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Preliminary communication

Tetrahydrofuran as an one-electron donor: Highly diastereoselective coupling of cobalt-complexed propargyl alcohol

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Abstract

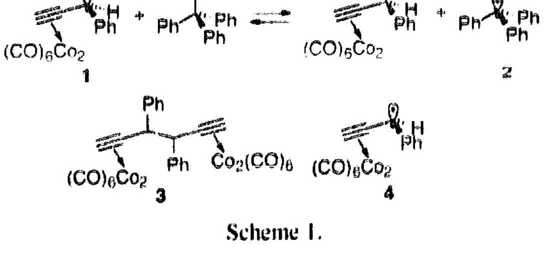
A novel one-step reductive dimerization of Co-complexed propargyl alcohol **5** has been developed producing dl- and meso-(3,4-diphenyl-1,5-hexadiyne)-bis-dicobalt hexacarbonyl (**8**,**9**) with unprecedented diastereoselectivity of 90%. A tandem action of a variety of one-electron/hydride ion donors and Brönsted Lewis acids has been tested both in one- and two-step methods with the latter including the isolation of propargyl cation **1**. © 1997 Elsevier Science S.A.

Keywords: Propargyl cation; Propargyl radical; Single-electron transfer; Reductive dimerization; Diastereoselectivity

1. Experimental

In connection with our program investigating the chemistry and electronic nature of transition metal complexed reactive intermediates [1] we studied an equilibrium between $Co_2(CO)_6$-complexed propargyl cation **1** and now-classical triphenylmethyl cation **2** [2]. To our surprise, we found that a *chemical reaction* occurs affording dimeric product **3**. Its formation can be interpreted in terms of one-electron transfer to propargyl cation **1** and subsequent coupling of cobalt-complexed propargyl radical **4**. This observation prompted us to examine various classes of organic compounds as prospective one-electron donors, and to establish diastereo- and chemoselectivities of the reaction, i.e. single electron transfer (SET) vs. hydride ion transfer (HIT). We report herein a novel one-step dimerization of Co-complexed propargyl alcohol mediated by Brönsted/Lewis acids and mild hydride ion donors, such as, tetrahydrofuran (THF) (Scheme 1).

The overall mechanism of the process is depicted on Scheme 2 with THF acting as a one-electron/hydride ion source. The first step includes a treatment of Co-complexed propargyl alcohol **5** with HBF_4 [3] and isolation of the cation **1** as a dark-red powder in 85% yield. At the second step, a solution of cation **1** in CH_2Cl_2 is treated at ambient temperature with a two-fold excess of THF or other donors (Table 1). While the mechanistic experiments are underway, the tentative hypothesis includes the coordination of 'hydride ion' with cationic center and formation of the transition state **6** with bridging hydrogen atom and three-center, two-electron molecular fragment. Alternative pathways are represented by a single electron transfer generating Co-complexed propargyl radical **4** and a hydride ion transfer affording hydrocarbon **7** [4]. The former undergoes an intermolecular dimerization producing diastereomers of Co-complexed 3,4-diphenyl-1,5-hexadiyne **8** and **9** [5]. Crucial parameters of the process are chemo- and diastereoselectivities indicated by ratios of SET (**8** + **9** + **10**): HIT (**7**) products and dl-(**8**): meso-(**9**) isomers, respectively. We found that SET and HIT are *competitive processes with the former one being inversely proportional to hydridic character of donor molecule.*



Scheme 1.

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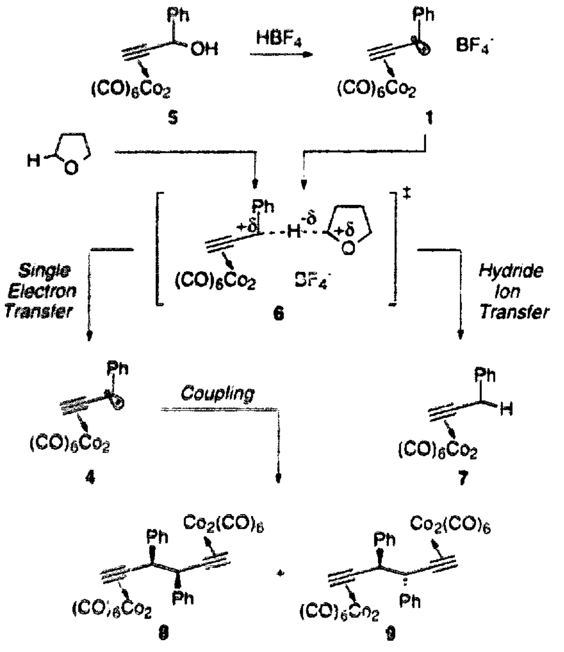
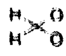
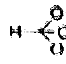


Scheme 2.

Thus, 1,4-cyclohexadiene and tributyltin hydride act as efficient hydride ion donors resulting in preponderant formation of hydrocarbon **7** (SET:HIT 39:61 and 4:96, respectively). To the contrary, milder hydride ion donors (Table 1) allow for a one-electron reduction to become a major reaction path. Among those tested, the most efficient reagents are THF and 1,3-dioxolane providing better yields (46% and 38%) and excellent chemo- (SET:HIT 99:1 and 94:6) and stereoselectivities (de 90% and 90%). It is noteworthy that the level of stereocontrol achieved in these reactions is rather unprecedented both for organic [6–8] and organometallic [9–12] radical dimerizations mostly occurring stereorandomly. Recent Zn-mediated coupling of Co-complexed propargyl cations occurs with de of 50% and constitutes the highest diastereoselectivity ever reported [13]. A remote analogy to the observed phenomenon is represented by an amply documented bridged electron transfer between transition metal ions [14]. The process is central to biology and chemistry [15] with halide atoms and hydroxy and cyano groups serving as monatomic bridges [14].

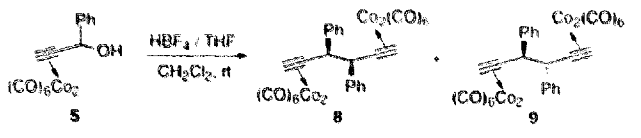
Table 1
Chemo- and diastereoselectivities of the interaction of carbocation **1** with one-electron/hydride ion donors

Entry	e⁻/H⁻ Donor	dl : meso : HIT **8** : **9** : **7**	SET^a : HIT	de	Yield, %^{b} **8**+**9**
1		93 : 5 : 1^c	99 : 1	90	46
2		88 : 5 : 6^c	94 : 6	90	38
3		95 : 3 : 0^{c,d}	100 : 0	94	32
4		92 : 8 : 0^d	100 : 0	84	27
5		70 : 13 : 14^c	86 : 14	68	37
6		90 : 5 : 0^c	100 : 0	90	26

[a] Includes bis-clusters **8** and **9** and mono-cluster **10**;
[b] Yields of reduction step;
[c] Formation of mono-cluster **10** was also observed; entries 1 (1%), 2 (1%), 3 (2%), 5 (3%) and 6 (5%);
[d] Complex [HC≡CCH(OMe)Ph]Co$_2$(CO)$_6$ derived from the MeO-group transfer to cation **1** was also isolated with the yield of 11% (entry 3) and 60% (entry 4).

To make the THF-induced reductive dimerization more attractive from the synthetic viewpoint, we developed its *one-step version, i.e. direct coupling of propargyl alcohol* **5** *without isolation of the intermediate carbocation* **1**. The method includes a tandem use of hydride ion donors and Brönsted/Lewis acids, and the major obstacle here is their compatibility. Multiple combinations of both components were tested and the best 'matching pair' appeared to be THF/HBF$_4$. An optimized procedure includes the treatment of Co-complex **5** with two-fold excess of HBF$_4$ and THF at ambient temperature in CH$_2$Cl$_2$ (4.5h). The formation of HIT product **7** was not observed at all, whereas dimerization occurs in a good yield (47%) producing diastereomers **8** and **9** in ratio of 95:5. The process features a remarkable simplicity combined with high chemo- and stereoselectivities [16]. Analogous results were obtained with 1,3-dioxolane/HBF$_4$ pair. Other acids were less efficient resulting in lower yields and decreased stereoselectivity (Brönsted/Lewis acid, de, yield: BF$_3$ · Et$_2$O, 84, 26; Tf$_2$O, 88, 24; TsOH, 72, 3).

To prove that the observed diastereoselectivity is genuine and not resulted from selective destruction of one stereoisomer, we carried out a control experiment with an increased five-fold excess of HBF$_4$. The ratio of isomeric dimers remained the same indicating that stability of isomers is comparable under reaction conditions. Another piece of evidence is provided by comparison of the stereochemical outcome in one- and two-step



Scheme 3.

processes. The latter is carried out in the absence of HBF_4, and higher de value can be anticipated if acid-induced selective decomposition does take place. In fact, diastereoselectivity remains the same (90%), as well as the yield of coupling products does (46–47%) (Scheme 3).

We also developed the '*column-chromatographic*' version of the parent reaction that includes filtration of alcohol **5** through Amberlyst-packed column (H^+-form) with THF as a coeluent. Although both yield and diastereoselectivity dropped (18%, de 44%), the method nevertheless affords dimeric product and further optimization can make it competitive with 'in-flask' procedure.

2. Representative experiment

dl- and meso-μ-η^2-(3,4-Diphenyl-1,5-hexadiyne)-bis-dicobalt hexacarbonyl (**8**,**9**).

Under nitrogen atmosphere, a solution of complex **5** (105 mg, 0.25 mmol) and THF (36 mg, 0.5 mmol) in CH_2Cl_2 (2.5 mL, 0.1M) was cooled down (-5°C) and treated with $HBF_4 \cdot Et_2O$ (74 μL, 81 mg, 0.5 mmol). The reaction mixture was allowed to warm over to room temperature (30 min) and stirred for 4.5h (TLC control). The products **8** and **9** were isolated by column chromatography (Florisil, anaerobic conditions, 60–100 mesh, 14 g, PE). Obtained were **8** and **9** (47 mg, 47%, 95:5, de 90%) as dark-red crystals which were identical by physico-chemical and spectral (TLC, NMR, FAB) data with authentic samples synthesized according to known procedure [13].

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References

[1] (a) G.G. Melikyan, V.M. Mkrtchyan, K.A. Atanesyan, G.Kh. Asaryan, Sh.O. Badanyan, Bioorg. Khim. 16 (1990) 1000; C.A. 113(25) 230995j; (b) G.G. Melikyan, A. Mineif, O. Vostrowsky, H.J. Bestmann, Synthesis (1991) 633; (c) G.G. Melikyan, O. Vostrowsky, W. Bauer, H.J. Bestmann, J. Organometal. Chem. 423 (1992) C24.

[2] H.H. Freedman, in: G.A. Olah, P.R. Schleyer (Eds.), Carbonium Ions, vol.4, Wiley, NY, 1973, p. 1501.

[3] K.M. Nicholas, Acc. Chem. Res. 20 (1987) 207.

[4] Alternative scenario includes a one-electron oxidation of C-H bond by cation **1**, and subsequent dimerization of propargyl radical **4**.

[5] Mono-cluster (3,4-diphenyl-1,5-hexadiyne)dicobalt hexacarbonyl (**10**) is also formed as a minor product.

[6] C. Ruchardt, Top. Curr. Chem. 88 (1980) 1; K.H. Eichin, K.J. McCullough, H.D. Beckhaus, C. Ruchardt, Angew. Chem., Int. Ed. Engl. 17 (1978) 934 and references therein.

[7] N.A. Porter, P.J. Krebs, in: E.L. Eliel, S.H. Wilen (Eds.), Topics in Stereochemistry 18 (1988) 97.

[8] L.A. Paquette, I. Itoh, K.B. Lipkowitz, J. Org. Chem. 41 (1976) 3524.

[9] (Pentadienyl)$Fe(CO)_3$: (a) J.E. Mahler, D.H. Gibson, R. Pettit, J. Am. Chem. Soc. 85 (1963) 3959; (b) A.J. Pearson, Y. Chen, M.L. Daroux, A.A. Tanaka, M. Zettler, J. Chem. Soc. Chem. Comm. (1987) 155.

[10] (Propargyl)$Cp_2Mo_2(CO)_4$: N. Berre-Cosquer, R. Kergoat P. L'Haridon, Organometallics 11 (1992) 721.

[11] (Benzyl)$Cr(CO)_3$: S. Top, G. Jaouen, J. Organomet. Chem. 336 (1987) 143.

[12] In some cases the stereoselectivity of dimerization has not been reported: (a) ferrocenylcarbinols: M. Cais, A. Eisenstadt, J. Org. Chem. 30 (1965) 1148; (b) $CpCo(\eta^5\text{-}C_7H_9)^+ PF_6$: W.E. Geiger, T. Genneth, G.A. Lane, Organometallics 5 (1986) 1352; (c) (propargyl)$Co_2(CO)_6$: S. Padmanabhan, K.M. Nicholas, J. Organomet. Chem. 212 (1981) 115.

[13] G.G. Melikyan, R.C. Combs, J. Lamirand, M. Khan, K.M. Nicholas, Tetrahedron Lett. (1994) 363.

[14] R.D. Cannon, Electron Transfer Reactions, Butterworths, London, 1980.

[15] Electron transfer in inorganic, organic and biological systems, in: J.R. Bolton, N. Mataga, G. McLendon, Advances in Chemistry, Series 228, ACS, Washington, 1991.

[16] A remote analogy is represented by a spontaneous dimerization of ferrocenylmethanol in the presence of sulfuric acid: K.L. Rinehart, C.J. Michejda, P.A. Kittle, J. Am. Chem. Soc. 81 (1959) 3162. For one-step hydrogenolysis see Refs. (1a) and P.L. Pauson, W.E. Watts, J. Chem. Soc. (1962) 3880.