The results of elementary analysis were in agreement with the calculated values.

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UNUSUAL REACTION OF A CYCLIC THIOCARBONATE WITH SECONDARY AMINES

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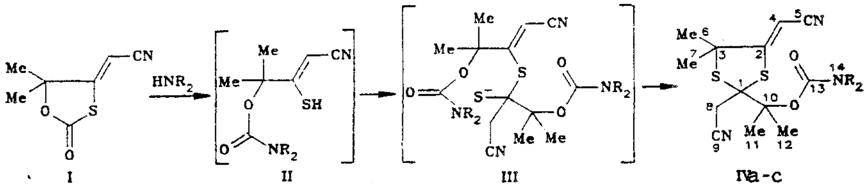
We have established that 2-[1-(N,N-dialkylcarbamoyloxy)-1-methylethyl]-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-dithiolanes IV are formed in up to 90% yields instead of the expected (in accordance with [2, 3]) carbamates II in the reaction of 1,3-oxathiolan-2-one I [1] with secondary amines.



IVa R=Et; b R=Pr; c R=Bu

Opening of the 1,3-oxathiolane ring with the formation of β-mercaptoalkylcarbamate II evidently occurs in the first step under the influence of the amine; the subsequent dimerization of II via the addition of the mercapto group of one molecule to the double bond of a second molecule leads to intermediate III. This is followed by intramolecular substitution of the carbamoyl grouping with the formation of the 1,3-dithiolane ring.

The structures of dithiolanes IVa-c were established by x-ray diffraction analysis and were confirmed by ^1H and ^{13}C NMR spectroscopy and the IR spectra.

2-[1-(N,N-Diethylcarbamoyloxy)-1-methylethyl]-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-2,3-dithiolane (IVa, $C_{17}H_{25}N_3O_2S_2$). This compound was obtained in 92% yield and had mp 158-160°C (from ether). IR spectrum ($CHCl_3$): 1570 (SC=CH), 1680 (C=O), 2215 (C=CHCN), 2245 cm^{-1} (CH_2CN). ^1H NMR spectrum ($CDCl_3$), δ: 5.26 (1H, s, =CH), 3.42 (4H, q, CH_2N), 3.17 (2H, s, CH_2), 1.84 (6H, s, CH_3),. 1.71 (6H, s, CH_3), 1.13 ppm (6H, t, CH_3). ^{13}C NMR spectrum ($CDCl_3$): 86.1 [$C_{(1)}$], 153.5 [$C_{(2)}$], 64.8 [$C_{(3)}$], 88.9 [$C_{(4)}$], 116.2 and 118.1 [$C_{(5)}$, $C_{(9)}$], 31.9 [$C_{(8)}$], 72.4 [$C_{(10)}$], 173.2 [$C_{(13)}$], 41.7 [$C_{(14)}$], 28.8, 31.6, 13.5 [$C_{(6)}$, $C_{(7)}$, $C_{(11)}$, $C_{(12)}$, $C_{(14)}$].

2-[1-(N,N-Dipropylcarbamoyloxy)-1-methylethyl[-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-dithiolane (IVb, $C_{19}H_{27}N_3O_2S_2$). This compound was obtained in 91% yield in the form of a light-yellow oil. IR spectrum (microlayer): 1560 (SC=CH), 1700 (C=O), 2220 (C=CHCN), 2250 cm^{-1} (CH_2CN). ^1H NMR spectrum ($CDCl_3$), δ: 5.27 (1H, s, =CH), 3.34 (10H, m, CH_2), 1.84 (6H, s, CH_3), 1.75 (6H, m, CH_3), 1.55 ppm (6H, m, CH_3).

2-[1-(N,N-Dibutylcarbamoyloxy)-1-methylethyl]-5,5-dimethyl-2-cyanomethyl-4-cyanomethylene-1,3-dithiolane (IVc, $C_{21}H_{33}N_3O_2S_2$). This compound was obtained in 92% yield in the form of a light-yellow oil. IR spectrum (microlayer): 1560 (SC=CH), 1700 (C=O), 2200 (C=CHCN), 2250 cm^{-1} (CH_2CN). ^1H NMR spectrum ($CDCl_3$), δ: 5.27 (1H, s, =CH), 3.29 (4H, q, CH_2), 3.21 (10H, m, CH_2), 1.77 (6H, s, CH_3), 1.71 (6H, d, CH_3), 0.94 ppm (6H, m, $2CH_3$).

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The results of elementary analysis were in agreement with the calculated values.

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FORMATION OF N-VINYL DERIVATIVES OF 1,2,4-TRIAZOLE

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Reactions for obtaining N-vinyl derivatives of 1,2,4-triazole either by the action of acetylene in an autoclave under pressure in the presence of catalysts [1, 2] or by transvinylation with vinyl acetate in the presence of sulfuric acid [3, 4] are known. Vinyl exchange of 5-substituted tetrazoles with vinyl acetate using the mercury acetate—boron trifluoride etherate catalytic system has been described for compounds of the heterocyclic series [5].

We have observed that for compounds of the triazole series transvinylation also takes place successfully in the presence of this catalytic system. In this case the undesirable resinification and polymerization processes are reduced to a minimum. The reaction time can be decreased from 48 h to 24 h. The catalytic system was tested with 1,2,4-triazole (I) and 3,5-dichloro-1,2,4-triazole (II).

A 0.4-ml sample of BF_3 etherate was added with stirring to a solution of 0.24 g of mercury acetate, 0.1 mole of I or II, and 0.005 g of hydroquinone in 15.7 ml of vinyl acetate, and the mixture was heated for 24 h at 50-60°C. At the end of the reaction, 0.6 g of sodium bicarbonate was added, the vinyl acetate was removed by distillation, and the residue was fractionated in vacuo. The yields of vinylation products ranged from 60% to 70%. The characteristics of the products were in agreement with the data for 1-vinyl-1,2,4-triazole [1, 2] and 1-vinyl-3,5-dichloro-1,2,4-triazole [6].

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