

TRANSITION METAL-STABILIZED CARBENIUM IONS

AS SYNTHETIC INTERMEDIATES. II.

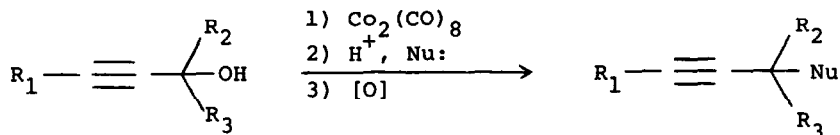
ALKYLATION OF β -DICARBONYL COMPOUNDS WITH
(PROPARGYL)DICOBALT HEXACARBONYL CATIONS

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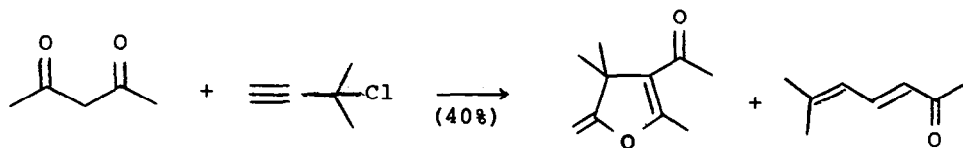
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As part of a program to investigate the potential synthetic utility of transition metal-stabilized carbenium ions, we have been interested in the chemistry of the cationic propargyl complexes $(RC\equiv CCR_2)Co_2(CO)_6^+$.¹ Since the activating $-Co_2(CO)_6$ moiety is efficiently introduced² and removed,³ these complexes appear to be attractive intermediates for application as electrophilic propargylic synthons (Scheme).



The limitations of propargyl halides and tosylates in this context, namely formation of allenic, elimination, and other by-products, are well-known⁴ and solutions to this general problem have been sought.^{5,6} These complications are particularly acute with β -dicarbonyl substrates as illustrated by the following example.⁷



In a previous study⁸ we found that the cationic cobalt complexes readily alkylate electron rich aromatics such as anisole and phenol to give propargyl derivatives exclusively and that elimination reactions could also be suppressed. We now report that these complexes likewise may be employed to effect selective propargylation of β -dicarbonyl compounds.

We chose acetylacetone and benzoylacetone as representative substrates and carried out their reactions with the in situ generated complexed cations according to the following generalized procedure. A methylene chloride solution of the dicarbonyl compound was added dropwise to a cooled (-78°) CH_2Cl_2 solution of the appropriate complexed alcohol and 0.5 - 1.5 equivalents of $\text{HBF}_4 \cdot \text{Me}_2\text{O}^9$ under N_2 . Brief warming to 0° (<1 hr.), neutralization with solid NaHCO_3 , and chromatography over silica afforded the product complexes as dark red oils or crystalline solids in good to excellent yield (Table).

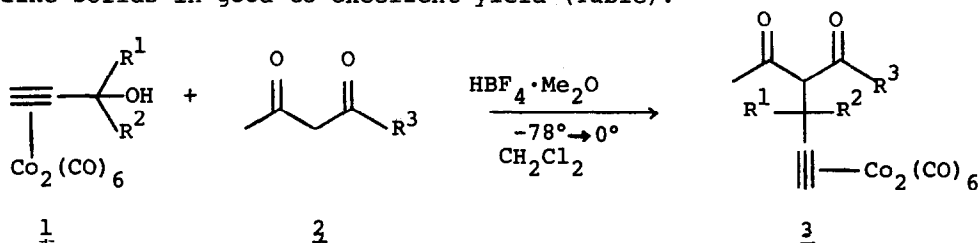
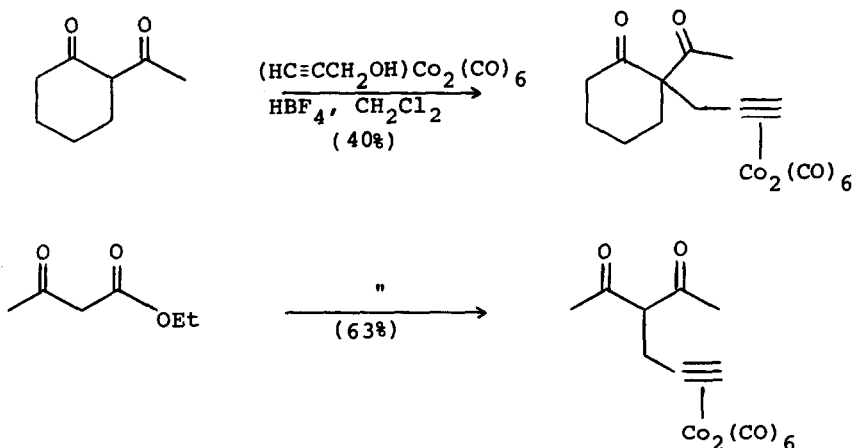


Table. Alkylations of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{R}^3$ with $[\text{HC}\equiv\text{C}(\text{OH})\text{R}^1\text{R}^2]\text{Co}_2(\text{CO})_6$.

Reaction	R^1	R^2	R^3	Yield of 3 (%)
1	H	H	CH_3	95
2	H	CH_3	CH_3	65
3	H	Ph	CH_3	91
4	H	H	Ph	90
5	H	CH_3	Ph	65
6	H	Ph	Ph	95

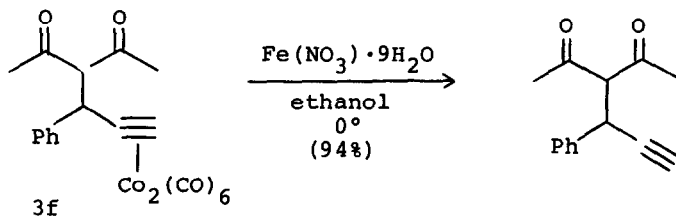
The structures of the products followed readily from their IR and ^1H NMR spectra.¹⁰ These indicated that except for the product from acetylacetone and the unsubstituted propargyl complex all the alkylated derivatives existed entirely (>95% by NMR) as the dicarbonyl tautomer in CS_2 . In no instance was any dialkylation observed, even with excess alkylating agent. The fifth and sixth entries in the Table are of particular interest because with the creation of a new asymmetric center the opportunity for asymmetric induction exists. Indeed significant stereoselectivity was observed, the ratio of diastereomers formed being 65:35 and 80:20 for reactions (5) and (6) respectively.¹¹ When the latter reaction was terminated after a few minutes at -78° , the ratio of diastereomers increased substantially to 93:7.¹²

In preliminary experiments we have also successfully alkylated 2-acetyl-cyclohexanone (to generate a quaternary center) and the β -ketoester ethylacetoacetate in moderate but unoptimized yield. No alkylated products were obtained,



however, from 1,3-cyclohexanedione or indanedione apparently owing to the extreme acid lability of these substrates. Alternative methods for generating the cations under neutral conditions are being examined.

The previously developed methods for demetalation of the (alkyne) $\text{Co}_2(\text{CO})_6$ complexes³ were effective for recovery of the alkylated dicarbonyl compounds. Thus, for example, treatment of **3f** with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 0° afforded the corresponding ligand in nearly quantitative yield.



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References and Notes

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9. For reactions with 1 ($R^1 = R^2 = H$ and $R^1 = H, R^2 = Ph$) 0.5 equiv. of acid was employed; with 1 ($R^1 = H, R^2 = CH_3$) 1.5 equiv. was required to suppress irreversible dehydration of the complex.
10. The product complexes were characterized further by elemental analysis and/or conversion to and spectroscopic analysis of the demetalated ligand.
11. Diastereomeric $C(O)CH_3$ resonances were observed at δ (ppm) 1.95 and 2.05 for 3e ($R^1 = H, R^2 = CH_3$) and 1.7 and 2.2 for 3f ($R^1 = H, R^2 = Ph$).
12. Determined by NMR at room temperature on isolated alkylation product. Presently we do not know whether the diastereomer ratio is kinetically or thermodynamically controlled.

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