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Communications

Co₂(CO)₈-Catalyzed Reaction of Benzylic Acetates with HSiMe₃ and CO. A Novel Method for Homologation of Alcohols

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Summary: In the presence of $Co_2(CO)_8$, the reaction of benzyl acetates with HSiMe3 and carbon monoxide under mild reaction conditions (25 °C, 1 atm of CO) resulted in the incorporation of CO to give β -phenethyl alcohols. The reaction is applicable to naphthyl-, furanyl-, thiophenyl-, and even ferrocenyl methyl acetates.

One-carbon homologation of alcohols, is an important transformation both in organic chemistry research and in chemical industry, but this conversion usually requires multistep operations.¹ This is mainly due to the relatively unreactive nature of the carbon-oxygen bond to be cleaved and also to the unavailability of suitable synthetic equivalents for nucleophilic oxymethylation² at the carbonoxygen bond. The use of carbon monoxide as a one-carbon source provides one method for alcohol homologation,³ the most common catalysts being those containing cobalt or



rhodium.⁴ Although this direct transition metal catalyzed homologation is appealing, a serious drawback may be the necessity of drastic reaction conditions (high reaction temperatures and high pressures). We report that the synthetically useful transformation illustrated in eq 1 can be attained by employing $HSiR_3/CO/Co_2(CO)_8$ in a catalytic reaction.⁵ This new one-carbon extension reaction proceeds under mild reaction conditions even at ambient temperature under carbon monoxide at atmospheric pressure.



⁽⁴⁾ Recent papers on homologation of alcohols, see: Matsuzaki, T.; (4) Recent papers on homologation of alcohols, see: Matsuzaki, T.;
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^aReaction conditions: benzylic acetate (2.5 mmol), $HSiMe_3$ (25 mmol, 2.9 mL), $Co_2(CO)_8$ (0.1 mmol, 34 mg), benzene (5 mL) at 25 °C under CO (1 atm). ^bGC yields based on benzylic acetate. Isolated yields are in parentheses.

The reaction of benzyl alcohol with $HSiMe_3^6$ and CO in the presence of $Co_2(CO)_8$ did not lead to incorporation of CO and the only product obtained was the trimethylsilyl ether of benzyl alcohol. It was found, however, that benzyl esters reacted catalytically with $HSiMe_3$ and CO to afford trimethylsilyl ethers of β -phenethyl alcohol 2 (benzyl acetate, reaction time 5 days, 43% yield; benzyl formate, 8 days, 44%; benzyl trifluoroacetate, 2 days, 0%).^{7,8} Benzyl methyl ether also gave similar results (7 days, 60%). Because of their availability, acetates were chosen as substrates for further study.

The catalytic reaction of eq 1 gave better results for benzyl acetates 1 bearing electron-donating substituents (2, R = p-OCH₃, 76% yield, reaction time 17 h; R = oCH₃O, 79%, 12 h; R = p-CH₃, 75%, 2 days; R = o-CH₃, 75%, 3 days; R = H, 43%, 5 days; R = p-Cl, 52%, 5 days; R = p-CN, 0%, 2 days). Apparently, the development of positive charge seems important at the step in which the carbon-oxygen bond is cleaved by R₃SiCo(CO)₄, which could be a key catalyst species.⁹ Once alkylcobalt intermediate 3^{10} is formed, it is transformed into 2 successively via acylcobalt carbonyl and aldehyde intermediates (Scheme I).¹¹

The new catalytic reaction was applicable to various benzylic acetates, and the results are summarized in Table I. The reaction tolerated functional groups such as methylenedioxy (run 1), furanyl (runs 3–7), and thiophenyl (run 8) groups. Even a ferrocenylmethyl acetate underwent homologation in good yield (run 9). The dicobalt hexacarbonyl complex of propargyl acetate, however, gave a mixture of many products. Under these mild reaction conditions, the acetates of secondary alcohols also gave good yields of the homologated products without competitive β -hydride elimination from the corresponding secondary alkylcobalt intermediates (runs 4–6).¹² The present homologation method also applicable to cinnamyl acetate as shown below (eq 2).

 $Ph \checkmark OAc \qquad \frac{\text{HSiMe}_3, \text{ CO}}{\text{cat. } \text{Co}_2(\text{CO})_8} \qquad Ph \checkmark OSiMe_3 \qquad (2)$ $C_6H_6 \qquad 73\%$ 25 °C, 1 atm

Further application of this straightforward and unique method for homologation is in progress.

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Supplementary Material Available: Typical experimental procedures and spectral data for products (9 pages). Ordering information is given on any current masthead page.

A Stereospecific Synthesis of 3,3-Disubstituted Allylic Alcohols. The Intermolecular Pinacol Cross-Coupling Reaction between α,α -Disubstituted α -(Diphenylphosphinoyl)acetaldehydes (Ph₂P(O)CR¹R²CHO) and Saturated Aldehydes

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Summary: High diastereofacial selectivity is observed in the intermolecular pinacol cross-coupling of α , α -disubstituted α -(diphenylphosphinoyl)acetaldehydes with sat-

urated aldehydes. The diols obtained from these reactions are converted to (E)-allylic alcohols via a Horner-Wittig elimination reaction.

⁽⁶⁾ We have designed a special apparatus for handling the volatile $HSiMe_{31}$ (bp 6-7 °C). See ref 5.

⁽⁷⁾ All new compounds obtained gave satisfactory spectra and analytical (C, H) data; see the supplementary material.

⁽⁸⁾ The major side reactions are hydrogenation to toluene and twocarbon extension reactions leading to PhCH₂CH(OSiMe₃)CH₂OSiMe₃ and PhCH₂CH(OSiMe₃)=CHOSiMe₃.

⁽⁹⁾ The reaction of $HSiR_3$ and $Co_2(CO)_8$ has been known to give $R_3SiCo(CO)_4$. Chalk, A. J.; Harrod, J. F. J. Am. Chem. Soc. 1967, 89, 1640. Baay, Y. L.; MacDiarmid, A. Inorg. Chem. 1969, 8, 986. Sisak, A.; Ungvary, F.; Marko, L. Organometallics 1986, 5, 1019.

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⁽¹¹⁾ This proposal is based on observations in our previous work on the catalytic reaction of oxiranes with $HSiR_3$ and CO. See ref 5.

⁽¹²⁾ A stereochemical test using optically pure (R)- α -methyl-2-furfuryl acetate (cf. run 4) showed 56% inversion in accordance with a transition state with carbenium ion character. Efforts to improve the optical yield are now in progress. We gratefully acknowledge Professors Fumie Sato and Yuichi Kobayashi for a gift of the above mentioned chiral acetate. Cf.: Kusakabe, M.; Kitano, Y.; Kobayashi, Y.; Sato, F. J. Org. Chem. 1989, 54, 2085.