

REACTION OF METAL-CARBENE COMPLEXES WITH DIAZOALKANES.

A VERSATILE VINYL ETHER SYNTHESIS.

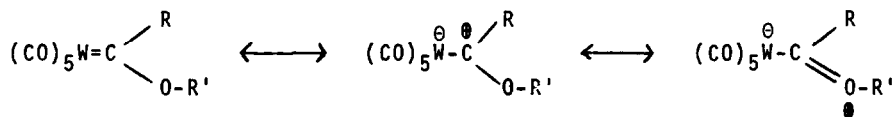
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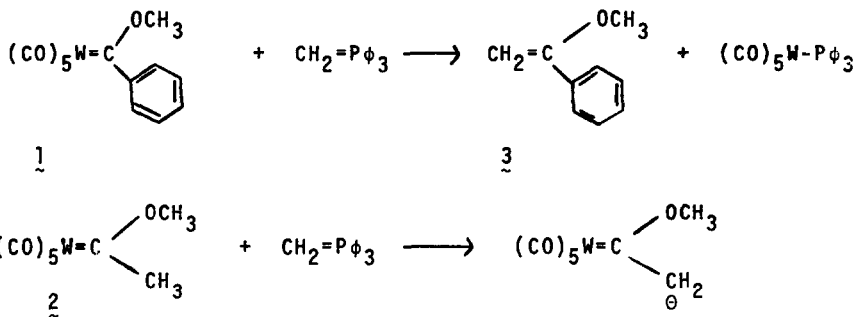
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In developing new approaches to the use of stable transition metal-carbene complexes in organic synthesis, we have focused our attention of the $M^{\ominus}-C^{\oplus}$ ylide nature of the metal-carbene bond and on the susceptibility of the electron deficient carbene carbon atom to nucleophilic attack.¹ In this regard, we

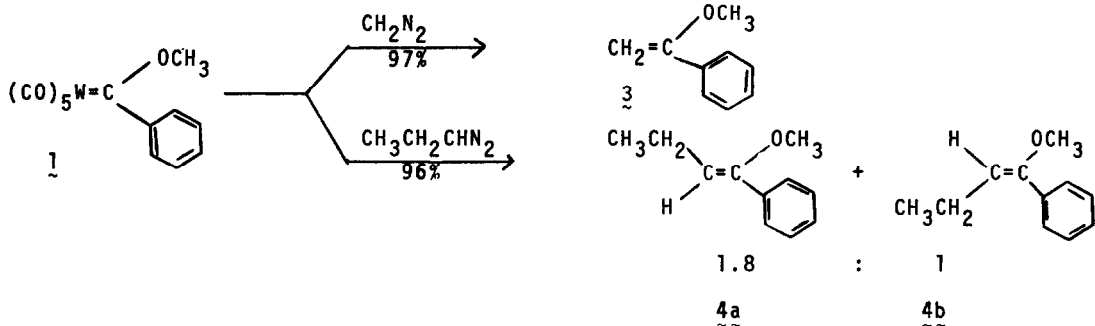


recently reported the reactions of arylmethoxycarbene complexes with phosphoranes which give high yields of vinyl ethers.² However, the reaction of phosphoranes with alkylmethoxycarbene complexes fails to produce vinyl ethers due to abstraction of a proton from the carbon α to the carbene carbon atom.³ To

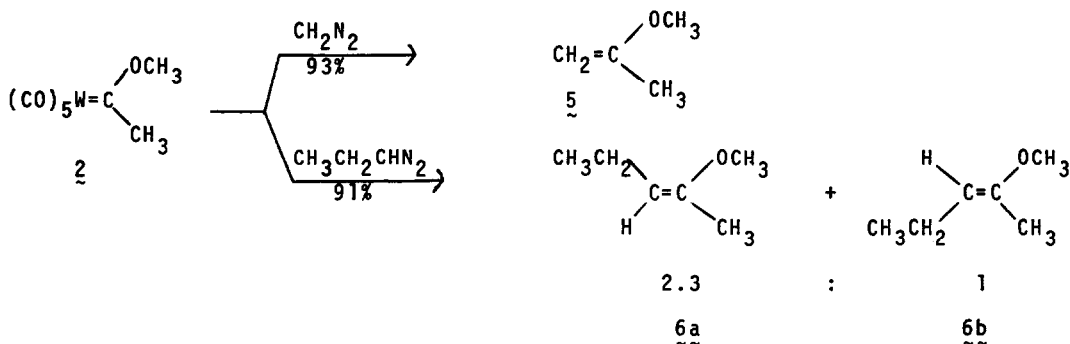


circumvent this problem, we began a study of the reaction of transition metal-carbene complexes with the more weakly basic diazoalkanes.

(Phenylmethoxycarbene)pentacarbonyltungsten(0), 1, undergoes facile reactions with excess diazomethane⁴ or n-diazopropane⁵ to give high yields⁶ of enol ethers. Whereas phosphoranes fail to produce enol ethers when added to



metal-carbene complexes containing α -hydrogens, both diazomethane and n-diazopropane give high yields⁶ of enol ethers when added to (methylmethoxycarbene)pentacarbonyltungsten(0), 2.

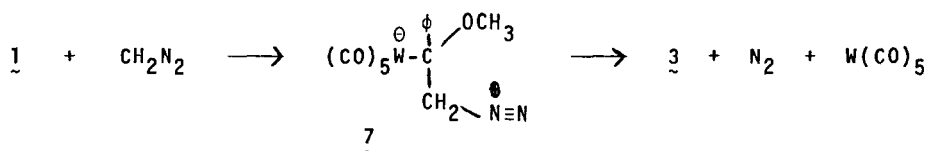


In a typical reaction, an ether solution of diazoalkane (10 ml, 0.1 M, 1 mmol, dried over K_2CO_3) was added to an ether solution of the metal-carbene complex (0.5 mmol) at 5° under a dry nitrogen atmosphere. An immediate reaction took place accompanied by vigorous gas evolution. The reaction of 1 with diazomethane is particularly easy to follow since the initial bright red color of the metal-carbene complex is destroyed in a matter of seconds leaving a yellow

solution containing excess diazomethane. Thin layer chromatography confirmed the complete reaction of the metal carbene complex.

The enol ethers were characterized by the nmr spectra of isolated samples (3, 4a, 4b) or of reaction mixtures run in benzene solution (5, 6a, 6b) and in all cases by hydrolysis (wet HCl in ether) to the corresponding ketones which were identified by comparison of their ir and nmr spectra and gas chromatographic retention times with those of authentic samples. The stereochemistry of enol ethers 4a and 4b were assigned on the basis of the relative chemical shifts of the vinyl proton resonances (4a, 5.31 δ ; 4b, 4.67 δ) and the chemical shift difference predicted from the correlations of Pascual, Meier, and Simon.⁷ The stereochemistry of 6a and 6b was tentatively assigned on the basis of the chemical shifts of the vinyl protons (6a, 4.49 δ ; 6b, 4.61 δ).

This reaction may be viewed as proceeding by nucleophilic attack by the diazo carbon atom at the electron deficient carbene carbon to form a betaine-like intermediate 7 which subsequently fragments to form enol ether, nitrogen, and coordinately unsaturated W(CO)₅. Evidence supporting the formation of



coordinately unsaturated W(CO)₅ was obtained by performing the reaction in the presence of pyridine as a trapping agent. When the reaction of excess diazomethane with 1 in ether at 5° was carried out in the presence of 10 equivalents of pyridine, the reaction proceeded normally with the usual rapid decolorization and gas evolution to give a 99% yield⁶ of the enol ether 3. In addition, Pyridinepentacarbonyltungsten(0) was isolated from the reaction mixture in 77% yield by low temperature recrystallization from hexane and was identified by nmr, ir, and mass spectral comparison with an authentic sample.⁸

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