

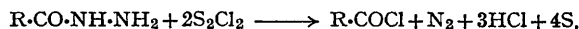
1112. *The Formation of Carboxylic Acid Chlorides and of Diacylhydrazines by the Action of Sulphur Monochloride on Monocarboxyhydrazides.*

By P. HOPE and L. A. WILES.

Although amides and amines react with sulphur monochloride to give sulphides, monoacylhydrazines form the acid chloride and diacylhydrazine.

MONOCARBOXYLIC ACID AMIDES, $R\cdot CO\cdot NH_2$, generally react with sulphur monochloride to form the monosulphides, $(R\cdot CO\cdot NH)_2S$.¹ Primary amines which have the amino-group linked to carbon also undergo replacement of the hydrogen atoms giving sulphides of various types.^{2,3}

The present work has shown that monoacylhydrazines, $R\cdot CO\cdot NH\cdot NH_2$, do not give sulphur compounds with sulphur monochloride. The reaction of one mole of hydrazide with two moles of sulphur monochloride gives the acid chloride,

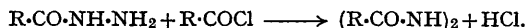


¹ P. Hope and L. A. Wiles, *J.*, in the press.

² M. Becke-Goehring and H. Jenne, *Chem. Ber.*, 1959, **92**, 1149.

³ W. K. Warburton, *Chem. Rev.*, 1957, **57**, 1011.

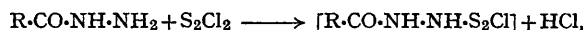
whilst equimolecular amounts of the reagents form the diacylhydrazine, $(R \cdot CO \cdot NH)_2$, presumably through the intermediate acid chloride,



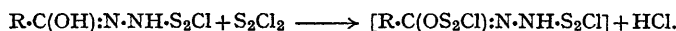
Acid chlorides have previously been obtained from monoacylhydrazines by the action of chlorine,⁴ whilst diacylhydrazines may be made from monoacylhydrazines by reaction with the corresponding acid chloride,⁵ or by oxidation.⁶ Diacylhydrazines are often prepared from hydrazine and the acid chloride, but the conversion of an ester into monoacylhydrazine by hydrazine, followed by application of the present method, has certain advantages. Esters are less easily hydrolysed than acid chlorides, and are more readily available. The diacylhydrazines are obtained in good yield, and the higher members in particular require little purification. The method is least successful for lower aliphatic acylhydrazines because of loss of the volatile intermediate acid chlorides, and the diacylhydrazines formed crystallise from benzene with sulphur.

On adding sulphur monochloride to a suspension of a monoacylhydrazine there is an exothermic reaction and the hydrazide hydrochloride is precipitated. This is similar to the deposition of the hydrochloride which occurs when a carboxylic acid amide is treated with sulphur monochloride.¹ In both reactions there is a brief pause before gas is evolved, and the hydrazide then gives a copious stream of nitrogen and hydrogen chloride.

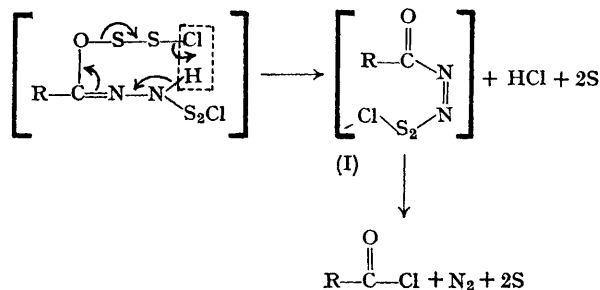
Sulphur monochloride is polarised as S_2Cl-Cl , and the chlorodithio-cation is an electrophilic substituent.^{7,8} Acylhydrazines are readily substituted at the primary amino-group,⁵ and we suggest that an intermediate *N*-chlorodithio-compound is formed,



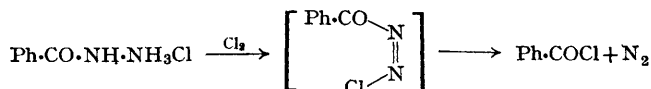
the hydrogen chloride then combining with unchanged hydrazide. Hydrazides are tautomeric,⁹ and a similar attack on the hydroxyl group is likely,



To account for the formation of the acid chloride we postulate the following changes:



An intermediate comparable with (I) has been suggested in the formation of an acid chloride by the action of chlorine on a hydrazide hydrochloride.⁴



⁴ L. A. Carpino, *J. Amer. Chem. Soc.*, 1957, **79**, 96.

⁵ H. L. Buning, *Rec. Trav. chim.*, 1921, **40**, 348.

⁶ L. Horner and H. Fernekes, *Chem. Ber.*, 1961, **94**, 712.

⁷ Z. S. Ariyan and L. A. Wiles, *J.*, 1962, 1725.

⁸ Z. S. Ariyan and L. A. Wiles, *J.*, 1963, 755.

⁹ H. T. Hayes and L. Hunter, *J.*, 1940, 332.

EXPERIMENTAL

The monoacylhydrazines were obtained commercially, or were prepared by the reaction of an ester with hydrazine hydrate solution (99%).¹⁰ Melting points were determined on a Kofler hot bench, and since some diacylhydrazines melt with decomposition, the figures now recorded for these are higher than the literature values. Infrared spectra were determined for mulls in hexachlorobutadiene using a Perkin-Elmer Infracord Spectrometer.

Diacylhydrazines.—Generally, purified sulphur monochloride (1 mole) was added drop-wise to a suspension of the hydrazide (1 mole) in benzene. When the initial vigorous reaction had subsided (5 min.) the mixture was refluxed (24 hr.). The diacylhydrazine was either insoluble, or separated immediately on cooling. Sulphur was slowly deposited. The following 1,2-diacylhydrazines were thus produced: di-*n*-propionyl (86%), m. p. 136° (lit.,¹¹ 136°) (from benzene), infrared spectrum in agreement with the literature¹² (Found: C, 50.1; H, 8.4; N, 20.3. Calc. for C₆H₁₂N₂O₂: C, 50.0; H, 8.3; N, 19.4%); di-isobutyryl (70%), m. p. 248° (lit.,¹³ 244—245°) (from methanol) (Found: C, 55.7; H, 9.5; N, 15.6. Calc. for C₈H₁₆N₂O₂: C, 55.8; H, 9.3; N, 16.3%); di-*n*-valeryl (52%), m. p. and mixed m. p. 163° (lit.,¹ 163°), (from ethanol-water), infrared spectrum identical with that of an authentic specimen;¹ di-isovaleryl (59%), m. p. 192° (lit.,¹⁴ 184°) (from ethyl acetate), infrared spectrum in agreement with the literature¹² (Found: C, 59.4; H, 10.4; N, 13.5. Calc. for C₁₀H₂₀N₂O₂: C, 60.0; H, 10.0; N, 14.0%); di-*n*-hexanoyl (63%), m. p. 159° (lit.,¹⁴ 159°) (from benzene) [Found: C, 63.6; H, 10.7; N, 11.7%; *M* (Rast), 205. Calc. for C₁₂H₂₄N₂O₂: C, 63.2; H, 10.5; N, 12.3%; *M*, 228]; di-*n*-octanoyl (68%), m. p. 153° (lit.,¹⁵ 154—155°) (from ethanol) [Found: C, 67.6; H, 11.5; N, 10.1%; *M* (Rast), 245. Calc. for C₁₆H₃₂N₂O₂: C, 67.6; H, 11.3; N, 9.9%; *M*, 284]; dibenzoyl (65%), m. p. 245° (lit.,¹⁶ 241°) (from ethanol), infrared spectrum identical with that of an authentic specimen; di-*p*-toluoyl (70%), m. p. 260° (decomp.) (lit.,¹⁷ 253—254°) (from ethanol-ethyl acetate) (Found: C, 70.9; H, 6.2; N, 9.8. Calc. for C₁₆H₁₆N₂O₂: C, 71.6; H, 6.0; N, 10.5%).

n-Octanoyl Chloride.—*n*-Octanohydrazide (6.0 g., 1 mole) and sulphur monochloride (10.1 g., 2 mole) were refluxed in chloroform (100 ml.) until hydrogen chloride ceased to be evolved (18 hr.). Distillation gave *n*-octanoyl chloride (2.5 g., 40%), b. p. 98—99°/25 mm.; 199°/760 mm. (lit.,¹⁸ 89.3—89.6°/20 mm., lit.,¹⁹ 194—196°/760 mm.).

Benzoyl Chloride.—Benzohydrazide (6.8 g., 0.05 mole) and sulphur monochloride (13.5 g., 0.1 mole) were refluxed in benzene (50 ml.; 24 hr.). Distillation gave benzoyl chloride (2.8 g., 40%) b. p. 194—197°.

p-Toluoyl Chloride.—*p*-Toluohydrazide (6.0 g., 1 mole) and sulphur monochloride (10.4 g., 2 moles) were refluxed in benzene (100 ml.; 12 hr.). On cooling, di-*p*-toluoylhydrazine (0.5 g.) was precipitated. Distillation gave *p*-toluoyl chloride (1.6 g., 27%), b. p. 113°/24 mm. (lit.,²⁰ 102°/15 mm., lit.,²¹ 125°/36 mm.) (Found: C, 61.9; H, 4.8; Cl, 22.7. Calc. for C₈H₇ClO: C, 62.1; H, 4.5; Cl, 23.0%).

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¹⁰ P. A. S. Smith, *Org. Reactions*, 1946, **3**, 366.

¹¹ T. Curtius and H. Hille, *J. prakt. Chem.*, 1901, **64** (II), 406.

¹² M. Mashima, *Bull. Chem. Soc. Japan*, 1962, **35**, 423.

¹³ H. Stetter and H. Spangenberg, *Chem. Ber.*, 1958, **91**, 1982.

¹⁴ W. Autenreith and P. Spiess, *Ber.*, 1901, **34**, 188.

¹⁵ S. Takase, *J. Chem. Soc. Japan*, 1958, **79**, 1500.

¹⁶ R. S. Curtiss, A. R. Koch, and E. J. Barrells, *J. Amer. Chem. Soc.*, 1909, **31**, 420.

¹⁷ W. Autenreith and G. Thomas, *Ber.*, 1924, **57**, 436.

¹⁸ E. B. Herschberg, *J. Amer. Chem. Soc.*, 1939, **61**, 3587.

¹⁹ L. Henry, *Bull. Classe Sci., Acad. roy. Belg.*, 1899, **37**, 63; *Chem. Centr.*, 1899, **I**, 968.

²⁰ P. Frankland and H. Aston, *J.*, 1899, **75**, 494.

²¹ G. T. Morgan and E. A. Coulson, *J.*, 1929, 2208.