 = CH_2Ph$, $R^3 = Me$, $R^4 = H$) respectively, in agreement with Diels's suggestion. The amounts of formaldehyde and benzaldehyde liberated on acid hydrolysis of these six compounds have been determined.

In his classical work on azodicarboxylic acid $(:N{\cdot}CO_2H)_2$ Diels investigated the reactions of its esters with amines. He showed that, whereas amides are formed from primary alkylamines (Diels and Fritzsche, *Ber.*, 1911, **44**, 3018), primary arylamines give either triazan addition compounds, *e.g.*, with aniline (I; $R^1 = Et$, $R^2 = H$, $R^3 = Ph$), or products of electrophilic substitution of the azo-group into the aromatic nucleus, *e.g.*, with naphthylamines (Diels, *Annalen*, 1922, **429**, 1). The secondary and tertiary alkylamines and alkylarylamines were found to give compounds corresponding in composition to the addition of one molecule of amine to one of azo-ester. Despite much experimental work with these adducts (Diels and Paquin, *Ber.*, 1913, **46**, 2000; Diels and Fischer, *Ber.*, 1914, **47**, 2043), Diels did not finally elucidate their structure. The principal evidence collected was that of acidic hydrolysis to an aldehyde, the correspondingly monodealkylated amine, and the hydrazo-ester. This was readily accommodated by structures of type (II), which were therefore favoured by Diels although the less conventional alternatives (III) and (IV) were also considered possible for the derivatives of tertiary amines. Interest in some possibilities arising out of Diels's work has led us to continue it; the additional results enable us to assign structures to these adducts of secondary and tertiary alkylamines.



$$\begin{array}{l} NR^2R^3{\cdot}N{\cdot}CO_2R^1 \\ \qquad | \\ \qquad NH{\cdot}CO_2R^1 \end{array}$$

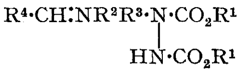
(I)



$$\begin{array}{r} NR^2R^3{\cdot}CHR^4{\cdot}N{\cdot}CO_2R^1 \\ | \qquad \\ NH{\cdot}CO_2R^1 \end{array}$$

(II)

(III)



$$\begin{array}{r} R^4{\cdot}CH{:}NR^2R^3{\cdot}N{\cdot}CO_2R^1 \\ | \qquad \\ HN{\cdot}CO_2R^1 \end{array}$$

(IV)

The adducts listed in the table were prepared by Diels's method, *viz.*, addition of the amine in portions to a boiling ethereal solution of the azodicarboxylic ester. Their hydrolysis was carried out in boiling 2N-sulphuric acid, with the results shown. In our hands, the most satisfactory of the various methods for specific colorimetric estimation of formaldehyde was the use of acidic Schiff's reagent according to Blaedel and Blacet (*Ind. Eng. Chem. Analyt.*, 1941, **13**, 449). Benzaldehyde was determined gravimetrically as its 2 : 4-dinitrophenylhydrazone (Mouton, *Chem. Abs.*, 1939, **33**, 5128), which was easily separated from 2 : 4-dinitrophenylhydrazine and the formaldehyde derivative by chromatography on silica (Roberts and Green, *Ind. Eng. Chem. Analyt.*, 1946, **18**, 335). Although this method gave good results for benzaldehyde, the values for formaldehyde were always lower than those obtained colorimetrically. We estimate the error in determination of benzaldehyde through the dinitrophenylhydrazone and of formaldehyde through acidic Schiff's reagent to be less than 10% in each case.

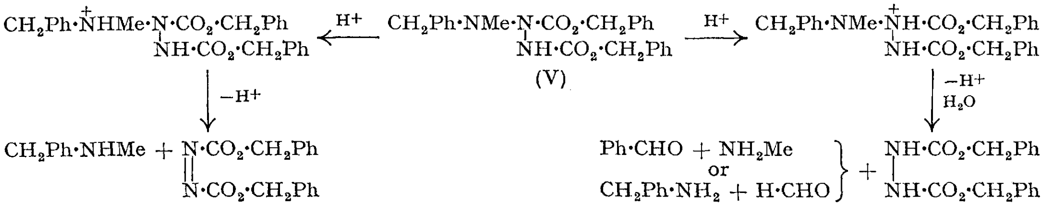
The adducts 1, 2, 4, and 5, derived from secondary amines, gave aldehydes in relatively low yields which varied with the conditions of hydrolysis. Moreover, in their preparation the yellow colour of the azo-ester is never completely discharged. The question therefore arises whether the production of aldehydes on acid hydrolysis indicates a structure of type (II), as supposed by Diels, or can also be explained by a labile triazan structure (I) (cf. Cooper and E. H. Ingold, *J.*, 1926, 1894). A plausible scheme is depicted below for the acid-catalysed decomposition of (V), *i.e.*, compound 5 formulated as dibenzyl 1-benzyl-1-methyltriazan-2 : 3-dicarboxylate (I; $R^1 = R^2 = CH_2Ph$, $R^3 = Me$).

Adduct from :			Mols., %, of aldehydes liberated by acid :	
Amine	Azodicarboxylate	M. p.	CH_2O	Ph·CHO
(1) Dimethyl	Diethyl	92·5—93° * ‡	40	—
(2) Dimethyl	Dibenzyl	98 *	44	<2
(3) Trimethyl	Diethyl	—	75	—
(4) Benzylmethyl	Diethyl	42—48 *	26	22 †
(5) Benzylmethyl	Dibenzyl	93—94 *	10	16
(6) Benzyldimethyl	Dibenzyl	84—85·5	90	<1

* With decomposition. ‡ Diels and Paquin (*loc. cit.*) record m. p. 95°.

† Estimated from the total weight of dinitrophenylhydrazone by subtraction of the amount of formaldehyde derivative.

Addition of a proton to the amine nitrogen regenerates the amine and dibenzyl azodicarboxylate, which is easily destroyed by acid; secondary amine was in fact detected in the acid hydrolysate of compound 1. On the other hand, addition of a proton to the central nitrogen liberates the hydrazo-ester and a cation which can lose a proton from either of two carbon atoms; the resulting Schiff's bases can then hydrolyse to benzaldehyde and methylamine or to benzylamine and formaldehyde. It is noteworthy that both aldehydes were obtained from adduct 5, apparently a single substance, although it might be argued that they arose by a dissociation and recombination process during the hydrolysis:



Adduct 4 likewise gave both aldehydes, but the amorphous character of this compound leaves its homogeneity more open to question. The failure to detect benzaldehyde on hydrolysis of 2 and 6 shows that it does not arise from the benzyl ester groups in 5. These experiments then support the formulation of all the adducts from secondary amines as triazans of type (I).

Acid hydrolysis of compounds 3 and 6, derived from tertiary amines, gave high yields of formaldehyde, which were unaffected by variation in the experimental conditions. Similarly, the adduct of dimethylaniline and diethyl azodicarboxylate (Diels and Fritzsche,

$$(II) \xrightarrow{H_2O} NHR^2R^3 + R^4{\cdot}CHO + ({\cdot}NH{\cdot}CO_2R^1)_2$$

loc. cit.) was found to give a quantitative yield of formaldehyde. These adducts are relatively stable; 3 was purified by high-vacuum distillation at 100°, and the yellow colour of the azo-ester is completely discharged in their preparation. They are therefore satisfactorily represented by Diels's structure (II). No matter which nitrogen atom in this structure is originally attacked by a proton, its acid hydrolysis can lead only to hydrazo-ester, dealkylated amine, and a single aldehyde. Only formaldehyde was obtained on acid hydrolysis of the benzyldimethylamine adduct 6, which must be dibenzyl *N*-(benzylmethylaminomethyl)hydrazine-*NN'*-dicarboxylate (II; $R^1 = R^2 = CH_2Ph$, $R^3 = Me$, $R^4 = H$). Whether an isomer (II; $R^1 = CH_2Ph$, $R^2 = R^3 = Me$, $R^4 = Ph$) existed in the liquors of its preparation was a point not settled by our experiments.

The assignment of structures of types (I) and (II) to the adducts derived from secondary and tertiary amines respectively requires that all these compounds should contain a single NH group. This was confirmed by determination of the active hydrogen content of compounds 1, 5, 6, and that from dimethylaniline and diethyl azodicarboxylate. In addition the infra-red spectra of compounds 1 (in Nujol suspension) and 3 (in thin film) showed NH peaks at 3·10, 6·58 and 3·04, 6·62 μ, respectively. The carbonyl band of compound 1 was resolved into a double peak at 5·70 and 5·92 μ, in agreement with a triazan structure and consequent differentiation of the two ester groups, whereas the spectrum of 3 showed a single broad band at 5·80 μ. Neither compound had selective absorption in the ultra-violet above 220 mμ.

Further confirmatory data were obtained by a study of the pyrolysis of adducts 1 and 3. Diels and Paquin (*loc. cit.*) described the pyrolysis of compound 1 (from dimethylamine) under two sets of conditions. Rapid heating at atmospheric pressure gave principally *NN'*-dimethylhydrazine, whereas careful decomposition under 30 mm. pressure yielded ethyl dimethylcarbamate amongst other substances. The complexity of these decompositions is clear from Diels and Paquin's work and it is therefore not surprising that we were unable to reproduce the second experiment, on which our attention was focused. Decomposition in boiling toluene, however, gave dimethylamine, identified as its picrate, and diethyl hydrazine-*NN'*-dicarboxylate. Ethyl dimethylcarbamate did result in small yield from the pyrolysis of compound 3 (from trimethylamine), a reaction not investigated by Diels; neither carbon monoxide nor diazomethane, which we considered as possible accompanying products, could be detected. In our view these decompositions, despite their obscure character, provide evidence that both compounds 1 and 3 contain the dimethylamino-group, as required by the structures diethyl 1 : 1-dimethyltriazan-2 : 3-dicarboxylate (I; $R^1 = Et$, $R^2 = R^3 = Me$) and diethyl *N*-(dimethylaminomethyl)-hydrazine-*NN'*-dicarboxylate (II; $R^1 = Et$, $R^2 = R^3 = Me$, $R^4 = H$), respectively.

The first step in the reaction between an amine and an ester of azodicarboxylic acid is presumably co-ordination of the basic nitrogen atom with the electrophilic azo-group. The resultant dipolar ion can then yield a stable structure either directly by migration of a proton in the case of secondary amines, or in two steps through an Ylide rearrangement (Wittig, *Angew. Chem.*, 1951, **63**, 15; Hauser and Kantor, *J. Amer. Chem. Soc.*, 1951, **73**, 1437) in the case of tertiary amines. The latter mechanism is substantially identical with that postulated by Böhme and Krause (*Ber.*, 1951, **84**, 170) for the reaction between halogens and tertiary amines; the adducts (II) correspond to the α-halogenated amines which were too unstable to be isolated.

The preparation of azodicarboxylic esters has commonly been achieved by nitric acid oxidation of the corresponding dialkyl hydrazine-*NN'*-dicarboxylates (Curtius and Heidenrich, *Ber.*, 1894, **27**, 773; Diels and Fritzsche, *loc. cit.*; C. K. Ingold and Weaver, *J.*, 1925, **127**, 378), but the method is rather uncertain and restricted in application. Chlorine in aqueous solution has been used as an alternative to nitric acid (Rabjohn, *J. Amer. Chem. Soc.*, 1948, **70**, 118; *Org. Synth.*, 1948, **28**, 58; Müller and Petersen, *Angew. Chem.*, 1951, **63**, 18). By means of bromine in aqueous acetic acid we were able conveniently to prepare diethyl, dibenzyl, and di-*p*-nitrobenzyl azodicarboxylates. The first two compounds were used in the work already described, but the last did not yield the expected highly crystalline adducts. Moreover, the preceding reaction between *p*-nitrobenzyl chloroformate and hydrazine was unsatisfactory owing, presumably, to reduction of the nitro-groups by hydrazine (cf. von Rothenburg, *Ber.*, 1893, **26**, 2060; Curtius, *J. pr. Chem.*, 1907, **76**, 233; Huang-Minlon, *J. Amer. Chem. Soc.*, 1948, **70**, 2802). The diaryl hydrazine-*NN'*-dicarboxylates were not accessible through the corresponding reaction with aryl chloroformates; free phenols were isolated from the reaction mixtures.

EXPERIMENTAL

M. p.s are corrected.

Diethyl Azodicarboxylate.—The following procedure is alternative to that of Rabjohn (*Org. Synth.*, 1948, **28**, 58). Bromine (12·3 c.c.) was added during ¼ hour to an ice-cooled suspension of diethyl hydrazine-*NN'*-dicarboxylate (35·2 g.; Rabjohn, *loc. cit.*) in water (250 c.c.). After a further ¼ hour, the product was extracted by ether (400 c.c.), which was washed at 0° successively with water, sodium carbonate solution, very dilute sodium thiosulphate solution (the product is unstable to thiosulphate), and water before being dried ($CaCl_2$). The orange oil, remaining after evaporation of the ether through a short fractionating column, was distilled at 60—70°/0·1 mm. (22 g., 63%).

*Dibenzyl Hydrazine-*NN'*-dicarboxylate.*—Potassium hydroxide (57 g.) in water (40 c.c.) was added cautiously to a hot solution of hydrazine sulphate (65 g.) in water (500 c.c.). Potassium sulphate was then precipitated by addition of ethanol (400 c.c.), removed from the cold mixture by filtration, and washed with ethanol (100 c.c.). Benzyl chloroformate (74 g., approx. 75% pure) was added to the combined filtrate and washings, which were boiled under reflux during 3½ hours before distillation of part (700 c.c.) of the solvent. Addition of water (1 l.) to the remaining solution afforded a crude solid which was pure enough for the next reaction after a single recrystallisation from carbon tetrachloride (34·9 g., 70%; m. p. 106—106·5°). The pure *ester* was obtained as prisms by two recrystallisations from benzene and one from water and had m. p. 106·5° on slow heating (fusion and resolidification at *ca.* 85° on rapid heating) (Found, in material dried at 60°: C, 63·9; H, 5·4; N, 9·7. $C_{16}H_{16}O_4N_2$ requires C, 64·0; H, 5·4; N, 9·3%).

Dibenzyl Azodicarboxylate.—Dibenzyl hydrazine-*NN'*-dicarboxylate (12 g.) was shaken during 3 hours with a solution of bromine (7·0 g.) in 50% aqueous acetic acid (130 c.c.). The yellow powder (10·2 g.), which separated when the mixture was poured into water (1 l.), was recrystallised from light petroleum (b. p. 40—60°; 850 c.c.); it had m. p. 46—47° (8·2 g., 69%). Recrystallisation from ether and then from acetone gave pure *dibenzyl azodicarboxylate*, orange plates, m. p. 46·5—47° (Found: C, 64·8; H, 4·8; N, 9·8. $C_{16}H_{14}O_4N_2$ requires C, 64·4; H, 4·7; N, 9·4%).

Di-p-*nitrobenzyl Hydrazine*-NN'-*dicarboxylate.*—A mixture of *p*-nitrobenzyl chloroformate (4·31 g.; Thiele and Dent, *Annalen*, 1898, **302**, 258) and hydrazine hydrate (1·50 g.) in dioxan (60 c.c.) was kept for ½ hour, during which it became cloudy, before the addition of much water. The precipitated oil solidified rapidly and was recrystallised from ethanol (1·45 g., 37%; m. p. 168—170°). After two further recrystallisations as colourless long prisms the *ester* had m. p. 170·5—172·5° (Found, in material dried at 80°: C, 49·3; H, 3·4; N, 14·0. $C_{16}H_{14}O_8N_4$ requires C, 49·2; H, 3·6; N, 14·4%).

Di-p-*nitrobenzyl Azodicarboxylate.*—The above hydrazo-ester (1·17 g.) was stirred during 1½ hours with a solution of bromine (10 c.c.) in acetic acid (70 c.c.) and water (30 c.c.). The mixture was diluted to 1 l. with water, and the pale yellow solid collected (0·94 g., 80%; m. p. 145—147°). The *di*-p-*nitrobenzyl azodicarboxylate* recrystallised from acetone in pale yellow prisms, m. p. 146·5—147·5° (Found: C, 49·9; H, 3·3; N, 14·5. $C_{16}H_{12}O_8N_4$ requires C, 49·5; H, 3·1; N, 14·4%).

Diethyl 1 : 1-*Dimethyltriazan*-2 : 3-*dicarboxylate* (I; $R^1 = Et, R^2 = R^3 = Me$) (Adduct 1).—This substance, prepared as by Diels and Paquin (*loc. cit.*) and recrystallised from ether, had m. p. 92·5—93° (Found: active H, 0·45. Calc. for $C_8H_{17}O_4N_3$: active H, 0·46%).

Dibenzyl 1 : 1-*Dimethyltriazan*-2 : 3-*dicarboxylate* (I; $R^1 = CH_2Ph$, $R^2 = R^3 = Me$) (Adduct 2).—An ethanolic solution of dimethylamine (1·80 c.c. of 25% w/v) was added to a solution of dibenzyl azodicarboxylate (2·98 g.) in boiling ether (5 c.c.). The evolution of heat and diminution in the colour indicated reaction. The orange syrup remaining on evaporation of solvent from the mixture, which had been kept for 1 hour at 20°, crystallised from ethereal solution on addition of light petroleum (b. p. 40—60°). Two further recrystallisations from ether then afforded the *adduct* as colourless plates, m. p. 98° (decomp.) (Found: C, 63·4; H, 6·0; N, 12·5. $C_{18}H_{21}O_4N_3$ requires C, 63·0; H, 6·2; N, 12·2%).

Diethyl (*Dimethylaminomethyl*)*hydrazine*-NN'-*dicarboxylate* (II; $R^1 = Et$, $R^2 = R^3 = Me$, $R^4 = H$) (Adduct 3).—On slow addition of an ethanolic solution of trimethylamine (17·8 g. of 34·7% w/w) to a solution of diethyl azodicarboxylate (17·4 g.) in boiling ether (35 c.c.), heat was evolved, and the orange colour was rapidly and completely discharged. The mixture was kept for 1 hour at 20° before evaporation under reduced pressure to an almost colourless syrup, which was distilled from glass-wool at 110—115°/0·5 mm. (bath-temp. 170°). A small quantity of diethyl hydrazine-*NN'*-dicarboxylate, m. p. 132—133°, separated from a solution of this syrup in acetone. The *adduct* itself was obtained by fractional distillation during 6 hours at 10^{-4} mm. along a 60-cm. tube (5-mm. bore) encased in a lagged copper tube, which fitted into the heating block maintained at 100°. It travelled further from the heater than the crystalline hydrazo-ester and was a colourless oil (Found: C, 45·5; H, 7·8; N, 18·0. $C_9H_{19}O_4N_3$ requires C, 46·3; H, 8·2; N, 18·0%).

Diethyl 1-*Benzyl*-1-*methyltriazan*-2 : 3-*dicarboxylate* (I; $R^1 = Et$, $R^2 = CH_2Ph$, $R^3 = Me$) (Adduct 4).—A solution of benzylmethylamine (1·21 g.; Wegler and Frank, *Ber.*, 1936, **69**, 2074) in ethanol (3 c.c.) was added slowly to a solution of diethyl azodicarboxylate (1·74 g.) in boiling ether (4 c.c.). The mixture was kept at room temperature during 1 hour before evaporation of the solvent. The *adduct* was obtained from the resultant deep yellow syrup, by seeding at −5° with solid from a previous batch, as a pale yellow solid, m. p. 42—48°, which readily decomposed with evolution of benzaldehyde and could not be further purified (Found: C, 56·1; H, 7·2; N, 15·3. $C_{14}H_{21}O_4N_3$ requires C, 56·9; H, 7·2; N, 14·2%).

Dibenzyl 1-*Benzyl*-1-*methyltriazan*-2 : 3-*dicarboxylate* (I; $R^1 = R^2 = CH_2Ph$, $R^3 = Me$) (Adduct 5).—Benzylmethylamine (1·21 g.) was added dropwise to a boiling solution of dibenzyl azodicarboxylate (2·98 g.) in ether (7 c.c.), whereupon a vigorous reaction took place with some diminution in the orange colour. After being left for 1 hour at 20° the mixture was diluted with ether (5 c.c.), seeded with crystals, obtained by addition of light petroleum (b. p. 40—60°) to a portion of the solution, and kept at −15° during 24 hours. The *adduct* (1·29 g., 31%; m. p. 90—92°) was twice recrystallised from ether and light petroleum (b. p. 40—60°), forming small colourless needles, m. p. 93—94° (Found: C, 68·4; H, 5·9; N, 10·0; active H, 0·27. $C_{24}H_{25}O_4N_3$ requires C, 68·7; H, 6·0; N, 10·0; active H, 0·24%).

Dibenzyl N-(*Benzylmethylaminomethyl*)*hydrazine*-NN′-*dicarboxylate* (II; $R^1 = R^2 = CH_2Ph$, $R^3 = Me$, $R^4 = H$) (Adduct 6).—Benzyldimethylamine (2·70 g.), prepared from benzylamine, formic acid, and formaldehyde, following the directions of Icke, Wisegarver, and Alles (*Org. Synth.*, 1945, **25**, 89, for *NN*-dimethyl-2-phenylethylamine), was added dropwise to a solution of dibenzyl azodicarboxylate (5·96 g.) in boiling ether (12 c.c.), which was rapidly decolorised. The solution was kept during 1 hour at 20° and then overnight at −15°. Recrystallisation of the deposited material from ether gave a colourless solid, m. p. *ca.* 75° (1·13 g.), two further recrystallisations of which afforded a small quantity of the pure *ester*, m. p. 84—85·5° (Found, in material dried at 40°: C, 69·1; H, 6·1; N, 9·6; active H, 0·24. $C_{25}H_{27}O_4N_3$ requires C, 69·3; H, 6·3; N, 9·7; active H, 0·23%).

Diethyl N-(*Methylanilinomethyl*)*hydrazine*-NN′-*dicarboxylate*.—The reaction between dimethylaniline and diethyl azodicarboxylate is very slow in boiling ether; Diels and Fritzsche's directions (*loc. cit.*) were therefore modified by carrying it out in dioxan during 3 hours at 100°. The product was crystallised from ether; it had m. p. 75—76° (Found: active H, 0·35. Calc. for $C_{14}H_{21}O_4N_3$: active H, 0·34%). Its hydrolysis by 2N-sulphuric acid gave 97% of the theoretical quantity of formaldehyde.

Determination of Formaldehyde produced on Acid Hydrolysis of the Adducts.—A solution of Schiff's reagent was prepared by adding sodium metabisulphite (5·15 g.), and then after ¼ hour 6N-hydrochloric acid (17 c.c.), to a solution of magenta (0·5 g.) in water (500 c.c.), and kept for 2 days before use. Colour intensities were measured with a Spekker photometer (blue filter) 4 hours after the reagent (10 c.c.) had been mixed with the formaldehyde solution (10 c.c.) and 75% sulphuric acid (2·4 c.c.). The formaldehyde concentration was then obtained from the almost linear calibration curve, constructed by dilution to 0·001—0·004% of a standard formaldehyde solution (*ca.* 0·1%, estimated by dimedone according to Meyer, "Nachweis und Bestimmung Organischer Verbindungen," Springer, Berlin, 1933, p. 48).

The adducts (*ca.* 50 mg.) were hydrolysed with boiling 2N-sulphuric acid (10 c.c.) during ½ hour before steam-distillation. The distillate (*ca.* 35 c.c.) was then diluted to an appropriate volume (50 or 100 c.c.) before colorimetric estimation. After neutralisation with sodium carbonate, the hydrolysate of Adduct 1 gave a positive Simon test (Schneider, "Qualitative Organic Microanalysis," Wiley, New York, 1947, p. 189) for secondary amines with sodium nitroprusside and acetaldehyde. Primary amines were not detected in the hydrolysate of Adduct 3 by the Rimini test (Schneider, *op. cit.*), *viz.*, treatment with sodium nitroprusside and acetone after neutralisation.

Determination of Benzaldehyde produced on Acid Hydrolysis of the Adducts.—A mixture of the adduct (*ca.* 120 mg.), water (10 c.c.), and concentrated sulphuric acid (0·5 c.c.) was boiled during 1½ hours, cooled, and filtered. The precipitated solid was washed with 1% ethanol (30 c.c.). To the combined filtrate and washings were added 2 : 4-dinitrophenylhydrazine solution (30 c.c. of 1% in 15% sulphuric acid) and concentrated sulphuric acid (5 c.c.). The yellow precipitate, which separated from the solution during 15 hours at −5°, was washed by decantation with water (4 portions of 10 c.c.) and dried in a vacuum (P_2O_5).

The crude dinitrophenylhydrazones were dissolved in benzene (10 c.c.) and adsorbed on a column (16 × 3 cm.) of silica (sieved through 80-mesh), which was then washed with benzene. The first orange band consisted of the benzaldehyde derivative, m. p. 238—240° undepressed by an authentic specimen, m. p. 240—242°. The formaldehyde derivative, m. p. 162—164° undepressed by an authentic specimen, m. p. 165—167°, formed the next, well-separated yellow band. A little orange material remained at the top of the column. The yields of formaldehyde derivative obtained by this method from adducts 2, 5, and 6 were 24, 4·4, and 63%, respectively.

Decomposition of Diethyl 1 : 1-*Dimethyltriazan*-2 : 3-*dicarboxylate* (*Adduct* 1) *in Boiling Toluene*.—A solution of the adduct (2 g.) in toluene (35 c.c.) was boiled under reflux during

3 hours, whilst a slow stream of nitrogen (washed with sulphuric acid) was bubbled through the solution, a trap cooled in liquid oxygen, and finally ammoniacal silver nitrate solution (from 3 g. of silver nitrate, 350 c.c. of 8% sodium hydroxide solution, and 63 c.c. of 8% aqueous ammonia). The toluene solution rapidly became yellow; there was no darkening of the silver solution to indicate any evolution of carbon monoxide (Manchot and Lehmann, *Ber.*, 1931, **64**, 1261). When a mixture of the contents of the liquid-oxygen trap and a boiling solution of picric acid (0·5 g.) in ethanol (14 c.c.) was cooled, crystals of dimethylamine picrate separated (0·37 g.; m. p. 159° undepressed by an authentic specimen). Diethyl hydrazine-*NN'*-dicarboxylate (0·33 g.; m. p. 130—132° undepressed by an authentic specimen) crystallised during distillation of the toluene in a stream of nitrogen. No dimethylamine could be detected on boiling of the toluene distillate with potassium hydroxide in aqueous 2-ethoxyethanol.

Pyrolysis of Diethyl N-(*Dimethylaminomethyl*)*hydrazine*-NN'-*dicarboxylate* (Adduct 3).—The crude adduct (11·5 g.) was heated with a free flame in a stream of nitrogen, whereupon rapid darkening occurred. The almost colourless mobile distillate (5·3 g.) was fractionally distilled through a 6-cm. vacuum-jacketed Vigreux column, yielding 3 c.c., b. p. *ca.* 67—82°, and 1·53 g., b. p. *ca.* 125—141°; these temperatures were not the true b. p.s owing to the very slow rate of distillation. Redistillation of the second fraction yielded ethyl dimethylcarbamate, b. p. 147·5° (corr.) (Siwoloboff method), n_D^{15} 1·4175 (Found: C, 51·7; H, 9·2; N, 11·8. Calc. for $C_5H_{11}O_2N$: C, 51·3; H, 9·5; N, 12·0%). An authentic specimen of ethyl dimethylcarbamate had b. p. 147·5° (corr.), n_D^{15} 1·4171. On repetition of the pyrolysis on a smaller scale (1·8 g.), no diazomethane could be detected in the distillate by means of *p*-nitrobenzoic acid (Marshall and Acree, *Ber.*, 1910, **43**, 2323), nor did ammoniacal silver nitrate solution (cf. preceding experiment) reveal the evolution of carbon monoxide.

The authors are grateful to Professor A. R. Todd, F.R.S., for his interest in this work, to Dr. R. N. Haszeldine for the infra-red spectra, determined with a Perkin-Elmer model 21 instrument, and to the Department of Scientific and Industrial Research for a Maintenance Grant (R. J. S.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, January 14th,* 1952.]