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CONVERSION OF OLEFINS TO ETHYLENE KETALS
WITH MERCURIC ACETATE AND PALLADIUM CHLORIDE

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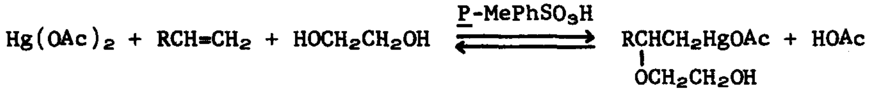
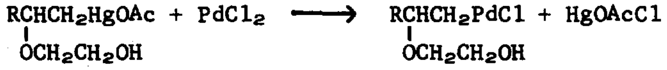
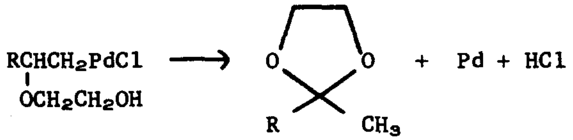
In this paper we describe a method for converting olefins to ethylene ketals which involves solvomercuration of the olefin (eq 1),[1] formation of a σ-bonded organopalladium derivative by a transmetallation reaction between the organomercurial and palladium chloride (eq 2),[2] and subsequent decomposition of the organopalladium intermediate (eq 3)[3].



$$Hg(OAc)_2 + RCH{=}CH_2 + HOCH_2CH_2OH \overset{\underline{P}\text{-}MePhSO_3H}{\rightleftharpoons} \underset{OCH_2CH_2OH}{RCHCH_2HgOAc} + HOAc \qquad (1)$$



$$\underset{OCH_2CH_2OH}{RCHCH_2HgOAc} + PdCl_2 \longrightarrow \underset{OCH_2CH_2OH}{RCHCH_2PdCl} + HgOAcCl \qquad (2)$$



(3)

A procedure for generating ketones from olefins which involves a similar set of reactions has been reported recently.[4]

As indicated in Table 1, treatment of olefins with mercuric acetate in 1:1 1,2-ethanediol-tetrahydrofuran followed by addition of the resulting solution to a mixture of Li_2PdCl_4 and lithium carbonate in tetrahydrofuran affords ethylene ketals. The reaction is usually complete in 30 min. at 64°.

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For terminal olefins the ketal group is selectively introduced at C_2 in high yield. Disubstituted olefins are converted to ketals in moderate yield and the procedure can be made catalytic in palladium chloride by adding copper (II) chloride to the reaction mixture. Products resulting from isomerization of the double bond[5] are not formed since the palladium catalyst does not encounter free olefin.

TABLE 1

CONVERSION OF OLEFINS TO ETHYLENE KETALS

Olefin	Products	Yield (%)[a] b	c
Styrene	2-Methyl-2-phenyl-1,3-dioxolane	60	95
Hex-1-ene	2-Butyl-2-methyl-1,3-dioxolane	82	95
Undec-1-ene	2-Methyl-2-nonyl-1,3-dioxolane	63	83
Oct-4-ene	2-Butyl-2-propyl-1,3-dioxolane	20[d]	50[d]
3,3-Dimethylbut-1-ene	2-t-Butyl-2-methyl-1,3-dioxolane	79	86
Cyclohexene	1,4-Dioxospiro [4.5] decane	13	40

[a] Analysis by GLC with an internal standard.

[b] Olefin (2 mmole), $Hg(OAc)_2$ (2 mmole), p-toluenesulfonic acid (0.02 mmole), Li_2PdCl_4 (0.2 mmole), ethylene glycol (2 ml), tetrahydrofuran (2 ml), $CuCl_2$ (6 mmole), Li_2CO_3 (6 mmole), stirred for 30 min. at 64°.

[c] Same as b except that 2.0 mmole of Li_2PdCl_4 was employed and the reaction was run without $CuCl_2$.

[d] 0.2 equivalents of p-toluenesulfonic acid were employed.

General Procedure: Preparation of 2-butyl-2-methyl-1,3-dioxolane

A stirred solution of anhydrous $Hg(OAc)_2$ (0.06 mole), hex-1-ene (0.06 mole), and p-toluenesulfonic acid (0.6 mmole) in 60 ml of anhydrous 1,2-ethanediol and 60 ml of anhydrous tetrahydrofuran was allowed to stand at room temperature for 30 min. The solution was then poured into 120 ml of anhydrous tetrahydrofuran containing $CuCl_2$ (0.18 mole), $LiPdCl_4$ (0.006 mole), and Li_2CO_3 (0.018 mole). The reaction mixture was heated at 64° for thirty min., cooled to room temperature, and then analyzed by GLC (8% SE-30 on 80-100 mesh Varoport 30). Isolation of the ketal product was accomplished by pouring the reaction mixture into 25 ml of 50% NH_4OH. The resulting mixture was extracted with diethyl ether (3x150 ml), dried ($MgSO_4$), filtered and the diethyl ether and tetrahydrofuran evaporated under reduced pressure. Distillation of the residue afforded 6.59g (77%) of 2-butyl-2-methyl-1,3-dioxolane: b.p. 63-64° (36 mm); n^{24} 1.419.

Evidence that the above method involves the intermediacy of a transmetallation step rather than a sequence involving deoxymercuration to give free olefin, and subsequent oxidation of the olefin directly to ketal with palladium chloride,[3] was obtained by subjecting undec-1-ene to the reaction conditions in the absence of mercuric acetate. GLC analysis of the reaction mixture failed to detect any ketal after 2 hrs.

In order to probe the mechanism by which the organopalladium intermediate is converted to the ketal product 2-d,-3,3-dimethylbut-1-ene (1) was prepared* and then treated with mercuric acetate and palladium chloride under the usual conditions.

Analysis of the reaction mixture by GLC-mass spectrometry showed that 86% of the deuterium label was retained in the ketal product 3. This result is consistent with the major reaction pathway involving concerted or stepwise palladium assisted 1,2-migration of deuteride from C_2 to C_1 in 2, elimination of palladium metal, and cyclization of the resulting species to form the ethylene ketal.[3]

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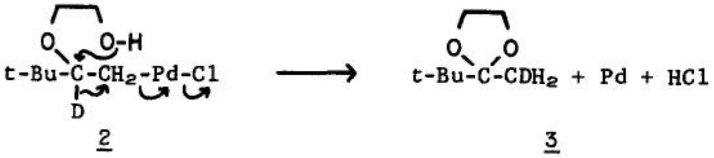
* Compound 1 was obtained by treating pinacolone with $LiAlD_4$ and then subjecting the acetate of the resulting alcohol to gas phase pyrolysis at 500° C.



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