OXIDATIVE HETEROCYCLIZATION OF DITHIOALKANOIC ACIDS

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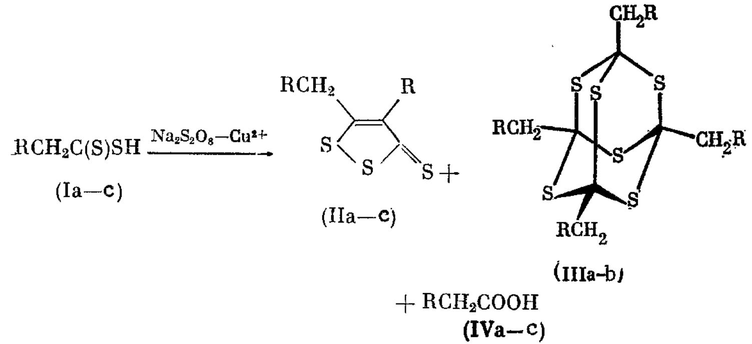
The oxidation of dithiocarboxylic acids usually leads to bis(thiocarbonyl) disulfides [1] or 1,2,4-trithiol derivatives [2, 3]. These acids are converted by the action of benzoyl peroxide to a complex mixture of products, among which 1,2,4,5-tetrathianes have been identified [3].

We have found that dithioalkanoic acids (Ia-c) undergo oxidative heterocyclization by the action of $Na_2S_2O_8$—$CuCl_2$ or $Na_2S_2O_8$—$CuSO_4$ systems to give 4,5-disubstituted 1,2-dithiol-3-thiones (IIa-c) and 1,3,5,7-tetraalkylhexathiaadamantanes (IIIa-c):



R = H (a), CH_3 (b), C_3H_7 (c)

The hydrolysis of (Ia-c) to the corresponding alkanoic acids (IVa-c) proceeds in competition to the heterocyclization reaction. For 100% conversion, (Ia) gives 10% (IIa), 15% (IIIa), and 60% (IVa); (Ib) gives 25% (IIb), 25% (IIIb), and 30% (IVb); and (Ic) gives 50% (IIc), 5% (IIIc), and 5% (IVc).

Dithioacyloxy radicals $RCH_2C(S)S^{\cdot}$ are most likely formed upon the one-electron oxidation of (I), and these radicals add to the sulfur atom of the thiocarbonyl group of (I) with the intermediate formation (after oxidation) of $RCH_2C(S)SSC(S)CH_2R$ (V). The enhanced C—H acidity of the hydrogens in the α position to the C(S)S group in (V) facilitates intramolecular oxidative cyclization to (II). This new reaction is the first example of the formation of 1,2-dithiol-3-thiones from dithioalkanoic acids. Tetraalkylhexathiaadamantanes were previously found upon the condensation of dithiocarboxylic acids by the action of $ZnCl_2$ [4].

A sample of 2.12 g (0.02 mole) propanedithio acid (Ib) was added to a solution of 3.42 g (0.02 mole) $CuCl_2 \cdot 2H_2O$ in 50 ml water at 80°C, and then a solution of 4.76 g (0.02 mole) $Na_2S_2O_8$ in 30 ml water was added dropwise. The reaction mixture was maintained for 3 h at 80°C and extracted with four 50-ml portions of $CHCl_3$. The extract was dried over $MgSO_4$ and evaporated. The residue was analyzed by gas—liquid chromatography and chromatography/mass spectrometry. Thin-layer chromatography on glass plates with an unattached layer of silica gel L 40/100 with 5:1 heptane—ethyl acetate eluent gave 0.35 g (20%) (IIb), Rf 0.65 as an oil, bp 88-92°C (0.35 mm). PMR spectrum (δ, ppm from TMS): 1.30 t (3H), 2.05 s (3H), 2.78 q (2H). ^{13}C NMR spectrum (δ, ppm from TMS): 13.5 and 15.2 ($2CH_3$), 29.7 (CH_2), 142.5 and 172.5 (C=C), 215.6 (C=S). Mass spectrum: m/z 176 (M^+, 100%). Then 0.36 g (21%) (IIIb) was isolated, Rf 0.8. ^{13}C NMR spectrum: 6.1 q (CH_3), 36.5 t (CH_2), 63.5 s (SCS). Mass spectrum (chemical ionization): 356 (M^+).

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SYNTHESIS OF 1,6-DI-tert-BUTOXY-2,4-HEXADIENE

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There is no information in the literature on the controlled catalytic dimerization of monosubstituted acetylenes containing a functional group.

We have carried out the synthesis of 1,6-di-tert-butoxy-2,4-hexadiene (I) by the controlled dimerization of the tert-butyl ether of propargyl alcohol (TBPE) and the concurrent hydrogenation of the dimer obtained to (I) on a fused catalyst containing 99% Fe_3O_4 and 1% SiO_2 at 130 °C and 50 atm pressure of synthesis gas ($CO + H_2$) (the $CO-H_2$ ratio was 1:1). The conversion of TBPE was 90-95% and the selectivity relative to (I) was 45-50%. Under these conditions, the hydrogenation of TBPE to tert-butoxypropene and tert-butoxypropane and the induced synthesis of tert-butoxyalcohols proceed along with the synthesis of (I).

Diene (I) was obtained from the reaction mixture by preparative thin-layer chromatography and identified by PMR, IR, and mass spectrometry. PMR spectrum at 60 MHz (TMS, CCl_4, δ, ppm): 1.2 [18H, $(CH_3)_3$], 3.87 (4H, CH_2O), 5.3-6.4 (4H, CH=CHCH=CH). IR spectrum, 0.004-mm-thick layer on KBr plate (ν, cm^{-1}): $(CH_3)_3C$ 2980 v.s, 1390-1350 s, 1250 m, 1197 v.s; OCH_2, 10.65 s, CH=CH–CH=CH 3035 w, 1650-1630 w, 992 s (trans). The mass spectrum was taken on an LKB-2091 mass spectrometer at 70 eV, m/z (intensity, % of maximum peak): 41 (15), 43 (5), 56 (3), 57 (100), 58 (5), 59 (4), 68 (8), 69 (13), 70 (5), 79 (3), 80 (3), 95 (21), 108 (8), 109 (3), 112 (3), 113 (2), 114 (3), 115 (1), 123 (0.8), 124 (1.5), 135 (2.5), 137 (3), 144 (1), 152 (6), 153 (3), 164 (0.5), 170 (3), 195 (0.2), 224 (0.5) M^+.

This example is the first case of the heterogeneous catalytic dimerization of functional acetylene derivatives with subsequent transformation of the dimer to a diene. This reaction became possible by the use of a bifunctional catalyst having both hydrogenating and polymerization properties.

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