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π-Complexes of Tellurium(II) with 1,1-Diarylethylenes. A Reinvestigation

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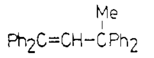
The reaction of tellurium tetrachloride with 1,1-diphenylethylene was reinvestigated. A reported novel π-olefin structure, tellurium dichloride–bis(1,1-diphenylethylene) (1), for one of the products was shown to be incorrect. Instead, both spectral and chemical evidence were presented in favor of a σ-bonded structure, bis(2,2-diphenylvinyl)tellurium dichloride (9), of this compound.

Introduction

In 1971 Patai and co-workers studied the reaction of some 1,1-diarylethylenes with tellurium(II) and tellurium(IV) halides.[1] When tellurium tetrachloride was allowed to react in ethyl ether with 1,1-diphenylethylene, a compound, 1, formulated as a π-complex of tellurium dichloride, was isolated in low yield in addition to 1,1,3,3-tetraphenylbut-1-ene (2) and some 2-chloro-1,1-diphenylethylene (3).

$(Ph_2C{=}CH_2)_2TeCl_2$

1


$Ph_2C{=}CH{-}\overset{\overset{Me}{|}}{C}Ph_2$

2

Structure 1 would represent a novel type of bonding between divalent tellurium and a π-donor. Furthermore, it would also constitute one of the very few examples[2,3] of isolable π-olefin complexes with non-transition metals.

The structure of compound 1 was based on spectral (NMR, MS, IR, UV) and analytical data as well as chemical evidence. (The chemical reactions are summarized in Scheme I.) However, several of the reported reactions are in disharmony with the chemical reactivity usually observed for organotellurium compounds.[4]

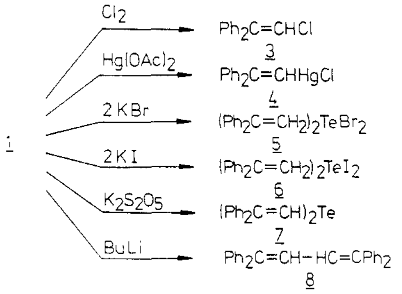
The novel structure 1 has received uncritical acceptance by some authors[5,6] while others,[7,8] without any comments, have reported it as a σ-bonded compound, 9. This apparent confusion in the literature has prompted us to carry out a reinvestigation of the reaction of 1,1-diphenylethylene with tellurium tetrachloride.

Results

1,1-Diphenylethylene was reacted in dry ethyl ether with tellurium tetrachloride as described by Patai.[1] The crystals that formed were light yellow and apparently contained some $TeCl_4$. After several recrystallizations from CCl_4 a white crystalline material was obtained with the same melting point (230–232 °C) as reported in the literature.

However, as seen from Table I the spectral data of our material were quite different from those reported in ref 1. The IR spectra had very little in common, and the ^1H NMR spectrum of our material lacked a vinyl proton signal at 7.22 ppm. The mass spectra showed some resemblance but were in disagreement at higher mass numbers.

Scheme I



Reduction of the white crystalline material melting at 230–232 °C with sodium disulfite according to Patai[1] afforded bis(2,2-diphenylvinyl) telluride (7). The melting point and spectral characteristics (IR, NMR) of this material were in good agreement with reported data.[1]

Treatment of compound 7 in CCl_4 with SO_2Cl_2 caused precipitation of a white material, mp 230–232 °C, identical in all respects (IR, NMR) with the material prepared above according to Patai.

When compound 7 was similarly treated with 1 equiv of Br_2, a yellow dibromide, 10, was formed. This material had the same melting point (241 °C) as reported by Patai for compound 5 (Scheme I). The IR data were also in close agreement, whereas the ^1H NMR spectrum of compound 10 was lacking the vinyl proton signal at 7.23 ppm reported by Patai.

Discussion

Patai and co-workers did not consider structure 9 in their discussion of possible structures of the reaction product of $TeCl_4$ and 1,1-diphenylethylene. The formulation of the compound as a π-olefin complex was based mainly on ^1H NMR and mass spectral data.

We repeated the preparation of compound 1 but obtained a substance with spectral data not in agreement with those reported by Patai. Most significantly, one of the two vinyl proton signals reported by Patai was not present. The mass spectrum of our material clearly indicated a $(M - 2Cl)^+$ fragment at *m/e* 488 that is two units lower than the reported value (*m/e* 490).

The spectral data of our material are clearly suggesting compound 9 as the reaction product of $TeCl_4$ and 1,1-diphenylethylene instead of compound 1 forwarded by Patai. The synthesis of compound 9 from bis(2,2-diphenylvinyl) telluride (7) and sulfuryl chloride provided conclusive evidence for the structure of bis(2,2-diphenylvinyl)tellurium dichloride.

$(Ph_2C{=}CH)_2TeCl_2$

9

$(Ph_2C{=}CH)_2TeBr_2$

10

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[1] Elmaleh, D.; Patai, S.; Rappoport, Z. *J. Chem. Soc. C* **1971**, 3100.

[2] Bilayet Hossain, M.; van der Helm, D. *J. Am. Chem. Soc.* **1968**, *90*, 6607.

[3] van den Hende, J. H.; Baird, W. C., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1009.

[4] Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974.

[5] Reference 4, p 36.

[6] Albeck, M.; Tamari, T. *J. Organomet. Chem.* **1982**, *238*, 357; see also: Albeck, M.; Shaik, S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1223, where evidence in favor of a σ-bonded structure is presented.

[7] Seyferth, D. *J. Organomet. Chem.* **1972**, *41*, 155.

[8] Sadekov, I. D.; Bushkov, A. Ya.; Minkin, V. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1979**, *48*, 343.

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Table I. Spectral Data of the Reaction Product of $TeCl_4$ and 1,1-Diphenylethylene

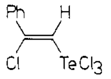
	found	reported[d]
UV[a] λ_{max}, nm	302 (ϵ 18300)	303 (ϵ 21800)
^{1}H NMR,[b] δ		7.22 (s, 1 H)
	7.33 (s, 5 H)	7.33 (s, 5 H)
	7.42 (s, 5 H)	7.43 (s, 5 H)
	7.97 (s, 1 H)	7.91 (s, 1 H)
IR,[c] cm^{-1}	1550 (w)	1605 (w)
	1485 (m)	1510 (s)
	1440 (m)	1450 (vw)
	745 (s)	825 (s)
	705 (s)	
MS, *m/e* (relative intensity)	178 (100), 179 (45), 180 (21), 214 (7), 267 (17), 279 (7), 281 (7), 306 (7), 308 (8), 358 (44), 359 (13), 484 (9), 486 (14), 488 (15)	178 (30),[e] 179 (100), 180 (57), 214 (77), 216 (27), 310 (40), 341 (13), 343 (21), 345 (25), 490 (7), 525 (5)

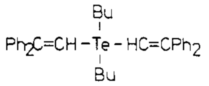
[a] Recorded in $CDCl_3$. [b] Recorded in CCl_4. [c] In KBr. [d] From ref 1. [e] The spectrum is reproduced in ref 1.

As a consequence of this finding, all structures formulated by Patai as π-olefin complexes **11** should be assigned a σ-bonded structure **12** (Ar = phenyl, 4-methylphenyl, or 2,4-dimethylphenyl; X = Cl, Br, I; Y = Cl, Br, I).

$(Ar_2C{=}CH_2)_2TeXY$ **11**

$(Ar_2C{=}CH)_2TeXY$ **12**


13


$$Ph_2C{=}CH{-}\overset{Bu}{\underset{Bu}{Te}}{-}HC{=}CPh_2$$
14

We can find no rational explanation for the spectral data (IR, ^{1}H NMR, MS) reported by Patai.

The chemical reactions of the purported compound **1** (Scheme I) can all be rationalized by assuming a revised structure **9** of the starting material.

(2-Chloro-2-phenylvinyl)tellurium trichloride (**13**) is known to undergo halodetelluration upon treatment with electrophilic reagents like iodine.[9] It is therefore not surprising that compound **9** is transformed into 2,2-diphenylvinyl chloride (**3**) and 2,2-diphenylvinylmercuric chloride (**4**), respectively, on treatment with chlorine and mercuric acetate.

The two halogen exchange reactions shown next in Scheme I are standard reactions for the interconversion of diorganyltellurium dihalogenides.[10] Treatment of compound **9** with KBr would therefore furnish the dibromide **10** (and KI similarly the corresponding diiodide).

Potassium bisulfite is commonly used in organotellurium chemistry for the dehalogenation of diorganyltellurium dihalides to diorganyl tellurides.[11] It is therefore remarkable that this reagent was used for a dehydrochlorination (the transformation **1** → **7** in Scheme I) by Patai.[1] A dehalogenation of compound **9** to give the telluride **7** would be in perfect harmony with the chemical reactivity usually observed for organotellurium compounds.

The formation of 1,1,4,4-tetraphenylbuta-1,3-diene (**8**) from compound **9** and 2 equiv of butyllithium might be rationalized assuming an intermediate tetraorganyltellurane, **14**. Tetraorganyltelluranes are unstable compounds that decompose into a diorganyltelluride and an organic coupling product.[12] The diene **8** could be formed as a coupling product of compound **14** in addition to dibutyl telluride.

The formation of compound **9** from tellurium tetrachloride and 2 equiv of 1,1-diphenylethylene might involve either two consecutive 1,2 additions accompanied by elimination of HCl or two consecutive electrophilic substitutions of hydrogen. Similar reaction pathways were forwarded to account for the reaction products of 1,1-diphenylethylene and phosgene,[13] oxalyl chloride,[14] and thionyl chloride,[15] respectively.

Experimental Section

Melting points were uncorrected. NMR spectra were obtained on a WP 200 or a JEOL PMX 60 SI instrument in $CDCl_3$ or CCl_4 solutions containing Me_4Si as internal standard. Mass spectra were recorded by using an LKB 9000 instrument. IR and UV spectra were obtained by using a Perkin-Elmer 257 and a Perkin-Elmer Hitachi 200 instrument, respectively.

Tellurium tetrachloride (10.0 g, 37.1 mmol) and 1,1-diphenylethylene (10.0 g, 55.6 mmol) were stirred in dry ethyl ether (50 mL) as described by Patai. The crystals that formed melted at 230–232 °C (CCl_4). All spectral data of this material are displayed in Table I together with published data.

Reduction of the material melting at 230–232 °C with sodium disulfite, following the procedure of Patai, afforded bis(2,2-diphenylvinyl)telluride (**7**): mp 119–120 °C; IR (KBr, cm^{-1}) 1490 (m), 1440 (m), 1260 (m), 800 (m), 750 (s), 700 (s); ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 1 H), 7.18–7.33 (several peaks, 10 H).

Bis(2,2-diphenylvinyl)tellurium Dichloride (9). To a solution of bis(2,2-diphenylvinyl) telluride (0.090 g, 0.19 mmol) in CCl_4 (4 mL) was added SO_2Cl_2 (0.042 g, 0.31 mmol) in CCl_4 (0.5 mL). Addition of petroleum ether (bp 40–60 °C) to cloudiness and cooling to −15 °C caused precipitation of 0.085 g (83%) of compound **9**, mp 230–232 °C. The spectral data of this material (^{1}H NMR, IR) were in all respects identical with those found for the reaction product of $TeCl_4$ and 1,1-diphenylethylene (Table I).

Bis(2,2-Diphenylvinyl)tellurium Dibromide (10). To a solution of bis(2,2-diphenylvinyl) telluride (0.020 g, 0.041 mmol) in CCl_4 (0.5 mL) was added Br_2 (0.007 g, 0.043 mmol) in CCl_4 (0.15 mL). Cooling to −15 °C caused precipitation of 0.020 g (75%) of compound **10**: mp 241 °C (CCl_4); IR (KBr, cm^{-1}) 1545 (m), 1485 (m), 1440 (m), 745 (s), 705 (s); ^{1}H NMR ($CDCl_3$) δ 7.97 (s, 1 H), 7.48 (s, 5 H), 7.39 (s, 5 H).

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Registry No. **7**, 33861-08-4; **9**, 34676-19-2; **10**, 34676-31-8; $TeCl_4$, 10026-07-0; 1,1-diphenylethylene, 530-48-3.

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