

The reaction of tropone and tropilidene derivatives with palladium acetate in benzene

Katsuhiro Saito

Department of Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi 466 (Japan)

(Received June 19th, 1987)

Abstract

Reaction of tropone or tropilidene derivatives with palladium acetate in benzene gave the following results. Tropone yielded 2-phenyltropone and 2,7-diphenyltropone. 2-Methoxytropone gave 2-methoxy-7-phenyltropone. Tropilidene yielded 1-phenyltropilidene but 7-methoxytropilidene gave tropone.

Much attention has been paid to substitution reactions of olefins in the presence of transition metal complexes. Heck et al. [1] and Moritani et al. [2] have reported the aromatic substitution of olefins in the presence of palladium salts. Horino et al. recently reported vinylic substitution reactions on halotropone and halotropolone derivatives catalyzed by a palladium(0) complex [3].

Few carbon–carbon bond formation reactions on the tropone nucleus are known [4]. There is no carbon–carbon bond formation on to tropone derivatives which have no suitable leaving group such as halogen atom, amino or alkoxy group [5]. The aromatic substitution reaction of tropone and tropilidene derivatives using a palladium complex was studied by the author who found that phenylation occurred at the tropone and tropilidene nuclei. The results of these reactions are reported here in.

Results and discussion

When tropone (**1**) was heated at 80 °C for 6 h in benzene in the presence of one molar equivalent of palladium acetate and five molar equivalents of sodium acetate, 2-phenyltropone (**2**) and 2,7-diphenyltropone (**3**) were obtained in 14 and 7% yields, respectively. Under analogous conditions, **2** gave **3** in 33% yield, whereas 2-methoxytropone (**4**) gave 2-methoxy-7-phenyltropone (**5**) in 19% yield. The same reaction but using tropilidene (**6**) in place of **1** afforded 1-phenyltropilidene (**7**) in 29% yield. Under the same conditions, 7-methoxytropilidene (**8**) gave **1** in a 27% yield.

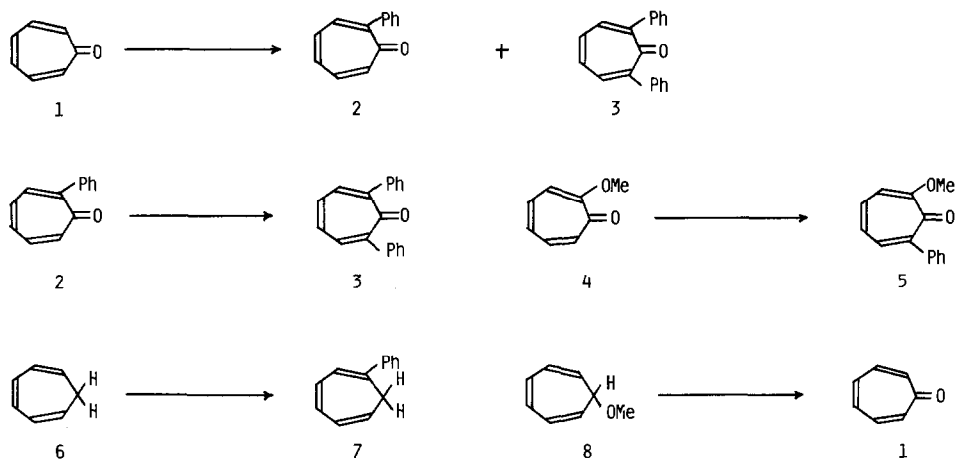


Fig. 1. Products of the reaction of troponone and tropilidene derivatives with palladium acetate in the presence of benzene.

The structures of the phenylated products **2** (m.p. 85–86°C, lit. [5] m.p. 85–86°C), **3** (m.p. 131–132°C, lit. [6] m.p. 133°C), **5** (m.p. 100–101°C, lit. [7] m.p. 101–102°C), and **7** [8] were determined on the basis of their spectra, especially NMR and assignments confirmed by agreement of these properties and/or their melting points with the literature values.

The phenylation reactions are considered to proceed as follows. The palladium salt (**9**) is formed reversibly from palladium acetate and benzene. Troponone or tropilidene coordinates with **9** to form complex **10**. Subsequent insertion of troponone or tropilidene into the aryl–palladium bond makes the new palladium–troponone or

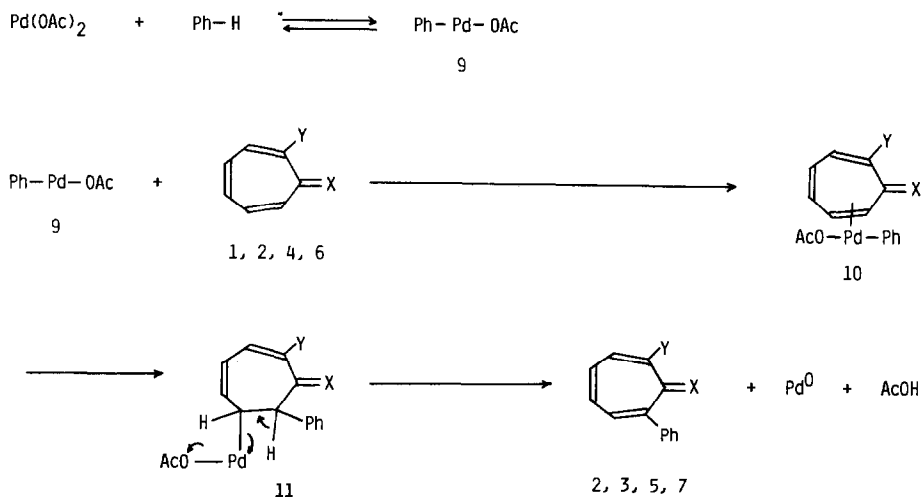


Fig. 2. Mechanism of reaction of troponone derivatives and tropilidene to give the phenylated products.

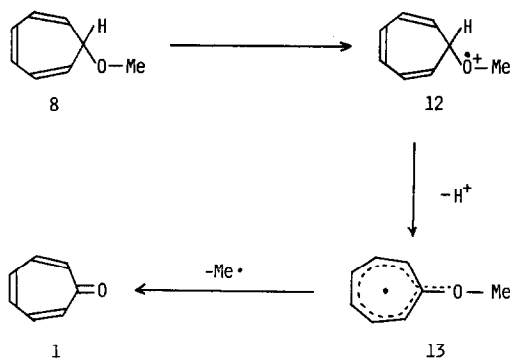


Fig. 3. Mechanism of reaction of 7-methoxytropilidene to give tropone.

palladium-tropilidene salt (**11**), which then decomposes to give the phenylated products, free palladium metal and acetic acid*.

Palladium acetate is known to react with *N,N*-dimethylaniline to form *N,N*,4-trimethylaniline via the radical cation of *N,N*-dimethylaniline by one-electron oxidation [10]. The reaction of 7-methoxytropilidene (**8**) to form tropone (**1**) probably proceeds via the radical cation of **8** as follows. One-electron oxidation of **8** by palladium acetate gives the cation radical of **8** (**12**). Elimination of a proton from **12** gives the radical intermediate **13**, which then yields tropone with loss of a methyl radical.

Experimental

Reaction of **1** with palladium acetate

A mixture of **1** (1060 mg, 10 mmol), palladium acetate (2280 mg, 10 mmol), and sodium acetate (4100 mg, 50 mmol) in anhydrous benzene (100 ml) was heated at

Table 1

Reaction conditions and yields of product of the reactions of tropone and tropilidene derivatives with palladium acetate in the presence of benzene

Reactant (mg (mmol))	Pd(OAc) ₂ (mg (mmol))	NaOAc (mg (mmol))	Benzene (ml)	Conditions (Temp. (°C), time (h))	Products and recovery (mg (%))
2	1140	2050	50	80, 10	3 , 427 (33)
910 (5)	(5)	(25)			2 , 336
4	2280	4100	100	80, 8	5 , 590 (19)
1360 (10)	(10)	(50)			4 , 380
6	2280	4100	100	80, 6	7 , 486 (29)
920 (10)	(10)	(50)			
8	2280	4100	100	80, 8	1 , 283 (27)
1220 (10)	(10)	(50)			

* The fact that tropones accept the phenyl group at the 2-position may suggest initial coordination of the carbonyl bond to the palladium in a manner analogous to that of magnesium in the Grignard reaction of tropones [9].

80 °C for 6 h. After removal of palladium and sodium acetate by filtration, the filtrate was poured into water, separated with a separating funnel, and the organic layer was washed with water, then dried over anhydrous sodium sulfate. After filtration, the solvent was removed by rotary evaporator to yield an oily material, which when subjected to preparative thin-layer chromatography on silica gel gave **3** (430 mg, 7%), **2** (478 mg, 14%), and unchanged **1** (570 mg).

Reactions of **2**, **4**, **6**, and **8** with palladium acetate were carried out similarly. The results are listed in Table 1.

Acknowledgement

The author is indebted to Professor H. Horino of Tohoku University for his fruitful suggestions.

References

- 1 R.F. Heck, *J. Am. Chem. Soc.*, 90 (1968) 5542. R.F. Heck and J.P. Jolly, *J. Org. Chem.*, 37 (1972) 2320. H.A. Deck and R.F. Heck, *J. Am. Chem. Soc.*, 96 (1974) 1133.
- 2 Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, 91 (1969) 7166. R. Asano, I. Moritani, A. Sonoda, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc. C*, (1971) 3691. H. Tanaka, Y. Fujiwara, I. Moritani, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, 48 (1975) 3372.
- 3 H. Horino, N. Inoue, and T. Asao, *Tetrahedron Lett.*, 22 (1981) 741.
- 4 F. Pietra, *Chem. Rev.*, 73 (1973) 293.
- 5 T. Nozoe, T. Mukai, and J. Minegishi, *Proc. Jpn. Acad.*, 27 (1951) 419.
- 6 T. Mukai, *Bull. Chem. Soc. Jpn.*, 31 (1958) 852.
- 7 T. Nozoe, T. Mukai, J. Minegishi, and T. Fujisawa, *Sci. Rep. Tohoku Univ. Ser. 1*, 37 (1953) 388. W. von E. Doering and L.H. Knox, *J. Am. Chem. Soc.*, 75 (1953) 297.
- 8 A.P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim., Pays-Bas*, 84 (1965) 241. T. Tezuka, M. Kimura, A. Sato, and T. Mukai, *Bull. Chem. Soc. Jpn.*, 43 (1970) 1120.
- 9 T. Nozoe, T. Mukai, and I. Murata, *Proc. Jpn. Acad.*, 28 (1952) 142. H. Tsuruta and T. Mukai, *Bull. Chem. Soc. Jpn.*, 41 (1968) 2489.
- 10 T. Sakakibara, J. Kotobuki, and Y. Dogomori, *Chem. Lett.*, (1977) 25. T. Sakakibara, Y. Dogomori, Y. Tsuzuki, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3592.