Chemistry

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Abstract

Full Text

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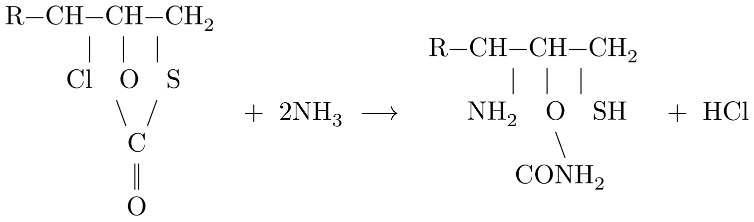
On the Interaction of Chloro Derivatives of Alkenethiocarbonates with Ammonia and with Amines

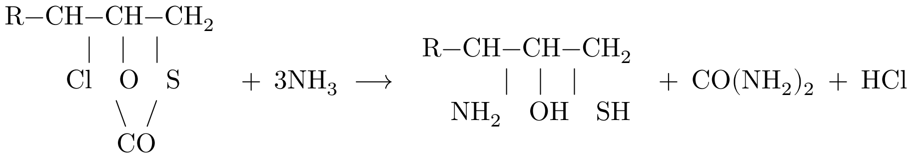
By the interaction of certain chlorine-containing epoxides with carbon oxysulfide at a temperature of 90-100° in the presence of tetraethylammonium bromide as a catalyst, under pressure, the corresponding chloroalkenethiocarbonates are obtained. It is known that the chlorine atom in epichlorohydrin is considerably reactive and can readily be replaced by other functional groups.

It was of interest to study the reactivity of the chlorine atoms in chloroalkenethiocarbonates (ChATC). It could be expected that, upon interaction of ammonia with ChATC, along with replacement of the chlorine atom, ammonolysis might occur with formation of carbamic acid esters:



$$\underset{\substack{|\qquad|\qquad|\\ \text{Cl}\quad \text{O}\quad \text{S}\\ \diagdown\ \diagup\\ \text{C}\\ \|\\ \text{O}}}{\text{R–CH–CH–CH}_2} + 2NH_3 \longrightarrow \underset{\substack{|\qquad|\qquad|\\ NH_2\quad \text{O}\quad \text{SH}\\ \diagdown\\ CONH_2}}{\text{R–CH–CH–CH}_2} + HCl$$

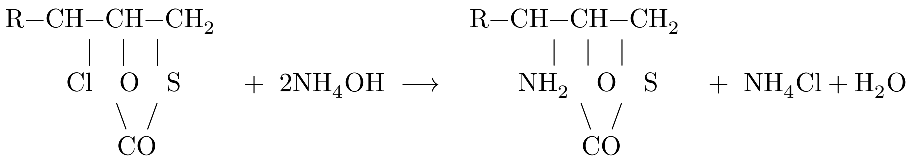
or urea and the corresponding thioglycol:



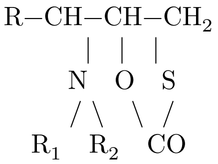
$$\underset{\substack{|\qquad|\qquad|\\ \text{Cl}\quad \text{O}\quad \text{S}\\ \diagdown\ \diagup\\ \text{CO}}}{\text{R–CH–CH–CH}_2} + 3NH_3 \longrightarrow \underset{\substack{|\qquad|\qquad|\\ NH_2\quad \text{OH}\quad \text{SH}}}{\text{R–CH–CH–CH}_2} + CO(NH_2)_2 + HCl$$

Experiments showed that ChATC react very vigorously at ordinary temperature with ammonia in alcoholic solution in sealed ampoules. As a result of the reaction, a difficultly separable mixture of organic and inorganic substances is obtained. Therefore we decided to carry out the reaction of ChATC with an aqueous solution of ammonia, reckoning that, as in the case of carbonates ([1]), formation of a carbamic acid ester would occur.

ChATC readily react at room temperature with concentrated (25%) aqueous ammonia solution; in this case only replacement of the α-chlorine atom relative to the thiocarbonate ring by the group $-NH_2$ takes place,



The reaction proceeds with evolution of heat; the ammonium chloride formed remains in the aqueous solution, and thus it is easy to separate the amino derivative, which precipitates as a crystalline substance in a sufficiently pure form, or separates as an insoluble oily layer. The reaction of ChATC also proceeds readily with aqueous solutions of other substituted amines, and amino derivatives of the following general formula are obtained in good yields:



Using 3-aminopropylenethiocarbonate, the structure of the thiocarbonate ring was additionally confirmed. A mixed melting-point test of 3-aminopropylenethiocarbonate obtained from 3-chloropropylenethiocarbonate synthesized from epichlorohydrin and COS with an amino derivative of thiocarbonate of known structure showed no depression. Fig. 1 gives the IR spectra of the indicated amino derivatives. Their complete analogy also indicates the identity of the two thiocarbonates.

In the reaction of 1,2-dichlorobutenethiocarbonate-3,4 with ammonia and with amines, compounds are obtained in which only one chlorine atom, the one located closer to the thiocarbonate ring, is replaced by an amino group. The principal physicochemical characteristics and yields of the new compounds obtained are given in Table 1. The elemental composition of the compounds is given in Table 2. The indicated compounds contain reactive functional groups and can serve as starting products for the synthesis of other organic compounds.

Fig. 1. IR absorption spectra of 3-aminopropylenethiocarbonates-2,3 obtained: **a** –from $ClCH_2CHOH-CH_2SH$ and $COCl_2$ with subsequent amination; **b** – from $ClCH_2CH-CH_2O$ and COS, with subsequent amination

Table 1

Physicochemical constants of the aminothiocarbonates obtained

Starting chloroalkenethio-carbonate	Aminoalkenethiocarbonate obtained	m.p., °C	Molecular weight, found	Molecular weight, calculated	Yield, % of chloroalkenethio-carbonate
$ClCH_2-C(O)H-CH_2-S-CO$	$H_2N-CH_2-C(O)H-CH_2-S-CO$	146–147.5	130	133	87.5
”	$CH_3HN-CH_2-C(O)H-CH_2-S-CO$	110–112	144	147	92.0
”	$(CH_3)_2N-CH_2-C(O)H-CH_2-S-CO$*	—	159	161	63.0
$ClCH_2-C(O)H-CH(SCO)-CH_3$	$H_2N-CH_2-C(O)H-CH(SCO)-CH_3$	104.5–105	145.5	147	41.0
”	$CH_3NH-CH_2-C(O)H-CH(SCO)-CH_3$	85.5–86	160.0	161	33.0
”	$(CH_3)_2N-CH_2-C(O)H-CH(SCO)-CH_3$**	—	175	175	65.0
$ClCH_2-C(Cl)H-C(O)H-CH_2SCO$	$ClCH_2-C(NH_2)H-C(O)H-CH_2SCO$	104.5–106	178.5	181.5	43.0
”	$ClCH_2-C(NHCH_3)H-C(O)H-CH_2SCO$	105–106	197.0	195.5	77.0
”	$ClCH_2-C[N(CH_3)_2]H-C(O)H-CH_2SCO$	184–185	206.0	209.5	82.5

* b.p. 96°/3 mm; 90°/1 mm, n_D^{20} 1.5033; d_4 1.1620; MR_D 41.10. Calculated 41.16.

** b.p. 114-115°/7 mm; n_D^{20} 1.4940; d_4 1.1150: MR_D 45.70. Calculated 45.81.

Experimental part

Into a pear-shaped flask equipped with a stirrer and a dropping funnel, a twofold excess of the amine was charged in the form of a 15-25% solution in water and from

from a dropping funnel, ChATC was added. Heating was observed, the solution became homogeneous, and after some time an amine began to separate. The reaction mixture was heated on a water bath to 60° and kept for 10-15 min. Then a double volume of water was added, the mixture was stirred, and the amine was filtered off. After drying, the amines were recrystallized from ethyl

Table 2

Results of analyses of aminothiocarbonates

Aminothiocarbonate	Found, % C	Found, % H	Found, % N	Found, % S	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % S
$H_2NCH_2-C(O)H-CH_2-SCO$, $C_4H_7NO_2S$	36.14	5.20	10.80	24.30	36.00	5.26	10.50	24.01
$CH_3NHCH_2-C(O)H-CH_2SCO$, $C_5H_9NO_2S$	40.70	5.95	9.82	21.88	40.70	6.10	9.50	21.80
$(CH_3)_2N-CH_2-C(O)H-CH_2SCO$, $C_6H_{11}NO_2S$	44.67	6.73	8.47	19.78	44.70	6.84	8.70	19.85
$H_2N-CH_2-C(O)H-CH(SCO)-CH_3$, $C_5H_9NO_2S$	40.72	6.13	9.25	21.80	40.70	6.10	9.50	21.80
$CH_3NH-CH_2-C(O)H-CH(SCO)-CH_3$, $C_6H_{11}NO_2S$	44.67	6.86	8.54	19.87	44.70	6.84	8.70	19.85
$(CH_3)_2N-CH_2-C(O)H-CH(SCO)-CH_3$, $C_7H_{13}NO_2S$	48.15	7.46	7.61	18.31	48.00	7.42	7.98	18.30
$ClCH_2-C(NH_2)H-C(O)H-CH_2SCO$*, $C_5H_8ClNO_2S$	33.25	4.50	7.63	17.10	33.00	4.40	7.72	17.65
$ClCH_2-C(NHCH_3)H-C(O)H-CH_2SCO$**, $C_6H_{10}ClNO_2S$	36.85	5.10	6.87	16.33	36.80	5.11	7.15	16.37
$ClCH_2-C[N(CH_3)_2]H-C(O)H-CH_2SCO$***, $C_7H_{12}ClNO_2S$	40.34	5.62	6.69	15.09	40.20	5.74	6.70	15.30

Aminothiocarbonate	Found, % C	Found, % H	Found, % N	Found, % S	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % S

* Cl, % 19.50, calculated 19.55.
** Cl, % 18.20, calculated 18.15.
*** Cl, % 16.94, calculated 17.00.

alcohol, using, when required, charcoal to decolorize the solution.

The samples were recrystallized to a constant melting point, after which they were analyzed. Liquid products were extracted with ether, dried with anhydrous sodium sulfate, and distilled in vacuum.

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1. W. T. Reppel, *Ind. and Eng. Chem.*, **50**, 767 (1958).

Note: Figure translations are in progress. See original paper for figures.