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Surprising Formation of a new Sulphurated Heterocycle by Cathodic Reduction of 2-Bromo-2,2-diphenylacetyl Bromide

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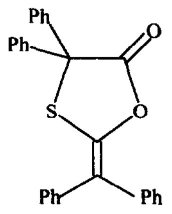
Abstract: The formation of 2-benzhydrylidene-4,4-diphenyl-[1,3]oxathiolan-5-one (1) was performed by cathodic reduction of 2-bromo-2,2-diphenylacetyl bromide in dichloromethane tetraethylammonium bromide on graphite cathode in the presence of inorganic sulphur compounds from the anodic compartment.

In previous papers we have described the formation of ketenes by cathodic reduction of suitable organic structures.[1,2] More recently the cathodic reduction of 2-chloro-2-phenylacetyl chloride led to a mixture of α- and γ-6-benzyl-3,5-diphenylhydroxypyranone, *via* a ketene intermediate.[3]

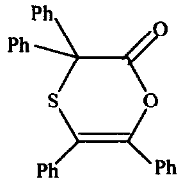
We carried out the cathodic reduction of 2-bromo-2,2-diphenylacetyl bromide in dichloromethane tetraethylammonium bromide on graphite cathode under an argon atmosphere in a divided cell.[4] To prevent the bromine formed in the anodic process from entering the cathodic compartment, a layer of solid sodium thiosulphate was placed on the diaphragm in the anodic side. Under these conditions an unexpected and surprising sulphurated heterocyclic compound was isolated after work up of the catholyte.

The product was purified by column chromatography (hexane-dichloromethane 7:3) and crystallized from hexane, mp 137-8 °C. (0.22 g, 21% yield). Elemental analysis C 79.91%, H 4.70%, O 7.72%, S 7.67%. This solid compound showed in MS a molecular ion M^+ m/z 420 and a strong band in the carbonyl range at 1788 cm^{-1} in IR; the ^{1}H-NMR only presents aromatic protons; signals at 171 ppm for CO, 118.09 and 137.3 ppm for C=C and 66.1 ppm for a quaternary aliphatic carbon were detected by ^{13}C-NMR. In light of these spectroscopic properties we have proposed two structures: 1 and 2.

In order to determine the right structure, ^{13}C proton-coupled spectra were performed. They showed a singlet for one of the C=C carbons which indicates the absence of protons in its neighbourhood, pointing to the structure 1.



1



2

This structure was confimed by chemical methods. It was saponified in 5% refluxing methanolic KOH, giving 2-mercapto-2,2-diphenylacetic acid[5] (mp 150-1°C) and diphenylacetic acid in rate 1:1. 1 was also reduced with $LiAlH_4$, and in this case we obtained 2,2-diphenylethanol and a new compound 3 which showed in IR absence of a carbonyl band and the presence of a broad band at 3426 cm^{-1} for OH group. A band at 2564 cm^{-1} for SH group was also present. In ^{1}H-NMR singlets appear at 4.25 ppm (2 H, CH_2OH), 2.5 ppm (1 H, SH) and 2.3 ppm (1 H, OH). Compound **3** was identified as 2,2-diphenyl-2-mercaptoethanol[6] .

The formation mechanism of 2-benzhydrylidene-4,4-diphenyl-*[*1,3*]*oxathiolan-5-one **(1)** is under study, but probably the process takes place by reaction of starting material with a sulphide anion in the presence of diphenyl ketene. This surprising reaction could open a way for the synthesis of new heterocycles with optimized reaction conditions.

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4. Electroreductions were performed in a concentric cell with two compartments separated by a glass frit diaphragm of medium porosity and under constant cathodic potential of -0.6 V vs SCE in dry CH_2Cl_2 - anhydrous $Et_4N^+ Br^-$ (0.2 M); 50 ml and 10 ml of this solution were placed in the cathodic and anodic compartments respectively and an argon atmosphere was used. A graphite disk was employed as cathode and a platinum plate as anode. A layer of sodium thiosulphate (6 g) was placed in the anodic side of the diaphragm. The catholyte was magnetically stirred and the temperature was kept at 20 °C by cooling.
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6. MS (chemical ionization) (m/z, %) 231 (M^++1, 0.52), 213 (M^++1 - H_2O, 37), 197 (M^++1 - H_2S, 100), 167 (49). IR cm^{-1} 3426, 3059, 3022, 2963, 2564, 1597, 1492, 1060, 747, 698, 655. δ_H ($CDCl_3$) 2.23 (1H, s, broad, OH), 2.50 (1H, s, SH), 4.25 (2H, s, broad, CH_2) and 7.20-7.43 (10H, m, 2xPh). δ_C($CDCl_3$) 60.10, 71.56, 126.51, 127.24, 127.55, 128.02, 128.31, 128.53, 128.45, 143.99.

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