ether to give 174 mg. (55% yield) of crude product, m.p. 242.5–246.5° with previous softening. Two crystallizations from acetone–petroleum ether gave 158 mg. of practically pure diol IId, m.p. 248.5–250.5° with previous softening.

B.—In another run, the product was purified for characterization by crystallization from acetone–petroleum ether, m.p. 249.5–250.5° with previous softening; $\lambda_{max}$ 241–242 mμ ($\epsilon$ 15,500); $\nu_{max}$ 3460, 1735, 1664, 1622cm.$^{-1}$; $[\alpha]^{25}D$ +223° (*c* 0.242, $\alpha_D$ +0.54°).

*Anal.* Calcd. for $C_{19}H_{26}O_4$ (318.40): C, 71.67; H, 8.23. Found: C, 71.73; H, 8.27.

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## Some 1-Alkyl-2-imidazolidinethiones

BY CHIEN-PEN LO

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This note reports the synthesis of the 1-*n*-octyl- 1-*t*-octyl-[1] and 1-*n*-octadecyl-2-imidazolidinethiones, the fungicidal properties of which have been discussed elsewhere by Rich and Horsfall.[2] The preparation of a series of 1-alkyl-2-imidazolidinethiones has just been reported by Thorn.[3]

Our 1-alkyl-2-imidazolidinethiones were prepared by a method similar to that used by Thorn.[4] N-Alkylethylenediamines were allowed to react with one mole of carbon disulfide to give the corresponding dithiocarbamic acids (inner salts)[5] which were isolated and characterized. These intermediate dithiocarbamic acids yielded the desired 1-alkyl-2-imidazolidinethiones upon heating above their melting points.

### Experimental[6]

**N-β-Aminoethyl-N-*n*-octyldithiocarbamic Acid (inner salt).**—N-*n*-Octylethylenediamine (172 g.) was treated with carbon disulfide (76 ml.) in acetone (500 ml.) to give 192 g. (77.5%) of a white solid melting at 116–118° (with effervescence).

*Anal.* Calcd. for $C_{11}H_{24}N_2S_2$: N, 11.3; $CS_2$, 30.6. Found: N, 10.8; $CS_2$, 30.3.

**1-*n*-Octyl-2-imidazolidinethione.**—The above dithiocarbamic acid (161 g.) was heated at 120–140° for two hours and the residue was crystallized from ethanol to give 122.5 g. (88%) of a white solid melting at 54–55°.[7]

*Anal.* Calcd. for $C_{11}H_{22}N_2S$: N, 13.1; S, 14.9. Found: N, 12.8; S, 15.0.

1-*n*-Octyl-2-imidazolidinethione was also prepared directly from N-*n*-octylethylenediamine and carbon disulfide by omitting the use of solvent and the isolation of the intermediate dithiocarbamic acid. The yield of the crude 1-*n*-octyl-2-imidazolidinethione (m.p. 42–43°) was 90%, based on the amine used.

**N-β-Aminoethyl-N-*t*-octyldithiocarbamic Acid (inner salt)** was obtained from N-*t*-octylethylenediamine and carbon disulfide in ethanol as a white solid, m.p. 144–146°, yield 57%.

*Anal.* Calcd. for $C_{11}H_{24}N_2S_2$: N, 11.3; $CS_2$, 30.6. Found: N, 11.0; $CS_2$, 30.3.

**1-*t*-Octyl-2-imidazolidinethione** was prepared by heating the above dithiocarbamic acid at 140–150° for three hours and obtained as a white solid (free ethanol); m.p. 164–165°, yield 66.5%.

*Anal.* Calcd. for $C_{11}H_{22}N_2S$: N, 13.1; S, 14.9. Found: N, 13.0; S, 15.1.

**N-β-Aminoethyl-N-*n*-octadecyldithiocarbamic acid (inner salt)** was obtained from N-octadecylethylenediamine and carbon disulfide in ethanol as a white solid, m.p. 106–108° (with effervescence), yield 83.5%.

*Anal.* Calcd. for $C_{21}H_{44}N_2S_2$: N, 7.2; $CS_2$, 19.6. Found: N, 6.8; $CS_2$, 19.2.

**1-*n*-Octadecyl-2-imidazolidinethione** was prepared by heating the above dithiocarbamic acid at 130–140° for 2.5 hours and obtained as a white solid (from ethanol), m.p. 80–81°, yield 84%.

*Anal.* Calcd. for $C_{21}H_{42}N_2S$: N, 7.9; S, 9.1. Found: N, 7.8; S, 9.1.

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[1] In the present work, *t*-octyl denotes 1,1,3,3-tetramethylbutyl.

[2] S. Rich and J. G. Horsfall, *Science*, **120**, 122 (1954). In this article these compounds were named as derivatives of ethylenethiourea.

[3] G. D. Thorn, *Can. J. Chem.*, **33**, 1278 (1955).

[4] For references on this general method of preparation of 2-imidazolidinethiones, see ref. 3.

[5] Because of the non-symmetry of the N-alkylethylenediamine molecule, there are two possible structures for the inner salt of the dithiocarbamic acid: $RN(CSSH)CH_2CH_2NH_2$ and $RNHCH_2CH_2NHCSSH$. Judging from the rather sharp melting point of the crude product, it appeared that one product was formed exclusively or predominantly in this reaction. In this work, the former structure is tentatively assigned to the product pending further structural proof. It is to be noted here that either of the structures would lead to the formation of the same 1-alkyl-2-imidazolidinethione by losing hydrogen sulfide.

[6] All melting points are uncorrected. Analyses were performed under the direction of Mr. Thomas Callan. Carbon disulfide was determined by the method of D. G. Clarke, H. Baum, E. L. Stanley and W. F. Hester, *Anal. Chem.*, **23**, 1842 (1951).

[7] Thorn (ref. 3) reported a melting point of 52–53°.

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## Acid-catalyzed Condensations. II.[1] The Condensation of Benzaldehyde with Substituted Acetophenones

BY ROBERT E. LYLE AND LEO P. PARADIS[2]

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The hydrogen chloride-catalyzed condensation of benzaldehyde with substituted acetophenones yields the hydrogen chloride addition compounds rather than the chalcones themselves.[3] In view, however, of the successful formation of 1,3,5-triarylbenzenes and substituted dypnones[1] by the hydrogen chloride-catalyzed self-condensation of substituted acetophenones, the application of similar conditions to the synthesis of chalcones appeared worthy of investigation.

The reaction of seventeen monosubstituted acetophenones with benzaldehyde in methanolic hydrogen chloride gave the corresponding chalcones

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[1] The first paper in this series is 1,3,5-Triarylbenzenes, R. E. Lyle, E. J. DeWitt, N. M. Nichols and W. Cleland, THIS JOURNAL, **75**, 5959 (1953).

[2] Abstracted from the thesis of Leo P. Paradis presented to the Graduate School of the University of New Hampshire in partial fulfillment of the requirement of the degree of Master of Science.

[3] L. Claisen and A. Claperde, *Ber.*, **14**, 2463 (1881); W. Dilthey, L. Neuhaus, E. Reis and W. Schommer, *J. prakt. Chem.*, **124**, 81 (1930); F. Bergel and A. L. Morrison and N. Rinderknecht, *J. Chem. Soc.*, 659 (1950); A. Bell, *ibid.*, 2834 (1953).