

PRELIMINARY COMMUNICATION

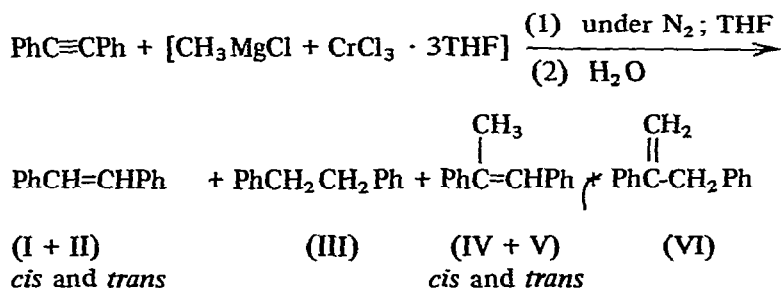
REACTIONS OF DIPHENYLACETYLENE WITH METHYLCHROMIUM σ -COMPLEXES: TRANSMETHYLATION, HYDROGEN TRANSFER REACTIONS AND CYCLIC CONDENSATION

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The reaction of diphenylacetylene with a methylchromium reagent¹ has been investigated. The latter was prepared from methylmagnesium halide (3 equiv.) and $\text{CrCl}_3 \cdot 3\text{THF}$ (1 equiv.) at -40° . Diphenylacetylene (0.3 equiv.) was then added and allowed to react at room temperature. The reaction mixture was then hydrolyzed after ca. 30 h. When used in these proportions the alkyne is fully consumed. The following products have been isolated by chromatography:



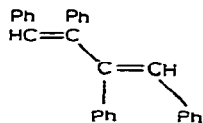
The products were identified by IR, NMR, mass spectra, gas chromatography, m.p. and compared with authentic samples. XII is an isomer of XI and not yet fully identified.

The Grignard reagent, or methyllithium, alone, did not react with diphenylacetylene. CrCl_3 , on the other hand, can be substituted by anhydrous CrCl_2 , NiCl_2 or CoCl_2 . Remarkably, an isolable methylchromium reagent $\text{Li}_3\text{Cr}(\text{CH}_3)_6$ ² failed to react.

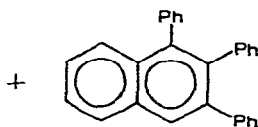
The process of transferring the metal-bonded methyl substituent to the alkyne is novel. The methyl hydrogens are also the major sources for the hydrogen transfer reaction. When CD_3MgI was used, large proportions of deuterium were found in the vinylic positions of stilbene and α -methylstilbene. Thus the hydrogen transfer reaction involved a process of α elimination in the methyl-metal complex.

The reaction exhibits a high degree of stereospecificity. *cis*-Stilbene and *cis*- α -

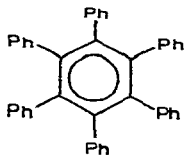
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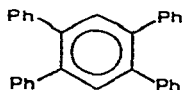
(VII)

cis, cis

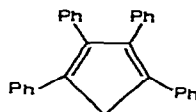
(VIII)



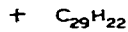
(IX)



(X)



(XI)



(XII)

methylstilbene are initially formed, and later isomerize to the corresponding *trans*-isomers. Tetraphenylbutadiene was isolated in the *cis, cis* form only. For this and other reasons the product ratios change considerably with time.

Detailed accounts of these reactions will be forthcoming.

ACKNOWLEDGEMENT

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