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105. Munemitsu Tomoeda, Saburo Kanahara,*1 Mutsuko Urata, and Junji Yoshizawa : Some Homolytic Reaction Behaviors of Diethyl Azodicarboxylate.*2

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Pyrolytic cleavage of the azo-bridge of diethyl azodicarboxylate (Ia) at 200～210° was studied and was shown to give diethyl oxalate (VI), tetraethyl hydrazine-N_1,N_1,N_2,N_2-tetracarboxylate (VIII), triethyl hydrazine-N_1,N_1,N_2-tricarboxylate (IX), diethyl hydrazine-N_1,N_2-dicarboxylate (X), and carbon dioxide, proving formation of the ethoxycarbonyl radical (III) as an important transitionally formed intermediate of the reaction. A homolytic mechanism with the diradical (IV) and ethoxycarbonyl radical (III) as intermediates was tentatively suggested for the reaction. Surprisingly, Ia, when treated with alumina or silica gel at room temperature, gave almost same pattern of products obtained by the pyrolysis, yielding VIII, IX, X and carbon dioxide. A photolysis of Ia on a tungsten lamp also gave IX, X, and carbon dioxide.

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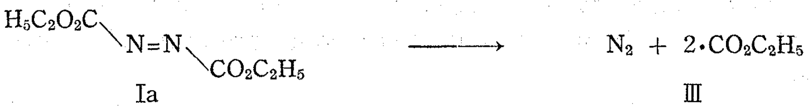
Introduction

Characteristic reactivity of the esters of azodicarboxylic acid (I) is well known.[1] Typical of the esters is the heterolytic and homolytic reactivity of the azo bridge itself and also its participation as dienophile in Diels-Alder reactions. They therefore constitute as regards such reaction behavior a link between the purely aliphatic and the purely aromatic azo derivatives.

I (Ia, R=C_2H_5)   II (IIa, X=N, n=2)

Chart 1.

For some time we have been interested in synthesis of a new class of small-membered heterocycles (II) such as cyclotetrazane (IIa). With this motivation behind, we have particularly been interested in the homolytic reactivity of the esters of azodicarboxylic acid appearing in the following papers. Huisgen and his colleagues[2] have predicted in their intensive work on the addition reaction of diethyl azodicarboxylate (Ia) to aromatic side chains, that the azo-ester (Ia), on pyrolytic cleavage, might afford nitrogen and ethoxycarbonyl radical (III).



Ia   III

Chart 2.

[*1] Present address : Ishikawa High Technological College, Tsubata, Ishikawa.

[*2] Presented in part at the Meetings of the Pharmaceutical Society of Japan held at Tokyo on 3rd of November, 1963, and at Toyama on 25th of June, 1966.

[*3] Takara-machi, Kanazawa (友枝宗光, 金原三郎, 浦田睦子, 吉沢潤治).

1) H. Zollinger; "Azo and Diazo Chemistry. Aliphatic and Aromatic Compounds," p. 286 (1961). Interscience Publishers, Inc., New York.

2) R. Huisgen, F. Jacob, W. Siegel, A. Cadus : Ann., **590**, 1 (1954).

Meanwhile, Schenck and his colleagues³⁾ have reported the homolytic cleavage, by light, of the azo bridge of the ester (Ia) in 2-propanol affording tetraethyl tetrazane-N_1, N_2,N_3,N_4-tetracarboxylate (V) and pinacone, possibly *via* the intermediacy of the diradical (Ⅳ).

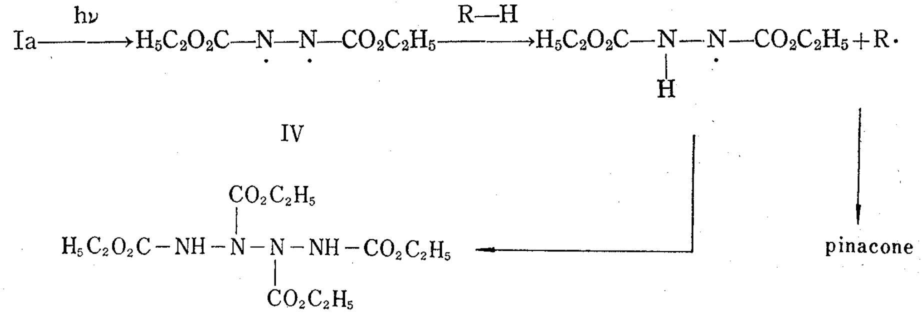


Chart 3.

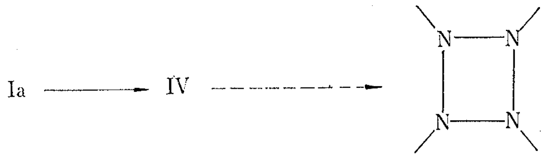


Chart 4.

It has thus appeared to be likely that the azodicarboxylic ester (I) might homolytically dimerize to the cyclotetrazane ring *via* the diradical intermediate (Ⅳ) as shown in the next diagram.

The present paper deals with the results of our work on pyrolyses of diethyl azodicarboxylate (Ia) and with the evidence for the formation of the ethoxycarbonyl radical (Ⅲ) as an intermediate. The paper also deals with the unique catalytic action of alumina and silica gel for the cleavage of the azo bridge of azodicarboxylic esters. A photochemical reaction behavior of the azo bridge of Ia by light, different from what Schenck has observed, is reported. A possible mechanism for the reaction referred to in the present paper is also presented.

Methods and Results

Pyrolyses——The azo-ester (Ia),⁴⁾ was pyrolyzed under the following conditions, *i.e.* i) in dark on a metal bath at 200~210°, ii) in dark on the metal bath at 200~210° with a catalytical amount of iodine, iii) on a 40W tungsten lamp at 200~210°, iv)on the 40W lamp at 200~210° with a catalytical amount of iodine, and v) under dispersed light on the metal bath at 200~210°. The pyrolyses were carried out under nitrogen and continued for 2 hr. Whichever the pyrolysis condition, the reaction appeared to proceed above 200°; when the temperature of the orange azoester (Ia) reached *ca.* 200°, a colorless oil began to reflux, and then a gas constantly evolved. The dark red oil thus formed, the weight of which reached in average *ca.* 80% of the starting material used, was subjected to fractional distillation under reduced pressure, and two fractions were separated, a) a more volatile light orange oil of b.p_3~120°, and b) the major fraction as a pale-yellow oil of b.p_3 120~160°; some amount of a brown oily residue always remained.

Constitution of the first fraction was analyzed gas chromatographically,[*4] and was proved to be a mixture of the starting material (Ia), and "diethyl oxalate" (Ⅵ) (Fig. 1). Formation of the oxalate (Ⅵ) was also proved by the evidence that the orange oil of the

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[*4] Two separate experiments according to the reaction condition (i) and (iii) were carried out for this purpose so that unnecessary complication of the analysis by presence of iodine in the reaction mixture might be avoided.

3) G. O. Schenck, H. Formanek: Angew. Chem., **70**, 505 (1958).
4) S. G. Cohen, R. Zand, C. Steel: J. Am. Chem. Soc., **83**, 2895 (1961).

first fraction was hydrolyzed with dilute alkali to afford oxalic acid (VII).[*5]

The major fraction was subjected to repeated column chromatography over alumina or silica gel[*6] (infrared (IR) spectra and thin-layer chromatography (TLC)). Change of refractory indexes of the oils obtained from fractions was also suggestive in separating products. Eventually the oil of the major fraction was proved to be a mixture of tetraethyl hydrazine-N_1,N_1,N_2,N_2-tetracarboxylate (VIII),[5] triethyl hydrazine-N_1,N_1,N_2-tricarboxylate (IX),[6] and diethyl hydrazine-dicarboxylate (X)[7] as follows.

Elution of the chromatogram with benzene gave first a colorless oil without any NH absorption in its IR spectrum. The oil, thin-layer chromatographically homogeneous, had b.p$_3$ 156~160°, and n_D^{25} 1.4402. The elemental analyses of the oil coupled with its Rast's molecular weight determination corresponded to the molecular formula of $C_{12}H_{20}O_8N_2$. The IR spectrum did not show any NH absorption as mentioned above but ν_{max} 1808 (s), 1768~1726 (s), 1275 (s) and 1100 (s) cm^{-1}, which corresponded to the N-CO_2-C_2H_5 group of the compound. The ultraviolet (UV) spectrum was transparent above 220 mμ, and the NMR spectrum showed a triplet at τ 8.67 with J=6.9 c.p.s. and a quartet at τ 5.74 with J=6.9 c.p.s. as the only peaks, providing further evidence for the presence of the N-$CO_2C_2H_5$ group as the only function in the compound. The oil was finally proved to be identical with

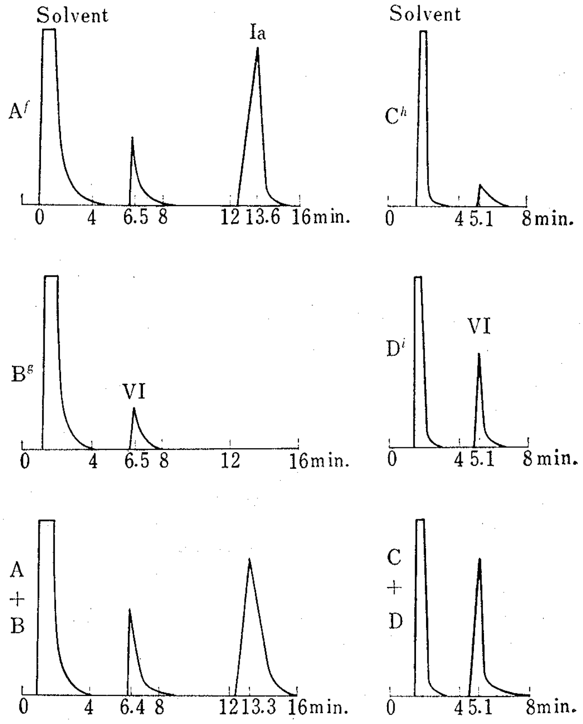
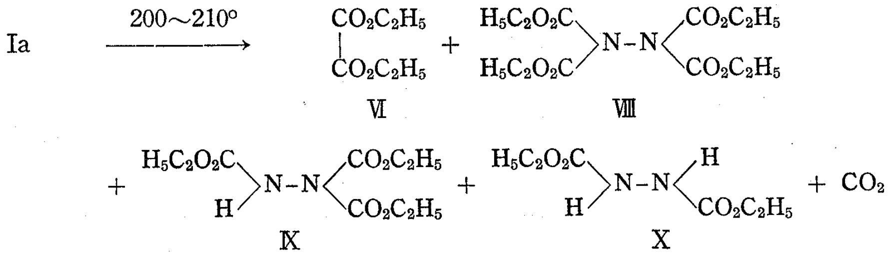


Fig. 1-1[a,c,d] Fig. 1-2[b,c,e]

Fig. 1. Gas Chromatographic Identification of Diethyl Oxalate (VI) in the Pyrolysis Product

a) The pyrolysis was carried out according to the condition (i).
b) The pyrolysis was carried out according to the condition (iii).
c) Shimadzu GC-1B with a tungsten filament detector, stainless steel column 6 mm.×3 m.×2 packed with Thermol 3.
d) Column temperature 150°, detector temperature 178°, sample temperature 160°, carrier gas He 48 ml./min.
e) Column temperature 150°, detector temperature 178°, sample temperature 160°, carrier gas He 60 ml./min.
f) Orange volatile fraction of b.p$_8$ 59~120° in acetone.
g) Diethyl oxalate (IV) in benzene.
h) Pale yellow volatile fraction of b.p$_8$ ~80° in benzene.
i) Diethyl oxalate (VI) in benzene.



$$\text{Ia} \xrightarrow{200\sim210^\circ} \underset{\text{VI}}{\begin{matrix} CO_2C_2H_5 \\ | \\ CO_2C_2H_5 \end{matrix}} + \underset{\text{VIII}}{(H_5C_2O_2C)_2N-N(CO_2C_2H_5)_2} + \underset{\text{IX}}{(H_5C_2O_2C)(H)N-N(CO_2C_2H_5)_2} + \underset{\text{X}}{(H_5C_2O_2C)(H)N-N(H)(CO_2C_2H_5)} + CO_2$$

Chart 5.

[*5] Alkaline hydrolysis of the azo-ester (Ia) itself was proved not to give oxalic acid.

[*6] Elution of the chromatogram was performed as rapidly as possible so that the products might not be further decomposed by catalytic action of adsorbents, which will be discussed in another section.

5) O. Diels, E. Borgwardt: Ber., **53**, 155 (1920).

6) R. Huisgen, F. Jacob: Ann., **590**, 53 (1954).

7) Org. Syn., Coll. Vol. III, 375 (1955).

an authentic specimen of the tetracarboxylate (VIII) synthesized according to the procedure of Diels and Borgwardt,[5] by comparison of their IR spectra and other physical properties.

Further elution of the chromatogram with benzene gave a colorless oil with NH absorption in its IR spectrum. Presence of the tricarboxylate (IX) together with the tetracarboxylate (VIII) and dicarboxylate (X) was supported by comparison of Rf values of the reaction product on TLC with those of authentic specimens of the synthetic compounds (Fig. 2).

Continuation of elution of the chromatogram with benzene and with benzene-ether, gave colorless needles of

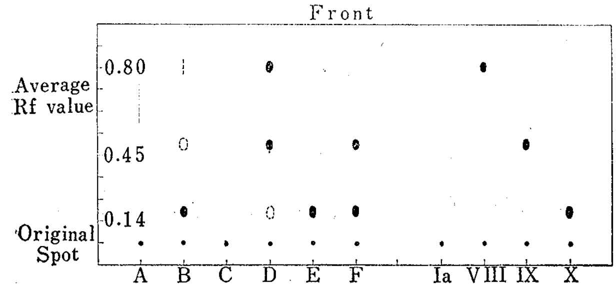


Fig. 2. Thin-layer Chromatography of the Pyrolysis Products[a,b] of the Azo-ester (Ia) at 200~210°[c]

a) Basic alumina (Wako Co.), deactivated with 6% H_2O, as 1 mm. plate of 200×100 mm. wide. 4:1 Benzene-ethyl acetate as eluent. Spots revealed with conc. sulfuric acid under ultraviolet lamp with the maximum absorption at 253.7 mμ.

b) A, B, C, D, E, and F are the materials obtained during the work up of the pyrolyzed azo-ester (Ia) as shown in the next diagram. The samples Ia, VIII, IX, and X are the synthesized specimens according to the literature.

c) According to the reaction condition (i), *i.e.* in dark without catalyst.

$$\text{Ia} \xrightarrow{200\sim210^\circ} \underset{\text{(A)}}{\text{oil}} \xrightarrow{\text{distillation}} \underbrace{\text{b.p}_3\ 59\sim120^\circ\text{(B)} + \text{b.p}_3\ 120\sim145^\circ + \text{residue(F)}}$$

$$\Big\downarrow \text{over } Al_2O_3 \text{ chromatography}$$

(C) first, and (D) second chromatograms with benzene as eluent, (E) crystals obtained with benzene-ether as eluent

Table I. Results of the Pyrolyses of Diethyl Azodicarboxylate (Ia) at 200~210°[a]

Reaction condition	Starting material (Ia) g. (mmole)	Yields of Products g. (mmole)			
		VIII	X	mixed oil of VIII, IX, and X	CO_2
a[b]	10 (57.4)	1.134 (3.54)	0.536 (3.04)	1.031	
	10 (57.4)	1.074 (3.36)	0.771 (4.38)	0.953	
	10 (57.4)	0.941 (2.94)	1.473 (8.37)	0.430	
	7 (40.2)	0.794 (2.48)	0.337 (1.91)	0.732	
	10 (57.4)				(10.7)
b[c]	10 (57.4)	1.111 (3.47)	0.544 (3.09)	0.433	
c[d]	10 (57.4)	0.519 (1.62)	0.801 (4.55)	0.613	
	10 (57.4)	0.389 (1.22)	1.153 (6.56)	0.841	
b[e]	10 (57.4)	0.981 (3.06)	0.718 (4.07)	0.370	
	10 (57.4)	1.088 (3.39)	0.904 (5.13)	0.671	
	10 (57.4)				(12.0)
e[f]	10 (57.4)	0.710 (2.21)	0.958 (5.44)	0.689	
	7 (40.2)	0.820 (2.56)	0.388 (2.21)	0.511	

a) The yields of tetraethyl hydrazine-N_1,N_1,N_2,N_2-tetracarboxylate (VIII), and diethyl hydrazine dicarboxylate (X) are based on the purified materials by chromatography of the reaction product. Triethyl hydrazine-N_1,N_1,N_2-tricarboxylate (IX) used to be obtained as a mixture with VIII and X. Carbon dioxide was characterized as $BaCO_3$ which was converted to $BaSO_4$ for the yield determination.

b) In dark on the metal bath.

c) In dark on the metal bath with iodine (0.73 g., 0.05 mmole).

d) On the 40 W tungsten lamp.

e) On the 40 W tungsten lamp with iodine (0.73 g., 0.05 mmoles).

f) Under dispersed light on the metal bath.

m.p. 132.5～133.5°. They were identified as the dicarboxylate (X) by mixed m.p. determination and comparison of its IR spectrum and other physical properties with those of an authentic specimen.[7]

TLC analysis of the brown oily residue suggested the presence of the tricarboxylate (Ⅸ) and dicarboxylate (X) (Fig. 2), however, further work up of the residue was not performed.

Formation of carbon dioxide during the pyrolysis was proved with two separate experiments according to the reaction conditions (i) and (iv). The exit gas from the reaction mixture on a nitrogen stream was collected during the pyrolysis into aqueous barium hydroxide solution; the precipitated barium carbonate was converted to barium sulphate for calculation of the yield (Table I).

Catalytic cleavage on alumina and silica gel——Alumina (basic, neutral or acidic) or silica gel was added to a benzene or ethanolic solution of Ia at room temperature with vigorous stirring under nitrogen, and the mixture was kept stirring for ～3 hr. The work up of the reaction mixture after filtration of the insoluble catalyst was carried out as usual (rapid chromatographic separation on silica gel, distillation under reduced pressure, and so on).

$$\text{Ia} \xrightarrow[\text{in 99\% EtOH (or benzene)}]{\text{alumina (or silica gel)}} \text{Ⅷ} + \text{Ⅸ} + \text{X} + \text{CO}_2$$

Chart 6.

The decomposition with silica gel appeared to proceed much slower than with alumina. As is shown in Table Ⅱ, very surprisingly, the tetracarboxylate (Ⅷ) could be isolated when Ia was decomposed on silica gel; the structure was identified by comparison of its IR spectrum and other physical properties with those of the authentic specimen of Ⅷ. Formation of Ⅷ with alumina as catalyst was also proved on TLC.

Formation of the tricarboxylate (Ⅸ), isolated as a homogeneous oil, which showed

TABLE Ⅱ. Catalytic Action of Alumina and Silica Gel toward the Azo-ester (Ia)[a)]

Starting material (Ia) g. (mmole)	Catalyst (g.)	Solvent (ml.)	Reaction time (hr.)	Yields[f)] g. (mmole)				
				Ia	Ⅷ	Ⅸ	X	CO_2
4.0 (2.30)	silica gel[b)] (20)	99% EtOH (40)	3	0.991 (5.68)	0.134 (0.418)	0.913 (3.68)	0.926 (5.26)	(3.22)
4.0 (2.30)	silica gel[b)] (20)	benzene (40)	3	0.764 (4.38)	0.051 (0.159)	1.231 (4.96)	0.525 (2.98)	(5.84)
4.0 (2.30)	neutral alumina[c)] (20)	99% EtOH (40)	1	0.865 (4.97)	trace	1.004 (4.06)	1.005 (5.71)	(5.27)
4.0 (2.30)	neutral alumina[c)] (20)	benzene (40)	1	1.710 (9.82)	trace	0.624 (2.52)	0.257 (1.46)	(4.33)
4.0 (2.30)	basic alumina[d)] (20)	99% EtOH (40)	1/3	0	trace	0.514 (2.07)	1.516 (8.62)	(13.75)
4.0 (2.30)	basic alumina[d)] (20)	benzene (40)	1	0.928 (5.33)	trace	0.693 (2.79)	0.788 (4.47)	(6.71)
4.0 (2.30)	acid alumina[e)] (20)	99% EtOH (40)	1	0.834 (4.79)	trace	0.643 (2.59)	1.085 (6.17)	(6.53)

a) Reaction temperature at 25°.
b) Purchased from Kanto Chemical Co., 100～200 mesh.
c) Purchased from M. Woelm Eschwege, neutral, grade I.
d) Purchased from Wako Chemical Co., basic.
e) Alumina, purchased from Wako Co., was shaken with 10% H_2SO_4 for 1 hr., and washed with water repeatedly until the pH of filtrate reached 4.0.
f) Yields of Ia, Ⅷ, Ⅸ, and X are based on the purified materials by distillation under reduced pressure or rapid chromatography over silica gel of the reaction product. Carbon dioxide is characterized as $BaCO_3$ which is then converted to $BaSO_4$ for the yield determination.

b.p.$_{0.10}$ 130°, ν_{max} 3318 (m) and 1514 (m) cm^{-1} for NH and ν_{max} 1804 (s) and 1762~1721 (s) cm^{-1} for N-$CO_2C_2H_5$ groups respectively, no intensive UV absorption, and n_D^{25} 1.4469, was observed with both alumina and silica gel as catalyst. These physical properties were completely identical with those of an authentic specimen of IX.

The dicarboxylate (X) was also identified among the products as colorless needles (m.p., IR spectra and TLC).

Formation of carbon dioxide was proved as barium carbonate as was performed in the pyrolytic experiment (Table II).

Photolysis——The azo-ester (Ia) was photolyzed on a 40W tungsten lamp in refluxing benzene. The reaction was carried out under nitrogen, and was followed by TLC. The reaction appeared to proceed much slower than the pyrolyses at 200° and more than 50% of the starting material was recovered after the prolonged exposure of the reaction mixture to light for 120 hr.

$$\text{Ia} \xrightarrow[\text{benzene}]{h\nu} \text{IX} + \text{X} + CO_2$$

Chart 7.

Presence of neither the tetracarboxylate (VIII) nor the oxalate (VI) was proved by TLC or gas chromatographic (GC) analyses of the reaction product. Formation of a certain amount of the tricarboxylate (IX) and dicarboxylate (X) was suggested by TLC. Isolation of these compounds was not performed. Formation of carbon dioxide during the photolysis was proved as barium carbonate.

Discussions

It would be unjustified to try, on the basis of the above evidence, to give any definitive explanation of the exact factors governing courses of the above reactions of three different types. However, a possible explanation on the mechanisms involved in the reactions referred to in the present paper might be tentatively put forward as follows.

The reaction at 200~210° begins, as many pyrolytic reactions do, with the homolytic cleavage of the azo-bridge giving the diradical (IV) which leads to several products as is shown below.

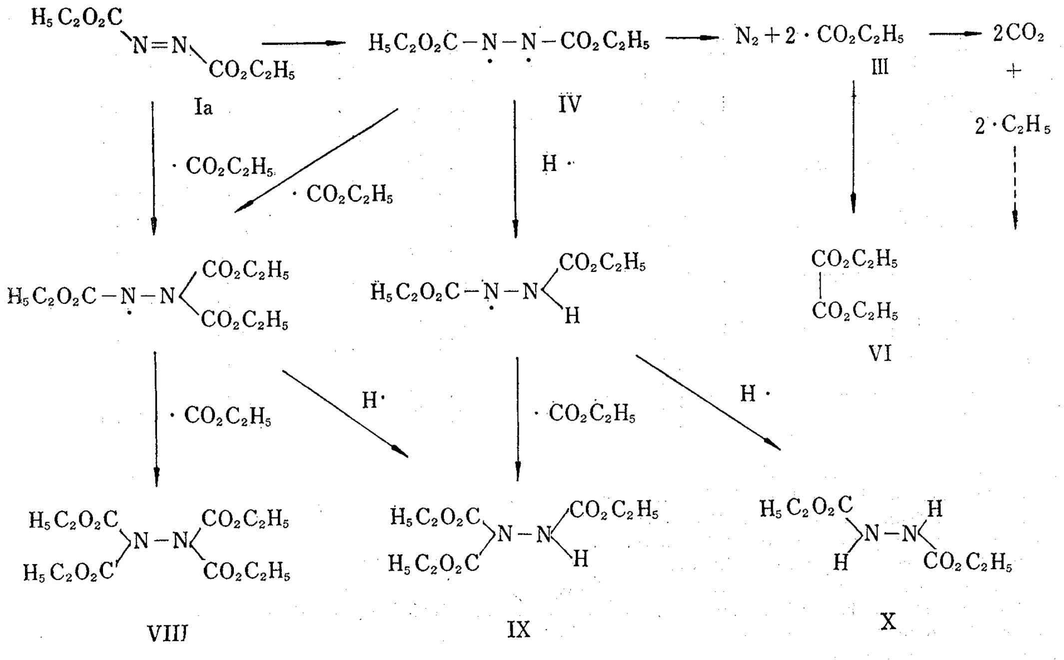


Chart 8.

Formation of the ethoxycarbonyl radical (Ⅲ) as important intermediate would definitely be supported by the evidence that both diethyl oxalate (Ⅵ) and carbon dioxide were identified among the products. The radical (Ⅲ) would then react with the azo-ester (Ia) or other transitionally formed free radical intermediates affording "higher ethoxycarbonylated" hydrazine derivatives, Ⅷ, and Ⅸ. Meanwhile, the hydrogen-abstraction reaction might be another process of the reaction during the course of the diradical (Ⅳ) to Ⅸ or Ⅹ.

It has been found that addition of iodine does not cause any important change to the result of pyrolyses. It would mean that iodine did not essentially alter the nature of the reaction at such high temperature either as initiator or suppressor[8)] for homolytic processes involved in the reaction. Unfortunately, an attempt to prove the homolytic character of the reaction by electron spin resonance (ESR) spectroscopy failed. The ESR analysis[*7] of the azo-ester (Ia) was carried out at 24° and 150°, and any detectable amount of free redical could not be proved at both temperatures. This would not however be an unexpected result in view of the fact that the reaction did not in fact proceed nearly at all below 150°, and also by the reasoning that the concentration of free radical, if present, might be too small to be detected due to equal distribution of electrons at high (excited) and low (ground) energy states at such temperature at 150°.

It was of particular interest that both alumina and silica gel catalyzed a homolysis-like reaction of the diethoxycarbonylated azo-ester (Ia) to the tetra- (Ⅷ) and tri- (Ⅸ) -ethoxycarbonylated hydrazine derivatives. The real nature of the reaction of the azo-bridge in Ia on such metal oxides as silica gel or alumina is however to be open to further discussions.

Finally, so far as the condition chosen in the present investigation for the photolysis of Ia is concerned, any tetrazane derivative (V) was not detected as product. Furthermore, presence of the tetracarboxylate (Ⅷ) and oxalate (Ⅵ) could not be proved by GC or TLC respectively, but were formed the tricarboxylate (Ⅸ), dicarboxylate (Ⅹ), and carbon dioxide as the isolable products. As it is an accepted knowledge that photochemical reactions, in general, begin with the homolytic cleavage of bond, the photolysis might follow the homolytic pathways shown above.

Experimental[*8]

Material

Diethyl Azodicarboxylate (Ia)——Prepared according to the procedure of Cohen, *et al.*[4)] as an orange oil, b.p$_3$ 86~87°(lit. b.p$_5$ 90~95°); λ_{max} mμ (ε): 402 (38) (N=N); ν_{max} cm^{-1}: 1790~1765 (s), 1252~1212 (s), 1020 (s) (N-$CO_2C_2H_5$)).

Tetraethyl Hydrazine-N_1,N_1,N_2,N_2-tetracarboxylate (VIII)——Prepared according to the procedure of Diels and Borgwardt,[5)] as a colorless oil, b.p$_3$ 155~157°(lit. b.p$_{0.65}$ 145~146°); n_D^{25} 1.4400; ν_{max} cm^{-1}: 1807 (s), 1770~1726 (s), 1285~1240 (s), 1100 (s) (N-$CO_2C_2H_5$).

Triethyl Hydrazine-N_1,N_1,N_2-tricarboxylate (IX)——Prepared according to the procedure of Huisgen, *et al.*[6)] as a colorless oil, b.p$_{0.4}$ 134~135°(lit. b.p$_{0.001}$ 120~125°); n_D^{25} 1.4473; ν_{max} cm^{-1}: 3305 (s), 1505 (s) (NH), 1800 (s), 1763~1723 (s), 1271 (s), 1108 (s) (N-$CO_2C_2H_5$).

Diethyl Hydrazine-N_1,N_2-dicarboxylate (X)——Prepared according to the literature[7)] as colorless needles, m.p. 132.5~134°(lit. 134~135°); ν_{max} cm^{-1}: 3245 (s), 1532 (s) (NH), 1740 (s), 1682 (s), 1240 (s), 1065 (s) (N-$CO_2C_2H_5$).

[*7] We are indebted to Dr. T. Takahashi of the Research Laboratories of Takeda Chemical Industries for the ESR analysis made on a Japan Electronics Optics Laboratory JES-3B ESR spectrometer.

[*8] M.p.s. were taken on a Kofler-type hot stage, and are uncorrected. IR spectra of oily compounds were taken as film, and those of solid compounds refer to nujol, and UV spectra to 95% ethanol, and NMR spectra (taken at 60 Mc on a Varian associates A-60 spectrometer) to carbon tetrachloride unless otherwise stated.

8) C. Walling: "Free Radicals in Solution," p. 3, 476, 543 (1957). John Wiley and Sons, Inc., New York.

Pyrolysis of Diethyl Azodicarboxylate (Ia) at 200∼210°——An example of the pyrolysis according to the condition (i), *i.e.* in dark on a metal bath at 200∼210°, is as follows. The orange azo-ester (Ia) (7.0 g., 40.2 mmoles) was heated on a metal bath at 200∼210° in a dark for 2 hr.; the whole reaction was carried out under nitrogen. The reddish oil thus obtained was fractionally distilled under reduced pressure into three fractions, a) an orange oil, b.p$_{1\sim2}$ 48∼89° (wt. 100 mg.), b) a pale yellow oil of b.p$_2$ 125∼155° (wt. 2.13 g.), and c) a brown oily residue (wt. 3.40 g.).

The orange oil of the first fraction was analyzed gas chromatographically using Shimadzu GC-1B with a tungsten filament detector, stainless steel column 6 mm. × 3 m. × 2 packed with Thermol 3 at a flow rate of 48 ml./min. with helium carrier, retention time (pyrolytic) 6.5 min., 13.5 min., (synthetic) 6.5 min. (diethyl oxalate (Ⅵ)), 13.4 min. (Ia)[*9] (Fig. 1). The rest of the oil (*ca.* 100 mg.) was dissolved in a mixture of 10% NaOH (2 ml.) and 99% EtOH (1 ml.), and the solution was refluxed for 20 min. and was concentrated *in vacuo* to *ca.* two third volume which was acidified with addition of some drops of dil. HCl and was extracted into ether.

The ethereal layer was washed with a small amount of water, and dried (anhyd. Na_2SO_4). Concentration of the ethereal filtrate afforded a solid which was dissolved in water, to which 5% $Ba(OH)_2$ was added, depositing a colorless precipitate. The precipitate was collected, washed with a small amount of water, and was treated with dil. HCl. The acid solution thus obtained was extracted into ether, and the ethereal layer was washed with a small amount of water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate gave a colorless solid which was recrystallized from a small amount of water to give Ⅶ as colorless prisms. The prisms sublimed on heat, and its IR spectrum showed $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3482∼3390 (s) (OH), 1703∼1670 (s), 1260 (s), 1125 (s) (COOH), which was completely superposable with that of an authentic sample of oxalic acid hydrate.

The pale-yellow oil of the major fraction showed $\nu_{\max}$ cm^{-1}: 3320 (s), 1505 (s) (NH), 1802 (s), 1772∼1725 (s), 1294∼1235 (s), 1108 (s) ($N{-}CO_2C_2H_5$), and was chromatographed on basic alumina (Wako Co.) (64 g.) deactivated with 6% H_2O when elution with benzene (90 ml.) afforded a colorless oil without any NH absorption in its IR spectrum. The oil was identified as the tetracarboxylate (Ⅷ) by comparison of its IR spectrum with that of an authentic sample of Ⅷ (wt. 794 mg., 2.48 mmoles). Repeated distillation under reduced pressure gave material of b.p$_3$ 156∼160°. *Anal.* Calcd. for $C_{12}H_{20}O_8N_2$: C, 45.00; H, 6.20; N, 8.75. Found: C, 45.05; H, 6.17; N, 8.60. Rast molecular weight determination, 311 (Calcd. 320.30); Rf (TLC over deactivated basic alumina (Wako Co.) with 4:1 benzene-ethyl acetate as eluent), (pyrolysis) 0.80, (synthetic) 0.80; n_{D}^{25} 1.4402; $\nu_{\max}$ cm^{-1}: 1808 (s), 1768∼1726 (s), 1275 (s), 1100 (s) ($N{-}CO_2C_2H_5$); NMR τ: 5.74 (2H, q, J=6.9 c.p.s.) ($N{-}CO_2\underline{CH_2}CH_3$), 8.67 (3H, t, J=6.9 c.p.s.) ($N{-}CO_2CH_2\underline{CH_3}$).

Further elution with benzne (630 ml.) afforded a colorless oil (wt. 732 mg.), which showed $\nu_{\max}$ cm^{-1}: 3333 (s), 1512 (m) (NH), 1804 (s), 1766∼1722 (s), 1289∼1227 (s), 1107 (s) ($N{-}CO_2C_2H_5$), Rf (TLC over deactivated basic alumina (Wako Co.) with 4:1 benzene-ether as eluent), (pyrolysis) 0.80, 0.45, 0.14, (synthetic) 0.80 (Ⅷ), 0.45 (Ⅸ), 0.14 (Ⅹ) (Fig. 2); these properties supported the constitution of the oil to be a mixture of the tetra- (Ⅷ), tri- (Ⅸ), and di (Ⅹ) -carboxylates.

The dicarboxylate (Ⅹ) was separated as colorless crystals by treatment of the oil with methanol. They were recrystallized from 95% EtOH to give colorless needles of m.p. 132.5∼133.5°, alone and on admixture with an authentic specimen of the dicarboxylate (Ⅹ)[7] (wt. 337 mg., 1.91 mmoles). *Anal.* Calcd. for $C_6H_{12}O_4N_2$: C, 40.90; H, 6.87; N, 15.90. Found: C, 40.49; H, 6.91; N, 16.16. $\nu_{\max}$ cm^{-1}: 3250 (s), 1536 (s) (NH), 1744 (s), 1690 (s), 1255 (s), 1070 (s) ($N{-}CO_2C_2H_5$). Rf (TLC over deactivated basic alumina (Wako Co.) with 4:1 benzene-ether as eluent), (pyrolysis) 0.14, (synthetic) 0.14 (Fig. 2).

The brown residue of the pyrolysis was analyzed on TLC over deactivated basic alumina (Wako Co.), showing Rf 0.45 and 0.14, which suggested the presence of both the tri- (Ⅸ) and di- (Ⅹ) -carboxylates (Fig. 2); further examination on the oil was abondoned.

Formation of carbon dioxide: Formation of carbon dioxide during the pyrolysis was characterized by the separate experiment according to the reaction condition (i) or (iv) as follows. The azo-ester (Ia) (10.0 g., 57.4 mmoles) in a 25 ml. round flask with a gas inlet and a reflux condenser which was connected with a gas outlet, was pyrolyzed at 200∼210° for 2 hr.; a nitrogen stream was introduced from the gas inlet and the exit gas on the nitrogen stream was collected from the gas outlet into dil. $Ba(OH)_2$ aq. when a colorless solid ($BaCO_3$) precipitated. The carbonate was filtered off, washed with a small amount of water, and was treated with dil. H_2SO_4 to give $BaSO_4$ as a colorless solid, which was dried until its weight reached a constant value (wt. 2.486 g., 1.07 mmoles as carbon bioxide).

Catalytic Action of Alumina or Silica Gel toward the Azo-ester (Ia)——An example of the catalytic action of alumina or silica gel toward the azo-ester (Ia) is as follows. To a suspension of silica gel (Kanto Chemical Co., 100∼200 mesh) (20 g.) in 99% EtOH (50 ml.), a solution of Ia (4.0 g., 23.0 mmoles) in 99% EtOH (10 ml.) was added dropwise with vigorous stirring at 22° in 5 min., and the reaction mixture was kept at the same temperature with stirring for 3 hr. During the procedure, a nitrogen stream was continuously

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[*10] Data of another example of gas chromatographic analysis of the pyrolysis product according to the condition (iii) is also shown in Fig. 1.

introduced from a gas inlet into the mixture. The exit gas on the nitrogen stream was collected from the top of the condenser into satd. $Ba(OH)_2$ aq. (150 ml.) when a colorless solid ($BaCO_3$) precipitated. The carbonate was filtered off, washed with H_2O, and dissolved in $2N$-HCl, to which $2N$-H_2SO_4 was added depositing a colorless solid ($BaSO_4$). The sulfate was filtered off, washed with H_2O, and dried (wt. 750 mg., 3.22 mmoles as CO_2).

Work up of the reaction mixture was carried out that silica gel was filtered off, and washed with 99% EtOH (50 ml.) five times. Concentration of the combined ethanolic filtrate *in vacuo* gave an orange oily residue (wt. 3.11 g.), which was treated with benzene (2 ml.) when the dicarboxylate (X) precipitated as colorless crystals, m.p. 130~133° (wt. 568 mg.). They were recrystallized from aqueous ethanol to give colorless needles of m.p. 132.5~133.5°, alone and on admixture with an authentic specimen of X (wt. 326 mg.). Their IR spectrum showed ν_{max} cm^{-1}: 3258 (s), 1528 (s) (NH), 1732 (s), 1685 (s), 1230 (s), 1065 (s) ($N-CO_2C_2H_5$), which was superposable with that of X.

The benzene filtrate of the crystals (X) was concentrated *in vacuo* to give an orange oily residue which was subjected to distillation under reduced pressure, giving an orange oil, b.p$_3$ 80° (wt. 980 mg.), and a pale yellow oily residue. The orange oil showed λ_{max} mμ (ε): 403 (36) (N=N); ν_{max} cm^{-1}: 1790~1765 (s), 1270~1220 (s), 1021 (s) ($N-CO_2O_2H_5$), and was proved to be identical with the azo-ester (Ia) by comparison of its IR spectrum with that of Ia.

To the residue was added benzene (1 ml.) when further X precipitated as colorless crystals, m.p. 117~130° (wt. 323 mg.). They were recrystallized from aqueous ethanol to give colorless needles, m.p. 132~133° (wt. 190 mg.) (mixed m.p. and IR determinations).

The benzene filtrate of the needles was concentrated under reduced pressure to give a pale yellow oil (wt. 1.126 g.), which was chromatographed over silica gel (Kanto Chemical Co., 100~200 mesh) (30 g.) when elution with benzene (80 ml.) afforded an orange oil, which was characterized as Ia by IR and TLC analysis (wt. 11 mg.). The yield of the recovered starting material (Ia) reached 991 mg. (57 mmoles).

Further elution with benzene (980 ml.) gave a colorless oil (wt. 134 mg., 0.42 mmoles as Ⅷ), which, after distillation at 3 mm. Hg and at 170° (oil bath), gave n_D^{25} 1.4399, ν_{max} cm^{-1}: 1819 (s), 1773~1717 (s), 1271 (s), 1107 (s) ($N-CO_2C_2H_5$), and was proved to be identical with Ⅷ by comparison of its IR spectrum with that of an authentic specimen of Ⅷ.

Further elution with 4:1 benzene-ether (780 ml.) afforded a colorless oil (wt. 913 mg., 3.70 mmoles as Ⅸ), which on distillation under reduced pressure gave b.p$_{0.3}$ 94°; n_D^{25} 1.4470; ν_{max} cm^{-1}: 3311 (m), 1503 (m) (NH), 1800 (m), 1734~1712 (s), 1260 (s), 1102 (s) ($N-CO_2C_2H_5$), and was proved to be identical with Ⅸ by comparison of its IR spectrum with that of an authentic specimen of Ⅸ.

Continuous elution with the same solvent (150 ml.) gave colorless crystals, m.p. 127~132°, alone and on admixture with an authentic specimen of X (wt. 35 mg.). The total yield of X then reached 926 mg. (5.26 mmoles).

Photolysis of the Azo-ester (Ia) with a 40 W Tungsten Lamp——A 100 ml. Erlenmyer flask with a gas inlet and a reflux condenser was placed on a 40 W tungaten lamp at a distance of *ca.* 1.5 cm. A solution of the azo-ester (Ia) (5.0 g., 28.7 mmoles) in benzene (50 ml.) was put into the flask when the light was on. The benzene solution began to reflux in a few min., and was kept illuminated for 120 hr. A nitrogen stream was continuously introduced into the solution from the gas inlet and the exit gas on the nitrogen stream was collected from the top of the condenser into dil. $Ba(OH)_2$ aq. when a colorless solid ($BaCO_3$) precipitated. This was converted to $BaSO_4$, and was weighed (99 mg., 0.42 mmoles as carbon dioxide).

The reaction was followed by TLC (over deactivated basic alumina with 4:1 benzene-ethyl acetate as eluent) which after 120 hr. showed Rf (photolysis) 0.27, 0.64, (synthetic) the tetracarboxylate (Ⅷ) 0.88, tricarboxylate (Ⅸ) 0.64, dicarboxylate (X) 0.27, suggesting presence of the tricarboxylate (Ⅸ) and dicarboxylate (X) in the reaction mixture.

After illumination for 120 hr., the solution was concentrated *in vacuo* to give an orange oil (wt. 4.33 g.), which was fractionally distilled under reduced pressure, and the azo-ester (Ia) of b.p$_{2.4}$ 64°, (wt. 3.27 g., 18.8 mmoles) was recovered (IR spectra).

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