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).

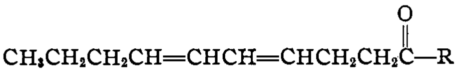
(6) Jacobson, THIS JOURNAL, **70**, 4234 (1948).

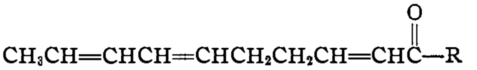
(7) Pendse, *et al.*, *J. Univ. Bombay*, **15A**, New Ser. Pt. 3, No. 20, 26 (1946).

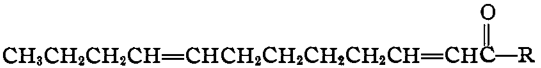
solve A extract of dry pellitory root (*Anacyclus pyrethrum* DC.)[8] was extracted with nitromethane, and the neutral fraction of the nitromethane-soluble portion was distilled. One crystallization, from Skellysolve A, of the fraction boiling at 155–165° (0.3–0.5 mm.) gave pure pellitorine in 0.14% yield, based on dry root.

Oxidation of pellitorine with alkaline permanganate resulted in the isolation of butyric, succinic and N-isobutyloxamic acids, showing that the double bonds occupy the 2- and 6-positions. Pellitorine is therefore N-isobutyl-2,6-decadienamide (IV).

In tests[9] conducted with house flies (*Musca domestica* L.), a Deobase (refined kerosene) solution of pellitorine, used as a spray, showed paralyzing action equal to, and mortality somewhat greater than one-half that of pyrethrins tested at the same concentration.


$\mathrm{CH_3CH_2CH_2CH{=}CHCH{=}CHCH_2CH_2\overset{\overset{O}{\|}}{C}{-}R}$ I


$\mathrm{CH_3CH{=}CHCH{=}CHCH_2CH_2CH{=}CH\overset{\overset{O}{\|}}{C}{-}R}$ II


$\mathrm{CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH{=}CH\overset{\overset{O}{\|}}{C}{-}R}$ III


$\mathrm{CH_3CH_2CH_2CH{=}CHCH_2CH_2CH{=}CH\overset{\overset{O}{\|}}{C}{-}R}$ IV

where R = $\mathrm{NHCH_2CH(CH_3)_2}$

Experimental[10]

Isolation of Pellitorine.—6070 g. of finely ground, dry pellitory root was extracted in a Soxhlet extractor with Skellysolve A. The solution was concentrated to *ca.* 700 ml. and extracted three times with 150-ml. and twice with 100-ml. portions of nitromethane. The combined nitromethane solution was freed of solvent under reduced pressure, the residue (27 g. of reddish-brown oil) taken up in ethyl ether, and the ether solution washed thoroughly with water, 5% hydrochloric acid solution, 5% potassium hydroxide solution, and finally with water. After being dried over sodium sulfate, the ether solution of the neutral fraction was freed of solvent completely, and the remaining 20 g. (0.33% of the bark) of viscous reddish-yellow oil solidified rapidly.

Vacuum distillation of this material, in an atmosphere of nitrogen, gave 8.5 g. of pale-yellow oil, b. p. 155–165° (0.3–0.5 mm.), which was dissolved in a small quantity of Skellysolve A, cooled in ice-salt, and filtered. The yield was 8.4 g. (0.14% based on dry bark) of colorless, feathery needles of pellitorine, m. p. 72° (lit.[4] m. p. 72°).

Oxidation of Pellitorine.—To a stirred suspension of 5 g. of pellitorine in 500 ml. of water, maintained at 70°, 18.8 g. of finely powdered potassium permanganate (equivalent to 4 moles of oxygen) was added in small portions. When the reaction mixture had become colorless, the manganese dioxide was filtered and washed thoroughly with warm water. The combined aqueous filtrates were concentrated down to 70 ml. and made acid to congo red with sulfuric acid. The solution was steam-distilled to remove the volatile acids and then extracted with ether in a continuous extractor. The ether solution was freed of solvent, and the residue was extracted with three 10-ml. portions of boiling Skellysolve B. Cooling of the hydrocarbon solution caused the separation of 2.5 g. (77%) of colorless feathery needles, m. p. 106–107°, containing nitrogen.

Anal. Calcd. for $C_6H_{11}NO_3$: N, 9.66; neut. equiv., 145. Found: N, 9.65; neut. equiv., 145.

The substance was identified as N-isobutyloxamic acid by a mixed melting-point determination with an authenic sample, m. p. 107°, prepared by the procedure of Malbot.[11]

The insoluble residue from the Skellysolve B extraction was taken up in a small amount of ethyl acetate, cooled in ice-salt mixture, and filtered. One recrystallization from a small amount of the same solvent gave 1.8 g. (69%) of colorless crystals in the form of clusters of needles, m. p. 188–189°.

Anal. Calcd. for $C_4H_6O_4$: mol. wt., 118. Found: mol. wt. (titration), 118.

The product was identified as succinic acid by a mixed melting point determination with an authentic specimen, m. p. 189°, and by preparing the *p*-phenylphenacyl ester, m. p. 208°.

The solution of steam-volatile acids obtained above was neutralized with sodium hydroxide solution, concentrated to a small volume on the steam-bath, and acidified to congo red with sulfuric acid. Steam distillation gave Duclaux values of 17.9, 15.9 and 14.6, identical with those given for butyric acid.[12]

The acid was shown to be butyric acid by evaporating the neutral solution to dryness and then preparing the *p*-phenylphenacyl ester, m. p. and mixed m. p. with an authentic sample, 81–82°.

---

(8) Obtained from S. B. Penick & Co., New York, N. Y.

(9) These tests were made by W. A. Gersdorff and Miss S. F. McDuffie, of this Bureau.

(10) All melting points are corrected.

(11) Malbot, *Compt. rend.*, **104**, 229 (1887).

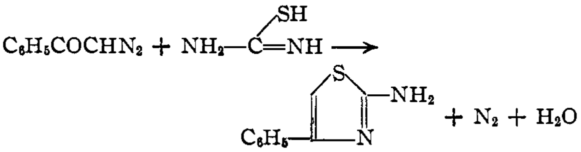
(12) McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 141.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
BELTSVILLE, MARYLAND
RECEIVED SEPTEMBER 30, 1948

The Reaction of Diazoketones with Thioamide Derivatives[1]

BY L. CARROLL KING AND F. M. MILLER

Werner[2] found that the action of diazomethane on thiourea produced S-methylpseudothiourea. We have now observed that diazoketones react with thiourea and other thioamide derivatives to furnish substituted thiazoles. The reaction between diazoacetophenone and thiourea is illustrative.



The reaction is effected either by heating an intimate mixture of the reactants on the steam-bath, or by refluxing an alcoholic solution of the reaction components. The reaction in alcoholic solution is more satisfactory.[3]

Thiourea and ethyl diazoacetate react to give

---

(1) For previous papers dealing with the synthesis of thiazoles, see King and co-workers: (a) THIS JOURNAL, **67**, 2242 (1945); (b) *ibid.*, **68**, 871 (1946); (c) *ibid.*, **69**, 1813 (1947).

(2) Werner, *J. Chem. Soc.*, **115**, 1168 (1919).

(3) A similar technique was employed for the preparation of quaternary salts from diazoacetophenone and salts of heterocyclic bases, King and Miller, THIS JOURNAL, **70**, 4154 (1948).