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METAL ATTACK AT THE CARBON-OXYGEN BOND

COUPLING OF ALLYLIC ACETATES BY NICKEL CARBONYL

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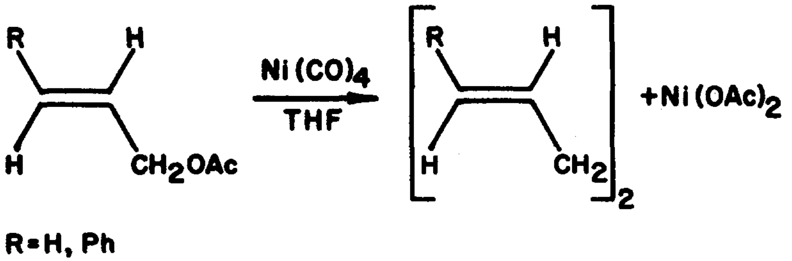
THOUGH reactions involving carbon-halogen bond rupture by metals are legion, analogous reactions at carbon-oxygen bonds are scarcely ever observed under conditions mild enough to be of more than esoteric interest. For example, cleavage of the C-O bond of allylic ethers is accomplished only under such relatively drastic conditions as sodium in liquid ammonia[2] (Na^+e^-, "sodium electride") and by sodium and other metals at temperatures exceeding 100°.[3]

In the course of a study of the detailed mechanisms of metal attack at carbon-halogen and carbon-oxygen bonds a novel reaction involving C-O cleavage under mild conditions has been unearthed. Rupture of the C-O bond of allylic acetates is effected when the esters are refluxed with equimolar amounts of nickel carbonyl in tetrahydrofuran solution for 2-3 hr (reaction temperature 45-65°). Specifically, allyl and cinnamyl acetates give 50 and 31 per cent conversions to biallyl and bicinnamyl, respectively (1).



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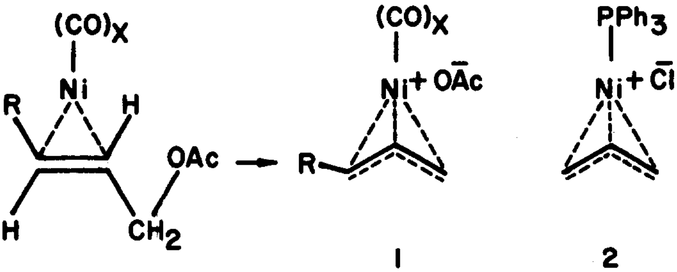
[2] A.J. Birch and H. Smith, Quart. Revs. 22 (1958).

[3] H. Dreyfus, F. Bryans and J.G.N. Drewett, U.S. 2,405,347; Chem. Abstr. 41, 148 (1947).

Since nickel carbonyl attacks only very reactive functional groups (such as acid chlorides) the procedure promises to be a reasonably general one for allylic esters.

The corresponding allylic alcohols and phenyl ethers were found inert, as were also all non-allylic esters investigated, including two homoallylic esters (*endo*-norbornenyl acetate and 3-buten-1-ol acetate). Even the frail C-O bonds of benzhydryl, phenacyl, and benzoin acetates were immune to attack. Since the C-O bond in the former is weaker than that in allyl acetate (*cf.* the resonance stabilization energies of allyl and benzhydryl radicals) it is inferred that *association of a nickel carbonyl moiety with an allylic C=C moiety is a prerequisite*. Moreover, the phenacyl and benzoin acetate failures indicate the specific need for carbon-carbon unsaturation, in accord with the expected firmer complexing at the weaker C=C pi bonds. Subsequent reaction may be envisioned as a metal-facilitated ionization of acetate ion (2). Postulated intermediate 1 is plainly analogous to complex 2 recently isolated by Heck, Chien and Breslow[4], which also decomposes to biallyl upon warming to room temperature.



1 2 (2)

Complex 1 also provides a ready explanation for the inertness of homoallylic acetates.

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[4] R.F. Heck, J.C.W. Chien and D.S. Breslow, *Chem. & Ind.* 986 (1961). Prepared from allyl chloride and triphenylphosphine nickeltricarbonyl at reduced temperatures. The reaction of nickel carbonyl with allylic halides is a general one.[5,6,7]

The reaction would thus seem to be fairly specific for allylic esters in the domain of oxygen functions. However, if the C-O bond is attenuated enough and/or a sufficiently nimble leaving group provided C-O cleavages should also be observable in non-allylic systems. The point is under scrutiny, and it thus far appears that certain active toluenesulfonate esters (e.g. benzhydryl) are coupled and certain active epoxides (styrene oxide) deoxygenated under our present mild conditions.

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[5] Belgian Patent 448,884 (1943).

[6] I.D. Webb and G.T. Borcherdt, J. Amer. Chem. Soc. **73**, 2654 (1951).

[7] I.D. Webb, U.S. Patent 2,654,787 (1953).