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; λ_{max} 241–242 mμ (ε 15,500); ν_{max} 3460, 1735, 1664, 1622cm.$^{-1}$; $[\alpha]^{25}D$ +223° (*c* 0.242, α_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.

Acknowledgment.—We are indebted to Messrs. Louis M. Brancone, Samuel S. Modes, Frank C. Geronimo, Alexander N. Prezioso and Harold J. Ferrari for the microanalytical data, and to Messrs. William Fulmor and George Morton and Miss Anne Callaghan for the optical rotation data and the infrared absorption spectra.

CHEMICAL RESEARCH SECTION
LEDERLE LABORATORIES, RESEARCH DIVISION
AMERICAN CYANAMID CO.
PEARL RIVER, NEW YORK

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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ROHM & HAAS COMPANY
PHILADELPHIA 37, PENNSYLVANIA

(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°.

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

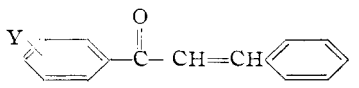
(1) The first paper in this series is 1,3,5-Triarylbenzenes, R. E. Lyle, E. J. DeWitt, N. M. Nichols and W. Cleland, THIS JOURNAL, **75**, 5959 (1953).

(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).

(see Table I). The product of the reaction of acetophenone under these conditions was β-chloro-β-phenylpropiophenone. The condensation of benzaldehyde with *p*-hydroxy-, *p*-methyl-, *p*-amino- and *o*-aminoacetophenones under these conditions did not give the corresponding chalcone.

TABLE I



Group Y	Yield, %	M.p., °C.	Lit. m.p., °C.
p-NO_2	100	146–147	149–150[a]
m-NO_2	100	129–130	131[a]
o-NO_2	98	125–126	128–129[a]
p-$(CH_3)_2N\cdot HCl$	76	165–167	165[b]
p-OH	68	171–174	171–172[c]
p-I	88	112–113	114–115[d]
p-Br	70	102–104	104–105[e]
p-Cl	69	97–98	101[e]
p-F	55	77–79	76–77[f]
m-I	46	83–84	[j]
m-Br	22	92–94	[k]
m-Cl	51	93–94	[l]
m-F	28	62–63	[m]
p-*t*-C_4H_9	54	97–98	98[g]
p-*i*-C_3H_7	68[n]	64–65	65[g]
p-C_2H_5	59[n]	59–61	61[h]
m-CH_3	65[n]	59–60	61[i]

[a] W. Dilthey, L. Neuhaus and W. Schommer, *J. prakt. Chem.*, **123**, 235 (1929). [b] H. Fecht, *Ber.*, **40**, 3902 (1907). [c] J. Simpson and S. Israelstam, *C.A.*, **44**, 5844 (1950). [d] O. Neuhoeffer and D. Roshal, *Ber.*, **86**, 229 (1953). [e] W. Dilthey, *et al.*, *C.A.*, **15**, 1292 (1921). [f] C. Allen, J. Norminton and C. Wilson, *J. Can. Research*, **11**, 382 (1934); *C.A.*, **29**, 135 (1934). [g] C. Weygand, L. Mensdorff and F. Strobelt, *Ber.*, **58**, 1832 (1935). [h] J. Michel, *C.A.*, **33**, 7650 (1939). [i] C. Weygand and F. Schacher, *Ber.*, **68**, 232 (1935). [j] *Anal.* Calcd. for $C_{15}H_{11}IO$: C, 53.99; H, 3.32. Found: C, 54.37; H, 3.44. [k] *Anal.* Calcd. for $C_{15}H_{11}BrO$: C, 62.45; H, 3.86. Found: C, 62.05; H, 3.94. [l] *Anal.* Calcd. for $C_{15}H_{11}ClO$: C, 74.23; H, 4.56. Found: C, 73.47; H, 4.91. [m] *Anal.* Calcd. for $C_{15}H_{11}FO$: C, 79.62; H, 4.90. Found: C, 79.29; H, 5.06. [n] These yields were obtained by distillation, at reduced pressure, of the halogen-containing oils which remained after removal of the starting materials.

From the reaction mixtures a non-crystallizable oil was usually isolated in addition to the chalcones. In those cases tested the oils contained halogen which could be removed, with the formation of the chalcone, by distillation under reduced pressure. Thus it is evident that the isolation procedure did not remove completely the hydrogen chloride from the addition compounds of the chalcones. That the hydrogen chloride addition compound was the initial product in every reaction was indicated by the formation of an unstable hydrochloride on treatment of 4′-iodo-chalcone with methanolic hydrogen chloride. 4′-Iodo-chalcone was regenerated by subjecting the hydrochloride to the usual isolation procedure. It is interesting to note that with the exception of the *m*-halogen series those chalcones having the lowest electron density in the vicinity of the carbonyl also formed the least stable hydrogen chloride addition compounds as evidenced by higher yields of chalcones. Thus, a hydrogen chloride-catalyzed condensation for the preparation of chalcones is most successful with acetophenones substituted with electron-withdrawing groups.

Experimental

Reaction of Benzaldehyde with Substituted Acetophenones in Alcoholic Hydrogen Chloride.—To 30 ml. of anhydrous methanol saturated at 0° with hydrogen chloride was added 4.0 ml. of benzaldehyde and 0.02 ml. of the acetophenone. The reaction mixture in a vented 125-ml. Erlenmeyer flask was allowed to stand at room temperature. The reaction proceeded at different rates with the various acetophenones as evidenced by the time which elapsed after mixing the reagents before precipitation began. For example, *p*-nitroacetophenone started precipitation after 5 min., while *p*-fluoroacetophenone required up to 42 hr. before precipitation began. At the end of 5 days the reactions were stopped by the addition of water, and the mixture was steam distilled to remove any unreacted starting materials. The residue was neutralized with sodium bicarbonate and, if the product crystallized, it was removed by filtration. Otherwise, the residue from the steam distillation was extracted with ether. After drying, the ether solution was distilled, and the residue was crystallized from petroleum ether or ethanol. The products from the reactions of *p*-isopropyl-, *p*-ethyl- and *m*-methylacetophenones failed to crystallize after this treatment and were distilled under reduced pressure and were isolated as the fractions: b.p. 233° at 12 mm., 213° at 4 mm., and 206° at 2 mm., respectively, which crystallized on standing.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE

Paper Chromatographic Separation of Phospholipids[1]

BY G. V. MARINETTI AND ELMER STOTZ

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The paper chromatographic separation of phosphatidylcholines and phosphatidylethanolamines has been difficult to achieve. Although Bevan and co-workers[2] have reported the separation of lecithin and cephalin, others[3] have been unable to confirm this work. Recently the chromatographic separation of various phospholipids has been reported.[4–6] Although the isoamyl alcohol–acetone system of Amelung and Bohm[4] can separate fairly simple mixtures of purified lecithin and cephalins, in our hands it was not capable of separating these lipids in a more complex phospholipid mixture extracted from various rat tissues. The reason for this is believed to be the significantly higher R_f values of the naturally occurring cephalins than those of the more saturated purified phosphatidylethanolamines. The paper chromatographic separation of acetal phospholipid from lecithin and cephalin has been difficult to achieve and has not been satisfactorily accomplished to date.

The authors and collaborators[7,8] have found solvent systems capable of separating unmodified phos-

(1) This investigation was supported in part by a research grant H-2063, from the National Heart Institute of the National Institutes of Health, Public Health Service.

(2) T. H. Bevan, G. I. Gregory, T. Malkin and A. G. Poole, *J. Chem. Soc.*, 841 (1951).

(3) C. H. Lea and D. N. Rhodes, *Biochem. J.*, **54**, 467 (1953).

(4) D. Amelung and P. Bohm, *Z. physiol. Chem.*, **298**, 199 (1954).

(5) C. H. Lea and D. N. Rhodes, *Biochem. J.*, **59**, v (1955); C. H. Lea, D. N. Rhodes and R. D. Stoll, *ibid.*, **60**, 353 (1955).

(6) J. W. Dieckert and R. Reiser, *Federation Proc.*, **14**, 202 (1955).

(7) G. Rouser, G. Marinetti and J. F. Berry, *ibid.*, **13**, 286 (1954).

(8) G. Rouser, G. Marinetti, R. F. Witter, J. F. Berry and E. Stotz, submitted for publication.