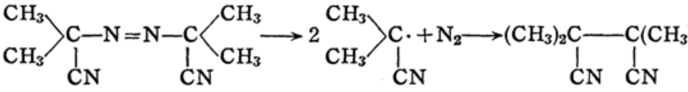
The Dimerization of Trichloroethylene Induced by the Decomposition of α, α'-Azodiisobutyronitrile and the Structure of the Dimer

By Osamu SIMAMURA and Naoki INAMOTO

(Received December 14, 1953.)

α, α'-Azodiisobutyronitrile first prepared by Thiele and Heuser[1] decomposes thermally to give tetramethylsuccinonitrile and nitrogen, involving homolysis to intermediate radicals $(CH_3)_2\dot{C}CN$:



$$(CH_3)_2\underset{CN}{C}-N=N-\underset{CN}{C}(CH_3)_2 \longrightarrow 2\,(CH_3)_2\underset{CN}{C}\cdot + N_2 \longrightarrow (CH_3)_2\underset{CN}{C}-\underset{CN}{C}(CH_3)_2$$

It acts therefore as a powerful initiator of the vinyl polymerization. The synthetical aspects of the chemistry of this and related compounds pertaining to this property have been reviewed by Ziegler[2]. The thermal decomposition of these compounds and the chemical nature of the radicals thereby produced have recently been the subject of numerous investigations[3]. It appeared to be of interest, as part of a study of chemical behavior of radicals in solution, to investigate the decomposition of **α, α'**-azodiisobutyronitrile in trichloroethylene which is known to give no high polymeric substances except in copolymerization with other reactive monomers[4]. In the present paper an account is given of the determination of the structure of the dimer of trichloroethylene produced by the agency of **α, α'**-azodiisobutyronitrile, and a mechanism of the dimerization is proposed.

By boiling trichloroethylene with 1 to 1.5 mole % of **α, α'**-azodiisobutyronitrile added in portions over a period of 35 to 64 hours and fractionating the reaction mixture a dimer, $C_4H_2Cl_6$, of trichloroethylene was obtained as a main product in 25 to 28% conversion (see Table I). The fractionation of higher polymeric products was not carried out, and the ratio of the weight of the dimer obtained to the weight of the residue from the distillation was shown in the column headed "Dimer/Polymers" in Table I. As Frank and Blackham[5] had reported the dimerization of trichloroethylene by means of dibenzoyl peroxide, we also repeated their experiment and the dimerized product was shown to be identical with that obtained by the action of **α, α'**-azodiisobutyronitrile by comparing their infrared spectra (see Fig. 1 and Table II).

TABLE I

DIMERIZATION OF TRICHLOROETHYLENE

Expt. No.	C_2HCl_3 g.	Azodinitrile mole %	Benzoyl peroxide mole %	Reaction time hrs.	Yield of dimer g.	B.p. °C/mm. Hg	Conversion %	Dimer/ Polymers
1	131	1.5		35.5	27	103–5/10	25.3	4.4
2	168	1.0		38	31	117–8/18	24.5	3.0
3	320	1.0		64	79.5	111–3/12	28.3	7.3
4	240		1.0	41	120	98–100/7–8	58.3	6.0
Data from ref. 5			1.2	95		104.4/10	68.3	9.0

TABLE II

PROPERTIES OF DIMER $C_4H_2Cl_6$

Source	B.p. °C/mm. Hg*	d_4^{20}	n_D^{20}	MR_D
Expt. 3	104/10	1.6786	1.5452	49.51
Expt. 4	98–100 /7–8	1.6727	1.5471	49.72
Ref. 5	104.4/10	1.6760	1.5461	49.66
				Calcd. 49.41

* Redistilled.

---

[1] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

[2] K. Ziegler, *Brennstoff-Chem.*, **30**, 181 (1949).

[3] See *Ann. Rep. on Progr. Chem.*, **49**, 115 (1952).

[4] K. W. Doak, *J. Am. Chem. Soc.*, **70**, 1525 (1948).

[5] C. E. Frank and A. U. Blackham, ibid., **72**, 3283 (1950).

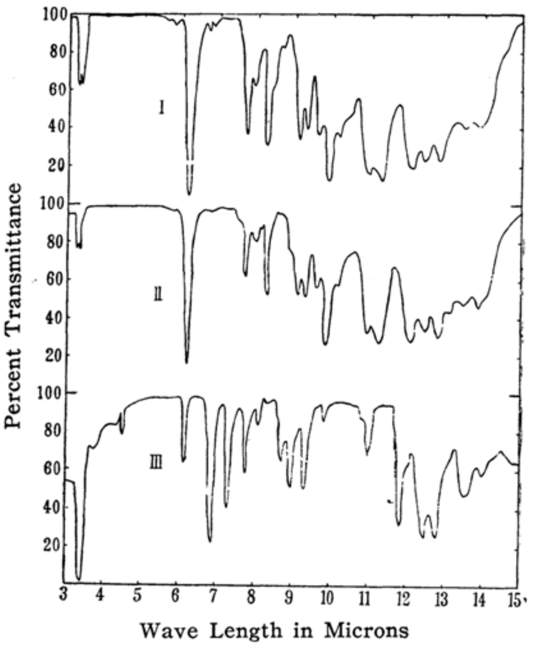
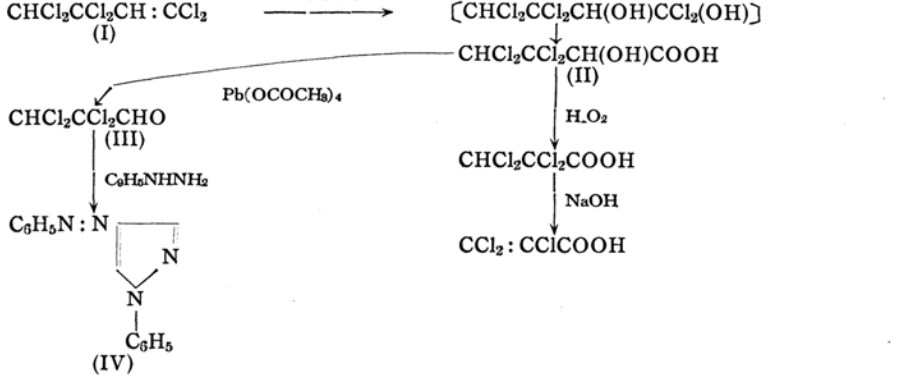


Fig. 1. Infrared absorption spectra of trichloroethylene dimers (I and II) obtained in the presence of azodiisobutyronitrile and dibenzoyl peroxide, respectively, and of 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene(III).

The chemical constitution of the dimer of trichloroethylene (I) was established to be 1, 1, 3, 3, 4, 4-hexachloro-1-butene on the basis of the following degradations (see the annexed scheme). The oxidation of the dimer with potassium permanganate in cold aqueous acetone gave a crude acid (II), but it could be neither crystallized nor distilled without decomposition, and no attempt at characterization was therefore made. It was shown, however, that it is an α-hydroxy acid, because, in the first place, the action of the Fenton reagent⁽⁶⁾ converted it to an acidic substance which gave a reddish brown precipitate with 2, 4-dinitrophenylhydrazine showing that an α-keto acid was formed, and secondly, on oxidation with lead tetraacetate according to Oeda⁽⁷⁾, it gave an aldehyde (III). This aldehyde also was not isolated in a pure state, but it developed a purple color with Schiff's reagent and gave with excess phenylhydrazine 1-phenyl-4-phenylazopyrazole (IV), m. p. 126–7°, demonstrating that the aldehyde (III) contains three carbon atoms. The formation of the pyrazole from aldehyde III, which must be 2, 2, 3, 3-tetrachloropropanal, as will be seen below, is readily understandable from its structure; for α and β carbon atoms of the aldehyde carry respectively two chlorine atoms and their function may therefore be equivalent to a carbonyl group. The same pyrazole is obtained by the action of phenylhydrazine on compounds with analogous structural features, namely, 1, 1, 3, 3-tetrachloropropanone⁽⁸⁾ and 1, 3-bisphenylhydrazone of propanonedial⁽⁹⁾. By heating the crude hydroxy acid (II) with 30% hydrogen peroxide 2, 2, 3, 3-tetrachloropropanoic acid, m. p. 79–80°, was obtained, which was dehydrochlorinated to 2, 3, 3-trichloropropenoic acid, m. p. 75–6°, by heating with aqueous sodium hydroxide. Thus, the grouping $CHCl_2CCl_2$- must be present in the dimer molecule and the double bond is accordingly located at the terminal position, the structure of the dimer having to be either $CHCl_2CCl_2CH:CCl_2$ or $CHCl_2CCl_2CCl:CHCl$. That the former structure is the correct one is shown by the formation of the three-carbon aldehyde (III) by the two-step cleavage of the double bond, which requires that carbon atom 2 of the dimer must bear a hydrogen atom. The structure of the hydroxy acid (II) must be 2-hydroxy-3, 3, 4, 4-tetrachlorobutanoic acid which is derived from the dimer (I) by hydroxylation at the double bond followed by hydrolysis and dehydration at carbon atom 1.



---

6) H. J. H. Fenton and H. O. Jones, *J. Chem. Soc.*, **77**, 71 (1900).

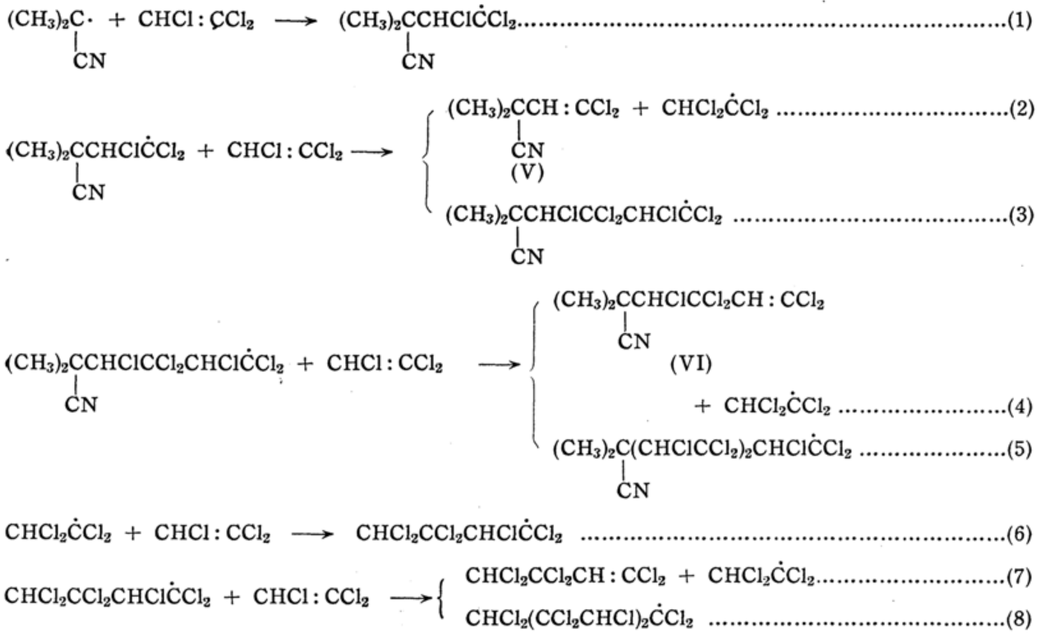
7) H. Oeda, This Bulletin, **9**, 8 (1934).

8) S. Levy and F. C. Witte, *Ann.*, **252**, 345 (1889); Th. Zincke and O. Kegel, *Ber.*, **22**, 1478 (1889).

9) H. v. Pechmann and L. Vanino, *Ber.*, **27**, 222 (1894).

Henne and Ruh[10] had attempted the determination of the structure of the trichloroethylene dimer obtained by means of dibenzoyl peroxide, but they could not decide between several possibilities. Frank and Blackham,[5] without presenting any experimental proof, had inferred the same structure as above by assuming that the dimerization of trichloroethylene follows a similar course to those of chlorinated olefins the structures of whose dimers are well established.[11,12] Since the identical dimer is obtained from trichloroethylene, as has been mentioned earlier, by means of either benzoyl peroxide or α, α′-azodiisobutyronitrile, the present structural proof is valid also for the dimers obtained by the American workers.

The residue from the fractionation of the dimer (Expt. No. 3) yielded a small amount of a new crystalline compound, m. p. 167–168°, which analyzed for $C_8H_8Cl_5N$ (see Fig. 1 for the infrared spectrum). In view of the established structure of the dimeric product and of the initiation of this reaction by α, α′-azodiisobutyronitrile, it is highly probable that this compound is 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene (VI), which should result from the successive addition of 1-cyano-1-methylethyl radical produced from an initiator molecule to two molecules of trichloroethylene followed by loss of a chlorine atom (reactions 1, 3 and 4 shown in the following scheme). The isolation of the compound $C_8H_8Cl_5N$ is significant in that, in the first place, it contains a radical moiety from the initiator molecule, thus demonstrating the mechanism of the initiation, and further, it affords an experimental proof of the chlorine atom being transferred from a growing radical chain to a molecule of trichloroethylene, a new chain being thereby initiated. Thus, we are led to formulate the initiation, propagation and termination of the dimerization as follows:



$$(CH_3)_2\underset{\underset{CN}{|}}{C}\cdot + CHCl:CCl_2 \longrightarrow (CH_3)_2\underset{\underset{CN}{|}}{C}CHCl\dot{C}Cl_2 \quad\text{......(1)}$$

$$(CH_3)_2\underset{\underset{CN}{|}}{C}CHCl\dot{C}Cl_2 + CHCl:CCl_2 \longrightarrow \begin{cases} (CH_3)_2\underset{\underset{\underset{(V)}{CN}}{|}}{C}CH:CCl_2 + CHCl_2\dot{C}Cl_2 & \text{......(2)} \\ (CH_3)_2\underset{\underset{CN}{|}}{C}CHClCCl_2CHCl\dot{C}Cl_2 & \text{......(3)} \end{cases}$$

$$(CH_3)_2\underset{\underset{CN}{|}}{C}CHClCCl_2CHCl\dot{C}Cl_2 + CHCl:CCl_2 \longrightarrow \begin{cases} (CH_3)_2\underset{\underset{CN}{|}}{C}CHClCCl_2CH:CCl_2 \;\; (VI) & \\ \qquad + CHCl_2\dot{C}Cl_2 & \text{......(4)} \\ (CH_3)_2\underset{\underset{CN}{|}}{C}(CHClCCl_2)_2CHCl\dot{C}Cl_2 & \text{......(5)} \end{cases}$$

$$CHCl_2\dot{C}Cl_2 + CHCl:CCl_2 \longrightarrow CHCl_2CCl_2CHCl\dot{C}Cl_2 \quad\text{......(6)}$$

$$CHCl_2CCl_2CHCl\dot{C}Cl_2 + CHCl:CCl_2 \longrightarrow \begin{cases} CHCl_2CCl_2CH:CCl_2 + CHCl_2\dot{C}Cl_2 & \text{......(7)} \\ CHCl_2(CCl_2CHCl)_2\dot{C}Cl_2 & \text{......(8)} \end{cases}$$

In the above formulation the transference of the chlorine atom is shown as occurring by a collision between a radical and a molecule of trichloroethylene. However, the possibility could not be excluded experimentally that the transference is effected by initial decomposition of the radical into a stable molecule and a chlorine atom, the latter adding subsequently to a molecule of trichloroethylene to give radical $CHCl_2\dot{C}Cl_2$.

A search for 1, 1-dichloro-3-cyano-3-methyl-1-butene (V) failed, the formation of which should be expected from the mode of initiation and the comparative ease of transference of the chlorine atom to trichloroethylene. Reactions 5 and 8 giving rise to higher polymeric products are of subordinate importance, as is seen from the last column in Table I, in line with the observation that trichloroethylene is unable to give high polymeric

---

[10] A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

[11] K. E. Wilzbach, F. R. Mayo and R. Van Meter, ibid., **70**, 4069 (1948).

[12] M. S. Kharasch and G. Büchi, *J. Org. Chem.*, **14**, 84 (1949).

substances on account of the steric hindrance exerted by the chlorine atoms at the double bond.

The dimerization by a chain transer reaction in which a halogen atom is transferred from the dimer radical to the monomer has originally been suggested by Wilzbach and Mayo[11] for methallyl chloride, and Kharasch and Büchi[12] explained the formation of 5-bromo-4-(bromomethyl)-1-pentene in the decomposition of acetyl peroxide in allyl bromide on the basis of a similar mechanism. The present study has brought foward another case in which such a mechanism is operative.

Experimental

Materials α, α'-Azodiisobutyronitrile was prepared according to Thiele and Heuser[1], and recrystallized from ether, m. p. 104° with decomposition. Commercial trichloroethylene was washed with aqueous potassium carbonate and then with water, dried with calcium chloride and fractionated. A fraction boiling at 87.0° was used.

Dimerization To boiling tricholoroethylene under reflux 1 to 1.5 mole % of α, α'-azodiisobutyronitrile was added in portions over a period of 35 to 64 hours, towards the end of which the temperature of the heating bath had to be elevated to 135° to keep the liquid refluxing. The results of three runs are shown in Table I. A reaction mixture, on cooling, deposited tetramethylsuccinonitrile (e.g., 0.14 g. in Expt. No. 3), m.p. 169°; the filtered solution was repeatedly fractionated through a Vigreux column 50 cm. in length; unreacted trichloroethylene was recovered and the dimer distilled over at 104° at 100 mm. Hg (Found: C, 18.7; H, 1.0; Cl, 80.86. Calcd. for $C_4H_2Cl_6$: C, 18.3, H, 0.8; Cl, 80.99%.). The residue from the fractionation, treated with ether, deposited 0.4 g. of 1, 1, 3, 3,4-pentachloro-5-cyano-5-methyl-1-hexene (VI), m. p. 167–8° (from alcohol) (Found: C, 32.7; H, 2.6; N, 4.73; Mol. wt. (Rast), 296. Calcd. for $C_8H_8Cl_5N$: C, 32.5; H. 2.7; N, 4.74 %; Mol. wt., 295.5). When the mother liquor was subjected to distillation at 0.04 mm. Hg., 5.6 g. of unidentified viscous oil (probably a trimer etc.) passed over at 122–124°, from which a further 0.3 g. of the pentachlorocyanomethylhexene crystallized out.

Degradation of the Dimer Potassium permanganate (6.5 g.) was added in portions with shaking to 5.0 g. of the dimer dissolved in 30 cc. of acetone and 5 cc. of water cooled with water at 10°. The mixture was filtered from the manganese dioxide, which was then washed with acetone. The filtrate and the washing were combined and evaporated on a water bath. The residue was neutralized with hydrogen sodium carbonate, the solution evaporated under diminished pressure of a water pump, and the residue extracted with ether to remove neutral substances. It was acidified with dilute hydrochloric acid and saturated with sodium chloride, and the solution was extracted repeatedly with ether. The ethereal extracts were combined and dried with anhydrous sodium sulfate and the ether was removed on a water bath giving 2.5 g. of a liquid residue comprising 2-hydroxy-3, 3, 4, 4-tetrachlorobutanoic acid (II), which could not be brought to crystallization by keeping over concentrated sulfuric acid in an evacuated desiccator for seven days.

To the crude α-hydroxy acid (II) (2.0 g.) in 5 cc. of water heated in a boiling water bath 30 % hydrogen peroxide was added drop by drop over a period of one hour until the presence of its excess was shown by potassium iodide-starch paper. The reaction mixture was cooled and extracted with ether and the ether removed. The liquid residue (1.2 g.), on being kept over concentrated sulfuric acid in an evacuated desiccator for three days, deposited 0.3 g. of hygroscopic crystals of 2, 2, 3, 3-tetrachloropropanoic acid, m. p. 79–80° (from petroleum ether, reported m. p. 76°[13]) (Found: Cl, 66.63; neutralization equivalent, 222. Calcd. for $C_3H_2Cl_4O_2$: Cl, 66.98 %; neutralization equivalent, 212). Further crops of the acid (a total of 0.8 g.) were obtained after several days. This acid (1 g.) was heated with 0.4 g. of sodium hydroxide in 5 cc. of water, the mixture acidified with hydrochloric acid and extracted with ether, the ether removed and the residue recrystallized from petroleum ether to give 0.8 g. of 2, 3, 3-trichlropropenoic acid, m. p. 75–6° (reported m. p. 76°[14]) (Found: neutralization equivalent, 182.5. Calcd. for $C_3HCl_3O_2$: 175.5).

To a stirred solution of 0.5 g. of the α-hydroxy acid (II) in 25 cc. of benzene at 60–80° lead tetraacetate was added in portions until the oxidizing power began to persist in the solution (potassium iodide-starch paper). It took about one hour. The excess lead tetraacetate was destroyed by heating for 30 minutes with anhydrous oxalic acid. The benzene solution developed a purple color with Schiff's reagent. It was distilled on a water bath to remove benzene, the residue added with 30 cc. of alcohol and filtered. The filtrate was heated with 2 g. of phenylhydrazine, some precipitate filtered off, and the filtrate concentrated on a water bath to give golden yellow crystals of 1-phenyl-4-phenylazopyrazole, m. p. 126–7° (from alcohol, yield 50 mg.) (Found: N, 22.9. Calcd. for $C_{15}H_{12}N_4$: 22.57%).

Infrared Data The infrared spectra were recorded on a Baird Double Beam Spectrophotometer equipped with rock salt optics. They were shown in Fig. 1. The spectrum of 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene suspended in liquid paraffin shows an absorption band of the nitrile group at 4.5 μ and that of the ethylenic bond at 6.13 μ.

Summary

1. Trichloroethylene has been dimerized by

---

[13] C. F. Mabery and A. W. Smith, *Ber.*, **22**, 2659 (1889).

[14] J. Böeseken and P. Dujardin, *Rec. trav. chim.*, **32**, 97 (1913).

boiling with α, α'-azodiisobutyronitrile to $C_4H_2Cl_6$, which has been identified as 1, 1, 3, 3, 4, 4-hexachloro-1-butene by degradation.

2. A compound of molecular formula $C_8H_8Cl_5N$, whose structure is presumably 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene, has been isolated. This fact indicates that the reaction is initiated by the addition of 1-cyano-1-methylethyl radical to trichloroethylene and propagated by the transference of a chlorine atom from the dimeric radical to a molecule of the monomer.

3. The decomposition of dibenzoyl peroxide in trichloroethylene gives the same dimer as above, the structural identity being confirmed infrared spectrometrically.

The authors' thanks are due to Dr. H. Kamada and Mr. S. Tanaka, Engineering Research Institute, for measuring the infrared spectra and to the Ministry of Education for a Grant-in-Aid for Scientific Research.

Department of Chemistry, Faculty of Science, Tokyo University, Tokyo