# Anti-Markownikoff 1,2-Hydrosulphonylation of 1,3-Dienes *via* π-Allylpalladium Complexes

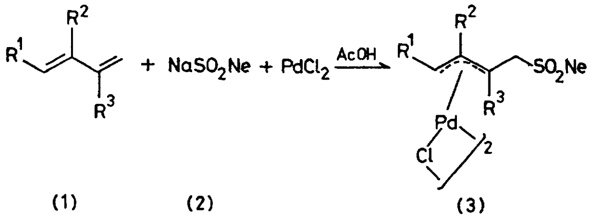
By Yoshinao Tamaru, Masahiro Kagotani, and Zen-ichi Yoshida*

(*Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto* 606, *Japan*)

*Summary* The reaction of palladium(II) chloride with 1,3-dienes and sodium alkanesulphinates in acetic acid produces di-μ-chloro-bis(1-*syn*-alkylsulphonylmethyl-π-allyl)dipalladium(II) complexes, which on treatment with dimethylglyoxime in methanol are degradated selectively to γδ-unsaturated sulphone.

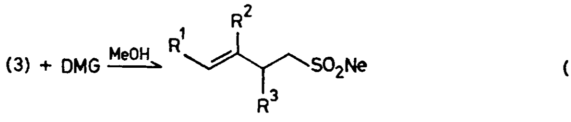
While sulphonyl and sulphinyl groups have played important roles in organic synthesis, little attention has been paid to these groups in organo-transition metal chemistry. However, studies on the insertion of sulphur dioxide into transition metal–alkyl bonds[1] and the reverse process, the extrusion of sulphur dioxide from arenesulphinate–transition metal complexes,[2] have been reported.

We report here the reaction of the alkanesulphinate (**2**) with the 1,3-dienes (**1a**)—(**1c**) in the presence of a stoicheiometric amount of $PdCl_2$; the sulphinate (**2**) reacted as an S-nucleophile[3] with the dienes to give the yellow chloro-bridged palladium(II) complexes (**3a**)—(**3c**) in good yields, the reaction selectively giving the thermodynamic product[4] [equation (1)]. 1,4-Disubstituted 1,3-dienes (*e.g.*, hexa-2,4-diene or cyclo-octa-1,3-diene) did not give products analogous to (**3**).



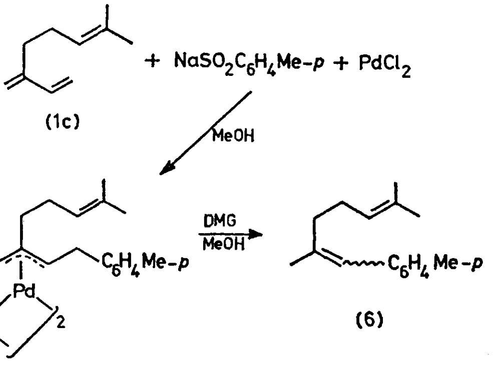
(1) (2) (3)

a, 80%; b,80%; c,52% (1)



(4)

a, 89%; b,90%; c,85% (2)



(5) (3)

Ne = neophyl = $CH_2CMe_2Ph$

**a**; $R^1$ = Et; $R^2$ = $R^3$ = H

**b**; $R^1$ = H, $R^2$ = $R^3$ = Me

**c**; $R^1$ = $R^3$ = H, $R^2$ = $CH_2CH_2CH{=}CMe_2$

In a typical preparation, hexa-1,3-diene (**1a**) (4 mmol), the sulphinate (**2**) (4 mmol), and $PdCl_2$ (2 mmol) were heated in acetic acid (22 ml) in a sealed tube purged with argon at 75 °C for 5 h. The reaction mixture, initially deep red probably owing to the presence of a sulphinate–palladium complex, turned yellow during the reaction. After extraction with ethyl acetate, drying ($MgSO_4$), and removal of solvent, the yellow residue was purified by column chromatography (silica gel, benzene–ethyl acetate, 8 : 1 v/v, as eluant) to give (**3a**) as a yellow oil (80% yield based on $PdCl_2$), which solidified on standing;† $\delta$ (100 MHz; $CDCl_3$; $Me_4Si$) 7·4 (m, 5H), 5·19 (t, *J* 11 Hz, 1H), 3·32 (s, 2H), 3·30 (dt, *J* 11 and 4 Hz, 1H), 3·19 (dt, *J* 11 and 6 Hz, 1H), 2·93 (dd, *J* 14 and 4 Hz, 1H), 2·58 (dd, *J* 14 and 11 Hz, 1H), 1·67 (s, 6H), 1·62 (m, 2H), and 1·11 (t, *J* 7 Hz, 3H); $\nu_{max}$ (KBr) 1620w, 1320s, 1145s, 1130s, 850m, 780s, 745s, and 705s $cm^{-1}$.

The reaction of (**3a**)—(**3c**) with dimethylglyoxime (DMG)[5] occurred selectively, the route being independent of their structures, to give the $\gamma\delta$-unsaturated sulphones (**4a**)—(**4c**), the products of formal anti-Markownikoff 1,2-addition of sulphinic acid to the 1,3-dienes [equation (2)]. For example, the reaction of (**3a**) (1 mmol) with DMG (2 mmol) in 10 ml of methanol (at room temperature for 3 h) gave the sulphone (**4a**) in 89% isolated yield; b.p. 140 °C at 0·01 mmHg; $\delta$ (60 MHz; $CCl_4$; $Me_4Si$) 7·45 (m, 5H), 5·28 (m, 2H), 3·14 (s, 2H), 2·20 (m, 4H), 2·1 (q, *J* 10 Hz, 2H), 1·66 (s, 6H), and 0·96 (t, *J* 10 Hz, 3H); $\nu_{max}$ (neat) 1320s, 1140s, 1135s, 850m, 780m, and 710s $cm^{-1}$; no isomer was detectable by g.l.c.

Similarly the reaction of (**3b**) and (**3c**) with DMG proceeded selectively to give the sulphones (**4b**) and (**4c**), containing terminal and less substituted olefinic groups, in 90 and 85% yields, respectively. These results are in marked contrast to those obtained for the reaction of a $\pi$-allylpalladium complex with DMG,[5] methanolic potassium hydroxide,[6] or potassium cyanide,[7] which usually produces a mixture of two possible olefins, the more highly substituted olefin predominating. In fact, treatment of the complex (**5**), which was prepared by sulphur dioxide extrusion from myrcene (**1c**), sodium toluene-*p*-sulphinate, and $PdCl_2$ in 47% yield, with DMG selectively gave the octa-2,6-diene (**6**) in 74% isolated yield [equation (3)].

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† All new compounds gave satisfactory elemental analyses and spectral data (i.r., n.m.r., and/or mass). However, the neophyl sulphone complexes (**3a**)—(**3c**) were difficult to recrystallize, and the corresponding t-buty sulphone derivatives were prepared and analysed instead.

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