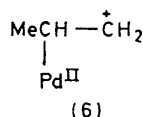
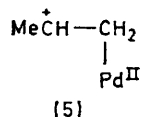
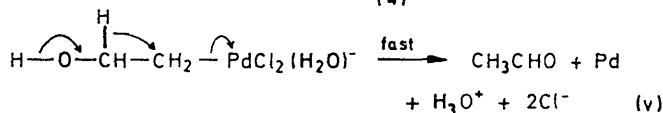
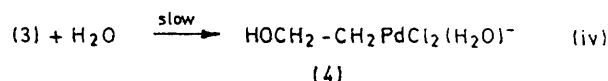
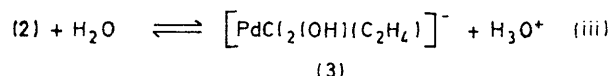
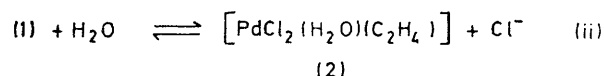
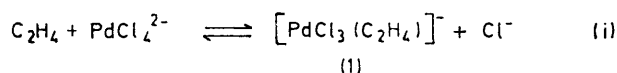


## Reactions of Palladium(II) with Organic Compounds. Part IV.<sup>1</sup> Oxidation of Some Substituted Stilbenes

By Ferrers R. S. Clark, Richard O. C. Norman,\* and C. Barry Thomas, Department of Chemistry, The University of York, Heslington, York YO1 5DD

The product distribution and the relative rates of reaction of some substituted stilbenes with palladium(II) chloride in aqueous 1,2-dimethoxyethane are consistent with there being small but significant carbocation character in the transition state of the oxypalladation step.

THE oxidation of ethylene by aqueous palladium(II) chloride is thought to occur as in reactions (i)–(v), where the species in square brackets represent olefin  $\pi$ -complexes.<sup>2</sup> The equilibrium constant for step (i) and the overall rate for steps (ii)–(v) have been measured in this case and for some higher olefins;<sup>3</sup> variations are relatively small. For example, the overall rate constant for steps (ii)–(v) for propylene is about one-third that for ethylene, from which it has been argued that, since the equilibrium constants for steps (ii) and (iii) are not likely



to differ much for the two olefins, step (iv) involves a concerted, non-polar, four-centre addition.<sup>3</sup> Now, propylene gives acetone as the main product,<sup>4</sup> rather than propionaldehyde, and this would be consistent either with a product-determining step which involves some significant carbocation character in the transition state for addition of electrophilic palladium(II), so that the  $\sigma$ -complex (5) is formed faster than (6) ('Markovnikov' orientation), or with hindrance to the uptake of palladium on to the methyl-substituted carbon; of these, the latter but not the former can be reconciled with the lower rate for propylene than for ethylene.† Moreover, the

† For example, in reactions considered to yield carbocations in the rate-determining step, but-1-ene reacts *ca.* 20 times as fast as ethylene with bromine in acetic acid<sup>5</sup> and propylene reacts *ca.* 150 times as fast as ethylene with thallium(III) acetate in aqueous acetic acid.<sup>6</sup>

<sup>1</sup> Part III, F. R. S. Clark, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1975, 121.

possible unimportance of carbocation character is indicated by the preferential formation of phenylacetaldehyde from styrene,<sup>4</sup> but this reaction may be anomalous since it has been suggested that the rate-determining step in the oxidation of styrene and its ring-substituted derivatives is the hydride shift analogous to reaction (v).<sup>7</sup> To seek evidence as to the possible significance of carbocation character in such reactions, we examined the oxidation of *para*-substituted *trans*-stilbenes by palladium(II) chloride in aqueous 1,2-dimethoxyethane; here, whereas the steric requirements of the two olefinic carbon atoms should be identical, their electronic properties are not.

### RESULTS AND DISCUSSION

Oxidations were carried out with an excess of palladium(II) chloride in initially homogeneous solutions in 1,2-dimethoxyethane–water (2 : 1) at 85–90 °C under nitrogen. In each case, both the possible deoxybenzoins were formed and the recovered stilbene was still entirely the *trans*-isomer. Yields, measured by g.l.c. to within  $\pm 3\%$ , are in the Table.

Products (mol %) from the oxidation of substituted *trans*-stilbenes, ArCH:CHPh, with palladium(II) chloride in aqueous 1,2-dimethoxyethane at 85–90 °C

Ar	Reaction time (h)	Yields (%)		
		Recovered stilbene	ArCO·CH <sub>2</sub> Ph	ArCH <sub>2</sub> ·COPh
<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub>	1	17	36	12
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	3	55	31	21
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	6	57	13	25
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	13.5	61	17	2

The relative amounts of the two deoxybenzoins from the *p*-OMe, *p*-Me, and *p*-Cl compounds are consistent with there being a small proportion of carbocation character in the transition state of the product-determining step; thus, the ions (7; Y = Pd<sup>II</sup>) are formed faster than (8; Y = Pd<sup>II</sup>) for X = OMe or Me, but slower for X = Cl, just as there is evidence that this is so for the addition of bromine<sup>8</sup> to give the ions (7) and (8) (Y = Br) (possible interactions between the carbocation and Pd<sup>II</sup> or Br are omitted in these representations).

<sup>2</sup> P. M. Maitlis, 'The Organic Chemistry of Palladium,' vol. 2, Academic Press, New York, 1971, pp. 78–93.

<sup>3</sup> P. M. Henry, *J. Amer. Chem. Soc.*, 1966, **88**, 1595.

<sup>4</sup> W. Hafner, R. Jira, J. Sedlmeier, and J. Smidt, *Chem. Ber.*, 1962, **95**, 1575.

<sup>5</sup> P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' Elsevier, Amsterdam, 1966, p. 84.

<sup>6</sup> P. M. Henry, *J. Amer. Chem. Soc.*, 1966, **88**, 1597.

<sup>7</sup> H. Okada, T. Noma, Y. Katsuyama, and H. Hashimoto, *Bull. Chem. Soc. Japan*, 1968, **41**, 1395.

<sup>8</sup> M. F. Ruasse and J. E. Dubois, *Tetrahedron Letters*, 1970, 1163.

2,4,6-Trimethylstilbene also gave a predominance of the 'Markovnikov' product, the ratio of the two being



greater in this case than in the others. However, reaction was much slower than with the *p*-Me compound, so that probably palladation is hindered at both olefinic carbons, the more so at the mesityl-substituted carbon.

In the light of these results, it seems likely that the slower oxidation of propylene than of ethylene is the result of steric hindrance to C-Pd  $\sigma$ -bond formation at each carbon atom, the preferred orientation being due at least in part to there being carbocation character in the formation of that bond. Moreover, *p*-chlorostilbene yields each possible ketone less rapidly than *p*-methylstilbene yields either, as expected for an electrophilic reaction, whereas *p*-chlorostyrene is reported to form *p*-chlorophenylacetaldehyde much faster than *p*-methylstyrene forms *p*-methylphenylacetaldehyde,<sup>7</sup> reinforcing the view that styrenes behave anomalously.

#### EXPERIMENTAL

**Materials.**—A solution of 4-methylbenzaldehyde (0.1 mol) in ether (50 ml) was added dropwise to a stirred solution of the Grignard reagent from benzyl chloride (0.1 mol) in ether (200 ml). After being stirred for a further 10 min the mixture was added to dilute sulphuric acid (200 ml) and the ether layer was concentrated, added to sulphuric acid (33% v/v in water; 150 ml), and heated under reflux for 3 h. The cooled mixture was diluted with water and the ether layer was dried (K<sub>2</sub>CO<sub>3</sub>) and evaporated to give 4-methyl-*trans*-stilbene (36%), m.p. 114—116° (from aqueous ethanol) (lit.,<sup>9</sup> 117°).

4-Chloriodobenzene (20 mmol), styrene (20 mmol), palladium(II) acetate (150 mg), and triethylamine (20 mmol) were stirred under reflux for 2 h. After cooling, the mixture was extracted with ether and the extract treated with 2M-HCl and water, dried (K<sub>2</sub>CO<sub>3</sub>), and evaporated to give 4-chloro-*trans*-stilbene (42%), m.p. 127—127.5° (from aqueous ethanol) (lit.,<sup>10</sup> 129°).

The Grignard reagent from 4-bromoanisole (46 mmol) was added under N<sub>2</sub> to styrene oxide (42 mmol) in ether (25 ml). Treatment with aqueous NH<sub>4</sub>Cl, followed by extraction with ether, drying (K<sub>2</sub>CO<sub>3</sub>), and concentration gave a gum (8.7 g, 99%) which was recrystallized with difficulty from ethanol-water to give 4-methoxy-*trans*-stilbene, m.p. 130—131° (lit.,<sup>11</sup> 132°).

The Grignard reagent from bromomesitylene (0.1 mol) was stirred in ether (60 ml) while phenylacetaldehyde (0.075 mol) in ether (20 ml) was added. After stirring for 10 min at

room temperature, the mixture was poured into 2M-HCl (200 ml) and the ether layer was washed with water, dried (K<sub>2</sub>CO<sub>3</sub>), and concentrated. The resulting oil was treated with H<sub>2</sub>SO<sub>4</sub> (150 ml; 50% v/v with water), mixed with acetic acid (20 ml), and heated at reflux temperature for 1 h. An ethereal extract of the cooled solution was washed with aqueous alkali, dried, and concentrated before distillation under reduced pressure. The fraction collected at 218° and 35 mmHg (5.0 g, 30%) gave 2,4,6-trimethyl-*trans*-stilbene as white needles, m.p. 49—51° (from ethanol) (lit.,<sup>12</sup> 53°).

Palladium(II) chloride (Fisons) was used without further purification.

Treatment with 4-methylbenzaldehyde (0.1 mol) of the Grignard reagent from benzyl chloride (0.1 mol) followed by oxidation with sodium dichromate (0.1 mol) in H<sub>2</sub>SO<sub>4</sub> (50% v/v with water; 30 ml) gave benzyl 4-tolyl ketone, m.p. 108—109.5° (from aqueous ethanol) (lit.,<sup>13</sup> 109—110°). 4-Tolylacetic acid (0.05 mol) was added to 2M-phenyl-lithium in ether (50 ml) to give 4-methylbenzyl phenyl ketone, m.p. 95—96° (from hexane) (lit.,<sup>13</sup> 95.5—96.5°).

Benzyl 4-chlorophenyl ketone was prepared from chlorobenzene, phenylacetyl chloride, and aluminium trichloride,<sup>13</sup> and had m.p. 103—103.5° (lit.,<sup>13</sup> 104.5—105°). 4-Chlorobenzyl phenyl ketone, obtained by the reaction of benzamide with the Grignard reagent from 4-chlorobenzyl chloride, had m.p. 137—138° (from ethanol) (lit.,<sup>13</sup> 136.5—137.5°).

Benzyl 4-methoxyphenyl ketone, prepared by the method of Curtin and Crew,<sup>13</sup> had m.p. 71—73° (lit.,<sup>13</sup> 75—76°). 4-Methoxybenzyl phenyl ketone, m.p. 94.5—95° (from hexane) (lit.,<sup>13</sup> 94.5—95°), was prepared by adding 4-methoxyphenylacetic acid (0.05 mol) to phenyl-lithium (0.1 mol) in ether (50 ml).

Benzyl mesityl ketone was prepared by the reaction in CS<sub>2</sub> between equimolar amounts of phenylacetyl chloride and mesitylene in the presence of an excess of aluminium trichloride; after distillation (b.p. 310° at 30 mmHg), it partly crystallized, and gave an n.m.r. spectrum identical with that previously reported.<sup>14</sup> Mesitylacetic acid<sup>15</sup> was added to an excess of phenyl-lithium in ether and refluxed for 6 h to give phenyl 2,4,6-trimethylbenzyl ketone, m.p. 148—151° (from ethanol) (lit.,<sup>16</sup> 147—148°).

**Oxidations.**—The olefin (1 mmol) and palladium(II) chloride (1.7 mmol) were mixed under N<sub>2</sub> with 1,2-dimethoxyethane (4 ml) and water (2 ml), both previously flushed with N<sub>2</sub>. Under a reflux condenser and in an atmosphere of N<sub>2</sub>, the mixture was stirred on an oil-bath (85—90°) for the times shown (Table). After cooling, a g.l.c. standard and water (40 ml) were added. An ethereal extract (3 × 20 ml) was dried (K<sub>2</sub>CO<sub>3</sub>) and concentrated and then analysed by g.l.c. on a Pye instrument (series 104) fitted with a flame ionisation detector; the columns contained either 10% Apiezon L or 3.5% polyethylene glycol adipate on Celite. Products were identified by g.l.c. followed by mass spectrometry, and comparison with authentic samples.

[4/2286 Received, 4th November, 1974]

<sup>9</sup> Heilbron's 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

<sup>10</sup> F. Bergmann, J. Weizman, and D. Schapiro, *J. Org. Chem.*, 1944, **9**, 408.

<sup>11</sup> M. S. Kharasch and H. G. Clapp, *J. Org. Chem.*, 1938, **3**, 355.

<sup>12</sup> P. S. Bailey and J. G. Burr, *J. Amer. Chem. Soc.*, 1953, **75**, 2951.

<sup>13</sup> D. Y. Curtin and M. C. Crew, *J. Amer. Chem. Soc.*, 1954, **76**, 3719.

<sup>14</sup> A. G. Pinkus, M. Z. Haq, and J. G. Lindberg, *J. Org. Chem.*, 1970, **35**, 2555.

<sup>15</sup> R. C. Fuson and N. Rabjohn, *Org. Synth.*, Coll. Vol. 3, 1955, p. 557.

<sup>16</sup> J. P. Freeman, *J. Org. Chem.*, 1961, **26**, 3507.