

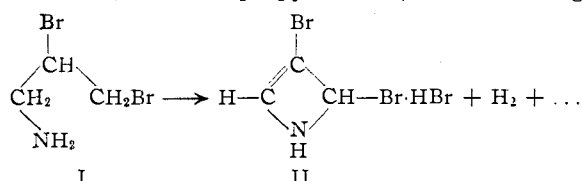
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

## Investigation of the Compound Described as Azacyclobutadiene

BY WALTER J. GENSLER

Azacyclobutadiene<sup>1</sup> (III) would be of interest as a compound vinylogous to pyridine and also as a compound related to the four-membered N-heterocyclic system in penicillin. The present work consists in the investigation of a compound synthesized by Abderhalden and Paquin<sup>2</sup> and assigned the structure of azacyclobutadiene.

These authors reported that a dry ethereal solution of 2,3-dibromopropylamine (I), on standing



was characterized by formation of the oxalic, picric and mandelic acid salts. Treatment with bromine resulted in the regeneration of II.

Consideration of these reported reactions suggests that compound II was not as shown but was probably the hydrobromide of the starting material I; and that compound III was not azacyclobutadiene but rather allylamine. The possibility is supported by a reexamination of the published analytical data which are found to contain a consistent error in calculation; the corrected figures agree more closely with calculated values for the revised structures than with those based on II and III (see table). The following observations have been made which further indicate the validity of this interpretation.

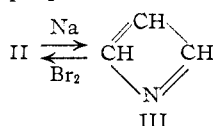
TABLE I

CORRECTED ANALYSES OF REPORTED COMPOUNDS COMPARED TO CALCULATED VALUES FOR THE REPORTED AND THE REVISED STRUCTURES

Compound reported <sup>2</sup>	Calcd. <sup>2</sup>				Found (cor.) <sup>2</sup>				Revised structure	Calcd.			
	C	H	N	Br	C	H	N	Br		C	H	N	Br
II hydrobromide	12.3	1.4	4.8	81.8	12.3	2.7	4.8	81.5	I hydrobromide	12.1	2.7	4.7	80.5
II nitrate	13.1	1.5	10.2	58.0	13.7	3.4	10.1	57.8	I nitrate	12.9	2.9	10.0	57.1
II sulfate	13.8	1.5	5.4	61.2	14.3	3.3	5.5	61.5	I sulfate	13.6	3.0	5.3	60.1
II formate	18.5	1.9	5.4	61.8	18.5	3.8	5.4	61.8	I formate	18.3	3.5	5.3	60.8
II oxalate	19.8	1.7	4.6	52.3	20.3	3.4	4.8	51.9	I oxalate	19.6	3.0	4.6	52.1
II picrate	24.5	1.4	12.7	36.3	25.0	2.4	12.8	36.1	I picrate	24.2	2.3	12.6	35.8
Bz derivative of II	38.0	1.9	4.4	50.7	38.5	3.7	4.9	50.1	Bz derivative of I	37.4	3.5	4.4	49.8
Me-II hydrobromide	15.6	2.0	4.6	78.0	18.3	3.9	4.7	77.4	DiMe-I hydrobromide	18.4	3.7	4.3	73.6
III oxalate	42.0	3.5	9.8	..	41.7	6.5	9.3	..	Allylamine oxalate	40.8	6.2	9.5	..
III picrate	37.9	2.1	21.1	..	37.8	4.1	19.7	..	Allylamine picrate	37.8	3.5	19.6	..
III mandelate (C <sub>10</sub> H <sub>7</sub> O <sub>2</sub> N?)	63.5	3.7	7.4	..	63.3	7.4	6.8	..	Allylamine mandelate	63.1	7.2	6.7	..
C <sub>2</sub> H <sub>3</sub> Br <sub>2</sub> N hydrobromide	21.7	1.8	4.2	72.3	21.8	3.7	4.2	72.3	IV hydrobromide	21.3	3.6	4.2	71.0
C <sub>2</sub> H <sub>3</sub> Br <sub>2</sub> N formate	28.3	2.4	4.7	53.9	28.2	4.8	3.8	55.6	IV formate	27.7	4.3	4.6	52.0

for several days, evolved hydrogen gas and deposited first a crystalline solid, m. p. 164° after purification, and then an amorphous solid. Structure II was suggested for the crystalline material. Complete analysis of a number of salts of II, as well as formation of the N-methyl, benzoyl, and benzenesulfonyl derivatives, was offered in support of this formulation.<sup>3</sup>

Treatment of an ethereal solution of the free base of II with sodium yielded a volatile base, C<sub>3</sub>H<sub>3</sub>N, for which the structure of azacyclobutadiene (III) was proposed. The C<sub>3</sub>H<sub>3</sub>N compound



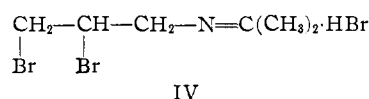
(1) Ring Index No. 38. Alternative names: azete or pyrculine;

(2) Abderhalden and Paquin, *Ber.*, **53**, 1125 (1920).

(3) Neither Hollins ["Synthesis of Nitrogen Ring Compounds," D. Van Nostrand, New York, N. Y., 1924, p. 23] nor Degering ["Outline of Organic Nitrogen Compounds," John S. Swift Co., Cincinnati, Ohio, 1942, p. 286] offers a satisfactory interpretation of the reaction.

In a repetition of the reported procedure, it has been found possible to isolate a solid from the first-formed crystalline precipitate (from ethereal 2,3-dibromopropylamine) which is identical with 2,3-dibromopropylamine hydrobromide and which agrees in melting point with that reported for II. No gas evolution is observed during the formation of the precipitate.

The compound, m. p. 198° dec., which was previously formed in the reaction of II and dry acetone may be obtained from 2,3-dibromopropylamine hydrobromide and acetone. The reported instability and ease of hydrolysis to the starting material may now be explained on the basis of the Schiff base structure IV



The oxalate and the picrate of allylamine have been prepared; the melting points, 128–130.5 and 141–141.5°, respectively, agree with those re-

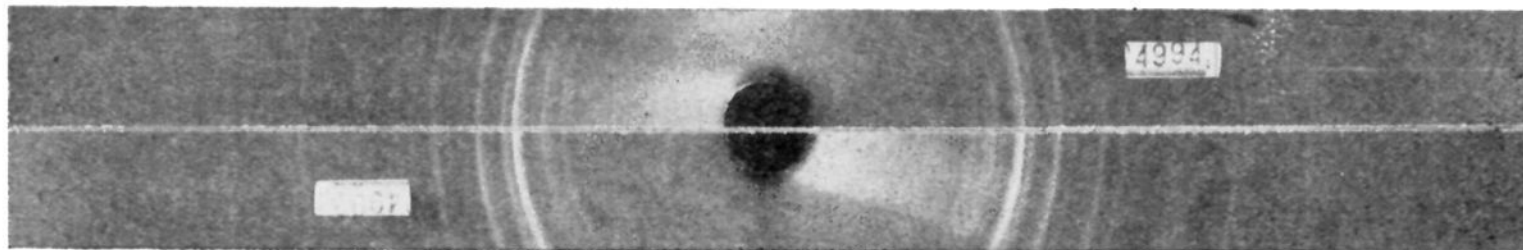
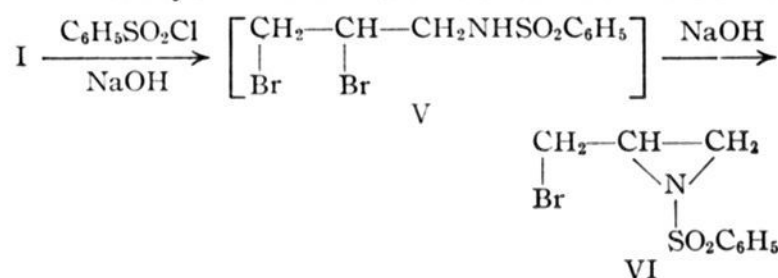


Fig. 1.—X-Ray diffraction patterns: no. 4993, 2,3-dibromopropylamine hydrobromide; no. 4994, material from ether solution of 2,3-dibromopropylamine. The Debye-Scherrer diagrams were taken using radiation from a copper target and nickel filter. The exposure was one and one-half hours at 20 milliamp.

ported for the corresponding salts of III (m. p. 127 and 141°).

Additional supporting evidence is found in the literature. The benzoyl derivative of 2,3-dibromopropylamine has been reported to melt at 135°<sup>4</sup>; the value for the melting point of the benzoyl derivative of II was given as 130°. The hydrobromide of the monomethyl derivative of II, reported m. p. 188° dec. was probably dimethyl-2,3-dibromopropylamine hydrobromide, m. p. 188–189° dec.<sup>5</sup> The dimethylation rather than the monomethylation of 2,3-dibromopropylamine may be explained on the basis of the large excess of formalin used in the reaction.<sup>2</sup> Conversion of II to III is interpreted as the sodium debromination of 2,3-dibromopropylamine to allylamine, an action shown to be possible by Paal.<sup>6,7</sup>

One piece of evidence which supported structure II and which does not agree with the present formulation was the reported formation of an alkali-insoluble benzenesulfonyl derivative. If II were actually 2,3-dibromopropylamine the benzenesulfonyl derivative V should be alkali-soluble.



On treatment of 2,3-dibromopropylamine (I) with benzenesulfonyl chloride in strong alkali a compound is formed which melts at 89–90° (85° was the melting point given for the benzenesulfonyl derivative of II), and which is *not* soluble in alkali. A plausible explanation of the anomalous behavior is indicated by the analytical figures, which agree not with V but with V minus a molecule of HBr. The alkali-insoluble ethylene-imine structure VI is proposed for the benzene-sulfonyl derivative on the basis of preliminary work.

### Experimental

**The Product from Ethereal 2,3-Dibromopropylamine.**—Twenty grams of 2,3-dibromopropylamine hydrobromide<sup>7</sup> was dissolved in 30 ml. of water and shaken with 100 ml. of ether and 10 ml. of 40% sodium hydroxide solution.

(4) Bergmann, Dreyer and Radt, *Ber.*, **54**, 2139 (1921).

(5) Partheil and v. Broich, *ibid.*, **30**, 618 (1897).

(6) Paal, *ibid.*, **21**, 3190 (1888).

(7) Paal and Hermann, *ibid.*, **22**, 3076 (1889).

After the ether layer was dried for a short time over powdered magnesium sulfate, it was removed by decantation and the magnesium sulfate rinsed thoroughly with 100 ml. of ether. The ethereal solution together with the wash-ether was stirred for four hours at room temperature with fresh magnesium sulfate, and the mixture filtered directly into a dry 300-ml. flask. Enough sodium-dried ether was added to fill the flask almost completely, a connecting tube was attached, and the solution was carefully boiled for a short time to remove most of the air. While ether vapor was still escaping from the connecting tube, the open end was placed in concentrated sulfuric acid, directly under the mouth of an inverted buret filled with concentrated sulfuric acid.

After two days at room temperature (27°) approximately 12 ml. of gas had collected in the buret. However, in a control experiment carried out exactly as described above but without the dibromopropylamine, approximately 13 ml. of gas was noted after the same period.

The crystals that had formed in the ether solution were collected and washed with dry ether. The material weighed 20 mg. and melted at 166.5–168.5° (sintering at 164°). Crystallization from absolute alcohol furnished white crystalline material melting at 168–168.5° (sintering at 165°) to a red-colored liquid. Mixed with authentic 2,3-dibromopropylamine hydrobromide<sup>7</sup> (m. p. 167–169.5°), the melting point was 168–169.5° (sintering at 166.5°).

When the decomposition of the 2,3-dibromopropylamine was carried out in more concentrated ethereal solution, in an apparatus that eliminated the gas space between the reaction mixture and the buret and in which any gaseous products could be trapped under ether, no gas formation was observed. Using this apparatus and starting with the dibromopropylamine from 40 g. of the hydrobromide in a total volume of 60 ml. of ether, 1.5 g. of crystalline precipitate was obtained after two days at 27°. Three crystallizations of this material from absolute alcohol brought the melting point to 166.5–169.5° (sintering at 165°), and the mixed melting point with the authentic material to 167–169.5° (sintering at 165°). Further evidence of identity was secured by comparison of the X-ray diffraction diagrams of the product and of the authentic material.<sup>8</sup>

**2,3-Dibromopropylamine Hydrobromide and Acetone.**—A mixture of 500 ml. of absolute acetone and 5.0 g. (0.017 mole) of powdered 2,3-dibromopropylamine hydrobromide was boiled for nine hours under a reflux condenser fitted with a drying tube. It was noted that although the solids did not dissolve the crystalline form changed. The white crystalline solids were collected at 10° and dried. The weight of IV was 4.8 g. (88%), m. p. 189° dec. with darkening. Crystallization from 100 ml. of 1:1 acetone-alcohol and then from 250 ml. of acetone containing 5 ml. of water afforded material that decomposed (preliminary darkening) at 192°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>NBr<sub>3</sub>: C, 21.3; H, 3.6. Found: C, 21.6; H, 3.7.

**Allylamine Oxalate.**—A solution of allylamine in alcohol was poured into a vigorously stirred alcoholic solution containing an equimolar amount of oxalic acid dihydrate.

(8) The pictures were obtained through the very kind cooperation of Professor Clifford Frondel and Mr. David Stewart of the Division of Geological Sciences at Harvard University.

The product which immediately precipitated was crystallized from absolute alcohol to a constant melting point of 128–130.5° (sintering at 126°).

*Anal.* Calcd. for  $C_6H_5NO_4$ : C, 40.8; H, 6.2. Found: C, 40.5; H, 6.3.

**Allylamine Picrate.**—Adding an ethereal solution of allylamine to an equimolar amount of picric acid in ether resulted in the immediate precipitation of the picrate. Three crystallizations from chloroform containing a small amount of absolute alcohol furnished small, matted, yellow-colored crystals melting at 141–141.5°.

*Anal.* Calcd. for  $C_9H_{10}N_4O_7$ : C, 37.8; H, 3.5. Found: C, 38.0; H, 3.5.

**Benzenesulfonyl Derivative of Dibromopropylamine.**—The benzenesulfonyl derivative of I was formed according

to the directions given for the preparation of the same derivative of II.<sup>2</sup> Recrystallization from alcohol yielded the alkali insoluble product VI, m. p. 89–90°.

*Anal.* Calcd. for  $C_9H_{10}NO_2SBr$ : C, 39.1; H, 3.7; N, 5.1. Found: C, 39.5; H, 3.5; N, 5.3.

### Summary

The crystalline precipitate formed in ethereal solution of 2,3-dibromopropylamine is 2,3-dibromopropylamine hydrobromide and not II as previously reported. The debromination product is allylamine and not azacyclobutadiene.

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[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & COMPANY, INC.]

## Pyrolysis of Polytetrafluoroethylene

BY E. E. LEWIS AND M. A. NAYLOR

Polytetrafluoroethylene is a new polymeric material possessing unusual heat stability and chemical inertness. A summary of its properties has been given by Renfrew and Lewis<sup>1</sup> and an attempt to explain these properties in terms of molecular structure has been given by Hanford and Joyce.<sup>2</sup>

Although the polymer is quite stable at the normal fabrication temperatures of 330 to 360°, it does undergo degradation if it is maintained at temperatures above 360° for extended periods of time. The extent and rate of this degradation increase as the temperature is raised. The materials obtained by cracking this polymer at 600 to 700° under reduced pressure are of particular interest because of their unexpected structure.<sup>3,4</sup>

It is generally believed that the products formed by the polymerization of tetrafluoroethylene are straight chains having the structure  $(-CF_2-CF_2-CF_2-CF_2-)_n$  terminated by as yet unidentified end-groups. If such is the case, one might expect the products of thermal cracking to have structural characteristics similar to those of the compounds obtained from the thermal cracking of high molecular weight straight chain hydrocarbons. This prediction would lead to the conclusion that the low molecular weight products formed should consist of straight- and branched-chain, saturated and unsaturated compounds along with carbon tetrafluoride. A broad range of molecular weights in the products would be expected.

Actually, however, the products obtained by cracking polytetrafluoroethylene at temperatures from 600 to 700° and at pressures between 5 and

760 mm. were of low molecular weight and consisted of  $C_2F_4$ ,  $C_3F_6$  and  $C_4F_8$  in varying quantities depending on conditions. Since the method of isolation employed, *i. e.*, Podbielniak distillation, is estimated to have accounted for 95 to 97% of the products formed, it is possible, of course, that small amounts of material of higher molecular weight and carbon tetrafluoride were formed but were not detected.

### Experimental

The equipment used is shown in Fig. 1. The decomposition chamber consisted of a 54" length of  $3/4$ " iron pipe with the middle 27 $1/2$ " section heated by three electrical resistance coils. Short lengths of galvanized-iron window screen were rolled into cylinders and then placed in the exit side of the heated zone of the pipe. Ground scrap polytetrafluoroethylene was fed from a hopper into the decomposition chamber by means of a hand-operated plunger. The decomposition products passed from the pipe through a glass tube into two or more vacuum flasks filled with glass wool and placed in series. The flasks removed solid particles that were being carried along in the gas stream. The filtered gas was compressed by means of a Model S Frigidaire refrigerating pump (driven by a  $1/4$  h. p. motor) into either of two gas cylinders. The cylinders were kept at approximately atmospheric pressure by cooling them in a methanol and Dry Ice mixture. The pressure in the system was checked by two manometers on the vacuum side (one at the pipe exit and one immediately before the compressor) and by a compound gage on the pressure side. The temperature of the reaction zone was measured by three thermocouples brazed to the outside of the pipe. During a run, the product was directed into the larger of the two receivers until constant conditions of pressure and temperature had been established. The product was then diverted into the previously evacuated smaller cylinder and the analytical sample collected. For experiments at pressures too low to be maintained by the Frigidaire compressor, a Cenco Megavac pump was used. In this case, the sample was collected by immersing the two traps in liquid nitrogen. Pressure was controlled either by varying the rate of feed or by a throttling valve.

The sample for analysis was transferred to a Podbielniak still and distilled. Three fractions were obtained boiling at -76, -29 and -6°. These were identified as follows:

$C_2F_4$ .—This was the lowest boiling compound obtained from the pyrolysis. It was identified as tetrafluoroethylene

(1) M. M. Renfrew and E. E. Lewis, *Ind. Eng. Chem.*, **38**, 870 (1946).

(2) W. E. Hanford and R. M. Joyce, *THIS JOURNAL*, **68**, 2082 (1946).

(3) A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,394,581 (February 12, 1946).

(4) E. E. Lewis, U. S. Patent 2,406,153 (August 20, 1946).