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THE THERMOLYSIS OF DI-*p*-TOLYLTITANOCENE AND DI-*m*-TOLYLTITANOCENE WITH ACETYLENES: FURTHER EVIDENCE FOR ARYNE- OR *o*-PHENYLENE-TITANOCENE INTERMEDIATES *

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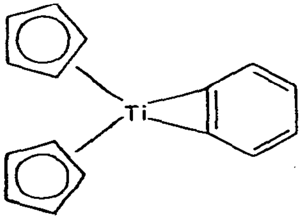
Summary

The thermolyses of di-*p*-tolyltitanocene and di-*m*-tolyltitanocene with diphenylacetylene, 2-butyne and hexafluoro-2-butyne have been investigated. Di-*p*-tolyltitanocene reacts with each acetylene to produce a mixture of two isomeric benzotitanoles in approximately equal amounts, whereas di-*m*-tolyltitanocene and each acetylene afford three isomeric benzotitanoles in an approximate 1 : 1 : 2 ratio, as evidenced by proton NMR analysis of the reaction products. These results lend further evidence for the formation of aryne- or *o*-phenylene-titanocene intermediates in the thermolyses of diaryltitanocenes. Steric effects play an important role in the addition of acetylene to these intermediates.

Introduction

The thermal degradation of diaryltitanocenes has been the subject of considerable study in recent years [1]. In an elegant series of experiments, Dvorak et al. [2] in 1970 demonstrated that the thermal decomposition of diphenyl-



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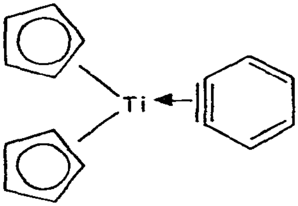

(III)

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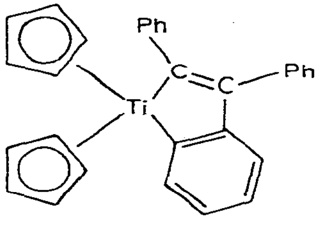
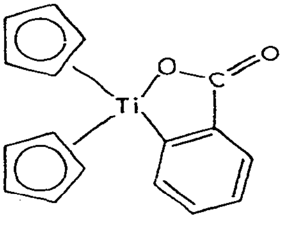
titanocene (I) in hydrocarbon solvents proceeds via formation of benzene and an apparent organotitanium species of composition $(C_5H_5)_2TiC_6H_4$, which may be regarded [1] either as an *o*-phenylene (II) or a benzyne (III) derivative of titanocene. Further evidence for the formation of a species such as II or III in the thermolysis of I was subsequently reported by Boekel et al. [3,4]. Species II or III have also been suggested as intermediates in thermal reactions of I with diphenylacetylene [2—5] and carbon dioxide [6—8] which led to the titanacycles IVa and V, respectively.



(IVa)



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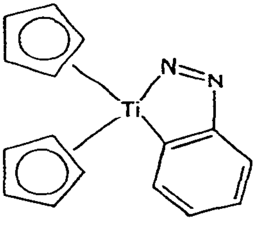


(VI)

The thermolysis of I in the presence of dinitrogen has been postulated [9—11] to proceed via formation of an intermediate such as VI, which after hydrolysis produced low yields of aniline. The metallacycle VI was not isolated, however. More recent studies by Volpin et al. [11] involving the thermolyses of ditolyltitanocenes and N_2 followed by hydrolysis showed that mixtures of isomeric toluidines could be produced, implicating in this case methyl-substituted derivatives of II or III.

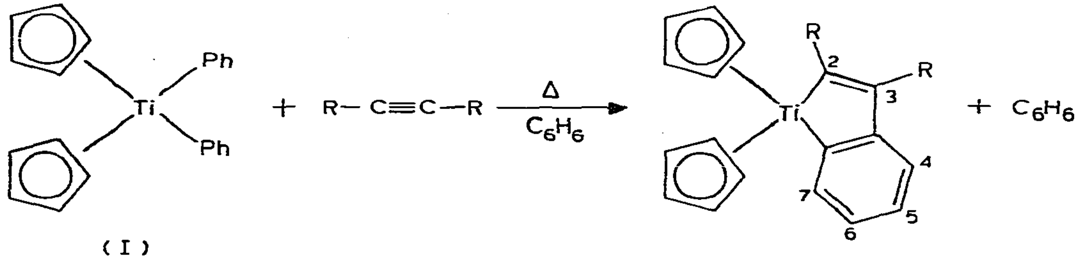
Although the evidence presented by Volpin and coworkers was consistent with aryne- or *o*-phenylene derivatives of titanocene being formed as intermediates under these conditions, their conclusions were based indirectly on hydrolysis products (aniline or toluidenes), and these products were in fact obtained in yields of only 1—2%.

In conjugation with our current program concerning reactions of dialkyl- or diaryltitanocenes under thermolytic [12,13,19,20] or photolytic [14—20] conditions, it was of interest to examine in detail the thermal reactions of both di-*p*-tolyltitanocene (VII) and di-*m*-tolyltitanocene (VIII) with a variety of acetylenes. From an analysis of the resulting isomeric benzotitanoles (titanaindenes) so produced, we hoped to gain further evidence for the possible intermediacy of species such as II or III in these types of reactions. Our results and conclusions are summarized in this paper.

Results and discussion

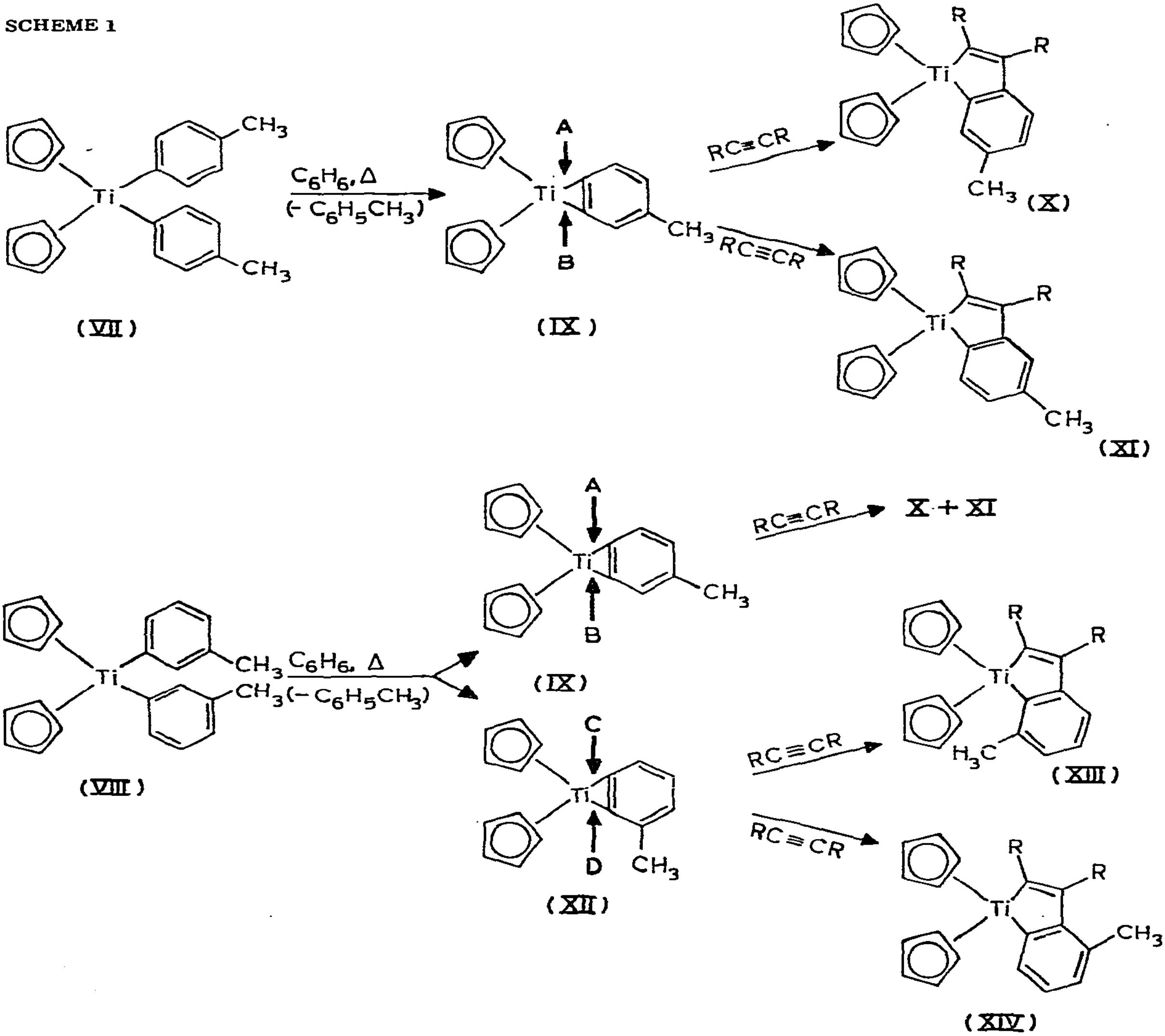
Hagihara and coworkers [5] have reported that the thermolysis of diphenyltitanocene (I) in the presence of diphenylacetylene in refluxing benzene produced 1,1-bis(η^5-cyclopentadienyl)-2,3-diphenylbenzotitanole (IVa) in moderate yield. Recent studies in our laboratory have shown that thermolysis of I with a variety of acetylenes which differ widely in steric and electronic properties produce corresponding benzotitanoles in good yields, thus illustrating the generality of this reaction [12,19,20].

In order to gain further insight as to the possible intermediacy of species



such as II or III in these reactions, the thermolyses of the ditolyltitanocenes VII and VIII in the presence of diphenylacetylene, 2-butyne and hexafluoro-2-butyne were investigated. As is outlined in Scheme 1, thermolysis of VII in

SCHEME 1



benzene can produce only intermediate IX, which would be expected to add an acetylene by either pathway A or B to produce benzotitanoles X and XI, respectively, in statistical amounts. Thermolysis of VIII, on the other hand, would be expected to produce intermediate XII as well as IX. If steric and electronic factors are minimal in the formation of IX and XII from VIII, then these intermediates would be formed in equal quantities. Intermediate IX could react as described above to produce benzotitanoles X and XI, whereas intermediate XII could add an acetylene by either pathway C or D to produce benzotitanoles XIII and XIV, respectively, resulting in a 1 : 1 : 1 : 1 mixture of benzotitanoles X, XI, XIII and XIV. It should be noted, however, that pathway D might be expected to be disfavored due to steric hindrance of the methyl group in the 3-position of intermediate XII.

The thermolysis of VII with diphenylacetylene, with 2-butyne, and with hexafluoro-2-butyne produced mixtures of the expected benzotitanoles in each reaction. In every case, a single η^5-cyclopentadienyl proton resonance and two methyl proton resonances were observed, the latter being of approximately equal intensity. The higher field methyl proton resonance for each set of isomers can be assigned to the respective benzotitanole X, since in this isomer the methyl protons would be closer to the shielding cones associated with the two η^5-cyclopentadienyl rings relative to the methyl protons in isomer XI. Benzotitanoles X and XI are therefore formed in approximately equal amounts, although it is interesting to note that isomer XI is favored slightly in each case. These results are summarized in Tables 1 and 2.

In an analogous manner, thermolysis of VIII with each of the above acetylenes also produced a mixture of benzotitanole isomers. In each case, two η^5-cyclopentadienyl proton resonances and three methyl proton resonances were observed, suggesting the presence of three isomers (Table 1). Of the three

TABLE 1

^{1}H AND ^{19}F NMR SPECTRA OF SOME SUBSTITUTED 1,1-BIS-(η^5-CYCLOPENTADIENYL)-BENZOTITANOLES [a]

Compound	Chemical shift and multiplicity [b]					
	η^5-C_5H_5	R_2	R_3	R_5	R_6	R_7
IVa	6.1(s) [c]	6.6(m) [c]	6.6(m) [c]			
XIa	6.33(s)	7.05(m)	7.05(m)	2.17(s)		
Xa	6.33(s)	7.05(m)	7.05(m)		2.08(s)	
XIIIa	6.38(s)	7.05(m)	7.05(m)			1.56(s)
IVb	6.17(s) [d]	1.23(q) [d,e]	1.62(q) [d,e]			
XIb	6.17(s)	1.23(q) [e]	1.61(q) [e]	2.21(s)		
Xb	6.17(s)	1.23(q) [e]	1.61(q) [e]		2.13(s)	
XIIIb	6.24(s)	1.29(q) [e]	1.61(q) [e]			1.46(s)
IVc	6.35(s) [d]	22.3(q) [d,f]	31.5(q) [d,f]			
XIc	6.35(s)	22.5(q) [f]	31.5(q) [f]	2.20(s)		
Xc	6.35(s)	22.5(q) [f]	31.5(q) [f]		2.12(s)	
XIIIc	6.42(s)	23.5(q) [f]	32.5(q) [f]			1.46(s)

[a] For IVa, Xa, XIa and XIIIa, $R_2 = R_3 = C_6H_5$; for IVb, Xb, XIb and XIIIb, $R_2 = R_3 = CH_3$; for IVc, Xc, XIc and XIIIc, $R_2 = R_3 = CF_3$. [b] Recorded in $CDCl_3$ unless otherwise indicated and given in δ(ppm) units; resonances for metallacyclic ring protons are not included. [c] Recorded in CCl_4; see ref. 5. [d] Refs. 19, 20. [e] $J = 1.5$ Hz. [f] ^{19}F resonance; $J = 17$ Hz.

TABLE 2

YIELDS AND PRODUCT RATIOS FOR SUBSTITUTED 1,1-BIS-(η^5-CYCLOPENTADIENYL)BENZOTITANOLES

Reaction	Yield (%)	Product ratio (%) [a]			
		X	XI	XIII	XIV
VII + $C_6H_5C{\equiv}CC_6H_5$	47	46	54	—	—
VIII + $C_6H_5C{\equiv}CC_6H_5$	24	22	33	45	—
VII + $CH_3C{\equiv}CCH_3$	37	43	57	—	—
VIII + $CH_3C{\equiv}CCH_3$	48	21	26	52	—
VII + $CF_3C{\equiv}CCF_3$	41	43	57	—	—
VIII + $CF_3C{\equiv}CCF_3$	46	26	34	40	—

[a] Product ratios were determined by integration of ^1H NMR spectra of the reaction products immediately following chromatography. Ratios are estimated to be accurate to ±3%.

methyl resonances, two had chemical shifts identical to the products assigned as isomers X and XI in each case, whereas the third resonance occurred consistently at much higher field. This new resonance can be assigned to benzotitanole isomer XIII, since in this isomer the methyl protons would be in even closer proximity to the η^5-cyclopentadienyl rings relative to the methyl protons in either isomer X or XI. This assignment is reinforced by the unique η^5-cyclopentadienyl resonance associated with the third isomer in each reaction, since a methyl group in the 7-position of this isomer (XIII) would be expected to exert a stronger influence on the η^5-cyclopentadienyl proton resonance than a methyl group in positions 4, 5 or 6 of isomers XIV, XI or X, respectively. The benzotitanole isomers X, XI and XIII were produced in each reaction in approximately a 1 : 1 : 2 ratio, and no product assignable to isomer XIV could be detected (Table 2) *.

Even with acetylenes which vary widely in electronic properties, the above results can be readily explained in terms of the mechanistic pathways shown in Scheme 1, when steric interactions are taken into account. Thermolysis of VII would lead to intermediate IX which could add acetylenes by either pathway A or B with little or no steric constraint. Thermolysis of VIII, in contrast, would be expected to produce an approximately equal ratio of intermediates IX and XII. Intermediate IX would behave as described above. For intermediate XII, however, in which there is a methyl group at the 3-position, attack of an acetylene by pathway D is disfavored relative to pathway C, due to steric hindrance. As a result, no isomer XIV was observed in any of these reactions.

Finally, while our findings are in general agreement with related studies reported earlier by Volpin et al. [11], they contrast in one important respect. Our results indicate that intermediates IX and XII are both formed upon the thermolysis of VIII in the presence of acetylenes, whereas Volpin et al. found that thermolysis of VIII in the presence of dinitrogen followed by hydrolysis

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[*] In the case of the reaction of diphenylacetylene with VII, HPLC analysis of the reaction mixture demonstrated the presence of two products, whereas reaction of diphenylacetylene with VIII upon HPLC analysis showed the presence of three products [21]. These findings are consistent with our NMR results.

produced only low yields of *m*- and *p*-toluidine. No *o*-toluidine was reported to be formed, a product which could arise together with *m*-toluidine from intermediate XII. The authors suggested that the formation of XII might be prevented by steric hindrance caused by the methyl group in XII, although they assumed the intermediacy of such a species in the thermolysis of a product assigned to be di-*o*-tolyltitanocene [11].

Experimental

All operations were conducted under an argon atmosphere. The argon was dried with P_2O_5 and H_2SO_4, and trace oxygen was removed using BTS Catalyst (BASF). Benzene and hexane were dried over calcium hydride and freshly distilled under argon. Reactions involving 2-butyne and hexafluoro-2-butyne were run in a heavy-walled Schlenk tube fitted with a 15 mm threaded connector and nylon plug (Ace Glass Co.) and a pressure stopcock (Eck and Krebs). Column chromatography was carried out under argon using Ventron-Alfa neutral grade alumina which had been degassed and deactivated with 5% water. ^1H NMR spectra were recorded on a Varian A-60 spectrometer and referenced to TMS. ^{19}F NMR were obtained on a Perkin-Elmer R-32 spectrometer and referenced to external CF_3COOH. IR spectra were recorded on a Beckman IR-10 spectrometer and were calibrated versus polystyrene. Mass spectra were obtained on a Perkin-Elmer-Hitachi RMU 6L instrument. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Di-*p*-tolyltitanocene and di-*m*-tolyltitanocene were prepared according to literature procedures [22].

Thermolysis of di-p-tolyltitanocene and diphenylacetylene

Di-*p*-tolyltitanocene (0.50 g, 1.4 mmol) and diphenylacetylene (0.25 g, 1.4 mmol) were dissolved in 15 ml of anhydrous benzene and refluxed for 1.5 h with magnetic stirring under argon. The reaction mixture was allowed to cool to room temperature and ca. 1 g of alumina was added. The solvent was removed in vacuo and the coated alumina was added to an alumina column (0.5 × 30 cm) which had been packed dry under argon. The column was initially eluted with hexane to remove unreacted diphenylacetylene. Subsequent elution with 5 : 1 hexane-benzene brought down a green band, which after removal of the solvent produced 0.29 g (47%) of a mixture of 1,1-bis(η^5-cyclopentadienyl)-2,3-diphenyl-5-methylbenzotitanole and 1,1-bis(η^5-cyclopentadienyl)-2,3-diphenyl-6-methylbenzotitanole. (Found: C, 83.59; H, 6.31. $C_{31}H_{26}Ti$ calcd.: C, 83.40; H, 5.87%). Mass spectrum: *m/e* 446 (M^+). ^1H NMR data are reported in Table 1.

Thermolysis of di-m-tolyltitanocene and diphenylacetylene

Di-*m*-tolyltitanocene (0.50 g, 1.4 mmol) and diphenylacetylene (0.25 g, 1.4 mmol) were allowed to react in the same manner as described above to produce upon work-up 0.15 g (24%) of a mixture of 1,1-bis(η^5-cyclopentadienyl)-2,3-diphenyl-5-methylbenzotitanole, 1,1-bis(η^5-cyclopentadienyl)-2,3-diphenyl-6-methylbenzotitanole, and 1,1-bis(η^5-cyclopentadienyl)-2,3-diphenyl-7-methylbenzotitanole. ^1H NMR data are reported in Table 1.

Thermolysis of di-p-tolyltitanocene and 2-butyne

Di-*p*-tolyltitanocene (0.70 g, 1.9 mmol) and 2-butyne (0.5 ml, 0.34 g, 6.3 mmol) were dissolved in 15 ml of benzene in a heavy-walled Schlenk tube. The tube was stoppered and then heated at 75° C for 4 h. The reaction was worked-up in the same manner as described above and produced 0.23 g (37%) of a mixture of 1,1-bis(η^5-cyclopentadienyl)-2,3,5-trimethylbenzotitanole and 1,1-bis-(η^5-cyclopentadienyl)-2,3,6-trimethylbenzotitanole. (Found: 78.62; H, 6.54. $C_{21}H_{22}Ti$ calcd.: C, 78.26; H, 6.88%). Mass spectrum: *m/e* 322 (M^+). ^1H NMR data are reported in Table 1.

Thermolysis of di-m-tolyltitanocene and 2-butyne

Di-*m*-tolyltitanocene (0.70 g, 1.9 mmol) and 2-butyne (0.5 ml, 0.34 g, 6.4 mmol) were allowed to react in the same manner as described above to produce on work-up 0.34 g (48%) of a mixture of 1,1-bis(η^5-cyclopentadienyl)-2,3,5-trimethylbenzotitanole, 1,1-bis(η^5-cyclopentadienyl)-2,3,6-trimethylbenzotitanole, and 1,1-bis(η^5-cyclopentadienyl)-2,3,7-trimethylbenzotitanole. ^1H NMR data are reported in Table 1.

Thermolysis of di-p-tolyltitanocene and hexafluoro-2-butyne

Di-*p*-tolyltitanocene (0.70 g, 1.9 mmol) was added to a heavy-walled Schlenk tube along with 10 ml of benzene. The tube was then immersed in liquid nitrogen, evacuated, and approximately a ten-fold excess of hexafluoro-2-butyne was bled into the tube. The reaction mixture was allowed to warm to room temperature and subsequently heated to 82° C for 5 h. After the reaction mixture had cooled to room temperature, the excess acetylene was vented and ca. 1 g of alumina was added. The solvent was removed in vacuo and the coated alumina was added to an alumina column (0.5 × 30 cm) which had been packed dry under argon. The column was eluted with 75 ml of hexane followed by 5 : 1 hexane-benzene to elute an orange band, which after removal of the solvent produced 0.37 g (41%) of a mixture of 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(trifluoromethyl)-5-methylbenzotitanole and 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(trifluoromethyl)-6-methylbenzotitanole. ^1H NMR data are reported in Table 1.

Thermolysis of di-m-tolyltitanocene and hexafluoro-2-butyne

Di-*m*-tolyltitanocene (1.00 g, 2.8 mmol) was added to a heavy-walled Schlenk tube along with 10 ml of benzene. The tube was then immersed in liquid nitrogen, evacuated, and approximately a ten-fold excess of hexafluoro-2-butyne bled into the tube. The reactants were then allowed to react in the same manner as described above to produce upon work-up 0.56 g (46%) of a mixture of 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(trifluoromethyl)-5-methylbenzotitanole, 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(trifluoromethyl)-6-methylbenzotitanole and 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(trifluoromethyl)-7-methylbenzotitanole. (Found: C, 59.38; H, 3.73. Calcd.: C, 58.62; H, 3.75%). Mass spectrum: *m/e* 436 (M^+). ^1H NMR data are reported in Table 1.

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