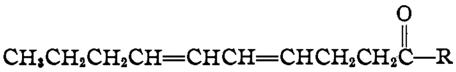
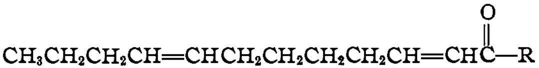
solve A extract of dry pellitory root (*Anacyclus pyrethrum* DC.)[8] was extracted with nitromethane, and the neutral fraction of the nitromethane-soluble portion was distilled. One crystallization, from Skellysolve A, of the fraction boiling at 155–165° (0.3–0.5 mm.) gave pure pellitorine in 0.14% yield,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

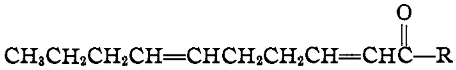
Oxidation of pellitorine with alkaline permanganate resulted in the isolation of butyric, succinic and N-isobutyloxamic acids, showing that the double bonds occupy the 2- and 6-positions. Pellitorine is therefore N-isobutyl-2,6-decadienamide (IV).

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.


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


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


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


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

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

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 $\mathrm{C_6H_{11}NO_3}$: 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 $\mathrm{C_4H_6O_4}$: 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°.

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BELTSVILLE, MARYLAND
RECEIVED SEPTEMBER 30, 1948

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[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.

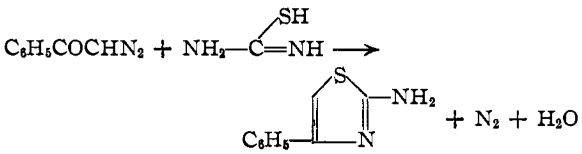
[11] Malbot, *Compt. rend.*, **104**, 229 (1887).

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

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

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[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).

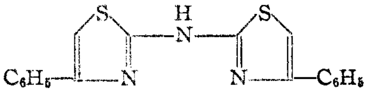
[3] A similar technique was employed for the preparation of quaternary salts from diazoacetophenone and salts of heterocyclic bases, King and Miller, THIS JOURNAL, **70**, 4154 (1948).

TABLE I

Compound	Formula	Yield, %	M. p., °C. Found[c]	M. p., °C. Reported	Composition,[h] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Amino-4-phenylthiazole	$C_9H_8N_2S$	67[a]	151–152	151–152[d]	...	...	..	..
Acetyl derivative	$C_{11}H_{10}ON_2S$		213–214	214.5–215[d]	...	...	..	..
2,4-Diphenylthiazole	$C_{15}H_{11}N_2S$	84[a]	91–92	92–93[e]	[i]	[i]	..	..
2-Amino-4-hydroxythiazole	$C_3H_4ON_2S$	34[a]	233–238, dec.	[f]	31.03	30.81	3.45	3.53
bis-(4-Phenyl-2-thiazolyl)-amine	$C_{18}H_{13}N_3S_2$	40, 78[b]	218–220	[g]	64.55	64.35	3.89	4.11
Acetyl derivative	$C_{20}H_{15}ON_4S_2$		132–133	[g]	63.16	63.45	4.25	4.14

[a] Based on the diazoketone. [b] The same compound was obtained with one or two molecular portions of diazoacetophenone, the latter giving the 78% yield, based on the dithiobiuret. [c] All melting points observed on a Fisher–Johns melting point block. [d] These compounds were compared with authentic material previously prepared in this Laboratory, reference 1.[a] [e] Hubacher, *Ann.*, **259**, 237 (1890). [f] Andreasch, *Monatsh.*, 8, 424 (1887), reported a melting point of 208° (dec.) for this material prepared by a different method. The compound from the diazoketone reaction melted in this range above. Similar results were obtained by Allen and VanAllan, "Organic Syntheses," **27**, 71 (1947). [g] Not previously reported. [h] Analysis by Miss P. Craig. [i] Calcd.: N, 5.62. Found: N, 5.69.

2-amino-4-hydroxythiazole (pseudothiohydantoin). Thiourea and thiobenzamide yield with diazoacetophenone, 2-amino-4-phenylthiazole and 2,4-diphenylthiazole, respectively. With the same diazoketone dithiobiuret gives bis-(4-phenyl-2-thiazolyl)-amine (I).[4]



I

Evidence for the structure of I lies in the method of formation, the analysis of the compound and its N-acetyl derivative, and the fact that it was unaffected by both acid and alkaline hydrolytic conditions, contrary to the known sensitivity of the thioureido group.[5] Compound I was also prepared by the action of phenacyl bromide on dithiobiuret.

Data for the compounds prepared are listed in Table I.

This investigation was supported by a grant from the Abbott Fund of Northwestern University.

Experimental

Preparation of Materials.—Diazoacetophenone was prepared as previously described.[3] Ethyl diazoacetate was prepared by the method of Curtius.[6] Thiobenzamide was prepared by suspending 60.5 g. (0.5 mole) of benzamide and 22.2 g. (0.10 mole) of phosphorus pentasulfide in 300 cc. of benzene and refluxing until the benzamide dissolved. The hot benzene solution was filtered and cooled, and the thiobenzamide collected. The material was recrystallized once from benzene m.p. 115–116°.[7] The dithiobiuret was a commercial sample, obtained through the courtesy of the American Cyanamid Company.

Preparation of the Thiazoles.—The techniques used will be illustrated by the following examples.

(a) **2-Amino-4-phenylthiazole.**—A solution of 1.46 g. (0.01 mole) of diazoacetophenone and 2.40 g. (0.012 mole) of thiourea in 20 cc. of absolute alcohol was refluxed for one hour. A portion of the alcohol was evaporated, a small amount of water and charcoal added, and the hot solution filtered and cooled. The separated material was collected and recrystallized from dilute aqueous alcohol.

(b) **bis-(4-Phenyl-2-thiazolyl)-amine.**—A solution of 2.92 g. (0.02 mole) of diazoacetophenone and 1.48 g. (0.011 mole) of dithiobiuret was refluxed for one hour in alcoholic solution. The product separated from the solution, was filtered and dissolved in excess acetone. Dilute aqueous alcohol was added and the acetone removed carefully on the steam-bath. The material crystallized on cooling and was recrystallized in the same manner.

bis-(4-Phenyl-2-thiazolyl)-amine was also prepared by refluxing 4.0 g. (0.02 mole) of phenacyl bromide and 1.50 g. (0.01 mole) of dithiobiuret in 25 cc. of alcohol for one hour. The separated material was suspended in alcohol and digested with ammonium hydroxide for one-half hour, filtered and washed with a small amount of alcohol. Recrystallization gave a material identical with that prepared above.

Acetyl Derivatives of Thiazoles.—These were prepared by the action of acetic anhydride on approximately 0.3 g. of the amino thiazole. The products were recrystallized from dilute aqueous alcohol.

Attempted Hydrolysis of I.—A solution of 0.1 g. of the material in 30 cc. of hot alcohol and 10 cc. of water was heated under reflux for three hours with 10 g. of barium hydroxide. Only the starting material was recovered, m.p. 217–218°.

Attempted acid hydrolysis performed in the same manner yielded identical results.

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RECEIVED AUGUST 23, 1948

The Verdet Constant of Certain Liquid Fluorocarbons

BY R. T. LAGEMANN

It is now known that certain fluorinated hydrocarbons possess some unusual physical properties. Although the density and viscosity are not particularly different from those of other liquids, the refractive index and ultrasonic velocity are both extraordinarily low. As an example, consider bis-(trifluoromethyl)-chlorononofluorocyclohexane. Here $n^{60}D$ is 1.3021,[1] only three liquids in Lange's "Handbook" have a lower value, and the ultrasonic velocity at 20° is 691.8 m./sec.,[1] also extremely low relative to other liquids. Since no values are known for the rotation of the plane of polarization of light by these liquids when placed in

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[4] The descriptive literature of the American Cyanamid Company records the reaction of chloroacetone and dithiobiuret to produce 2-thioureido-4-methylthiazole. Attempts to obtain the analogous 2-thioureido-4-phenylthiazole were not successful.

[5] Mehta and Krall, *J. Indian Chem. Soc.*, **12**, 635 (1935), report the effects of acid and basic hydrolysis of phenylthiourea.

[6] Curtius, *J. prakt. Chem.*, **38**, 401 (1888).

[7] Gabriel and Heyman, *Ber.*, **23**, 158 (1890).

[1] Lagemann, Woolf, Evans and Underwood, THIS JOURNAL, **70**, 2994 (1948).