

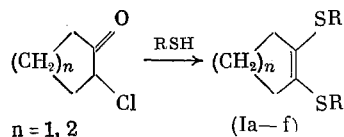
6. E. F. Litvin, A. B. Shapiro, L. M. Kozlova, É. G. Rozantsev, and L. Kh. Friedlin, Zh. Org. Khim., **6**, 2365 (1970).
7. V. M. Frolov, O. P. Parenago, G. N. Bondarenko, L. S. Kovaleva, A. I. Él'natanova, L. P. Shuikina, G. M. Cherkashin, and E. Ya. Mirskaya, Kinet. Katal., **22**, 1356 (1981).
8. É. G. Rozantsev, V. A. Golubev, M. B. Neiman, and Yu. B. Kokhanov, Izv. Akad. Nauk SSSR, Ser. Khim., 572 (1965).
9. L. P. Shuikina, Dissertation [in Russian], Moscow (1983).
10. É. G. Rozantsev, Free Iminoxyl Radicals [in Russian], Khimiya, Moscow (1970), p. 128.

SYNTHESIS OF BISALKYLTHIO DERIVATIVES OF CYCLOPENTENE AND CYCLOHEXENE

É. A. Ramazanov, F. F. Kerimov,
I. G. Mursakulov, and A. M. Moiseenkov

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The wide use of unsaturated sulfides in modern organic synthesis is prevented by the absence of methods for the preparation of their individual functionalized members, for example, the dialkylthiocycloalkenes (I) discussed below. Previously it was shown that, under the standard conditions for the synthesis of cyclic α -haloketone thioacetals, the reaction of α -haloketones with mercaptans leads to the formation of halogen-free 1,4-dithienes in moderate yields [1, 2]. We found that the related monocyclic tetrasubstituted olefins (Ia-f) can be synthesized in up to 90% yield by simply keeping a mixture of either the α -chlorocyclopentanone or α -chlorocyclohexanone and 2 mole equivalents of the appropriate mercaptan in cyclohexane at $\sim 25^\circ\text{C}$ (Table 1).^{*} In all cases the thioacetals corresponding to the starting chloroketones were not detected in the reaction mixtures.



The structure of the previously unknown olefins (I) was confirmed by the elemental and spectral analysis data. Thus, in their IR spectra are present the absorption bands of the C-S ($520\text{--}600\text{ cm}^{-1}$) and C=C ($1570\text{--}1610\text{ cm}^{-1}$) bonds, while the PMR spectra have the signals of the protons of all of the structural fragments of the discussed compounds. In particular, the multiplet signals of the cycloalkene allylic methylenes are located in the $\delta \sim 3$ ppm region, the remaining methylenes at $\delta \sim 2$ ppm, while the signals of the ethyl, propyl, and butyl substituents have standard tabular values.

EXPERIMENTAL

1,2-Diethylthio-1-cyclopentene (Ia). To a stirred solution of 12.4 g (0.2 mole) of EtSH in 150 ml of cyclohexane at 0°C was added in 15 min a solution of 11.9 g (0.1 mole) of α -chlorocyclopentanone in 25 ml of cyclohexane. Then the reaction mass was heated to $\sim 25^\circ\text{C}$ and stirred for 8 h. The obtained aqueous layer was separated, the organic layer was washed with water, dried over MgSO_4 , and the residue after removal of the solvent was vacuum-distilled. We obtained 14.1 g (75%) of (Ia) as a pale yellow oil, bp $90\text{--}95^\circ$ (2 mm); n_D^{20} 1.5546. Found: C 57.31; H 8.43; S 33.94%. $\text{C}_9\text{H}_{16}\text{S}_2$. Calculated: C 57.39; H 8.56; S 34.05%.

1,2-Di-n-propylthio-1-cyclopentene (Ib) was obtained the same as (Ia) from n-PrSH and α -chlorocyclopentanone. Yield of (Ib) 87%, bp $105\text{--}110^\circ$ (3 mm); n_D^{20} 1.5454. Found: C 61.19; H 9.24; S 29.45%. $\text{C}_{11}\text{H}_{20}\text{S}_2$. Calculated: C 61.05; H 9.32; S 29.63%.

1,2-Di-n-butylthio-1-cyclopentene (Ic). Similarly from 18.0 g (0.2 mole) of n-BuSH we obtained 20.7 g (85%) of (Ic), bp $140\text{--}142^\circ$ (3 mm); n_D^{20} 1.5318. Found: C 63.69; H 9.81; S 26.13%. $\text{C}_{13}\text{H}_{24}\text{S}_2$. Calculated: C 63.87; H 9.90; S 26.23%.

^{*}Table 1 has apparently been omitted from the Russian — Publisher.

Institute of Chloroorganic Synthesis, Academy of Sciences of the Azerbaidzhan SSR, Baku.
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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1,2-Diethylthio-1-cyclohexene (Id). Similarly from 12.4 g (0.2 mole) of EtSH and 13.3 g (0.1 mole) of α -chlorohexanone we obtained 17.8 g (88%) of (Id), bp 110–115° (1 mm); n_D^{20} 1.5522. Found: C 59.25; H 8.86; S 31.52%. $C_{10}H_{18}S_2$. Calculated: C 59.35; H 8.96; S 31.69%.

1,2-Di-n-propylthio-1-cyclohexene (Ie). Similarly from 15.2 g (0.2 mole) of n-PrSH we obtained 19.8 g (86%) of (Ie), bp 138–141° (5 mm); n_D^{20} 1.5436. Found: C 62.38; H 9.57; S 27.78%. $C_{12}H_{22}S_2$. Calculated: C 62.55; H 9.62; S 27.83%.

1,2-Di-n-butylthio-1-cyclohexene (If). Similarly from 18.0 g (0.2 mole) of n-BuSH we obtained 21.9 g (85%) of (If), bp 128–132° (1 mm); n_D^{20} 1.5336. Found: C 64.95; H 10.04; S 24.65%. $C_{14}H_{26}S_2$. Calculated: C 65.05; H 10.14; S 24.81%.

CONCLUSIONS

Alkyl mercaptans react with α -chlorocyclopentanone and α -chlorocyclohexanone to give the corresponding 1,2-bisalkylthiocyclenes.

LITERATURE CITED

1. H. Rubinstein and M. Wuerthele, J. Org. Chem., **34**, 2762 (1969).
2. I. G. Mursakulov, F. F. Kerimov, N. K. Kasumov, E. A. Ramazanov, and N. S. Zefirov, Azerb. Khim. Kh., No. 1, 93 (1979).

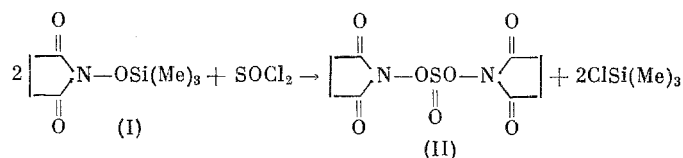
SYNTHESIS OF N-HYDROXSUCCINIMIDE ESTERS OF N-PROTECTED AMINO ACIDS AND PEPTIDES USING N,N'-DISUCCINIMIDYL SULFITE

A. V. Il'ina, Yu. A. Davidovich,
and S. V. Rogozhin

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The N-hydroxysuccinimide esters of N-protected amino acids and peptides have found wide use at the present time in the synthesis of peptides [1–3], since racemization is practically not observed when they are used. The N-hydroxysuccinimide that is formed during reaction is readily soluble in water, which greatly facilitates the isolation of the end products [4]. Among the known methods for obtaining the N-hydroxysuccinimide esters of N-protected amino acids the carbodiimide method is used most frequently [5]. A disadvantage of this method is the formation of the corresponding N-acylureas, and also the high toxicity and allergenicity of dicyclohexylcarbodiimide. The methods for obtaining the N-hydroxysuccinimide esters of N-protected amino acids and peptides by the mixed anhydride method [6] or using N,N'-disuccinimidyl carbonate [7], which permit obtaining the activated esters in good yields, also have important disadvantages.

In order to create a new efficient method for obtaining the N-hydroxysuccinimide esters of N-protected amino acids and peptides we synthesized N,N'-disuccinimidyl sulfite (II) by the following scheme.



The reaction was run in an inert organic solvent with cooling. The trimethylsilyl ether of N-hydroxysuccinimide (I) is a stable crystalline compound, which is easily formed by the silylation of N-hydroxysuccinimide. Compound (II) is formed in 80–85% yield, is stable when stored, and is readily soluble in most of the organic solvents used in peptide synthesis. The esterification of the N-protected derivatives of amino acids and peptides using (II) proceeds easily in up to 100% yield in the presence of organic bases in 1–1.5 h at 20°C in such solvents as DMF, DMSO, THF, MeCN, dioxane, and CH_2Cl_2 .

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 5, pp. 1163–1165, May, 1984. Original article submitted June 3, 1983.