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pressure (approximately 7 mm.) below which adduct formation does not occur for crystals of the dimensions used in these experiments.

The reaction between urea crystals and n-octane vapor in the presence of water vapor was also observed by a photomicrographic technique. At water vapor pressures of 14 to 15 mm. the reaction was observed to proceed quite readily. This was shown by the loss of transparency of the urea crystal and the formation of a fuzzy, opaque, somewhat larger crystal.

Photomicrographic evidence appears to indicate that not all the urea crystals react at once. However, once initiation of reaction occurs on a given crystal, the reaction progresses rapidly through that crystal. When water vapor was present to the extent of 7 to 8 mm. no reaction occurred after 24 hr., indicating again the presence of a limiting water vapor pressure below which adduct formation does not occur.

The fact that water vapor promoted the adduct formation led to an investigation of other possible promoters. Methanol and ethanol, at pressures in the region of 10 to 15 mm., promoted the reaction after considerable time. There is some indication that nitromethane and ethylenediamine behave in a similar manner. The effect of other substances is being studied.

Work is being carried out on the adsorption of water vapor on urea, the determination of the change in surface area on removal of hydrocarbons at low pressure, and more extensive utilization is being made of X-ray techniques. The results will be reported in a subsequent paper.

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1-ALKYL-2-IMIDAZOLIDINETHIONES1

By G. D. Thorn²

For the study in this laboratory of the fungicidal activity of compounds containing the thiocarbamoyl grouping, it became necessary to have a series of 1-alkyl-2-imidazolidinethiones. Except for a paper by Rich and Horsfall (10) in which is reported the fungitoxicity of n-octyl-, t-octyl-, and n-octadecylethylenethiourea (for which no physical characteristics are given), no reference to simple 1-alkyl-2-imidazolidinethiones is to be found in the literature.

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THORN: 1-ALKYL-2-IMIDAZOLIDINETHIONES

The reaction of equimolar amounts of ethylenediamine and carbon disulphide was shown by Hofmann (4) to yield N-(β -aminoethyl)dithiocarbamic acid (I, R = H). Thermal decomposition of this inner salt gave 2-imidazolidinethione (II, R = H). These reactions were later extended to various Nand N,N'-substituted 2-imidazolidinethiones by van Alphen (1), Baum (2), Donia, Shotton, Bentz, and Smith (3), Hurwitz and Auten (5), Lob (7), Newmann (8), Schmidt (11), Vaugh and Bean (12), and Zienty (13).

Following the classical procedures, a series of 1-alkyl-2-imidazolidinethiones has been prepared.



EXPERIMENTAL³

The N-alkylethylenediamines were prepared either by reaction of the requisite alkylamine with 2-bromoethylamine (9) (R = ethyl through hexyl), or by reaction of an alkyl halide with 98% ethylenediamine (6) (R = heptyl through dodecyl).

The N-alkyl-2-imidazolidinethiones were prepared essentially according to the method given by Donia *et al.* (3). The reaction of the amine with carbon disulphide was carried out in ether to give a fine white precipitate of the dithiocarbamic acid inner salt. The use of acetone (3) as the reaction medium resulted in yellow gummy precipitates, which could however be triturated with ether to give more tractable material.

A typical preparation is described, in which the alkyl group is octyl: A solution of 10.1 gm. (0.059 mole) of N-octylethylenediamine in 80 ml. ether was cooled to 10° C. in an ice-bath, and stirred vigorously while 4.72 gm. (0.062 mole) of carbon disulphide in 30 ml. ether was added dropwise. Stirring was continued for 30 min. after addition was completed. The precipitate was removed by filtration, washed with ether, and air-dried. The yield was 14.3 gm. (98%). Found: N, 11.2%. Calc. for $C_{11}H_{24}N_2S_2$: N, 11.3%.

The inner salt was heated for two hours in a wide-mouthed Erlenmeyer flask immersed in an oil bath at 130° C. The dark residue was crystallized from hexane to give 9.7 gm. (77%) of 1-octyl-2-imidazolidinethione. The material was then recrystallized from hexane to constant melting point (Table I).

The yields given in Table I are calculated from the amount of material obtained after one crystallization of the crude imidazolidinethione. Hexane was the preferred solvent for recrystallization, except for the first three members of the series, where ether or hexane-acetone was used.

³All melting points are uncorrected and were obtained on the Fisher-Johns block.

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CANADIAN JOURNAL OF CHEMISTRY, VOL. 33 TABLE I

1-Alkyl-2-imidazolidinethiones						
R in formula II	Yield, %, from I	m.p., °C.	Analyses			
			Found		Calc.	
			С	H	C	Н
Ethyl	72	79-80	46.1	7.56	46.2	7.69
Butyl	70	7879	53.3	8.87	53.2	8.87
Pentyl	81	68 - 68.5	55.8	9.35	55.8	9.30
Hexvl	90	71 - 72	57.9	9.57	58.1	9.68
Heptyl	81	69 - 70	60.0	10.15	60.0	10.00
Octvĺ	77	52 - 53	61.7	10.36	61.7	10.28
Nonvl	73	56 - 57	63.2	10.38	63.2	10.53
Decvl	81	64.5 - 65	65.0	10.38	64.5	10.74
Dodecyl	74	6061	66.9	10.91	66.8	11.10

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