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SYNTHESIS OF STYRENE AND STILBENE DERIVATIVES BY THE PALLADIUM-CATALYSED ARYLATION OF ETHYLENE WITH AROYL CHLORIDES

ALWYN SPENCER

Central Research Laboratories, Ciba-Geigy AG, CH-4002 Basel (Switzerland)

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Summary

The arylation of ethylene with aroyl chlorides, catalysed by palladium(II) acetate, leads to styrene and stilbene derivatives. By appropriate choice of reaction conditions, particularly the ethylene pressure, the reaction can be made to produce either styrene or stilbene derivatives selectively. The reaction tolerates those common substituents which do not react with aroyl chlorides. Only *trans*-stilbene derivatives are formed.

Introduction

The arylation of mono- [1] and di-substituted [2] activated alkenes by aroyl chlorides catalysed by palladium(II) acetate has been recently reported by us. We describe here the arylation of ethylene to give styrene and stilbene derivatives [3]. Similar arylations with aryl halides have been reported by Mizoroki [4] and by Heck [5].

Results

Preliminary experiments involving benzoyl chloride and ethylene showed that both styrene and *trans*-stilbene were formed. No *cis*-stilbene could be detected by gas-chromatographic or NMR studies. The ratio of styrene to stilbene was found to be very dependent on the ethylene pressure. Accordingly, optimisation of the

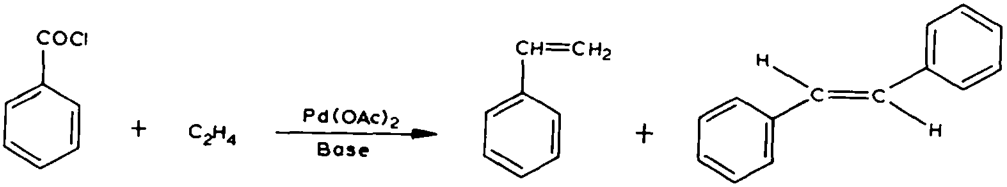

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TABLE 1. EFFECT OF ETHYLENE PRESSURE ON THE FORMATION OF STYRENE
(Benzoyl chloride 50 mmol, *N*-benzyldimethylamine 50 mmol, ethylene (as below), palladium acetate 0.5 mmol, toluene 100 ml, n-hexadecane 1 g (GC standard), 100°C, 4 h)

Ethylene [a] (atm.)	Styrene [b] (%)	Stilbene [b] (%)
5	35	trace
10	58	7
15	37	0

[a] Gauge pressure. [b] Yields by gas chromatography.

reaction conditions was carried out for both products. Both reactions were found to tolerate a variety of substituents in the aroyl chloride.

Styrene formation

Toluene was the preferred solvent for styrene formation, though 1,4-dioxane, propionitrile and ethyl acetate were also used with success. The styrene selectivity decreased slightly with increasing temperature and 100°C was generally used. As in previous studies, *N*-benzyldimethylamine as base gave in general better results than tri-n-butylamine or *N*-ethylmorpholine [1,2], but here also, *N*-ethylmorpholine was preferred when strongly electron-withdrawing groups were present in the aroyl chloride.

Ethylene reacts far more slowly than the simple activated alkenes, e.g. acrylates [1] and 1 mol% palladium acetate was used as catalyst. Other palladium(II) or palladium(0) complexes could be used but they provided no advantage over the acetate. Both the yield and selectivity are affected by the ethylene pressure, as shown in Table 1. A pressure of 10 atm. was used for further work. Under the conditions so obtained a series of ten substituted aroyl chlorides were investigated (Table 2). No attempt was made to isolate the accompanying stilbenes, which were present in very low yields only. The appropriate styrene derivatives were obtained in all cases in moderate yields, suggesting that the reaction will tolerate all substituents that do not react directly with the acid chloride group.

Stilbene formation

p-Xylene was found to be the best solvent for stilbene formation. Toluene, 1,4-dioxane and chlorobenzene can also be used. Best results were obtained at 120°C. Reflux conditions should be avoided as the yields are then very low, presumably due to the low ethylene concentration in solution. Once again, 1 mol% palladium acetate was used as catalyst.

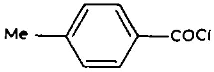
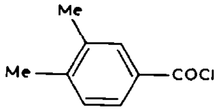
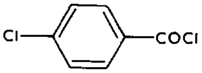
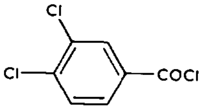
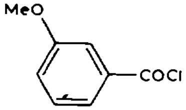
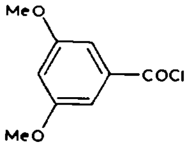
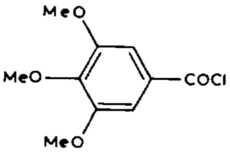
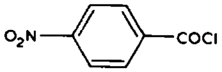
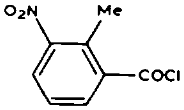
The ethylene was passed over the surface of the reaction mixture under normal pressure to minimise its concentration in solution. Nevertheless, the selectivity towards stilbene was never more than ca. 67%. At pressures marginally above atmospheric the reaction time was considerably reduced, but the selectivity was displaced slightly towards styrene (Table 3).

Table 4 shows the results obtained with eight substituted aroyl chlorides. Again, it was found that those with strongly electron-withdrawing substituents gave better results with *N*-ethylmorpholine as base than with *N*-benzyldimethylamine. In all

TABLE 2

FORMATION OF STYRENE DERIVATIVES BY ARYLATION OF ETHYLENE WITH AROYL CHLORIDES

(Aroyl chloride 50 mmol, base 50 mmol, ethylene 10 atm. (gauge, at 100°C), palladium acetate 0.5 mmol, toluene 100 ml, 100°C, 4 h)

Aroyl chloride	Base [a]	Styrene yield [b] (%)
	BDA	36
	BDA	53
	BDA	55
	BDA	18
	BDA	48
	BDA	60
	BDA	42
	EM	30
	EM	42
	EM	51

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[a] BDA = *N*-benzyldimethylamine, EM = *N*-ethylmorpholine. [b] Isolated yield.

TABLE 3. EFFECT OF ETHYLENE PRESSURE ON THE FORMATION OF STILBENE
(Benzoyl chloride 50 mmol, *N*-benzyldimethylamine 50 mmol, ethylene (as below), palladium acetate 0.5 mmol, *p*-xylene 100 ml, n-hexadecane 1 g (GC standard), 120°C)

Ethylene [a] (atm.)	Time (h)	Styrene [b] (%)	Stilbene [b] (%)
1	8	30	60
1.13	2	34	55
1.26	2	38	42

[a] Total pressure (absolute). [b] Yield by gas chromatography.

cases, the expected stilbene derivative was obtained, but the yields were slightly lower than those in Table 2, due to the lower selectivity prevailing in stilbene formation. Again, it appears that most substituents are tolerated. The ^{1}H NMR spectra of the stilbene derivatives showed them to be *trans* [6], with the vinylic protons in the range δ 6.94–7.04 ppm. The two nitro derivatives were not investigated because of their low solubility.

Discussion

The mechanism of the reaction has been discussed previously [1]. The effect of pressure on the selectivity is exactly as would be expected, a higher ethylene concentration in solution constraining more of the aroyl chloride to react with ethylene and less with the styrene derivative formed, and vice versa. It is noticeable that the product selectivity obtained towards styrene (89%) is significantly better than that towards stilbene (67%). This surely reflects the superior coordinating ability of ethylene, permitting it to compete successfully for the palladium even when present at low concentration relative to the styrene formed.

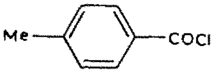
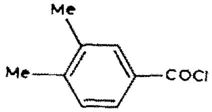
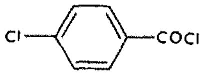
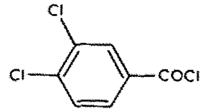
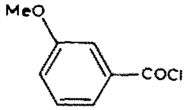
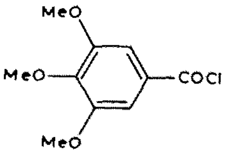
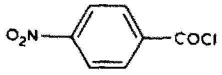
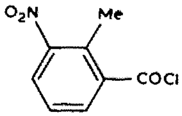
The rate of reaction of ethylene, both in styrene and stilbene formation, is very much less than those of simple activated alkenes such as ethyl acrylate, *N*,*N*-diethylacrylamide or even styrene itself [1]. As ethylene is a far better ligand than the activated alkenes, it may be that the ethylene complexes resulting are less active catalysts than alkene-free species. Any reduction in the electron density on the metal in the palladium(0) species would be expected to hinder the oxidative addition of the aroyl chloride. Further, the alkene must subsequently insert into the polar palladium–phenyl bond. Conceivably the non-polar ethylene reacts less readily than polarised double bonds of the activated alkenes.

The formation of *trans*-isomers only of the stilbene derivatives is to be expected as a result of the steric interactions of the two phenyl groups in the alkylpalladium(II) species which eliminate the final product, and the expected *cis* (suprafacial) nature of the elimination of the palladium(II) hydride [2].

It is noticeable that the total conversion of benzoyl chloride is lower in styrene formation. This is most probably due to the accumulation of carbon monoxide, which at 60% conversion would approach a pressure of 6 atm. in the apparatus used, neglecting its solubility in toluene. In stilbene formation, the carbon monoxide is largely removed by the ethylene stream.

TABLE 4. FORMATION OF STILBENE DERIVATIVES BY ARYLATION OF ETHYLENE WITH AROYL CHLORIDES

(Aroyl chloride 200 mmol, base 200 mmol, ethylene (normal pressure), palladium acetate 2 mmol, *p*-xylene 400 ml, 120°C)

Aroyl chloride	Time (h)	Base [a]	Stilbene yield [b] (%)
	7.5	BDA	45
	6.5	BDA	45
	6.5	BDA	45
	6.5	BDA	45
	7.5	BDA	45
	4.5	BDA	45
	6	EM	45
	6.5	EM	45

[a] BDA = *N*-benzyldimethylamine, EM = *N*-ethylmorpholine. [b] Isolated yield.

Experimental

Palladium acetate was obtained from Engelhard. Ethylene was from Carbagas. Other chemicals were from Fluka or Merck. Aroyl chlorides were prepared as described previously [1]. ^1H NMR spectra were recorded with a Varian XL-100; IR spectra with a Perkin–Elmer 157; and mass spectra with Varian CH5 and CH7 instruments. Elemental analyses were carried out by the Microanalytical Laboratory at Ciba-Geigy.

The preparation of styrene derivatives was carried out in Fischer–Porter Aerosol Compatability bottles attached to a constant pressure apparatus. For the stilbene derivatives, a conventional reflux apparatus was used. Reactions slightly above normal pressure were performed by passing the effluent ethylene stream through an appropriate column of mercury.

Styrene derivatives

Toluene (100 ml) was placed in a 12 oz Fischer-Porter bottle and argon was passed for 5 min. with magnetic stirring. To this were added palladium(II) acetate (0.1122 g, 0.5 mmol), aroyl chloride (50 mmol) and base (50 mmol, see Table 2). The bottle was then connected to the constant pressure apparatus and flushed three times with argon by evacuating and refilling to normal pressure. The argon was then replaced by ethylene (5 atm.) and the bottle was heated in an oil-bath to 100°C. The pressure (7–8 atm.) was then raised to 10 atm. and the reaction mixture was stirred for the appropriate time. After cooling it was extracted with 2*N* hydrochloric acid (2×50 ml), 2*N* aqueous sodium hydroxide (50 ml) and water (50 ml), and then dried for 15 min. with magnesium sulphate (10 g). After removal of the solvent under reduced pressure, the crude product was chromatographed on a Kieselgel 60 column using an appropriate solvent, usually dichloromethane. The product fractions were collected and the solvent removed. In some cases it was necessary to chromatograph the product twice. After characterisation by IR and NMR spectroscopy, it was treated with the stoicheiometric amount of bromine in carbon tetrachloride at 0°C. The resulting dibromides were purified by recrystallisation and fully characterised.

Stilbene derivatives

p-Xylene (400 ml) was placed in a three-necked flask and ethylene was passed with magnetic stirring. To this were added palladium(II) acetate (0.4488 g, 2 mmol); aroyl chloride (200 mmol); and base (200 mmol, see Table 4), and the mixture was stirred at 120°C for the appropriate time with the ethylene now being passed over the surface at ca. 10 ml/min. After the reaction, the mixture was filtered hot and the precipitate was washed with hot toluene (80 ml). The solvents were then removed under reduced pressure and the residue was stirred with methanol (100 ml). The suspension was filtered and the product washed with methanol (20–40 ml). Purification was effected by recrystallisation.

Satisfactory elemental analyses were obtained for all 1,2-(dibromoethyl)benzene and stilbene derivatives.

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