NOTES

Thiocarbonyls. III. The Willgerodt Reaction with Thioacetophenone[1]

By E. Campaigne and Phyllis V. Rutan

To account for the reaction of ketones in the Willgerodt reaction, King and McMillan[2] proposed the following sequence of steps: ketone → thioketone → mercaptan → olefin → mercaptan → etc. To show that these substances could act as intermediates in the reaction, mercaptans and olefins were successfully converted to the corresponding amides by the Willgerodt procedure. However, no thioketone has been shown to undergo a Willgerodt reaction. King and McMillan[2] found that "duplodithioacetone" was converted to propionamide when heated with ammonium polysulfide, but "duplodithioacetone" is neither dithioacetone nor trithioacetone.[3]

Trithioacetophenone has been found to yield phenylthioacetomorpholide by the Kindler procedure in better yield than that obtained from acetophenone in a parallel experiment. Since the refluxing temperature was well above the melting point of trithioacetophenone (122°) it was assumed to act through the monomeric form. The Kindler modification of the Willgerodt reaction was used to eliminate the possibility of hydrolysis of thioacetophenone to acetophenone as one step in the reaction.

In one experiment, acetophenone (12 g., 0.1 mole), morpholine (8.7 g., 0.1 mole), and sulfur (3.2 g., 0.1 mole) were mixed, refluxed for eight hours, and the mixture poured into 50 ml. of hot ethyl alcohol. The crystals of phenylthioacetomorpholide which formed on cooling melted at 78–79.5°, and weighed 15.9 g., which is equivalent to 72% of the theoretical yield.

In a second experiment, morpholine (4.4 g., 0.05 mole), sulfur (1.6 g., 0.05 mole) and trithioacetophenone (6.8 g., 0.017 mole) were mixed and refluxed for seven and one-half hours at a temperature of 145–150°. A copious evolution of hydrogen sulfide occurred in this case. Worked up in an identical manner, the yield of phenylthioacetomorpholide, m.p. 77–79°, was 9.2 g. or 83%. A mixed melting point determination of the two products showed no depression.

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[1] For the second paper of this series, see This Journal, **68**, 769 (1946).

[2] King and McMillan, *ibid.*, **68**, 1369 (1946).

[3] Campaigne, *Chem. Rev.*, **39**, 22 (1946).

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The Conversion of Certain Mercaptans into Acetates and Sulfides[1]

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In connection with certain research projects in these Laboratories, 2-hydroxyethylmercaptan and *t*-butylmercaptan were converted into 2-chloroethylthiol acetate, *t*-butyl chlorothiol acetate, *t*-butyl 2-hydroxyethyl sulfide and *t*-butyl 2-chloroethyl sulfide. They were isolated in a state of purity and several density, freezing point and vapor pressure determinations made.

Experimental

The intermediates, 2-hydroxyethyl and 2-chloroethyl mercaptan, were prepared according to the method of Bennett.[3] Yields were considerably lower than reported by Bennett, particularly for the 2-chloroethyl mercaptan. The 90% yield reported for the chloro compound was obtained for the crude product, but on distillation extensive polymerization could not be prevented. Yields of 33 to 44% for the purified material were obtained.

2-Chloroethylthiol Acetate.[4]—2-Chloroethyl mercaptan (50 g., 0.52 mole) was added dropwise with stirring to 0.9 mole of acetyl chloride at a reaction temperature of 50°. After the addition was complete, about fifty minutes, the reaction mixture was stirred at 50° for an additional two hours to complete the reaction. The large excess of acetyl chloride was unnecessary if its loss through volatilization was prevented by a carbon dioxide–acetone cooled scrubber. The reaction mixture was then fractionated in vacuum and the fraction of b. p. 74–76° at 17 mm. collected. For material of 99% purity see Table I.

***t*-Butyl Chlorothiol Acetate.**—*t*-Butyl mercaptan (50 g., 0.56 mole) was heated gently with 69 g., 0.62 mole, of chloroacetyl chloride for two hours at 60–90°. The mixture ceased refluxing at 90°, which indicated that the reaction was complete. The reaction mixture was then fractionated under vacuum and the fraction of b. p. 82–84° at 15–19 mm. collected. For material of purity of 99% see Table I.

***t*-Butyl 2-Hydroxyethyl Sulfide.**—This intermediate was prepared by condensing the sodium salt of *t*-butyl mercaptan with aqueous ethylene chlorohydrin at 60–70° with good stirring. The crude hydroxy sulfide which separated as an insoluble oil was drawn off, dried over silica gel and fractionated in vacuum. Yield of the once distilled product of b. p. 89–93° at 17 mm. was 80–85%. *Anal.* Calcd. for $C_6H_{14}OS$: S, 23.88. Found: S, 22.89.

***t*-Butyl 2-Chloroethyl Sulfide.**—*t*-Butyl 2-hydroxyethyl sulfide (116.5 g., 0.87 mole) was diluted with 30 ml. of ether and the mixture added beneath the surface of an ether–thionyl chloride mixture containing 114 g., 0.96 mole of thionyl chloride and 30 ml. of ether. The reaction was conducted in a 3-necked flask of the proper ca-

Table I

Analyses and Properties of Certain Acetates and Sulfides

Compound			2-Chloroethyl thiolacetate	*t*-Butyl chlorothioacetate	*t*-Butyl-2-chloroethyl sulfide
Formula			C_4H_7OClS	$C_6H_{11}OClS$	$C_6H_{13}ClS$
B. p.	°C.		76–76.5	89	81–82
	Mm.		17	21	30
Yield, %, once distd.			90	80	80
F. p., °C.			...	Below −70	−49 ± 1
Density	g./ml.		1.2010	1.1023	1.0001
	at °C.		20	25	25
Vapor. p.	Mm.		1.68	0.549	1.46
	°C.		30	25	25
Analyses, %	Cl	Calcd.	25.59	21.27	23.22
		Found	25.36	21.08	23.24
	S	Calcd.	23.14	19.24	21.00
		Found	22.81	18.83	20.85

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[1] Published with the permission of the Chief, Chemical Corps.

[2] Chemical Corps Technical Command, Edgewood Arsenal, Md.

[3] Bennett, *J. Chem. Soc.*, **121**, 2139 (1922).

[4] Alderman, U. S. Patent 2,212,141 (1941); prepared by author in 1938, E. A. T. R. 279.