

TRANSITION METAL-PROMOTED REACTIONS

VI *. PALLADIUM(II)-PROMOTED OXIDATIVE COUPLING OF ETHYL ACRYLATE AND RELATED TERMINAL OLEFINS IN THE PRESENCE OF BENZENESELENYL BROMIDE

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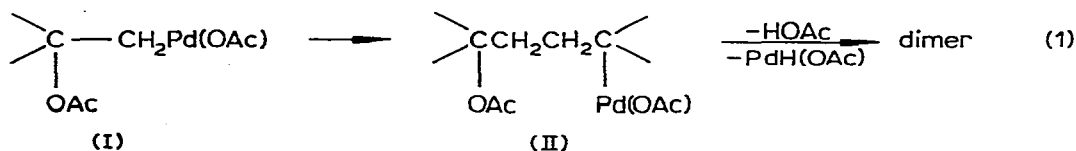
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Summary

Treatment of ethyl acrylate and related terminal olefins with benzeneselenenyl bromide under the conditions of the Heck reaction yields oxidative coupling products incorporated with two phenylselenenyl groups. The mechanism for this reaction is briefly discussed.

Introduction

Oxidative coupling reactions of terminal olefins are known involving palladium compounds as stoichiometric reagents [2,3] as well as catalysts [4]. The mechanism of these reactions is not clear, but a binuclear palladium complex [2] or palladium(II) hydride species [4] has been proposed as the possible reaction intermediate. More recently, the acetoxy-palladation adduct (I) has also been suggested to be an intermediate, which undergoes insertion reaction to afford a



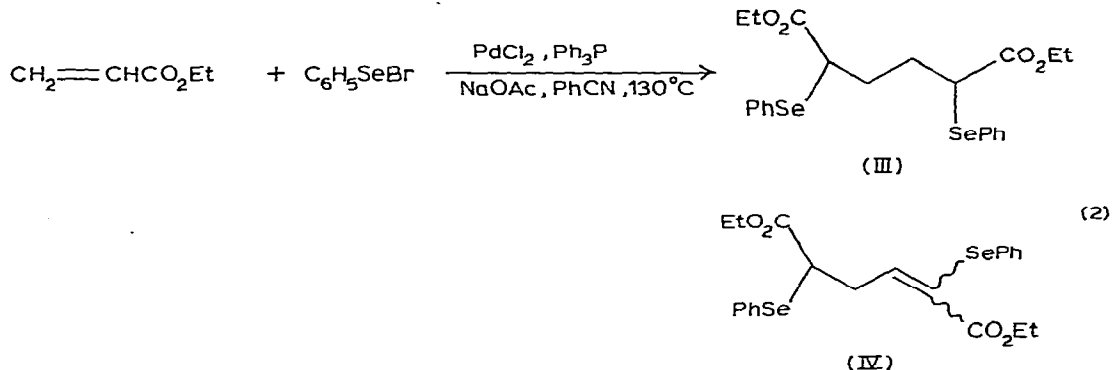
dimer (eq. 1) [3]. The species II was not trapped, however, and the elimination of acetic acid from II appears unusual. We now wish to report our investigation on the palladium(II)-promoted oxidative coupling of ethyl acrylate and related compounds in the presence of benzeneselenenyl bromide. The reaction may be

* For parts IV and V see ref. 1.

synthetically useful and the product distribution may aid understanding of the course of the coupling reactions.

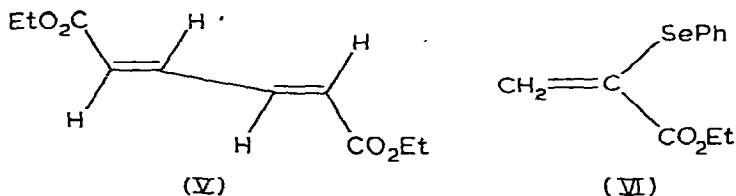
Results and discussion

In the presence of catalytic amounts of palladium chloride, triphenylphosphine, and sodium acetate, benzeneselenenyl bromide reacts with ethyl acrylate in benzonitrile to give a mixture of III and IV in 37% and 30% yield, respectively (eq. 2). The structures of III and IV were unambiguously assigned on the



basis of their spectra. Moreover, upon oxidation with hydrogen peroxide [5], III afforded diethyl *trans,trans*-muconate (V) in essentially quantitative yield.

The reaction is extremely sensitive to the variation in conditions. Thus, no coupling occurred when triethylamine or tributylamine was employed as base, while the presence of trace amount of water or isopropanol slightly increased the yield. An entirely different product (VI) was obtained when the reaction

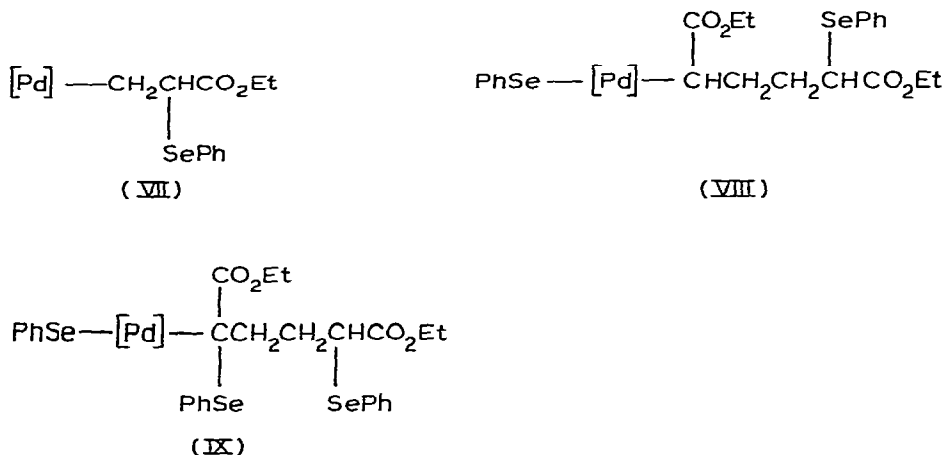


mixture contained no benzonitrile, or when the reaction was carried out at lower temperature (e.g. 25°C), or when sodium carbonate was used as base in place of sodium acetate. Compound VI is obviously obtained from the base-promoted elimination of the benzeneselenenyl bromide adduct.

It is noteworthy that acetate ligand can form dimeric or trimeric species [2,6]. The monomeric species, $\text{Na}_2\text{Pd}(\text{OAc})_4$ has recently been found to be unreactive in the oxidative dimerization reactions [6], and our results confirm this observation. It is noteworthy that VI does not undergo dimerization under the reaction conditions. Interestingly, no oxidative coupling product was found for other 1,1-disubstituted olefinic system (e.g. ethyl methacrylate) under the same conditions, although dimerization of these olefins carrying two alkyl or aryl substituents at the β -carbon atom has been reported in other media [2].

Presumably, steric effects play an important role here.

Our reaction conditions are quite similar to those of the Heck reaction [7] except that benzeneselenenyl bromide is used in place of aryl bromide. It has been proposed that the palladium(II) salt may somehow be reduced to palladium(0) in the Heck reaction. Benzeneselenenyl bromide is itself an oxidizing agent. In the absence of olefin, diphenyldiselenide was formed rapidly. The role of the palladium(II) catalyst in this reductive process is not clear, but a palladium-selenium bond might be formed during the reaction. This suggestion is supported by comparing our product distributions as shown in eq. 2 with those in related studies [2-4]. The mechanism for the formation of III and IV has not been fully established, but it seems plausible that benzeneselenenyl group could be transferred from palladium to the α -carbon of ethyl acrylate to give a benzeneselenenylpalladate adduct (VII) which is structurally similar to I. The adduct VII might then undergo an insertion to give the intermediate VIII,



which could contain the benzeneselenenyl group as a ligand. However, it is not clear whether the intermediate VII is a mononuclear or dinuclear complex. Reductive elimination of VIII would afford the product III and the lower-valent palladium species, which should be effective in starting another catalytic cycle. On the other hand, VI might also be inserted into the palladium-carbon bond of VII to give the intermediate IX. There is substantial steric crowding around the metal in IX, and elimination of a palladium-hydride species might become feasible, to give the product IV.

Styrene, acrylonitrile, and 1-hexene were also used as substrate and gave approximately the same yields and product distribution. In addition, various Group VIII transition metal halides were screened as catalyst, and the results indicate that palladium(II) is a unique catalyst for these transformations.

In conclusion, we have described the first example of the oxidative coupling reaction promoted by palladium(II) compounds and benzeneselenenyl bromide. Our results support the proposed mechanism for the oxidative coupling [3]. In particular, the product distribution in this study suggests that II or a related species may be the intermediate in the palladium(II)-catalyzed coupling reactions.

Experimental

Materials

Benzeneselenenyl bromide was prepared according to literature procedures [5]. Palladium chloride was obtained from Fluka AG, Switzerland. Infrared spectra were measured on a Perkin-Elmer 283 spectrophotometer. NMR spectra were taken on a JEOL C-60HL spectrometer. Mass spectra were recorded using a VG 7070F mass spectrometer.

General procedure

To a solution of benzeneselenenyl bromide (10 mmol) in benzonitrile (6 ml) was added the olefin (10–20 mmol), sodium acetate (11 mmol), palladium chloride (0.1 mmol), and triphenylphosphine (0.2 mmol). The mixture was heated in an oil bath at 130–140°C, and the progress of reaction was monitored with TLC. After 6–8 h, the mixture was cooled, filtered and the excess olefin and benzonitrile were removed in vacuo. The residue was chromatographed on an alumina column.

In a typical experiment, ethyl acrylate (2 g, 20 mmol) was transformed to III, (0.47 g, 37%*), a thick oil which decomposes upon heating, δ (CDCl₃) 1.15 (t, 6 H), 1.90 (m, 2 H), 3.50 (m, 4 H), 4.05 (d, 4 H), 7.20–7.60 ppm (m, 10 H) and IV (0.38 g, 30%), also a viscous liquid, δ (CDCl₃) 1.15 (t, 3 H), 1.18 (t, 3 H), 2.95 (t, 2 H), 3.60 (t, 1 H), 4.05 (d, 2 H), 4.15 (d, 2 H), 6.10 (t, 1 H) and 7.10–7.70 ppm (m, 10 H), and diphenyldiselenide (1.60 g, 50%).

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* The yield was calculated on the basis of unrecovered selenium compound isolated as diphenyldiselenide.