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O-ALKYL S-CHLOROFORMYL DITHIOCARBONATES FOR PEPTIDE SYNTHESIS

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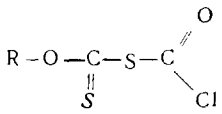
In order to study the condensing properties of compounds of the O-alkyl S-chloroformyl dithiocarbonate series and their subsequent use in the synthesis of peptides, we have performed the synthesis of O-ethyl and O-butyl S-chloroformyl dithiocarbonates with the general formula



(R—C_2H_5, —C_4H_9).

The O-ethyl and O-butyl S-chloroformyl dithiocarbonates were obtained by the reaction of the corresponding potassium O-alkyl dithiocarbonates with phosgene in absolute ether, benzene, or carbon tetrachloride at −10-5°C with vigorous stirring and the subsequent raising of the temperature of the reaction mixture to room temperature. The O-alkyl S-chloroformyl dithiocarbonates obtained were yellow liquids with a specific odor readily soluble in organic solvents but insoluble in water.

The structures of the compounds that we had obtained were confirmed by mass and IR spectroscopy and refractometry. The mass spectrum of O-butyl S-chloroformyl dithiocarbonate contained strong peaks of the following fragments: *m/z* 212 (*m*+); 177 (—Cl); 149 (—C(=O)Cl); 117 (—S—C(=O)Cl); 57 (—O—C(=S)—S—C(=O)Cl); 43 (—CH_2—O—C(=S)—S—C(=O)Cl); 29 (—CH_2—CH_2—O—C(=S)—S—C(=O)Cl).

TABLE 1. Compounds Synthesized with the Aid of S-(Butoxythiocarbonyl)chlorothioformate and Their Main Constants

Compound	Yield %	mp, °C found	mp, °C lit.	$[\alpha]_D^{20}$, deg	R_f in system* 1	R_f in system* 2
Benzyloxycarbonyl-Gly-pentachlorophenyl	71,4	126—128	128—130 [3]		0,77	0,80
Benzyloxycarbonyl-Ala-pentachlorophenyl	86,7	100—102	100—104 [4]		0,92	0,94
Benxyloxycarbonyl-Gly-para-nitrophenyl	50,5	125—127	126—128 [5]		0,74	0,91
Benxyloxycarbonyl-Gly-Gly-OOH	65,4	62—65	64—66 [6]		0,89	0,92
Benzyloxycarbonyl-Ala-Gly-OOH	61,4	73—76	74—76 [6]	—19,1 (*c* 6; $CHCl_3$)	0,83	0,89
o-NPS-Ser-Gly(γ-benzyl)-2,4,5-trichlorophenyl	67,0	amorph.	Oil —[7]	—22,55 (*c* 4; ethyl acetate	0,92	0,90

*Systems: 1) butan-1-ol—water—acetic acid (4:1:1); 2) butan-1-ol—water—acetic acid—pyridine (30:24;6:20).

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Analysis of the IR spectrum of O-butyl S-chloroformyl dithiocarbonate showed characteristic absorption bands in the following regions (cm^{-1}): 1200 (C=S); 750 (—C—S—); 1800 (—C(=O)—Cl); 1100 (—C=O); 2950, 2870 (CH_3); 1925, 1440 ($—CH_2—$).

O-Ethyl S-chloroformyl dithiocarbonate was obtained with a yield of 50%, bp 29-30°C (0.2 mm Hg); $MR_{D_{calc}} = 45.45$; $MR_{D_{found}} = 45.35$; $n_D^{20} - 1.5572$; $d_4^{20} - 1.3099$.

O-Butyl S-chloroformyl dithiocarbonate was obtained with a yield of 50%, bp 58-60°C (0.2 mm Hg); $MR_{D_{calc}} = 53.62$; $MR_{D_{found}} = 54.18$; $n_D^{20} - 1.5341$; $d_4^{20} - 1.2190$.

The reagents that we synthesized were used in the activation of the α-carboxy groups of N-substituted amino acids for the formation of ester and peptide bonds. As concrete examples we synthesized a number of compounds known in the literature that had been obtained with the aid of other condensing agents [1, 2]. Since O-butyl S-chloroformyl dithiocarbonate proved to be more active than the O-ethyl compound, the results obtained with its aid are given in Table 1.

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SYNTHESIS OF AFFINITY SORBENTS AND THEIR TESTING ON AMYLORIZIN

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In consideration of the hydrophobic nature of the active sites of the proteolytic enzymes of microrganisms, we have synthesized a number of affinity sorbents the ligands of which are hydrophobic amino acids and a number of dipeptides and tripeptides. These ligands were bound to the support used with the aid of dicyclohexylcarbodiimide.

Estimates of the sorption capacities of the sorbents were made by incubating them with an extract of Amylorizin at pH 8.0 followed by washing out the nonsorbed proteins and eluting the sorbed proteolytic enzymes with various concentrations of sodium chloride at the same pH value. All the sorbents were present in the moist state and had different volumes ranging from 5 to 12 cm^3, and therefore, in order to evaluate the results obtained they were recalculated to unit volume (cm^3) of moist sorbent.

The sorption capacities of the sorbents synthesized differed considerably from one another. The largest amount of aminopeptidase (substrate: leucine p-nitroanilide) [1] was sorbed on the sorbent glycyl-phenylalanine-support (22.25 units/cm^3), but at the same time 45.3 units/cm^3 of endopeptidases (proteolytic activity on casein) was sorbed [2]. The sorbent leucyl-glycyl-glycine-support sorbed less than a quarter of the amount of aminopeptiodase (5 units/cm^3) but almost as much of endopeptidases. Comparatively small amounts of these enzymes were sorbed by the other sorbents (Table 1).

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