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SYNTHESIS OF SKIPPED (1,4) DIYNES VIA COUPLING OF (PROPARGYL ACETATE)DICOBALT HEXACARBONYL COMPLEXES WITH ALKYNYL ALANES

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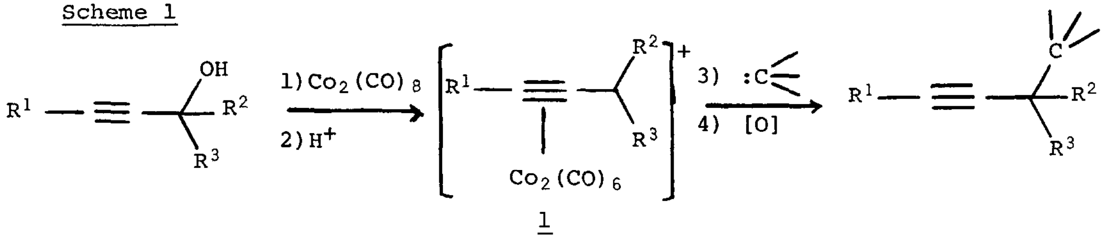
Abstract: A general, highly selective route to skipped (1,4) diynes, including the hitherto unknown 3-substituted derivatives, is provided by the reactions of (propargyl acetate)$Co_2(CO)_6$ complexes with trialkynyl alanes and subsequent demetallation.

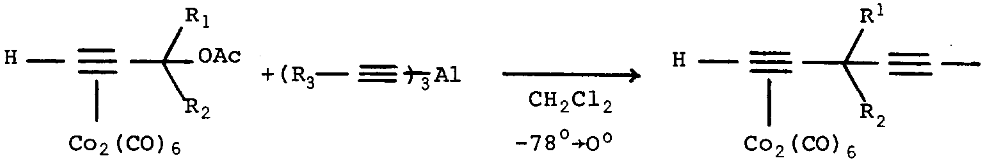
We have been interested in the synthetic potential of the cobalt-stabilized propargyl cations 1, particularly with respect to their function as propargyl electrophiles in carbon-carbon bond-forming reactions (Scheme 1).

Scheme 1



In earlier studies we found the coupling of cations 1 with a variety of nucleophiles including aromatics,[1] β-dicarbonyls,[2] ketones and enol derivatives,[3] allyl silanes,[4] and trimethylaluminum[5] to be an efficient propargylation method, free from the allenic by-products associated with reactions of typical propargyl electrophiles.[6] This result combined with the ready introduction[7] and removal[8] of the $-Co_2(CO)_6$ moiety under mild conditions single out Scheme 1 as the preferred method in most instances for introduction of the synthetically versatile propargyl function.

In the course of our current efforts to develop general methods for propargyl/alkyl coupling utilizing 1 (or appropriate precursors) and metal alkyls, we have now found that (propargyl acetate)$Co_2(CO)_6$ complexes 2 react smoothly and efficiently with trialkynyl alanes to form the corresponding 1,4-diyne complexes 3 and 4 (eq. 1).



(eq. 1)

2

a: $R_1=R_2=H$
b: $R_1=CH_3$; $R_2=H$
c: $R_1=H$; $R_2=Ph$
d: $R_1=R_2=CH_3$

3 (R_3=n-Bu)
4 (R_3=n-Hex)

Simple addition of a methylene chloride solution of freshly prepared trialkynyl alane (R_3 = C_4H_9, C_6H_{13})[9] to the acetate complexes 2[5] in CH_2Cl_2 at 0° (or better, -78°) resulted in a rapid reaction (20-30 min. at 0°; 3-4 hrs at -78°) as indicated by TLC (silica). Aqueous workup followed by preparative TLC or flash column chromatography afforded the pure diyne complexes as dark red oils in moderate to excellent yields (Table).[10]

Table. Coupling Reactions of $[HC{\equiv}CC(OAc)R_1R_2]Co_2(CO)_6$ with $(R_3C{\equiv}C)_3Al$

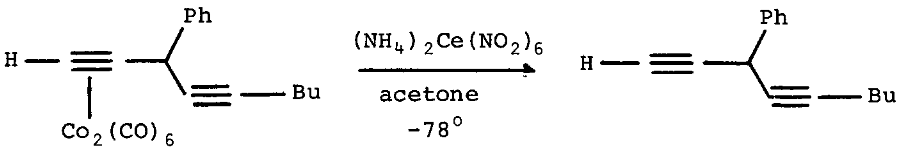
Complex	$(R_3C{\equiv}C)_3Al$	Product	Yield (%)[a]
2a	$(n\text{-}BuC{\equiv}C)_3Al$	3a	66
2b	$(n\text{-}BuC{\equiv}C)_3Al$	3b	61
2b	$(n\text{-}BuC{\equiv}C)_3Al$	3b	94[b]
2c	$(n\text{-}BuC{\equiv}C)_3Al$	3c	77
2d	$(n\text{-}BuC{\equiv}C)_3Al$	3d	48[c]
2c	$(n\text{-}HexC{\equiv}C)_3Al$	4c	46

[a] Reactions conducted at 0° unless otherwise indicated. [b] Reaction at -78°.
[c] The elimination product $[HC{\equiv}CCMe{=}CH_2]Co_2(CO)_6$ (14%), was also formed.

The ready availability of a wide variety of the precursor propargyl alcohols and alkynylalanes makes the present reaction a convenient, selective, and flexible route to 1,4-diynes including the apparently hitherto unknown 3-substituted derivatives (e.g. 3b-3d). Formation of a quaternary center in 3d with only a modest (and separable) amount of elimination product is particularly noteworthy. Prior preparative reports of unsubstituted skipped diynes involving copper-catalyzed coupling of propargyl halides and alkynyl

Grignard reagents indicate in several instances the co-production of the conjugated diyne and allene derivatives.[11]

The free diynes and alkynes in general may be recovered from their -$Co_2(CO)_6$ complexes upon mild oxidative treatment.[8,12] Typical is the low temperature demetallation of 3c with $(NH_4)_2Ce(NO_2)_6$ affording 3-phenyl-1,4-nonadiyne [b.p.(Kugelrohr) 70°/0.2mm; IR(CH_2Cl_2): 3290 (s, H-C≡C-), 2260 (vw, -C≡C-), 2120 (w, HC≡C-)cm^{-1}; ^1H NMR(CD_2Cl_2): δ7.3(m,5H), 4.65(m,1H), 2.3(d,1H), 2.2(m,2H), 1.45(m,4H) and 0.9(t,3H); MS m/e 196; Anal. Calcd. for $C_{15}H_{16}$: C, 91.84; H,8.16. Found: C, 91.50; H, 8.27%] in 83% isolated yield:[13]



3c

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10. The structures of all new compounds were confirmed by their IR and NMR spectra and by satisfactory elemental analyses.

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13. To 0.8g (1.7mmol) of **3c** dissolved in 30ml of acetone, cooled to -78° was added portionwise a large excess (15g) of ceric ammonium nitrate over one hour. After stirring for an additional hour, the mixture was poured into 200ml of ice-cold water and extracted with ether (3x100ml). The ether extracts were dried over $MgSO_4$ and concentrated. Kugelrohr distillation of the crude mixture at 70°/0.2mm afforded the pure compound in 83% yield.

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