TABLE I

KETENE DIMERS

-Cyclohexyl, ketene dimers	B. p.		Yield,[a]			Analyses, %					
						Mol. wt.[b]		Carbon		Hydrogen	
	°C.	Mm.	%	n^{20}_D	Formula	Found	Calcd.	Found	Calcd.	Found	Calcd.
,ketene	108–111	2	28	1.5001	$C_{16}H_{24}O_2$	250.7	248.4	76.68	77.36	10.08	9.74
,methyl	190–191	6	40	1.4925	$C_{18}H_{28}O_2$	281.9	276.4	78.09	78.22	10.38	10.21
β-, ethyl	115–120	2	18	1.4850	$C_{20}H_{32}O_2$	278.2	304.5	79.15	78.91	10.64	10.52
γ-, propyl	150–152 (m. p., 16–17)	1	25	1.4860	$C_{22}H_{36}O_2$	331.8	332.5	79.53	79.39	11.04	10.90
δ-, butyl	128–130 (m. p., 33–35)	1	36	....	$C_{24}H_{40}O_2$	351.6	360.5	80.46	79.88	11.56	11.18

[a] Based upon the amount of unrecovered acid chloride. [b] Determined cryoscopically.

The ketene dimers thus formed have not been previously reported.

The dimers gave a negative test with silver nitrate; positive tests with potassium permanganate, and bromine. *p*-Nitrophenylhydrazine reacted with the dimers to yield the hydrazones.

Experimental

The procedure followed in dehydrohalogenation of the the acid chlorides was similar to that reported by Sauer.[2] Equal molar quantities of acid chloride and triethylamine were allowed to react in dilute ether solution. Each dimer was isolated in its pure form by distillation under diminished pressure. A quantity of unreacted acid chloride was recovered from each experiment.

Analytical data and physical constants of the five ketene dimers are shown in Table I.

***p*-Nitrophenylhydrazones.**—The hydrazones were prepared according to the procedure described by McElvain.[3] The color of the hydrazones varied from lemon to deep orange.

Analytical data and physical properties of the hydrazones are given in Table II.

TABLE II

p-NITROPHENYLHYDRAZONES OF DIMERS

-Cyclohexyl, ketene dimer	Hydrazone	N, %		M. p.,[a] °C.	Yield, %
		Found	Calcd.		
,ketene	$C_{28}H_{34}O_4N_6$	16.29	16.21	102–103 d.	19
,methyl	$C_{30}H_{38}O_4N_6$	14.89	15.38	104–105 d.	41
β-, ethyl	$C_{32}H_{42}O_4N_6$	14.05	14.63	110–111 d.	53
γ-, propyl	$C_{34}H_{46}O_4N_6$	14.10	13.95	113–114 d.	44
δ-, butyl	$C_{36}H_{50}O_4N_6$	[b]	...	84–85	57

[a] Melting points are uncorrected. [b] Compound decomposed upon prolonged drying.

---

(3) McElvain, "Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 199.

DEPARTMENT OF CHEMISTRY
TENNESSEE A. AND I. STATE COLLEGE
NASHVILLE 8, TENNESSEE

RECEIVED AUGUST 25, 1948

The Preparation and Vapor Pressure of Bromopentachloroethane; the Vapor Pressures of Heptachloropropane and Dibromotetrachloroethane

BY TAKERU HIGUCHI,[1] NOBORU ENDOW[2] AND JOHN E. WILLARD

When confronted with a need for a sample of bromopentachloroethane we were not able to find any record of its preparation in the literature. We have prepared a sample by the photobromination of pentachloroethane at elevated temperature, using a technique similar to that previously employed in this laboratory for the preparation of bromotrichloromethane from chloroform and bromine.[3] The over-all reaction is

$$C_2Cl_5H + Br_2 \longrightarrow C_2Cl_5Br + HBr$$

Eastman Kodak Co. technical pentachloroethane was washed several times with concentrated sulfuric acid, with water, with 20% potassium hydroxide solution and again with water. After drying with phosphorus pentoxide, approximately 1 mole (125 cc.) was then mixed with one mole (55 cc.) of bromine and 75 cc. of carbon tetrachloride. This mixture was illuminated by two 500-watt Mazda projection bulbs placed next to the flask which was sealed to a water-cooled reflux condenser. The heat from the bulbs was sufficient to maintain the solution at or near the boiling temperature. Since the photobromination of chloroform has been found to be inhibited by both oxygen and water, the following precautions were taken to exclude gross amounts of these substances: (a) a slow stream of nitrogen was bubbled through the solution and allowed to pass out through the condenser throughout the course of the reaction; (b) 5 g. of phosphorus pentoxide was added to the reaction flask.

Initial attempts to prepare bromopentachloroethane by this method, from mixtures of bromine and pentachloroethane without carbon tetrachloride, led to a mixture of products. Because of the possibility that this might be the result of reactions favored by the relatively high temperature of the boiling point of the pentachloroethane (155°), carbon tetrachloride was added to reduce the boiling point.

After a week of continuous illumination the reaction solution solidified on cooling. The weight of this crude product was 200 g. Following three recrystallizations from small amounts of carbon tetrachloride large white crystals were obtained which melted with decomposition in the range of 180 to 200° when heated in sealed evacuated tubes. An estimate of the molecular weight and vapor pressure was obtained from this sample by measuring the gas pressure produced in a known volume by a weighed sample as a function of temperature. This was accomplished by placing the sample in an evacuated sealed bulblet in a sidearm of an evacuated thermostated flask which was connected to an open-end mercury manometer,[4] the middle section of which was made of flexible rubber suction tubing. The sample tube was broken with a glass-enclosed magnetic hammer. By means of a leveling bulb the mercury was maintained at an index mark on the glass side arm of the flask which connected with the manometer, thus maintaining a constant gas volume as the pressure

---

(1) Present address: Department of Pharmacy, University of Wisconsin, Madison, Wis.

(2) Present address: Hanford Engineer Works, General Electric Co., Richland, Wash.

(3) (a) Bohlmann and Willard, THIS JOURNAL, 64, 1342 (1942); (b) Higuchi, Ph.D. Thesis, University of Wisconsin, 1943.

(4) The apparatus used in these determinations was constructed by Norman W. Rosenberg with the aid of funds from the National Youth Administration. Details of modifications and applications are given in the Masters' degree thesis of Noboru Endow filed with the Library of the University of Wisconsin in January, 1948.

changed due to vaporization of the sample. The pressure was read as the difference in heights of the mercury columns. The connection from the flask to the manometer entered the mineral oil thermostating-bath through a bushing in the bottom of the silver-soldered copper can and the index mark was viewed through a window in the side of the can. Experiments showed that no correction was necessary for the vapor pressure of mercury, thus indicating that the time required for the mercury vapor (which was always at a lower pressure than the organic vapor) to diffuse from the narrow side arm into the flask was long compared to the time involved in the experimental measurements.

Three experiments made on the freshly purified samples believed to be bromopentachloroethane gave linear plots of the logarithm of the sublimation pressure against the reciprocal of the absolute temperature over the temperature range of about 110 to 160°. A sharp break in the curve was found in each case at the temperature of total vaporization of the sample. The average molecular weights calculated for the totally vaporized system at the break in the curve were 280, 280 and 285 as compared to the theoretical value of 281 for C_2Cl_5Br. Chemical analysis of a sample of the compound by the Carius wet oxidation method combined with the Moser-Miksh iodide metathesis method gave the results:

	Experimental	Theoretical (C_2Cl_5Br)
Bromine	27.8	28.3
Chlorine	61.2	63.2

Samples of the compound prepared by the photobromination of pentachloroethane with radiobromine of known specific activity showed a specific activity corresponding to the formula C_2Cl_5Br.

The average vapor pressure of the C_2Cl_5Br over the range tested is given by the relation $\log p = (-2.32 \times 10^3/T) + 6.33$, where p is the pressure in cm. of Hg and T is the absolute temperature.

Heptachloropropane.—A single series of measurements of the vapor pressure of $CCl_3CCl_2CHCl_2$ as a function of temperature with the apparatus described above gave a straight line plot of $\log p$ *vs.* $1/T$ for five points taken over the range of 140 to 200°. These data gave the expression $\log p = (-1.82 \times 10^3/T) + 5.11$. The sample used was obtained from the Eastman Kodak Company, which specified its melting point as 30°. The fact that the molecular weight of the sample calculated from the observed pressure at the temperature of total vaporization was 278 as compared to the theoretical value of 285 indicates that the sample was probably not highly impure. Prins,[5] Farlow[6] and Henne and Ladd[7] have reported values for the boiling point of $CCl_3CCl_2CHCl_2$ at several pressures. Their values are shown in Table I for comparison with those determined from the equation given above.

TABLE I

Pressure, mm.	Obs. b. p., other workers. °C.	B. p. from vapor pressure equation, °C.
10	110–113 (Farlow)	83
32	137–140 (Farlow)	122
43	147 (Prins)	133
90	164 (Prins)	
	163–166 (Henne and Ladd)	165

The relation of $\log p$ to $1/T$ for Farlow's data is not in agreement with that for Prins' data and neither is in agreement with our vapor pressure determinations. These latter show a consistent relationship over a 60° range under conditions of measurement which have given agreement with well established values for the vapor pressure of carbon tetrachloride and have given consistent vapor pressure and molecular weight values for a number of compounds tested.

Dibromotetrachloroethane.—A similar determination of the vapor pressure of $C_2Cl_4Br_2$ gave the expression $\log p = (-2.74 \times 10^3/T) + 7.18$ over the range from 110 to 180°. These results are in satisfactory agreement with those of Carrico and Dickinson[8] who made similar measurements from 50 to 150°. At 50° they observed a pressure of 0.4 mm. while the value calculated from our data is 0.5 mm. At 150° they found 51 mm. and our data indicate 50 mm. Following complete vaporization of the $C_2Cl_4Br_2$, the vapor was heated to 215° without more than a few per cent. decomposition over the period of about half an hour, indicating greater thermal stability than that of the C_2Cl_5Br reported above.

The work reported here was done as part of a program to which support was given by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

---

(5) Prins, *J. prakt. Chem.*, **89**, 414 (1914).

(6) Farlow, "Organic Synthesis," **17**, 58 (1937).

(7) Henne and Ladd, THIS JOURNAL, **60**, 2491 (1938).

(8) Carrico and Dickinson, THIS JOURNAL, **57**, 1344 (1935).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

RECEIVED JUNE 22, 1948

The Structure of Pellitorine[1]

BY MARTIN JACOBSON

The isolation from plant materials of several pungent N-isobutylamides of aliphatic unsaturated acids has been reported, namely, spilanthol (N-isobutyl-4,6-decadienamide)(I) from the flower heads of *Spilanthes oleraceae* Jacquin[2] and *S. acmella* Murr.,[3] pellitorine (the N-isobutylamide of a decadienoic acid) from the roots of *Anacyclus pyrethrum* DC.,[4] N-isobutyl-2,6,8-decatrienamide (II) from the roots of *Heliopsis longipes* (A. Gray) Blake[5]; and herculin (N-isobutyl-2,8-dodecadienamide) (III) from the bark of *Zanthoxylum clava-herculis* L.[6]

Gulland and Hopton[4] had identified pellitorine as an isomer of spilanthol, but they did not determine the positions of the double bonds in the molecule. In view of the insecticidal activity of compounds I,[3,7] II[5] and III,[6] and since preliminary tests in the laboratories of the Bureau of Entomology and Plant Quarantine had indicated that pellitorine was also insecticidal,[6] it was of considerable interest to determine the points of unsaturation in this compound, with a possible consequent correlation between insecticidal activity and molecular structure.

The procedure used in this Laboratory for isolating pure pellitorine eliminated the repeated fractional distillations found by Gulland and Hopton to be necessary for its purification. A Skelly-

---

(1) Report of a study made under the Research and Marketing Act of 1946.

(2) Gerber, *Arch. Pharm.*, **241**, 270 (1903); Asano and Kanematsu, *Ber.*, **65B**, 1602 (1932).

(3) Pendse, *et al.*, *Current Sci.*, **14**, 37 (1945); Gokhale and Bhide, *J. Indian Chem. Soc.*, **22**, 250 (1945).

(4) Gulland and Hopton, *J. Chem. Soc.*, 6 (1930).

(5) Jacobson, Acree and Haller, *J. Org. Chem.*, **12**, 731 (1947).

(6) Jacobson, THIS JOURNAL, **70**, 4234 (1948).

(7) Pendse, *et al.*, *J. Univ. Bombay*, **15A**, New Ser. Pt. 3, No. 20, 26 (1946).