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THE REGIOSPECIFIC COBALT CARBONYL CATALYZED SYNTHESIS OF DIENONES AND TRIENONES BY PHASE TRANSFER CATALYSIS

Howard Alper* and Janie K. Currie
Department of Chemistry, University of Ottawa
Ottawa, Ontario, Canada K1N 9B4

Summary: The phase transfer catalyzed, cobalt carbonyl catalyzed reaction of dienes, and a triene, with methyl iodide and carbon monoxide [r.t., 1 atm. P] is highly regiospecific, affording E-conjugated enones.

We have recently noted that 1,3-dienes can be acylated by phase transfer catalyzed[1] reaction of the organic substrates with methyl iodide and carbon monoxide in the presence of catalytic amounts of dicobalt octacarbonyl.[2] Not only is this process effected under very gentle conditions [r.t., 1 atm. P], but the yields of <u>isolated</u> products are significantly superior to those obtained by carrying out the reaction under homogeneous conditions [at 50-85°C, 50-130 p.s.i.; 10-23% yields].[3] We now wish to report on the remarkable regiospecificity of this reaction for a variety of conjugated dienes and trienes.

1-Vinylcyclohexene (1) undergoes acylation [conditions as previously described][2] only at the least substituted carbon of the diene to give <u>only</u> the E(trans) isomer, 2, in 60-63% yield (Table 1). Acylation of 2-methyl-1,3-butadiene [isoprene] occurs at the terminal carbon furthest removed from that bearing the methyl substituent (4). Both 1-ferrocenyl (5) and 1-phenyl-1,3-butadiene (7) experienced acylation at the 4-position to give the E-products only (i.e. 6 and 8, respectively). Furthermore, the all-trans trienone (10) was obtained from 1-phenyl-1,3,5-hexatriene (9).

This regiospecific synthesis of conjugated dienones and trienones may occur via 1,2-addition of the <u>in situ</u> generated acetylcobalt tetracarbonyl [from $Co(CO)_4^-$, CH_3I, and CO] to the least substituted double bond of the diene or triene to give the σ-allyl complex (e.g. 11 from 1). Carbon monoxide loss from 11 would afford the π-allyl complex 12. Simple π-allyl complexes can be synthesized by phase transfer catalysis.[4] Here, the methylene hydrogens of the β-keto π-allyl system are expected to be acidic, and 13 could then be formed by proton removal under the phase transfer conditions. Decomplexation of 13 in the presence of CO would afford the product, 2, and regenerate the $Co(CO)_4^-$ ion. It is

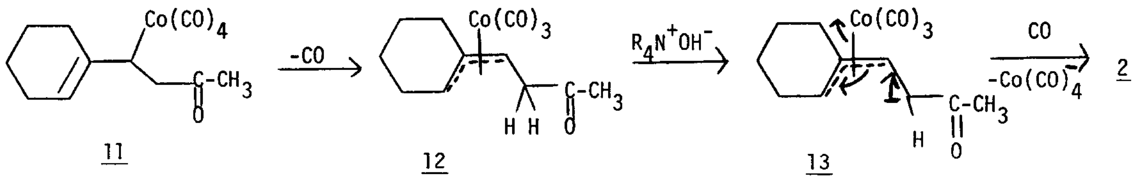
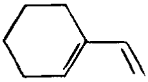
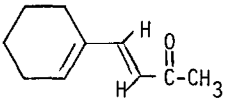
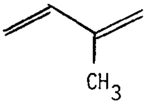
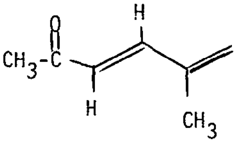
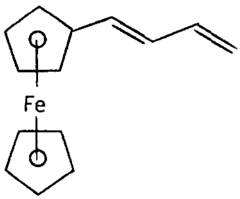
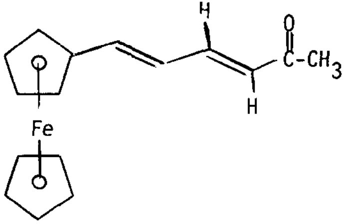
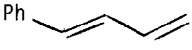
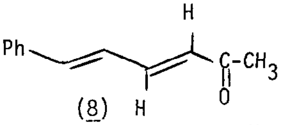
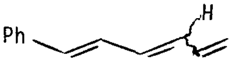
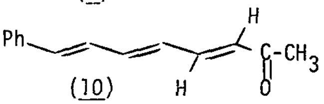


Table 1: DI- AND TRIENONE SYNTHESIS BY PHASE TRANSFER CATALYSIS

Reactant	Product[a]	Yield[b], %
 (1)	 (2)	60-63
 (3)	 (4)	42
 (5)	 (6)	82
 (7)	 (8)	86
 (9)	 (10)	43

[a] The structures of the products were determined on the basis of analytical and spectral data [ir,uv,ms,nmr(^{1}H,^{13}C--operating in FD and SFORD modes]. [b]The yields are of pure materials.

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conceivable that the already substantial sp^2 character of carbanion 13 [in contrast to normal Elcb processes where there is little sp^2 character in the carbanion intermediate] is responsible for producing the more thermodynamically stable E isomer.

The regiospecific nature of the above reactions makes the phase transfer catalyzed acylation procedure one of considerable potential in synthetic organic chemistry.

ACKNOWLEDGMENT

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