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Preliminary communication

THE PHOTO-CATALYSED REACTION OF SULFUR WITH DIALKYLTITANOCENES

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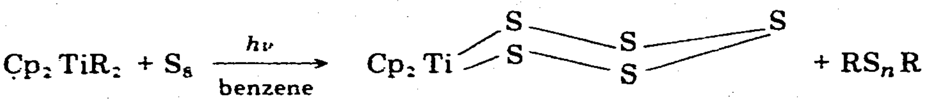
Summary

Photolysis of dialkyltitanocene compounds Cp_2TiR_2 ($R = CH_3$, $CH_2C_6H_5$) in presence of elemental sulfur produces titanocene pentasulfide Cp_2TiS_5 along with other organic polysulfides.

Reactions of cyclooctasulfur with transition metal complexes are known to proceed thermally [1,2] and photochemically [3,4], but examples of such reactions are rather rare. We now describe the results of the photo-catalysed reaction of elemental sulfur S_8 with dialkyltitanocene compounds.

When Cp_2TiR_2 (R = methyl or benzyl) is added to a saturated solution of cyclooctasulfur in benzene and the mixture is photolyzed in a Pyrex vessel with a high pressure mercury vapor lamp (using a copper sulfate solution as a filter [5]) the mixture turns dark red in a few minutes. After half an hour the reaction is complete and Cp_2TiS_5 [6,7,8] I can be isolated in a 70% yield (eq. 1). The compound is characterized by its color, NMR spectrum (Cp proton peaks at τ 3.8 and 3.9 ppm in $CDCl_3$ at 20°C) and melting point.



(1)

This reaction is believed to proceed through photolytic cleavage of the Ti—R bond to form a coordinatively unsaturated titanocene [9], followed by opening of the S_8 ring and chelation of an S_5 fragment with titanocene to form the six-membered titanium—sulfur heterocycle.

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The organic reaction products could not be characterized for R = CH_3 because of their volatile nature. However, for R = benzyl, it was possible to isolate by TLC a polysulfide of composition $C_6H_5CH_2{-}S_6{-}CH_2C_6H_5$ as a main product. Analysis: Found: C, 45.7; H, 3.8; S, 50.3. $C_{14}H_{14}S_6$ (calcd: C, 44.91; H, 3.7; S, 51.3%.) The NMR spectrum shows peaks at τ 5.83 (CH_2) and 2.69 ppm (C_6H_5) of integrated intensity 2:5. The mass spectrum of this compound shows along with the parent ion peak at *m/e* 374, intense peaks at 342, 310, 278, 246 and 214 due to successive loss of sulfur atoms.

Photolysis of dimethylzirconocene under the same reaction conditions as above did not yield the zirconium analog of I. Instead a yellow sulfur-containing zirconocene compound was isolated from which the two methyl groups of the starting product were absent as shown by its NMR spectrum (a single peak at τ 6.38 ppm in $CDCl_3$ due to Cp protons). It could not be isolated pure or characterized because of loss of sulfur upon recrystallization or sublimation.

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