

CATALYZED CYCLOADDITION OF ACETYLENES TO CYCLOHEXENE, FORMATION OF 2:1 ADDUCTS

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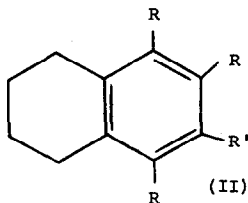
Metal-catalyzed reaction of acetylenes with activated olefins, to form 2:1 cycloadducts, is known to occur in the presence of zerovalent iron or nickel complexes or of Ziegler-Natta catalysts. Usually, the olefins are strained, e.g., norbornadiene¹ or allene or else are activated by conjugation, e.g., butadiene or ethyl acrylate².

The literature contains a number of examples of reactions in which a σ -bonded hydrocarbon ligand has been incorporated into an organic product during reaction of acetylenes with an organometallic complex. Ethyl derivatives of chromium and nickel, for example, form 1,2,3,4-tetraphenylbenzene and 1,2,3,4-tetraphenylcyclohexadiene respectively upon treatment with diphenylacetylene³. Many similar examples are known.⁴ Since the completion of the present work, Chalk⁵ has shown that (2:1) co-condensation of terminal or conjugated acetylenes with *n*-methylmaleimide can be catalyzed by $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$. No cases seem to have been reported, however, in which simple, nonactivated olefins have been catalytically condensed with internal acetylenes. In this communication, such a reaction is disclosed and a possible route to certain alkyl-substituted naphthalene and anthracene derivatives is thus opened.

The standard procedure employed $[\text{C}_2\text{H}_4]_2\text{RhCl}]_2$ ⁶ (I) as catalyst and cyclohexene as solvent/reactant. Reactions were carried out in an autoclave under argon or nitrogen, at ca 160°C for 10-16 hours.

When a 7.5:1 molar ratio of cyclohexene and 2-butyne was employed, together with 0.8% m (I), over 90% of the acetylene was consumed and two products were detected and separated by GLC. Component A (80% selectivity) was readily identified as hexamethylbenzene (NMR, mass spectrometry and GLC retention time). Component B (20% selectivity) showed a molecular ion at $m/e = 188$ in the mass spectrum, corresponding to $\text{C}_{14}\text{H}_{20}$. The NMR spectrum showed multiplets centered at δ 2.77 ppm from TMS [2H] and δ 1.83 [2H], and two singlets at δ 2.30 [3H] and δ 2.23 [3H]. The data is in accord with structure IIa for component B, i.e., 1,2,3,4-tetra-

methyl-5,6,7,8-tetrahydronaphthalene:



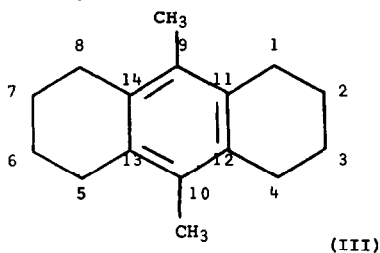
- a) $R=R'=\text{CH}_3$
- b) $R=R'=\text{n-C}_3\text{H}_7$
- c) $R=\text{CH}_3, R'=\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_4$

This product must arise by dehydrogenative aromatization of a 2:1 acetylene:olefin adduct, probably under the influence of rhodium metal. (The rhodium complex decomposes thermally to yield traces of the metal which is known to be a potent hydrogen-transfer agent). Repetition of this experiment using an olefin: acetylene molar ratio of 11.2:1 and 0.06 %m catalyst gave an increase in the selectivity of the 2:1 cross-adduct to 33%. Little or no reaction could be detected when 0.14 %m 1,5-cyclooctadiene rhodium chloride or 0.13 %m $(\text{Rh}(\text{CO})_2(\text{acac}))^7$ were employed as catalysts, using the same reactant ratio.

When a 21:1 (molar) mixture of cyclohexene and 4-octyne containing 2.5 %m $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ was heated, over 92% of the acetylene was consumed and much of the solvent underwent disproportionation into benzene and cyclohexane. Two major products were observed in 35:65 proportions. Mass spectrometry indicated that the predominant product was hexa(n-propyl)benzene $\text{C}_{24}\text{H}_{42}$ (m/e 330.32901 theoretical 330.32863, prominent M-29 ion). Upon GLC isolation, the minor product showed three parent ions at m/e 300, 298, and 296 (low resolution mass spectrometry), corresponding to $\text{C}_{22}\text{H}_{36}$, $\text{C}_{22}\text{H}_{34}$, and $\text{C}_{22}\text{H}_{32}$, respectively. This material is believed to be a mixture of 1,2,3,4-tetrapropyl-5,6,7,8-tetrahydronaphthalene (IIb) and its di- and tetradehydroderivatives⁸.

A 21-fold molar excess of cyclohexene was heated with 2,8-decadiene in the presence of 2.9 %m(I) and yielded fluffy white crystals (~ 25% yield based on actual structure) and a red oil. The oil appeared (by mass spectrometry) to be a mixture of rhodium complexes. The white product was shown to consist of 92% $\text{C}_{16}\text{H}_{22}$ (m/e 214.17150 - calculated value is 214.17214) and 8% $\text{C}_{20}\text{H}_{30}$ (m/e 270.35044, calculated value is 270.23474). This material was fractionally sublimed at ~ 125-128°/35 mm to yield crystals which were > 98% homogeneous (by NMR). The ¹H NMR spectrum showed a sharp singlet at δ 2.1 (3H) and multiplets at δ 2.7 (2H) and δ 1.8 (2H). The ¹H NMR spectrum, including decoupling experiments, together with the mass spectrum, suggest that this compound is 1,2,3,4,5,6,7,8-octahydro-9,10-dimethylantracene (III), formed by a 1:1 polycyclic condensation between cyclohexene and the acetylene. This structure is confirmed by the proton-

decoupled ^{13}C NMR spectrum, which shows peaks at δ 14.1 ppm from TMS ($2 \times \text{CH}_3$), δ 23.7 ppm ($\text{C}_2 + \text{C}_3 + \text{C}_6 + \text{C}_7$), δ 28.4 ppm ($\text{C}_1 + \text{C}_4 + \text{C}_5 + \text{C}_8$), δ 132.2 ppm ($\text{C}_9 + \text{C}_{10}$) and δ 132.8 ppm ($\text{C}_{11} + \text{C}_{12} + \text{C}_{13} + \text{C}_{14}$).



A comparison of NMR spectra taken prior to, and after, sublimation, together with the mass spectrum, is consistent with the expected structure (IIC) for the trace component. This compound, 1,3,4-trimethyl-2-(5-heptenyl)-5,6,7,8-tetrahydronaphthalene, is the partly-hydrogenated product of a 1:1 condensation between two moles of diacetylene (analogous to trimerization of a monoacetylene).

It is possible that a labile cyclobutadiene complex is formed in these transformations and that the observed (Kekule-type) products are derived from this perhaps via "Dewar benzene" intermediates. A transformation of this type has been reported⁹. In the closely-related trimerization of acetylenes, cyclobutadiene intermediates have been implicated in a few cases¹⁰, but more frequently, have been eliminated¹¹ and metallocyclopentadienyl intermediates have been suggested. (These two types of complex are interconvertible in some cases¹².) Schrauzer has suggested¹³ a third mechanism involving cis-complexed acetylenes. While neither the cyclobutadiene nor the Schrauzer route can be excluded, the products in these reactions are readily explained by the intervention of rhodiacyclopentadiene intermediates¹⁴ in a process similar to that favored by Chalk⁵.

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- 8) When isolated by column chromatography, on neutral alumina, this material showed a single parent ion at m/e 300.28136 (theoretical for $C_{22}H_{36}$ is 300.28169). Although it is possible that the dehydroderivatives observed are artifacts of the GLC separation, it is believed that they were present in the original mixture in view of the extensive disproportionation of the cyclohexene. Thus, it must be assumed that they were selectively lost during column chromatography.
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