Synthesis of Conjugated Dienes using Cobalt Acetylene Complexes

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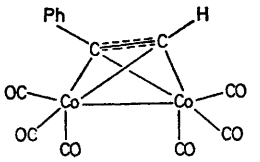
Summary Unsaturated aldehydes, ketones, esters and nitriles add acetylenes in the form of their hexacarbonyldicobalt complexes to give the corresponding conjugated dienes.

PREVIOUSLY we have shown[1] that reaction of strained alkenes with acetylenehexacarbonyldicobalt complexes provides a useful synthesis of cyclopentenone derivatives. Simple unstrained alkenes are unreactive under the same conditions, but we now find that those bearing one or more electron-withdrawing groups yield conjugated dienes by addition to the acetylenic ligand. Thus ethyl crotonate reacts with (phenylacetylene)hexacarbonyldicobalt according to equation (1). The ester produced (*ca.* 45%) is a mixture of the *trans,trans* and 2-*cis*,4-*trans* isomers (*ca.* 3·5 : 1) and was identified by m.s., n.m.r., hydrolysis to the corresponding acids which were separated, and by i.r. and n.m.r. comparison of the mixed esters and *trans,trans*-acid with authentic samples.[2]

Crotonaldehyde added similarly to the complex to give chiefly the *trans,trans*-aldehyde from which the same acid was obtained by silver oxide oxidation. Acrylonitrile gave the analogous product, cinnamylidene-acetonitrile and we have further demonstrated the applicability of the reaction to unsaturated ketones and diesters.



+MeCH=CHCO$_2$Et → PhCH=CHCMe=CHCO$_2$Et (1)

The direction of addition to the acetylene appears to be highly specific and we are continuing to explore this specificity and the range of applicability of this new synthesis with other alkyne and alkene components.

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