Catalytic Diacetoxylation of *cis-* and *trans*-Dichloroethylenes by Means of Palladium(II) Chloride

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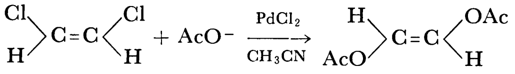
It is well known that palladium(II) chloride and sodium acetate cause the displacement reaction of vinylic halides to give vinyl acetate derivatives.[1] However, examples are limited to only monohalides such as vinyl chloride or 2-chloropropylene. In order to study whether dihalides also undergo displacement reaction or not, we have carried out the reactions of *cis-* and *trans*-dichloroethylenes. Interestingly enough we have found that in the presence of catalytic amounts of palladium(II) chloride, *cis*-dichloroethylene reacts with acetate ions to produce *trans*-diacetoxyethylene[2] in high yield with a small amount of unidentified products. Similarly *trans*-dichloroethylene afforded *trans*-diacetoxyethylene in a 137% yield based on palladium(II) chloride used.



$$\overset{\mathrm{Cl}}{\underset{\mathrm{H}}{>}}\mathrm{C{=}C}\overset{\mathrm{Cl}}{\underset{\mathrm{H}}{<}} + \mathrm{AcO^-} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{PdCl_2}} \overset{\mathrm{H}}{\underset{\mathrm{AcO}}{>}}\mathrm{C{=}C}\overset{\mathrm{OAc}}{\underset{\mathrm{H}}{<}}$$

AcO: CH_3COO

This is the first example of direct diacetoxylation ethylene derivatives to give unsaturated diacetates by the nucleophilic substitution of halides with an acetate anion.

The following procedure is a representative one. A mixture of 0.09 mol of *cis*-dichloroethylene, 0.18 mol of sodium acetate, and 0.03 mol of $PdCl_2$ in 200 m*l* of acetonitrile under air was stirred at 80°C for 8 hr. The resulting mixture was filtered to remove $PdCl_2$ and Pd metal, and the filtrate was poured into water, and the organic layer was then separated. After drying over $MgSO_4$, the solvent was evaporated. The residual heavy oil crystallized on standing. The mixture was filtered and the crystals were washed with petroleum ether. From the mother liquor, a very small amount of two unidentified products was detected by glpc. The crude substance was recrystallized from ether-petroleum ether, then sublimed at 4 mmHg, to give 5.31 g (123% yield based on $PdCl_2$) of *trans*-diacetoxyethylene[3] as colorless crystals, mp 44—44.5°C, IR, 1720 (C=O), 1600 (C=C), 1188 (C-O-C) and 970 cm^{-1} (*trans*-C-H); NMR,[4] 3.29 (olefinic protons, s, 2H) and 7.80 τ (methyl protons, s, 6H).

The reaction provides an extremely convenient method for the synthesis of olefinic diacetate derivatives.

Further works on this reaction are now in progress together with mechanistic investigation, and details will be described in a full paper.

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[1] E. W. Stern, M. L. Spector and H. P. Lefti, *J. Catalysis*, **6**, 152 (1966); C. F. Kohll, R. Van Helden, *Rec. Trav. Chim. Pays-Bas*, **87**, 481 (1968); H. C. Volger, *ibid.*, **87**, 501 (1968); M. Tamura and A. Yasui, *Kogyo Kakagu Zasshi*, **72**, 572 (1969).

[2] No *cis*-isomer was obtained, but it is presumably formed at first and then rapidly isomerized to a *trans*-isomer in the reaction.

[3] M. F. Shostakovskii, N. V. Kuznetsov and Chemin Yang, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1962**, 710; *Chem. Abstr.*, **57**, 16389 (1962).

[4] Taken with a Japan Electron Optics JNH-MH-100 spectrometer.