

REACTIONS OF 2,4-DIMETHYLPHENYLMERCURY AND PENTAMETHYLPHENYLMERCURY
ACETATES WITH OLEFINS IN THE PRESENCE OF Pd(II) AND Pt(IV) COMPLEXES

G. V. Nizova and G. B. Shul'pin

UDC 542.97:547.559.
49:547.538.141

Arylmercury compounds form diaryls in the presence of Pd(II) complexes [1, 2] and arylated olefins in the presence of olefins (Heck reaction) [2, 3]. Previously it was shown that the reaction with the PtCl_6^{2-} complex ion occurs similarly and affords the same products [4-7]. The σ -aryl complexes of Pd(II) and Pt(IV) are formed as intermediate substances, and these compounds can be isolated in the second case [7, 8]. Recently it was found [5] that the reaction of α -dinaphthylmercury with Pt(IV) affords α, α' -dinaphthyl, whereas in the reaction of pentamethylphenylmercury acetate with Pt(IV) or Pd(II) only free pentamethylbenzene is obtained. It is important to emphasize that in the case of α -naphthyl and pentamethylphenyl and σ -aryl complexes of Pt(IV) cannot be formed because of steric factors, and the reaction is apparently induced by Pt(II) compounds.

In the present paper, we investigated reactions of 2,4-dimethylphenyl and pentamethylphenyl derivatives of mercury acetate (Ia, b) with olefins in the presence of Pt(IV) and Pd(II). As the olefin component we chose styrene, which, as is known, readily undergoes arylation in the presence of Pd(II) or Pt(IV) complexes.

In the case of (Ia), arylation occurred rather readily in the presence both of a Pd(II) complex and a Pt(IV) derivative. However, the reaction with (Ib) afforded the arylation product of styrene only when the Pd(II) complex was used. The use of a Pt(IV) complex in this reaction gave only free pentamethylbenzene in 35% yield. The difference in the behavior of (Ia) and (Ib) may be because the pentamethylphenyl radical exerts a stronger screening effect and is a stronger electron donor. Thus, the reaction of (Ib) with Pt(IV) in the presence of styrene affords the same product as in its absence [5]. It is of interest that the direction of the reaction in the presence of Pd(II) depends on the presence of an olefin. Thus, whereas the reaction of (Ib) with Pd(II) gave only the free arene and dimerization products were not formed, in the presence of styrene the corresponding substituted stilbene was obtained in 40% yield.

We also found that arylation of the stilbene with mercury derivative (Ib) occurred neither when a Pt(IV) complex was used nor in the presence of a Pd(II) compound. In both cases, the free arene was formed from the mercury compound.

Experimental

Reaction of 2,4-Dimethylphenylmercury Acetate (Ia) with Styrene in the Presence of PtCl_6^{2-} . A solution of 0.182 g (0.5 mmole) of (Ia), 0.5 ml (4.5 mmoles) of styrene, and 0.281 g (0.5 mmole) of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 14 ml of acetone was boiled for 3.5 h and then evaporated at lowered pressure. We recovered isomeric substituted stilbenes by thin-layer chromatography on Silufol UV-254 plates (the eluent was hexane). The yield of trans-1-phenyl-2-(2',4'-dimethylphenyl)-ethylene was 0.08 g (38%); mp 40-41°C. Found, %: C 92.56, H 7.77. $\text{C}_{16}\text{H}_{16}$. Calculated, %: C 92.26, H 7.74. Proton NMR spectrum (in CDCl_3 , δ , ppm): 7.15 multiplet (aromatic and olefinic protons), 2.31 singlet (CH_3), 2.26 singlet (CH_3). The yield of the cis isomer was 0.003 g (2%). Proton NMR spectrum: 6.97 multiplet (aromatic protons), 5.70 doublet and 5.12 doublet (olefinic protons), 2.36 singlet and 2.02 singlet (CH_3). During irradiation by light from a high-pressure mercury lamp in an alcoholic solution, the cis isomer was converted to the trans derivatives.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 9, pp. 2070-2071, September, 1987. Original article submitted July 9, 1986.

Reaction of Pentamethylphenylmercury Acetate (Ib) with Styrene in the Presence of PtCl_6^{2-} . A solution of 0.436 g (1 mmole) of (Ib), 0.5 ml (4.5 mmoles) of styrene, and 0.4 g (0.9 mmole) of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 20 ml of acetone was boiled for 3 h. We recovered 0.052 g (35%) of pentamethylbenzene by thin-layer chromatography. Other organic products were not detected.

Reaction of Bis(2,4-dimethylphenyl)mercury with Styrene in the Presence of PdCl_4^{2-} . A solution of 0.3 g (1.1 mmoles) of anhydrous Na_2PdCl_4 in 5 ml of MeCN was added to a suspension of 0.41 g (1 mmole) of bis(2,4-dimethylphenyl)mercury and 0.5 ml (4.5 mmoles) of styrene in 15 ml of MeCN. The solution was stirred for 20 h at -20°C . The precipitate was filtered and washed with CHCl_3 . The combined organic solution was evaporated at reduced pressure, and the organic products were recovered by thin-layer chromatography on silica gel (the eluent was hexane). The yield of trans-1-phenyl-2-(2',4'-dimethylphenyl)ethylene was 0.042 g (20%), and the yield of the cis isomer was 0.005 g (2%).

Reaction of (Ib) with Styrene in the Presence of PdCl_3^- . To a solution of 0.436 g (1 mmole) of (Ib) and 0.5 ml (4.5 mmole) of styrene in 9 ml of MeCN was added 11 ml of a 0.1 M solution of LiPdCl_4 in MeCN. The solution was stirred for 30 h at -20°C . The product was recovered as described above. The yield of 1-phenyl-2-(pentamethylphenyl)ethylene was 0.067 g (40%), mp 154°C (cf. [9]).

The authors thank V. I. Sokolov for valuable advice.

Conclusions

1. 2,4-Dimethylphenylmercury acetate arylates styrene in the presence of chloro complexes of Pd(II) and Pt(IV), but pentamethylphenylmercury acetate forms with styrene the corresponding substituted stilbene only in the presence of PdCl_3^- , and only the free arene is formed in the presence of PtCl_6^{2-} .
2. In the presence of Pd(II) or Pt(IV) complexes the trans-stilbene is not arylated by pentamethylphenylmercury acetate.

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