

A CONVENIENT PREPARATION OF DI- η^5 -CYCLOPENTADIENYLTITANA(IV)-CYCLOHEXASULFANE

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Summary

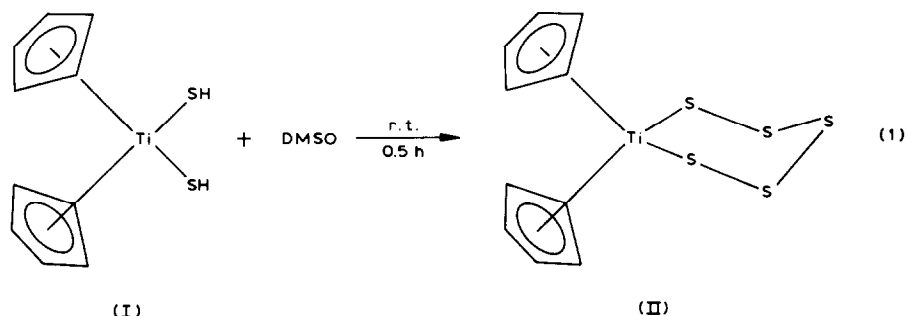
DMSO was found to be an active reagent for the transformation of di- η^5 -cyclopentadienylbis(hydrosulfido)titanium(IV) to di- η^5 -cyclopentadienyltitana(IV)-cyclohexasulfane.

Introduction

There has been considerable interest in recent years in transition metal complexes containing a catenated polysulfur metallocycle [1]. One of the more important representatives of this type of compound is Cp_2TiS_5 (II), which was first prepared in 1966 by the reaction of Cp_2TiCl_2 with $(\text{NH}_4)_2\text{S}_5$ [2] and several other thermal and photochemical syntheses of II with yields between 30–93% were subsequently developed [3]. We now report a very convenient preparation of Cp_2TiS_5 in 55% yield.

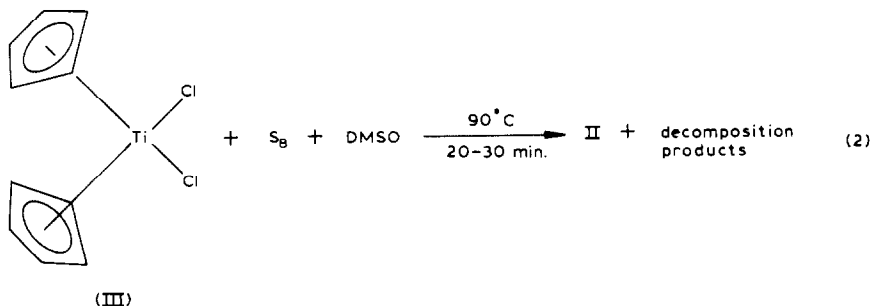
Results and discussion

When a solution of I in DMSO was stirred at room temperature for $\sim 1/2$ h and then evaporated under reduced pressure, II was obtained along with an insoluble, yellowish decomposition product (eq. 1).



The product II was purified by chromatography on silica gel (CH_2Cl_2 as eluant) and identified by its melting point, elemental analysis, and ^1H NMR and mass spectra [5] (Yield: 55%). Formation of II was also found to take place in tetrahydrofuran and dioxane, but in markedly decreased yields.

Since we suspected that the DMSO played an active part in the reaction we examined the interaction of titanocene dichloride (III) with elemental sulfur in DMSO (eq. 2) and isolated II in 20% yield.



This supports our view that the formation of II in DMSO proceeds through an intermediate titanocene - DMSO complex. Furthermore the reaction shown in 2 represents to our knowledge the simplest preparation of II without use of sulfur-transfer agents such as Li_2S_x or 1,1'-thiobisbenzimidazole [4].

Experimental

(a) *Reaction of di- η^5 -cyclopentadienylbis(hydrosulfido)titanium(IV) with DMSO.* A solution of I (50 mg; 0.2 mmol) in 50 ml of DMSO was stirred for $\sim 1/2$ h at room temperature, then evaporated under reduced pressure. The residue was extracted with dichloromethane and the insoluble yellowish material was filtered off. The extract was purified by chromatography on silica (CH_2Cl_2) to give II (38 mg, 55%).

(b) *Reaction of di- η^5 -cyclopentadienyltitanium dichloride with elemental sulfur in DMSO.* A solution of III (50 mg; 0.2 mmol) and sulfur (50 mg; 0.2 mmol) in 50 ml of DMSO was stirred for 20–30 min at 90°C then evaporated under reduced pressure. Work-up as in (a) gave II (14 mg, 20%).

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- 5 M.p. 199–201°C (lit. m.p. 201–202°C); MS: m/z , M^+ 338; $^1\text{H NMR}$ (CD_2Cl_2): δ 6.35 (s, 5H), 6.08 (s, 5H) ppm. Elemental analysis. Found: C, 35.38; H, 3.06; S, 46.69. $\text{C}_{10}\text{H}_{10}\text{S}_2\text{Ti}$ calcd.: C, 35.49; H, 2.98; S, 47.37%.