

A Mild, Regiospecific But-2-enolide Synthesis and a Convenient Preparation of Acylated Dienes

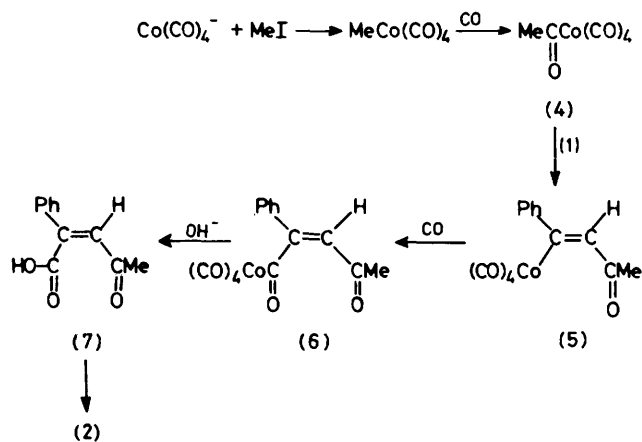
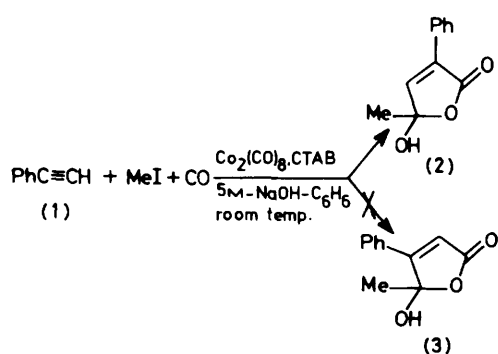
By HOWARD ALPER,* JANIE K. CURRIE, and HERVÉ DES ABBAYES

(Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5)

Summary Phase transfer-catalysed, cobalt carbonyl-catalysed reaction of alkynes with carbon monoxide and methyl iodide affords but-2-enolides; acylation occurs if dienes instead of alkynes are used as reactants.

BUT-2-ENOLIDES are an important class of naturally occurring compounds, some derivatives of which possess significant biological activity.¹ We now report a very mild, regiospecific synthesis of hydroxybutenolides, by cobalt carbonyl catalysed carbonylation of alkynes using phase transfer catalysis. Recent results have shown the latter technique to be an excellent one for effecting metal carbonyl-catalysed reactions.²⁻⁴

The cobalt tetracarbonyl anion, generated^{2,5} by vigorous stirring of a mixture of $\text{Co}_2(\text{CO})_8$ in benzene and 5M-NaOH containing cetyltrimethylammonium bromide (CTAB), was treated with an excess of methyl iodide, phenylacetylene (1) (25:1 ratio of alkyne to Co), and carbon monoxide (1 atm.) at room temperature to give the hydroxybutenolide (2) in 44% yield.† None of the isomeric butenolide (3) was detected. Hydroxybutenolides were similarly obtained from cyclohexylacetylene (18% yield) and from 17-ethynyltestosterone (68% yield).



SCHEME

† The structures of the products were determined on the basis of analytical and spectral data (i.r., n.m.r., m.s.), and in several instances by comparison of properties with authentic materials.

A possible mechanism for formation of the but-2-enolides is outlined in the Scheme. Addition of the acylcobalt tetracarbonyl^{2,3} to the alkyne would give the vinylcobalt complex (5). Carbon monoxide-induced ligand migration⁶ of (5) would afford (6) which, on hydroxide cleavage, would be converted into (7), the open-chain form of the butenolide (2). In the absence of OH⁻, (6) would be converted into a π -allyl complex, a much less favourable alternative pathway.⁷

Acylated dienes can be conveniently synthesized by phase transfer catalysis, simply by use of a diene instead of an alkyne as a reactant (other reaction conditions being the

same as for the synthesis of butenolides). For instance, cyclohexa-1,3-diene gave 1-acetylcyclohexa-1,3-diene in 54% yield and an isomeric mixture of diacylated cyclohexadienes in 21% yield. 1,4-Diphenylbuta-1,3-diene, 1-methoxybuta-1,3-diene, and cyclo-octa-1,3-diene were acylated under identical conditions (room temperature, atmospheric pressure) to give monoacylated dienes in 32, 13, and 40% yields, respectively.

We are indebted to the National Research Council of Canada for support of this research.

(Received, 17th November 1977; Com. 1188.)

¹ S. F. Martin and D. R. Moore, *Tetrahedron Letters*, 1976, 4459 and references cited therein.

² H. Alper and H. des Abbayes, *J. Organometallic Chem.*, 1977, **134**, C11.

³ L. Cassar and M. Foa, *J. Organometallic Chem.*, 1977, **134**, C15.

⁴ H. Alper, K. D. Logbo, and H. des Abbayes, *Tetrahedron Letters*, 1977, 2861

⁵ H. Alper, H. des Abbayes, and D. Des Roches, *J. Organometallic Chem.*, 1976, **121**, C31.

⁶ F. Calderazzo, *Angew. Chem. Internat. Edn.*, 1977, **16**, 299.

⁷ R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2819.