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Preliminary communication

STEREOSPECIFIC ALKYLATION OF ALKYNES BY BIS(π-ALLYL)NICKEL AND THE MECHANISM OF OLIGOMERIZATION OF ALKYNES BY NICKEL(0)

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Summary

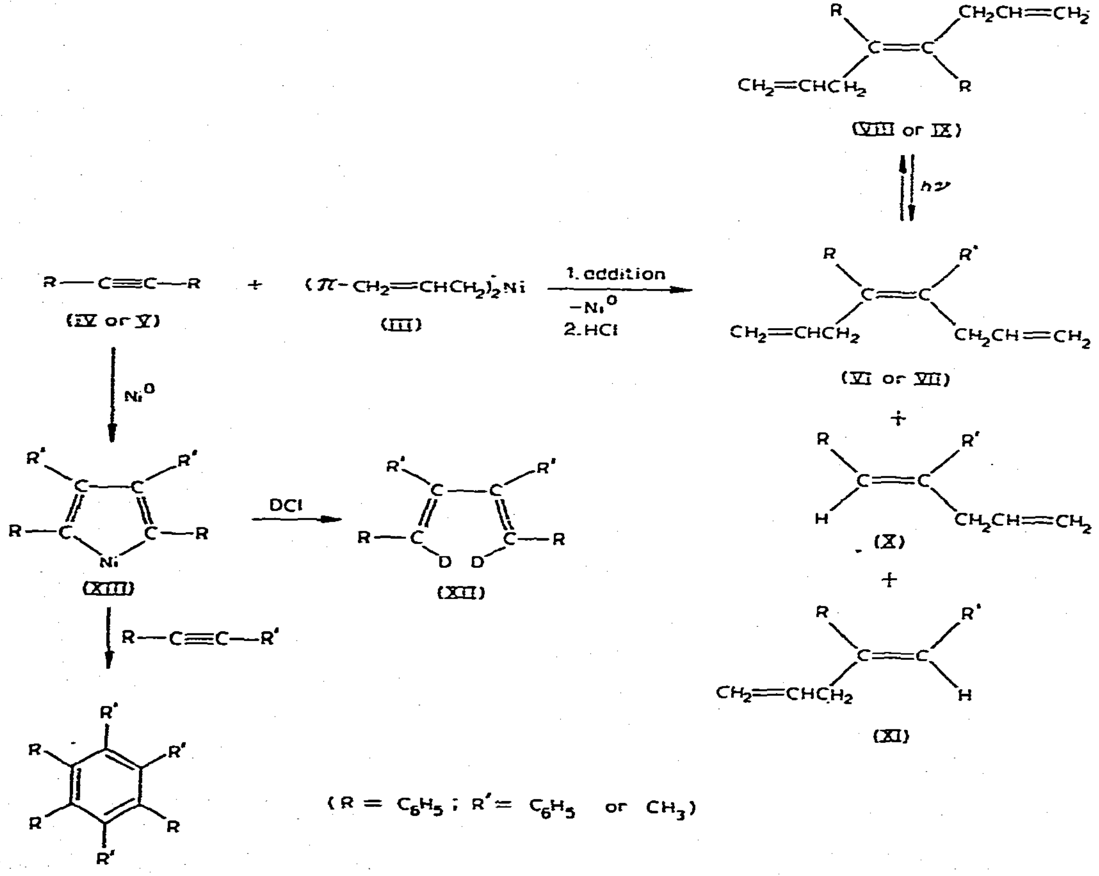
Bis(π-allyl)nickel effects the stereospecific *cis*-diallylation of methyl(phenyl)-acetylene and diphenylacetylene in 30-50% yield. The former acetylene also gives minor amounts of both *cis*-regioisomers of monoallylated product and some (allyl)propenyl adducts. The nickel(0) generated in the diallylation causes the reductive dimerization and cyclotrimerization of the alkyne. Since deuterolytic workup either of the allylation reaction mixture or of a mixture of alkyne and $(c\text{-}C_8H_{12})_2Ni$ leads to a 1,4-dideuterioalkadiene, it is proposed that the alkyne oligomerization proceeds via a nickelole intermediate.

The transition metal-catalyzed alkylation of alkynes can yield *cis,trans*-isomeric mixtures of mono- and di-alkylated products [1-8]. By examining the influence of ligands in such catalysts and the behavior of preformed transition-metal alkyls, the conclusion has been reached that the alkyne coordinates with the intermediate transition-metal-alkyl before inserting into the carbon—metal bond. Recently, the pathway for the dialkylation of alkynes by α,ω-octadienyl-nickel triphenylphosphine (I) has been clarified [9], by showing that I reacts with diethyl acetylenedicarboxylate to form the isolable *cis*-monoalkyl adduct, which upon carbonylation collapses to the *cis*-dialkyl adduct, a *cis, cis, trans*-1,4,7-cyclodecatriene derivative (II). However, the pertinence of the exclusive *cis*-dialkylation observed with I to the preferred stereochemistry to be expected from other transition-metal-alkyls remains unclear, for the structures of I and II do not readily permit of a *trans*-addition of I.

Accordingly, we have investigated the stereochemistry of the dialkylation of alkynes by the prototype of I, namely bis(π-allyl)nickel [10] (III), for this reagent could, in view of its structure, give either the *cis*- or *trans*-diallyl adduct. Nevertheless, the action of III on both methyl(phenyl)acetylene (IV) and diphenylacetylene (V) in ethereal solution was found to form exclusively the *cis*-

diallyl adducts, VI and VII, in at least 30-50% yield. Thus, the bis(π-allyl)nickel reagent was prepared by treating a suspension of 30 mmol of anhydrous nickel(II) bromide in 25 ml of diethyl ether or tetrahydrofuran with 75 mmol of allylmagnesium bromide in the same solvent at –20 °C. The reagent was then allowed to react with 25 mmol of the alkyne (25 h at 25 °C for $C_6H_5C{\equiv}CCH_3$; 20 h at 35 °C for $C_6H_5C{\equiv}CC_6H_5$). Hydrolysis was conducted with 6 *N* aqueous HCl under a nitrogen atmosphere. The structures of VI and VII were determined by their photoisomerization (254 nm) to the respective *trans* isomers, VIII and IX, and then by correlation of their methylene or methyl NMR chemical shifts with those of suitable models, i.e., the β-methylstyrenes and the stilbenes (CH_3 on δ-scale: VI, 1.55; VIII, 1.80; CH_2: VII, 3.40; and IX, 3.86) (Scheme 1).

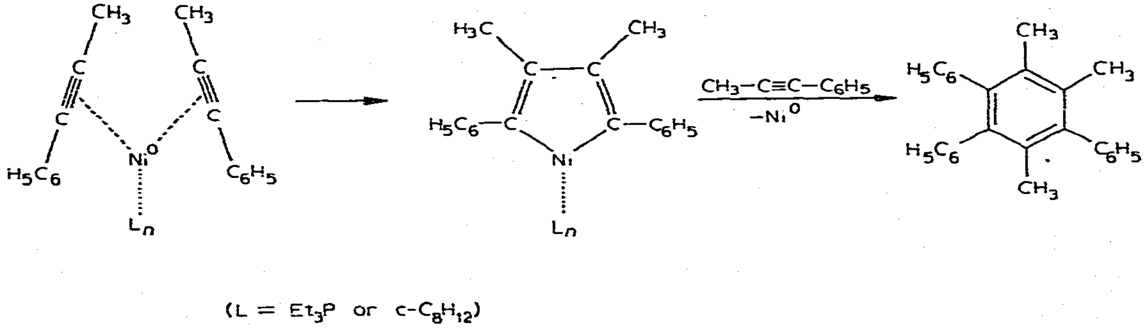
The minor products formed in these diallylations are highly relevant to the alkylation reaction pathway and to nickel(0)-catalyzed oligomerization of alkynes. First, methyl(phenyl)acetylene also gave a 5-10% yield of a 3/2 mixture of the monoallyl adducts, X and XI, the regioisomers of presumably *cis*-adducts (comparison of the experimental vinyl NMR chemical shifts with those calculated from empirical relationships [11]). This finding is in accord with a stepwise course for the diallylation [9] by III. Secondly, the detection of some



SCHEME 1

allyl → 1-propenyl group isomerization of VI (2-4%) in the methyl(phenyl)-acetylene reaction and of 8-10% of *cis*-stilbene with diphenylacetylene implies the occurrence of nickel hydride reactions. Thirdly, and most significantly, both alkynes yielded reductive dimers and cyclotrimers in variable amounts (5-10%). Furthermore, when the methyl(phenyl)acetylene reaction mixture was worked up with DCl, the *E*,*E*-2,3-dimethyl-1,4-diphenylbutadiene (XII) isolated was shown to be dideuterated at C(1) and C(4).

These latter results suggested that the nickel(0) generated in the diallylation of the alkyne caused a reductive dimerization of some alkyne to yield a nickelole intermediate (XIII), which in turn underwent a Diels--Alder reaction to form the cyclotrimer and to regenerate nickel(0) (Schemes 1 and 2). Although nickel(0) trimerizations of alkynes are well-known [12], dimers are not commonly encountered. Therefore, the behavior of two nickel(0) catalysts toward IV was scrutinized. Heating IV with 0.33 equiv. of $(Et_3P)_4Ni$ in toluene solution gave, upon hydrolysis with 6 *N* aqueous HCl, a 70% yield of the unsymmetrical and symmetrical trimethyltriphenylbenzenes in a ratio of 96/4. Treatment of IV with 0.25 equiv. of $(c\text{-}C_8H_{12})_2Ni$ in hexane solution at 25 °C gave, after 30 minutes, 60% of the trimers in a ratio of 58/42 (unsym/sym), together with XII and a lesser amount of its *E*,*E*-1,3-dimethyl-2,4-diphenyl isomer. Work-up of a similar reaction mixture with 4 *N* DCl in D_2O gave XII that was completely deuterated at C(1) and C(4) (Scheme 2)*. Again, these observations offer strong support for the occurrence of nickelole intermediates in nickel(0) oligomerizations of alkynes. The variable proportions of the cyclotrimeric isomers of IV appear to be related to steric factors in the preferential formation of the isomeric nickeloles involved.



SCHEME 2

Since the case for nickelole intermediates in such reactions could be made more cogent by synthesizing and examining the chemical behavior of isolated nickeloles, such a study has been carried out and is reported in the accompanying communication.

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*The structures of the reductive dimerization and cyclotrimerization products were readily determined from spectral comparisons with authentic samples [13].

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