period of 8 hr. with occasional swirling until 24 g. (0.367 mole) of zinc and 24 g. (22.8 ml., 0.40 mole) of acetic acid had been added. The reaction mixture was then filtered and the residue of zinc and zinc acetate washed with a small portion of acetic acid. The combined filtrates were evaporated *in vacuo* on a hot water bath. The greenish residue (the reaction mixture itself exhibited a green fluorescence) was stirred with 20% sodium hydroxide and then extracted with ether. After drying over sodium sulfate, the ether was evaporated. The residual oil was distilled to give 1.78 g. (64%) of colorless liquid product, b.p. 131–132°/0.4 mm. The product formed a dipicrate, m.p. 210–211°, which was used for analysis.

Anal. Calcd. for $C_{25}H_{20}N_8O_{14}$: C, 45.74; H, 3.07; N, 17.07. Found: C, 45.94; H, 3.06; N, 16.88.

***N*-Acetyl-1-phenyl-2-(2-pyridyl)ethylamine (IX).**—A solution of 3.5 ml. (0.037 mole) of acetic anhydride, 7.5 ml. of glacial acetic acid, and 1.78 g. (0.009 mole) of VIII were heated on a steam bath for 30 min. The acetic acid and excess acetic anhydride were removed by evaporation *in vacuo*. Upon cooling, the residue solidified to a yellow solid. Recrystallization from 1:1 benzene–ligroin gave 1.41 g. (65%) of white product, m.p. 114–117°. Two more recrystallizations raised the m.p. to 123.5–124.5°.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.02; H, 6.77; N, 11.42.

Attempted Synthesis of 3*H*-1-Methyl-3-phenylpyrido[1,2-*c*]pyrimidine. Method A.—One gram (0.004 mole) of IX, 2 ml. (3.35 g., 0.02 mole) of phosphorus oxychloride, and 6 ml. of anhydrous benzene were refluxed for 4 hr. The reaction mixture was extracted with chloroform, the extract dried over anhydrous sodium sulfate, and then evaporated to dryness on a steam bath to give a sticky, yellow solid. This solid was eluted from an alumina column with benzene to give a white solid contaminated with yellow oil. The oil was removed by vacuum filtration giving 0.67 g. of product, m.p. 74–84°. Recrystallization of this crude product from dioxane gave an amount of white material, m.p. 140–143°, too small for analysis. The filtrate was evaporated to dryness and the residue (0.63 g.) recrystallized from a minimum of 1:1 benzene–ligroin to give a good recovery of solid, m.p. 91–92°, which did not have the correct analysis for the desired pyridopyrimidine. This material, 0.55 g. (60%), did not show a mixed melting point depression with an authentic sample of 2-stilbazole (XI), and the elemental analysis is in good agreement with that expected for XI.

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.14; H, 6.12; N, 7.73. Found: C, 86.29; H, 6.37; N, 7.53.

Method B.—One gram (0.004 mole) of IX and 5.7 g. (0.04 mole) of phosphorus pentoxide were heated overnight in 10 ml. of refluxing benzene. The resulting mixture was made basic with 15% ammonium hydroxide and the light tan product, 0.15 g. (21%), proved to be 2-stilbazole as determined by its mixed melting point with an authentic sample.

2-Stilbazole (XI).—2-Stilbazole, for mixed melting point determinations, was prepared according to the directions of Shaw and Wagstaff.[9]

***N*-Benzoyl-1-phenyl-2-(2-pyridyl)ethylamine (X).**—Two grams (0.01 mole) of VIII was placed in 25 ml. of benzene with 1.41 g. (1.16 ml., 0.01 mole) of benzoyl chloride and 1.5 ml. of pyridine. The resulting solution was refluxed overnight and the precipitate filtered and stirred with an excess of 20% sodium hydroxide. The crude light brown solid was filtered and dried to give 2.05 g. (67%) of product, m.p. 147–148°. One recrystallization from 80% methanol raised the m.p. to 148–149°.

Anal. Calcd. for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.27. Found: C, 79.39; H 6.01; N, 9.55.

Attempted Synthesis of 3*H*-1,3-Diphenylpyrido[1,2-*c*]pyrimidine. Method A.—A solution of 0.80 g. (0.00265 mole) of X in 7 ml. of benzene was refluxed with 3.76 g. (0.0265 mole) of phosphorus pentoxide for 2 hr. The benzene was removed and the residue stirred with ice water. The resulting mixture was made basic with 20% sodium hydroxide and the white precipitate filtered and dried. The melting point and mixed melting point were identical to that of the starting material. The recovery was quantitative.

Method B.—A solution of 0.80 g. (0.00265 mole) of X and 2 ml. (3.35 g., 0.0219 mole) of phosphorus oxychloride in 6 ml. of benzene was refluxed for 4 hr. The benzene and excess phosphorus oxychloride were evaporated *in vacuo* and the residue collected as in method A. The recovery was 0.60 g. of solid (75%), m.p. 110–112°. Two recrystallizations from 80% methanol raised the m.p. to 148–149°, that of the starting benzamide.

Acknowledgment.—The authors wish to express their thanks to Dr. C. H. Tilford and the Wm. S. Merrell Co. for their interest and financial assistance during the course of this work. Our thanks go also to Dr. V. B. Fish of Lehigh University who performed the analyses.

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[9] B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 77 (1933).

Decomposition of Mixed Carboxylic-Dithiocarbamic Anhydrides

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A number of mixed carboxylic-dithiocarbamic anhydrides, derived from aromatic carboxylic acids and piperidine—or methyldithiocarbamic acids, have been prepared and characterized. They have been found in each case to decompose on heating to the corresponding amide and carbon disulfide; the reaction takes place at a measurable rate in refluxing cyclohexane, and can be followed spectrophotometrically. It is catalyzed by triethylamine.

The behavior[2] of the mixed carboxylic-carbonic anhydrides (I), particularly the mechanism of their decomposition[3] has been studied. The present paper reports some observations on the decomposition of the mixed carboxylic-dithiocarbamic anhydrides (*S*-acyldithiocarbamates, II).

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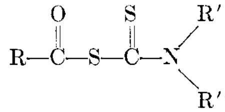
[1] Aided by Grant NSF-G11240 from the National Science Foundation.

[2] (a) D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1957). (b) D. S. Tarbell and N. A. Leister, *ibid.*, **23**, 1149 (1958). (c) N. A. Leister and D. S. Tarbell, *ibid.*, **23**, 1152 (1958).

[3] (a) D. S. Tarbell and E. J. Longosz, *ibid.*, **24**, 774 (1959). (b) E. J. Longosz and D. S. Tarbell, *ibid.*, **26**, 2161 (1961).

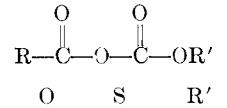
TABLE I

MIXED CARBOXYLIC-DITHIOCARBAMIC ANHYDRIDES,

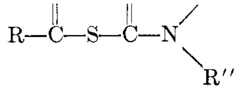


R	R′	R″	M.p.[a]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_6H_5	—$(CH_2)_5$—		100–102[b]	$C_{13}H_{15}NOS_2$	58.92	59.14	5.71	5.85
p-$CH_3OC_6H_4$	—$(CH_2)_5$—		82– 84[c]	$C_{14}H_{17}NO_2S_2$	57.00	57.20	5.81	6.04
p-$O_2NC_6H_4$	—$(CH_2)_5$—		133–135	$C_{13}H_{14}N_2O_3S_2$	50.36	50.90	4.55	4.63
C_6H_5	CH_3	H	90– 91[d]	$C_9H_9NOS_2$	51.23	51.34	4.30	4.62
p-$CH_3OC_6H_4$	CH_3	H	95– 97	$C_{10}H_{11}NO_2S_2$	49.83	50.09	4.60	4.58
p-$O_2NC_6H_4$	CH_3	H	100–101	$C_9H_8N_2O_3S_2$	42.22	43.17	3.15	3.02

[a] All of the melting point reported were with decomposition. [b] Levi[5c] reports m.p. 99°. [c] V. Braun[5a] reports m.p. 62–65°. [d] Bodendorf[5b] reports m.p. 91°.

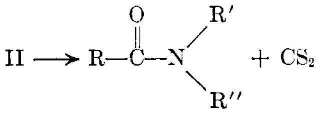


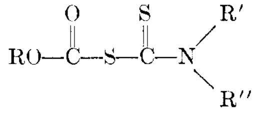
I



II

The chemistry of the dithiocarbamates has been extensively investigated,[4] and the mixed anhydrides II, prepared by several workers,[5] have been found to be rather unstable and form the corresponding amide and carbon disulfide. The anhydrides of type III have been prepared from the action of chlorocarbonates on dithiocarbamates,[5a,6] and the thiuram monosulfides and disulfides,





III

$(R_2N\overset{\overset{S}{\|}}{C})_2S$ and $(R_2NCSS)_2$, are well known.

The mixed carboxylic-dithiocarbamic anhydrides prepared in the present work are listed in Table I; they were prepared by the action of the acid chloride on the dithiocarbamate, in chloroform or acetonitrile solution, and were obtained as pure crystalline solids after recrystallization. All of them were shown to yield the corresponding amide when heated in cyclohexane solution; the amides were identified by mixed melting points with authentic samples, or in the case of anisic piperidinedithiocarbamic anhydride, by agreement of the infrared spectrum with that of a known sample of the noncrystalline amide. Most of these anhydrides are too unstable to be recrystallized from a refluxing solvent, and were therefore recrystallized from a solvent pair, benzene–petroleum ether, ether–petroleum ether, or chloroform–petroleum ether, at room temperature. The anhydrides undergo decomposition on prolonged standing at room temperature, with loss of carbon disulfide; decomposition appears to be accelerated by light. The p-nitrobenzoyl derivatives decompose more rapidly than the others.

The mixed anhydrides II showed absorption in the 220–430-mμ range, and the corresponding amides did not absorb in the longer wave length part of this region. Hence it was possible to follow the conversion of the anhydrides to the amides readily by measuring the optical density at wave lengths where the amides did not absorb. The results and the absorption data are given in Table II.

It has been shown[3b] that the decomposition of mixed carboxylic-carbonic anhydrides is strongly catalyzed by a variety of nucleophiles, by strong acids and by dimethylformamide as solvent. The effect of several additives is shown in Table II; lithium chloride and sodium acetate were without effect, in contrast to the previous case, probably because of their lack of solubility in cyclohexane. Dimethylformamide was inactive in the present case at a concentration of 3.77×10^{-4}.

Elaboration of a reaction mechanism for the decomposition of the mixed carboxylic-dithiocarbamic anhydrides will require a more detailed kinetic study. The uncatalyzed decomposition may involve a cyclic four-membered transition state[2a,7] such as the following:

(4) For a review, see P. Chabrier and G. Nachmias, *Bull. soc. chim.*, **17**, D-51 (1950).

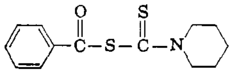
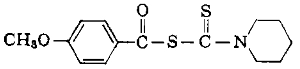
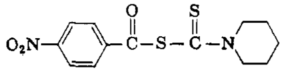
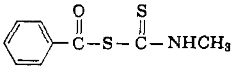
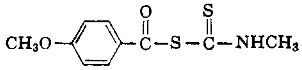
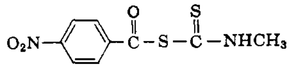
(5) (a) J. v. Braun, *Ber.*, **36**, 3520 (1903). (b) K. Bodendorf, *J. prakt. Chem.*, **126**, 233 (1920). (c) T. G. Levi, *Gazz. chim. ital.*, **61**, 719 (1931). (d) There are several references in the patent literature, *e.g.*, G. W. Watt, Canadian Patent 388,587 [*Chem. Abstr.*, **34**, 5314 (1940)]; Wingfoot Corp., British Patent 525,173 [*Chem. Abstr.*, **35**, 6835 (1941)].

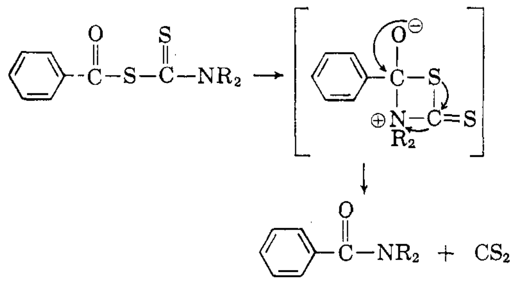
(6) E. R. Buchman, A. O. Reims, and H. Sargent, *J. Org. Chem.*, **6**, 764 (1941); cf. T. B. Johnson, A. J. Hill, and E. B. Kelsey, *J. Am. Chem. Soc.*, **42**, 1711 (1920); R. Andreasch, *Monats.*, **27**, 1220 (1906); O. F. Williams, O. H. Johnson, and J. R. Graham, U. S. Patent 2,796,-376: *Chem. Abstr.*, **51**, 16526 (1957).

(7) *Cf.*, D. H. Powers and D. S. Tarbell, *J. Am. Chem. Soc.*, **78**, 70 (1956), and references therein.

TABLE II

CONVERSION OF MIXED CARBOXYLIC-DITHIOCARBAMIC ANHYDRIDES (II) TO THE AMIDES IN CYCLOHEXANE SOLUTION (7.54×10^{-3} M) at 81°

Compound	Lifetime, hr.	Effect of additives 7.54×10^{-3} M Lifetime, hr.		Absorption maxima, mμ		ε
		$(C_2H_5)_3N$	CH_3COOH			
	28	1	20	$\frac{230}{14,080}$	$\frac{275}{7,480}$	$\frac{410}{224}$
	34	1	32	$\frac{220}{12,740}$	$\frac{270}{16,170}$	$\frac{410}{162}$
	26	0.6	2.8	$\frac{220}{10,836}$	$\frac{260}{18,318}$	$\frac{360}{2064}$
	3.5			$\frac{230}{11,550}$	$\frac{270}{4,900}$	$\frac{375}{196}$
	3			$\frac{220}{16,400}$	$\frac{290}{23,000}$	$\frac{360}{448}$
	0.5			$\frac{220}{9,257}$	$\frac{255}{16,000}$	$\frac{320}{4479}$



The catalytic effect of triethylamine can be readily accommodated on an analogous scheme.

Experimental[8]

Benzoic-Piperidinedithiocarbamic Anhydride.—To 20 ml. of ice-cold chloroform, containing 2.36 g. of the piperidine salt of piperidinedithiocarbamic acid,[9] was added 1.4 g. of benzoyl chloride; a yellow solution formed immediately. The chloroform solution was evaporated by an air jet, and the yellow residue was extracted with ether and filtered, to separate the piperidine hydrochloride. Evaporation of the ether solution yielded a residue, which was recrystallized from ether to give 1.70 g. (64%) of yellow needles, m.p. 100–102° with decomposition.

The corresponding *p-anisic* and *p-nitrobenzoic* mixed anhydrides were prepared similarly; the former, obtained in 51% yield, was recrystallized from ether–petroleum ether, and the latter was obtained in 70% yield from the same solvents.

Benzoic-methyldithiocarbamic anhydride was prepared by a modification of Bodendorf's[5b] method. To 1.4 g. of benzoyl chloride dissolved in 10 ml. of ice-cold acetonitrile was added a concd. aqueous solution of 1.4 g. of the methylamine salt of methyldithiocarbamic acid. A white precipitate formed immediately; recrystallization from benzene–petroleum ether gave 1.5 g. (70%) of white needles, m.p. 90–91° with decomposition.

The *p-anisic* analog was prepared similarly and was recrystallized from the same solvents in 60% yield; the *p-nitrobenzoic* was prepared similarly and was recrystallized from chloroform–petroleum ether.

Thermal Decomposition of Carboxylic-Dithiocarbamic Anhydrides.—The mixed anhydride in cyclohexane (7.54×10^{-3} M) was refluxed. Care was taken to exclude light from the reaction flask, since it was demonstrated that the decompositions of these anhydrides, particularly the *p*-nitro substituted analogs, were photocatalyzed.

At regular intervals, 2-ml. aliquots were withdrawn by pipette, and diluted with an additional 4 ml. of cyclohexane. Dilution was necessary during the early stages of the decomposition, in order to obtain a measurable optical density on the Beckman spectrophotometer. To achieve constant results, this dilution was continued during the entire course of the decomposition.

Each aliquot was rapidly scanned using the Beckman spectrophotometer. In the case of the piperidinedithiocarbamic derivatives, the region observed was between 400 mμ and 430 mμ, at 10-mμ intervals. The methyldithiocarbamate derivatives were scanned between 340 mμ and 390 mμ, at 10-mμ intervals. The taking of aliquots was continued until a constant or null reading was obtained for the optical density. Absence of absorption in the above-mentioned areas was indicative that the decomposition had gone to completion, thus determining the lifetime.

In the case of catalyzed thermal decompositions of the mixed anhydrides, 7.54×10^{-3} mole of catalyst (equimolar amounts) was used.

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[8] All melting points are uncorrected; microanalyses are by Mr. Victor Landeryou. Absorption spectra were taken with a Beckman DU spectrophotometer, using spectroscopic cyclohexane and 95% ethanol.

[9] A. Ladenburg and C. F. Roth, *Ber.*, **17**, 513 (1884).