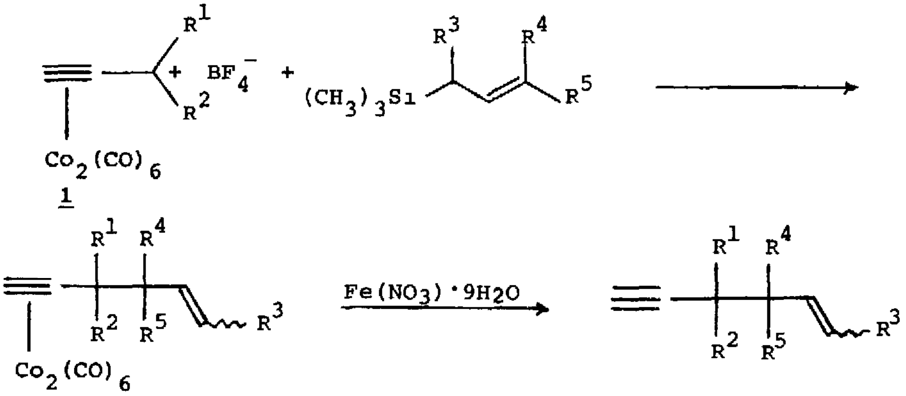
Tetrahedron Letters Vol. 21, pp 1595 - 1598
© Pergamon Press Ltd. 1980. Printed in Great Britain
0040-4039/80/0422-1595$02.00/0

SYNTHETIC APPLICATIONS OF METAL-STABILIZED CARBENIUM IONS.IV. PREPARATION OF 1,5-ENE-YNES VIA COUPLING OF [(PROPARGYL)DICOBALT HEXACARBONYL] CATIONS WITH ALLYL SILANES.

Joseph E. O'Boyle and Kenneth M. Nicholas*
Department of Chemistry, Boston College
Chestnut Hill, Massachusettes 02167

Abstract: A highly selective and flexible route to 1,5-ene-ynes is provided by the reactions of [(propargyl)dicobalt hexacarbonyl] cations with allyl silanes.

We have been exploring the potential of the cobalt complexes $[(RC{\equiv}CCR_2)$-$Co_2(CO)_6]BF_4$(1)[1] as propargyl cation equivalents and have found these species to be highly effective propargylating agents for aromatics[2], β-dicarbonyl compounds[3], ketones[4], and enol derivatives of ketones[4]. A crucial feature of these reactions is a total absence of the allenic by-products which generally mar conventional reactions involving propargyl halides (as electrophiles) or propargyl Grignard reagents (as nucleophiles)[5,6]. We now report a highly selective route to 1,5-ene-ynes, useful intermediates in the synthesis of acyclic isoprenoids[7], via coupling of readily available, nucleophilic allyltrimethyl silanes[8] with the propargyl complexes 1.



Simple admixture of a methylene chloride solution of allyl silanes 2-4 and the cobalt salts 1[1] at 0° results in rapid reaction from which the ene-yne complexes 5-7 can be isolated, generally in good to excellent yields (See Table).

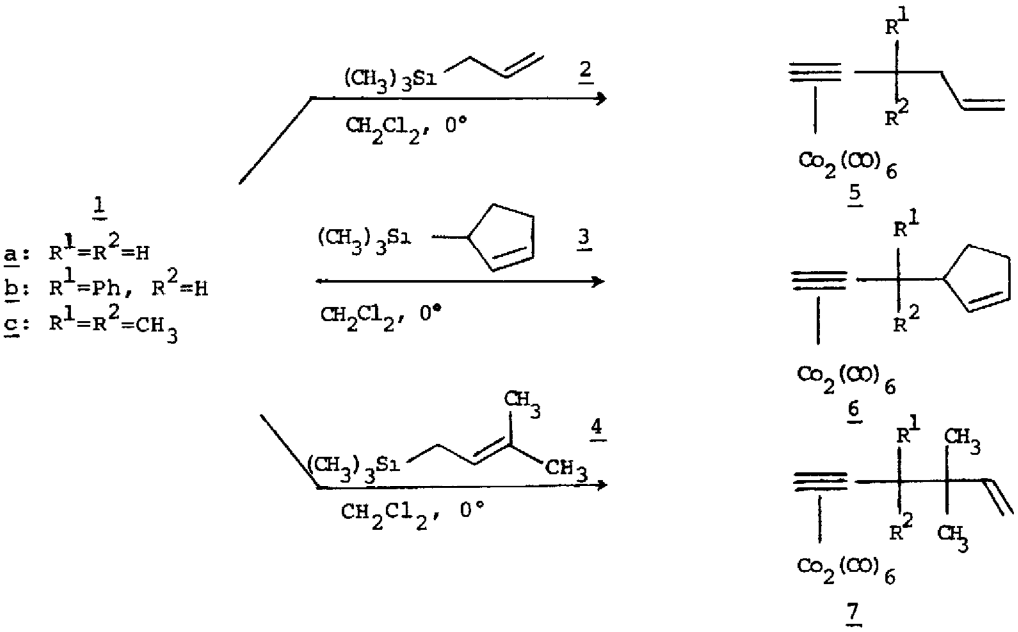


Table. Coupling Reactions of $[(HC{\equiv}CCR^1R^2)Co_2(CO)_6]BF_4$ with Allyl Silanes

Silane	Complex	Product	Yield(%)
2	1a	5a ($R^1=R^2=H$)	83[a]
	1b	5b ($R^1=Ph$; $R^2=H$)	92[a]
	1c	5c ($R^1=R^2=CH_3$)	70[a]
3	1a	6a	79[a]
	1b	6b	97[b]
	1c	6c	92[a]
4	1a	7a	95[b]
	2a	7b	91[b]
	3a	7c	0

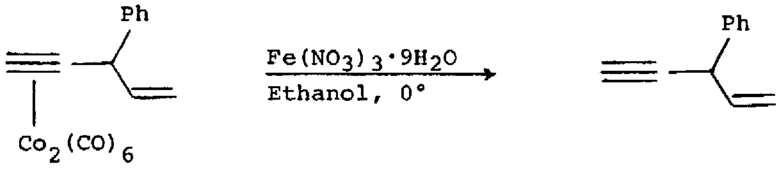
[a] After column chromatography.

[b] Before column chromatography; TLC (silica gel, petroleum ether) exhibited only one spot.

The general procedure employed was as follows: a solution containing 1 - 2 mmol of the silane in dry CH_2Cl_2 (7 - 10 ml) was added to 1.0 mmol of the cobalt complex under N_2 and stirred at 0° for approximately 30 minutes. Excess solid $NaHCO_3$ and $MgSO_4$ were added and stirring continued for an additional 10 minutes. After filtration, evaporative removal of volatiles from the filtrate left the product complexes as dark red oils or low melting solids, essentially pure judging by TLC and ^{1}H NMR[9]. Analytically pure samples were obtained by column chromatography over silica gel (petroleum ether eluant)[11].

An important feature of this reaction is its flexibility for producing a wide variety of substituted 1,5-ene-ynes. In particular, we note the efficient generation of quarternary centers without competing elimination by combining the dimethyl-substituted cation 1c with silanes 2 and 3. As is generally observed, electrophilic substitution of the silane proceeds with allylic inversion[12] as illustrated by the reaction of 3,3-dimethylallyl silane 4 (i.e. 1a + 4 → 5a, 1b + 4 → 5b). The reaction between 4 and cation 1c was very sluggish and afforded after several hours only the products of deprotonation - $(HC{\equiv}CCMe{=}CH_2)Co_2(CC)_6$ (21%) and its dimer, $[HC{\equiv}CC(CH_2)CH_2C(CH_3)_2C{\equiv}CH][Co_2(CO)_6]_2$ (8%) - and hydrolysis, $[HC{\equiv}CC(CH_3)_2OH]Co_2(CO)_6$ (∿50%).

Decomplexation is readily achieved as reported previously[13], by treatment of the (alkyne)$Co_2(CO)_6$ complexes with excess $Fe(NO_3)_3{\cdot}9H_2O$ in ethanol. Typical is the oxidative demetallation of 5b to afford 3-phenyl-5-hexene-1-yne in 96% isolated yield[14].



5b

Acknowledgments: We are grateful for support provided by the National Institutes of Health (GM 26760-01) and the Donors of the Petroleum Research Fund, administered by the American Chemical Society (#11519-AC 1,3).

References and Notes

1. R.E. Connor and K.M. Nicholas, J. Organometal. Chem., 125, C45 (1977).
2. R.F. Lockwood and K.M. Nicholas, Tetrahedron Lett., 4163 (1977).
3. H.D. Hodes and K.M. Nicholas, ibid, 4349 (1978).
4. K.M. Nicholas, M. Mulvaney, and M. Bayer, J. Am. Chem. Soc., in press.
5. a) L. Gouin, M.-C. Faroux, and O. Riobe, Bull. Soc. Chem. France, 2320 (1966);
   b) G. Fontaine, C. Andre', J. Jolivet, and P. Maitte, ibid, 1447 (1963);
   c) A. Schaap, L. Brandsma, and J.F. Arens, Rec. Trac. Chim., 86, 393 (1967);
   d) J.H. Wotiz, J. Am. Chem. Soc., 72, 1639 (1950) and 73, 693 (1951);

e) T.L. Jacobs, R. Akawie, and R.G. Cooper, *ibid*, *73*, 1273 (1951);
f) A.F. Bramwell, L. Crombie, and M.H. Knight, *Chem. Ind.*, 1265 (1965) and references therein.
g) G.F. Hennion and F.X. Quinn, *J. Org. Chem.*, *35*, 3054 (1970).

6. Corey and coworkers have described the use of $(CH_3)_3SiC{\equiv}CCH_2Li$ for highly (but not completely) selective introduction of the *unsubstituted* propargyl group (ref. 7a).

7. a) E.J. Corey and H.A. Kirst, *Tetrahedron Lett.*, 5041 (1968);
   b) E.J. Corey, J.A. Katzenellenbogen, N.W. Gilman, S. Roman, and B. Erickson, *J. Am. Chem. Soc.*, *90*, 5618 (1968);
   c) E.J. Corey and K. Achiwa, *Tetrahedron Lett.*, 2245 (1970).

8. Review: E.W. Colvin, *Chem. Soc. Rev.*, *7*, 15 (1978).

9. We suspect that $(CH_3)_3SiF$ and BF_3 are the other products because of the white vapor produced upon exposure of the reaction mixture to air and the absence of NMR resonances attributable to the $(CH_3)_3Si$- group in the reaction residues after solvent removal. Additionally, the cleavage of t-butyldimethylsilyl ethers by $LiBF_4$ has recently been reported (ref. 10).

10. B.W. Metcalf, J.P. Burkhart, and K. Jund, *Tetrahedron Lett.*, 35 (1980).

11. The structures of all new compounds were confirmed by their IR and NMR spectra and, in most cases, by satisfactory elemental (C,H) analyses.

12. R. Calas and E. Frainnet, *Compt. Rend.*, *240*, 203 (1955); *ibid*, 243, 595 (1956); J.-P. Pillot, J. Dunogues, and R. Calas, *Tetrahedron Lett.*, 1871, 2449 (1971).

13. K.M. Nicholas and R. Pettit, *Tetrahedron Lett.*, 3475 (1971).

14. To 1.37g (3.10 mmol) of *5b* dissolved in 10 ml of absolute EtOH was added portionwise a large excess of $Fe(NO_3)_3 \cdot 9H_2O$ over one hour. After stirring for 5 hours, the mixture was poured into 100 ml of H_2O and extracted thrice with ether (50 ml). The ether extracts were dried over $MgSO_4$ and concentrated to provide 0.45g (2.87 mmol) of 3-phenyl-5-hexene-1-yne [Bp. 85 - 90°/20 mm; IR (CCl4): 3300, 2110, 1650 cm^{-1}; NMR ($CDCl_3$): δ7.1 (bs, 5H), 4.8 - 6.0 (m,3H), 3.6 (dt, J=7Hz, J=2Hz, 1H), 2.6 (m,2H), and 2.1 (d, J=2Hz, 1H); MS: m/e 156 (P)].

(Received in USA 6 February 1980)