

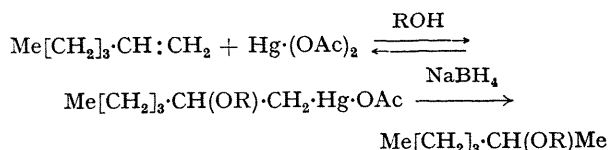
Conversion of Olefins into Ketones with Mercuric Acetate and Palladium Chloride

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Summary A convenient laboratory procedure for converting olefins into ketones by oxymercuration, involving transmetallation of the resulting oxymercurial with palladium chloride, is described.

TREATMENT of olefins such as hex-1-ene with mercuric acetate in aqueous tetrahydrofuran or methanol produces the corresponding oxymercurials (I) and (II) in high yield. These in turn are easily converted into alcohol¹ and methyl ethers² by addition of an alkaline solution of sodium borohydride.

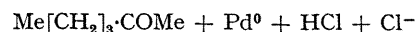
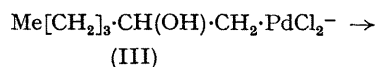


(I); R = H

(II); R = Me

In contrast to oxymercurials, the analogous palladium compounds, *e.g.* (III), are unstable in solution and undergo a rapid reductive elimination to give ketones and palladium metal.³ We describe here a procedure for converting

olefins into ketones by oxymercuration of the olefin, formation of a palladium compound by transmetallation of the



oxymercurial with palladium chloride,⁴ and subsequent decomposition of the organo-palladium intermediate.

On addition of oxymercurial (I) in tetrahydrofuran-water (3:1) to an equimolar amount of Li_2PdCl_4 in tetrahydrofuran at 25°, palladium metal was immediately precipitated and a quantitative yield of hexan-2-one was obtained in 2 h. High yields can also be obtained with catalytic quantities of palladium chloride as long as copper(II) chloride is added to oxidize the palladium metal generated (see Table). Although only 2 equiv. of CuCl_2 are required to oxidize 1 g atom of Pd^0 , we found that the yield of ketone reached a maximum with 3 equiv. of CuCl_2 . It appears that the mercury(II) salt liberated in the transmetallation step forms a complex with palladium chloride thus making it unavailable for further reaction. Since CuCl_2 also forms a complex with the mercury(II) salt, an additional 1 equiv. is added to absorb the mercury(II) species as it is produced.

Hydrochloric acid, formed by hydrolysis of CuCl_2 and by the decomposition of the palladium adduct, catalyses the conversion of the oxymyrcerial into olefin and mercury(II) salt. The low yield of acetophenone is due in part to this effect.

similar capacity and we are currently investigating this possibility.

In methanol the yields of ketones are good (see Table), and the following procedure is representative. Mercuric acetate (2 mmol) and hex-1-ene (2 mmol) were stirred at 25° for

TABLE

Olefin	t/min^a	Product	Yield (%) ^b	
			c	MeOH
Hex-1-ene	30	Hexan-2-one	84	100
Undec-1-ene	30	Undecan-2-one	89	89
<i>trans</i> -Oct-4-ene	240	Octan-2-one	0 ^d	82
Styrene	120	Acetophenone	40	90
3,3-Dimethylbut-1-ene	90	3,3-Dimethylbutan-2-one	—	100

^a Time following addition of the oxymyrcerial to a solution of Li_2PdCl_4 and CuCl_2 .

^b Analysis by g.l.c. with an internal standard.

^c Tetrahydrofuran-water (3:1).

^d Formation of the required oxymyrcerial did not occur under these conditions.

In order to minimise the effect of acid, the reaction was studied in methanol. Here, conversion of an olefin into an enol-ether or dimethyl acetal was expected but in fact the corresponding ketone was produced directly. Drying of both reagents and solvent failed to reduce the yield of ketone, so it is unlikely that water participates in the hydrolysis of the enol-ether or dimethyl acetal. Clement and Selwitz⁵ have reported that palladium chloride catalyses the conversion of vinyl acetate into acetaldehyde and acetic anhydride in glacial acetic acid containing sodium acetate. Palladium chloride may be functioning here in a

15 min in methanol and then added to a stirred methanolic solution of cupric chloride (6 mmol) and Li_2PdCl_4 (0.2 mmol). Formation of ketone was monitored by g.l.c. after hydrolysis of samples with aqueous NaHCO_3 . At 65° a quantitative yield of hexan-2-one was obtained after 30 min. In the absence of CuCl_2 , equimolar quantities of oxymyrcerial and Li_2PdCl_4 in methanol afforded a quantitative yield of hexan-2-one after 2 h at room temperature.

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⁵ W. H. Clement and C. M. Selwitz, *Tetrahedron Letters*, 1962, 1081.