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Preliminary communication

On the stability of α-(alkynyl)dicobalt hexacarbonyl carbonium ions

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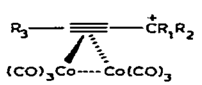
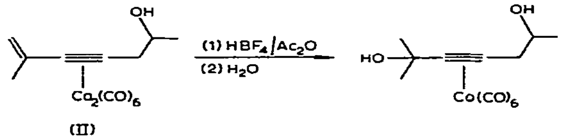
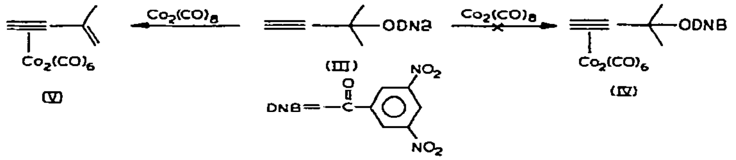
The greatly enhanced stability of carbonium ions α to an organometallic substituent has been recognized for some time. This phenomenon, which is typified by the facile hydration of vinylferrocene[1], has been of considerable interest, and suggestions as to its origin have been advanced[2, 3, 4, 5]. The effect is illustrated by the following examples: (1) The rate of solvolysis of α-ferrocenylcarbinyl acetate is approximately equal to that of trityl acetate[2], (2) (benzyl chloride)-chromium tricarbonyl solvolyzes 10^5 times faster than benzyl chloride itself[6] and (3) chloromethylcyclobutadieneiron tricarbonyl solvolyzes about 10^8 times faster than benzyl chloride[5].

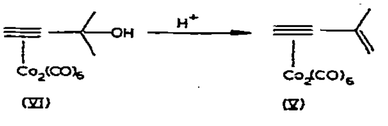
We wish to report the preliminary results of a study to evaluate the stability of α-(alkynyl)dicobalt hexacarbonyl carbonium ions (I).



(I)







In a previous publication[7] we reported the facile hydration of the complex II; under the same conditions the uncomplexed ligand was unreactive.

In an effort to obtain a suitable complexed derivative for solvolytic study, the dinitrobenzoate of 2-methyl-3-butyn-2-ol (III) was treated with dicobalt octacarbonyl in benzene solution at 25°. Instead of the desired dinitrobenzoate complex IV, the product obtained was the ene–yne complex V resulting from formal elimination of 3,5-dinitrobenzoic acid from IV. The possibility that this was an acid-catalyzed elimination prompted us to investigate the acid-catalyzed dehydration of propargyl alcohol complexes.

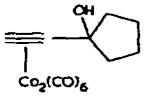
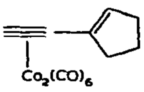
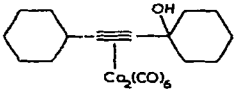
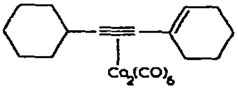
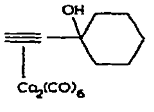
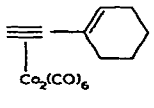
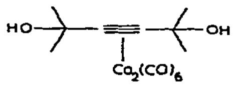
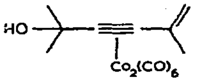
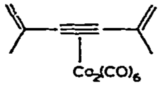
We have found that tertiary propargyl alcohol complexes readily undergo acid-catalyzed dehydration to give conjugated ene–yne complexes. For example, the carbinol VI when treated with 35 mole % of trifluoroacetic acid in benzene (25°, 24 h) was converted to the complex V in 72% yield. A summary of yields for several other dehydrations is shown in Table 1.

Under the same reaction conditions the uncomplexed carbinols were unchanged. Dehydration of free tertiary propargyl alcohols requires considerably high temperatures (80–200°) and usually employs more strongly acidic conditions[8].

An effort to extend the dehydration reaction to secondary propargyl complexes met with only partial success. Thus the complex VII when treated with CF_3CO_2H in

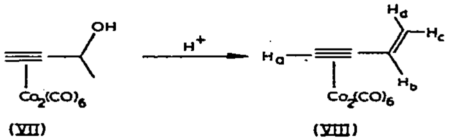
TABLE 1

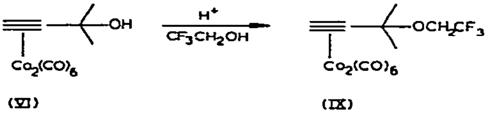
ACID-CATALYZED DEHYDRATION OF TERTIARY PROPARGYL ALCOHOL COMPLEXES

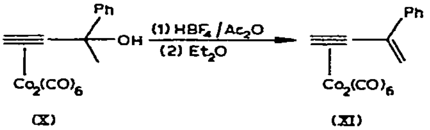
Alcohol complex	*Product*	*Yield (%)*
		81
		76
		65
		9
		79

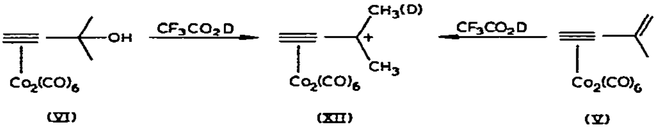
benzene (25°, 24 h) gave a mixture of products. An NMR spectrum of the mixture indicated the presence of the vinyl acetylene complex VIII as a major component. The complex VIII exhibits absorptions at δ 6.8 (8 lines, doublet (J_{bd} 16.5 Hz) of doublets (J_{bc} 9 Hz) of doublets (J_{ab} 1 Hz), H_b), 6.2 (doublet, H_a), 5.6 (doublet of doublets (J_{cd} 1.5 Hz), H_c), and 5.5 (doublet of doublets, H_d).[*] Dehydration of free secondary propargyl alcohols requires extremely forcing conditions, and few of these reactions have been successful[8].

That our reactions involve the intermediacy of a carbonium ion is supported by the following observations: (1) Treatment of the carbinol VI with a catalytic amount of CF_3CO_2H in trifluoroethanol led to the quantitative formation of the trifluoroethyl ether IX after 75 min at 25°; (2) under identical conditions only about 10% of the ene–yne V had reacted. This latter result indicates that ether formation via V is a minor pathway at best.









Attempts to isolate the proposed intermediate carbonium ion were unsuccessful although NMR evidence confirms their stability in solution. The alcohol complex X when treated with fluoboric acid in acetic anhydride gave, upon addition of ether, only the product of dehydration XI.

Solution of either the alcohol VI or the ene–yne V in CF_3CO_2D at 0° produced the carbonium ion XII. An NMR spectrum of this solution at 10° exhibited absorptions

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[*] The NMR spectrum of vinyl acetylene itself[9] has the following coupling constants: J_{ab} 2.1 Hz, J_{bd} 17.3 Hz, J_{bc} 11.5 Hz, J_{cd} 2.0 Hz.

at δ 7.9(singlet) and 2.3(singlet) with relative areas 1/6 when generated from VI and 1/5 when generated from V. Under the same conditions the uncomplexed alcohol underwent a slow reaction to give an intractable mixture of products.

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