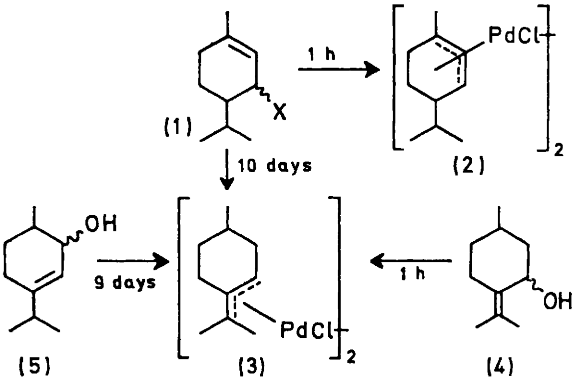
Rearrangements in the Formation of Some π-Allylpalladium Compounds

By **G. A. Gray, W. R. Jackson,*** and **J. J. Rooney,** Department of Chemistry, Queen's University, Belfast BT9 7AG

A reaction of *p*-menth-1(2)-en-3-ol with palladium(II) chloride, lithium chloride, and carbon monoxide which was worked up as soon as the passage of gas had ceased gave di-μ-chloro-bis-[(1,2,3-*trihapto*-*p*-menth-1-ene)palladium(II)] (2). When the mixture was set aside for several days di-μ-chloro-bis-[(3,4,8-*trihapto*-*p*-menth-3-ene)palladium(II)] (3) was isolated. The preparation of (3) from other cyclic monoterpene derivatives is described.

THE reaction of palladium(II) chloride with a mixture of *cis*- and *trans*-*p*-menth-1(2)-en-3-ols (1; X = OH) was studied under the conditions described by Dent, Long, and Wilkinson.[1] A reaction for 1 h gave di-μ-chloro-bis-[(1,2,3-*trihapto*-*p*-menth-1-ene)palladium(II)] (2) (24%) as a yellow, gummy solid. The structure was established from its n.m.r. spectrum and from oxidation with chromic acid which gave *p*-menth-1(2)-en-3-one. The same π-allylpalladium compound (2) was obtained by treatment of the 3-chloro-*p*-menth-1-enes (1; X = Cl) under similar conditions but in even lower yield (12%). The low yields of π-allylpalladium compounds were associated with the formation of large amounts of a black, solid, polycarbonylpalladium compound.

In an attempt to obtain higher yields of (2), the reaction mixture with *p*-menth-1(2)-en-3-ol was set aside for 10 days at room temperature after brief passage of carbon monoxide. A pure crystalline π-allylpalladium compound was obtained which showed only one allylic proton in its n.m.r. spectrum. Di-μ-chloro-bis-[(3,4,8-*trihapto*-*p*-menth-3-ene)palladium(II)] (3) contains the only conceivable tetrasubstituted π-allylic system which has not involved drastic rearrangement of the menthane ring system. Reaction of the *p*-menth-4(8)-en-3-old (4) with palladium chloride and lithium chloride for 1 h in the presence of carbon monoxide gave (3) in low yield. Reaction for this short time is less likely to be accompanied by rearrangement and the result provides further evidence for the structure of (3). A reaction of *p*-menth-4(8)-en-3-ol which was allowed to proceed for 4 days gave a higher yield of (3) (54%); compound (3) was also isolated from a reaction with *p*-menth-3-en-2-ol (5) which was allowed to proceed for 9 days.



An interesting parallel with these rearrangements is the reported isomerisation of *p*-menth-1-ene to *p*-menth-4(8)-ene over a palladium catalyst.[2] However, it has not proved possible to increase the yield of (2), and attempts to isomerise (2) to (3), *e.g.* in methanolic solutions of dry hydrogen chloride, have led only to decomposition.

EXPERIMENTAL

I.r. spectra were recorded either for liquid films or for potassium bromide discs with a Perkin-Elmer Infracord 137 spectrometer. N.m.r. spectra were recorded by R. Spratt or I. Jack with a Varian HA100 spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal standard. G.l.c. was carried with a Perkin-Elmer F11 chromatograph. Alumina refers to Spence grade H deactivated by treatment with 5% of aqueous acetic acid (10% by volume of acid). Light petroleum refers to the fraction with b.p. 40—60°.

Materials.—(±)-*cis* and -*trans* *p*-Menth-1-en-2-ols (1; X = OH), b.p. 72—86° at 2 mmHg (lit.,[3] b.p. 60—70° at 0·5 mmHg) were prepared by lithium aluminium hydride reduction of (±)-*p*-menth-1-en-2-one. Reduction of *p*-menth-3-en-2-one gave the diastereoisomeric *p*-menth-3-en-2-ols (5), b.p. 70—80° at 2 mmHg, n_D^{20} 1·477 (lit.,[4] b.p. 107—109° at 16 mmHg, n_D 1·479); reduction of *p*-menth-4(8)-en-3-one gave a mixture of the diastereoisomeric *p*-menth-4(8)-en-3-ols (4), b.p. 76—86° at 3·5 mmHg, n_D^{19} 1·470 (lit.,[5] b.p. 91·5° at 12 mmHg, n_D^{18} 1·471.

(±)-cis- and -trans-3-*Chloro*-p-*menthenes* (1; X = Cl).—*p*-Menth-1-en-3-ol (19·7 g), conc. hydrochloric acid (38 ml) and freshly prepared copper(I) chloride solution (6 ml; prepared as described by Vogel[6]) were placed in a flask fitted with a reflux condenser and cooled in an ice-bath. Sulphuric acid (13·6 ml) was added dropwise through the condenser with shaking and the turbid liquid was set aside for 2 h. The upper layer was separated, washed twice with water, dried ($CaCl_2$), and distilled under reduced pressure with dibutyl phthalate as an antifoaming agent. The allylic chlorides were obtained as a colourless oil (13·5 g, 62%), b.p. 34—44° at 0·2 mmHg, n_D^{19} 1·4831 (lit.,[7] 92—98° at 13 mmHg).

---

[1] W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1964, 1585.

[2] G. V. Smith, J. A. Roth, and J. L. Kosco, American Chemical Society, 154th National Meeting, Chicago, 1967, Abstract U32, and personal communication from Dr. Smith.

[3] A. K. MacBeth, B. Milligan, and J. S. Sharmon, *J. Chem. Soc.*, 1953, 901.

[4] O. Wallach, *Annalen*, 1918, **414**, 202.

[5] V. Paolini, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1919, **28**, 190, 236.

[6] A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' 3rd edn., Longmans, London, 1966, p. 276.

[7] A. Kotz and G. Busch, *J. prakt. Chem.*, 1942, **7**, 397.

Di-μ-chloro-bis-[(1,2,3-trihapto-p-*menth*-1-*ene*)*palladium*-(II)] (2).—Palladium(II) chloride (930 mg, 5·3 mmol) and sodium chloride (380 mg, 6·5 mmol) were dissolved in methanol (10 ml) by shaking overnight. *p*-Menth-1-en-3-ol (1·0 g, 6·6 mmol) was added to the filtered solution and carbon monoxide was passed through for 1 h.[1] The resulting clear yellow solution was poured into water and immediately extracted with chloroform (3 × 200 ml). Large amounts of a black product were filtered off with the magnesium sulphate used to dry the chloroform solution. A sample of the black solid showed strong i.r. absorptions at 2005 cm^{-1}. The chloroform was removed under reduced pressure and the residual yellow oil was chromatographed on silica gel. Elution with chloroform–light petroleum (3 : 7) gave *di-μ-chloro-bis-*[(1,2,3-trihapto-p-*menth*-1-*ene*)*palladium*(II)] as a yellow oil (358 mg, 24%) (Found: C, 43·8; H, 6·4. $C_{10}H_{17}ClPd$ requires C, 43·0; H, 6·2%); τ 4·74 (d, $J_{2,3}$ 6·5 Hz, 2-H), 5·32 (d, 3-H), 8·56 (s, Me), 9·04, and 9·08 (d, CH*Me*$_2$, *J* 6·5 Hz).

The π-allyl compound (287 mg, 12%) was also prepared by reaction of the 3-chloro-*p*-menth-1-enes (1·68 g, 6·7 mmol) under similar conditions.

Chromic Acid Oxidation of (2).—A solution of (2) (358 mg) in ether (7 ml) was stirred for 2 h at 20° with a solution of sodium dichromate dihydrate (700 mg) in 98% sulphuric acid (0·5 ml) and water (2·5 ml). The mixture was extracted with ether, and the ether layer was washed with hydrogen carbonate solution and water, and dried ($MgSO_4$); the ether was removed through a short distillation column. The residue was chromatographed on alumina in light petroleum to give *p*-menth-1-en-2-one (65 mg, 33%) (retention time identical with that of an authentic sample on a 2 m-column of Antarox CO-990 on AW-DMCS Chromosorb W, 80—100 mesh); 2,4-dinitrophenylhydrazone, m.p. 115—118° (lit.,[8] 119°).

Di-μ-chloro-bis-[(3,4,8-trihapto-p-*menth*-3-*ene*)*palladium*-(II)], (3).—(a) *From* p-*menth*-1-*en*-2-*ol*. *p*-Menth-1-en-2-ol (1·54 g, 10 mmol) was added to a solution of lithium chloride (832 mg, 19·8 mmol) and palladium(II) chloride (1·55 g, 8·7 mmol) in methanol (15 ml) and carbon monoxide was passed through for 50 min. The tube containing the resulting clear yellow solution was stoppered and set aside for 10 days at room temperature during which time a mirror of palladium metal formed on the side. The mixture was poured into water and again a black solid was deposited. The product was isolated in chloroform as a yellow oil and chromatographed on alumina. Elution with chloroform–light petroleum (1 : 1) gave *di-μ-chloro-bis-*[(3,4,8-trihapto-p-*menth*-3-*ene*)*palladium*(II)] as a yellow wax (498 mg, 20%). Trituration with light petroleum gave a yellow solid which was recrystallised from ether–light petroleum to give prisms, m.p. 127° (decomp.) (Found: C, 43·3; H, 6·4. $C_{10}H_{17}ClPd$ requires C, 43·0; H, 6·2%); τ 5·75 (s, 3-H), 9·02 (d, *J* 6·8 Hz, Me), and 8·84 and 8·76 (each s, 3H). The separation of the last two singlets decreased to 3·4 Hz when the spectrum was taken at 40 MHz.

(b) *From* p-*menth*-3-*en*-2-*ol*. (5) *p*-Menth-3-en-2-ol (1·54 g), palladium chloride (1·5 g), and lithium chloride (0 8 g) in methanol (15 ml), treated with carbon monoxide for 50 min and set aside for 9 days at ambient temperature, gave the π-allyl compound (3) (1·13 g, 48%).

(c) *From* 3-*chloro*-p-*menth*-1-*ene* (1; X = Cl). The allylic chlorides (1·3 g, 7·7 mmol), lithium chloride (0·7 g, 17·5 mmol), and palladium chloride (1·54 g, 8·7 mmol) gave (3) (640 mg, 34%) after 1 week at ambient temperature.

(d) *From* p-*menth*-4(8)-*en*-3-*ol* (4). *p*-Menth-4(8)-en-3-ol (1·55 g), lithium chloride (1·25 g), and palladium chloride (1·4 g) were treated with carbon monoxide for 50 min and the mixture was set aside for 1 h. Isolation with chloroform gave (3) (179 mg, 8%). A reaction on a similar scale for 4 days gave (3) (1·24 g, 54%).

We thank the Ministry of Education, Northern Ireland, for the award of a post-graduate studentship (to G. A. G.) and Dr. P. Bladon, University of Strathclyde, for a 40 MHz n.m.r. spectrum.

[9/1998 *Received, November* 20*th*, 1969]

---

[8] W. Kuhn and H. Schinz, *Helv. Chim. Acta*, 1953, **36**, 161.