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Catalytic Oligomerization in the Reaction of Diphenylacetylene with Chromium Vapor

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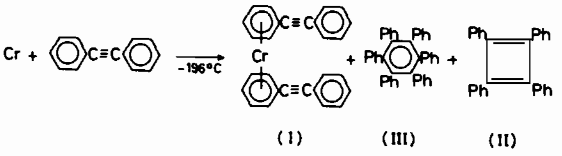
The condensation of alkynes with transition-metal atoms causes catalytic oligomerization and high oligomers are found [1–3]. Some alkynes have been trimerized to benzene by reaction with chromium vapor, but no bis(arene)chromium compounds have been detected among the reaction products. On condensation of chromium vapor with benzonitrile, bis(benzonitrile)chromium forms, but this major process is accompanied by cyclotrimerization of benzonitrile to form a small amount of 2,4,6-triphenyltriazine [4]. Reported here is the reaction of chromium atoms with diphenylacetylene to give bis(diphenylacetylene)chromium, 1%(I), together with a mixture of dimers 34%(II) and trimers 65%(III) of diphenylacetylene as determined by mass spectrometry.



Method A

Chromium (0.7 g) was condensed at −196 °C and 10^{-4} torr with a decane solution of biphenylacetylene (*ca.* 5 g in 20 ml) during 1.5 hours from a closely-wound, conical tungsten basket in a 1 L. flask as described previously [5]. The mixture was allowed to warm to room temperature and the excess decane was removed in a vacuum at 50 °C. The unreacted diphenylacetylene was sublimed onto a cold finger in a vacuum at 40 °C. The residue was analyzed by mass spectrometry. The residue contained bis(diphenylacetylene)chromium(0) (m/e = 408) together with a mixture of dimers (m/e = 356) and the cyclic trimers of (m/e = 534) biphenylacetylene.

The residue was recrystallized from light petroleum (−20 °C) to give dark crystals of bis(diphenylacetylene)chromium(0). The mass spectrum has m/e 408(M), 231(ML) and 52(Cr). The ESR spectrum of the cationic analogue bis(diphenylacetylene)chromium(I) has g = 1.9878, $A(H_{Ar})$ = 3.75 gauss, which is the same range as ESR parameters of a series of substituted bis(arene)chromium(I) compounds [6].

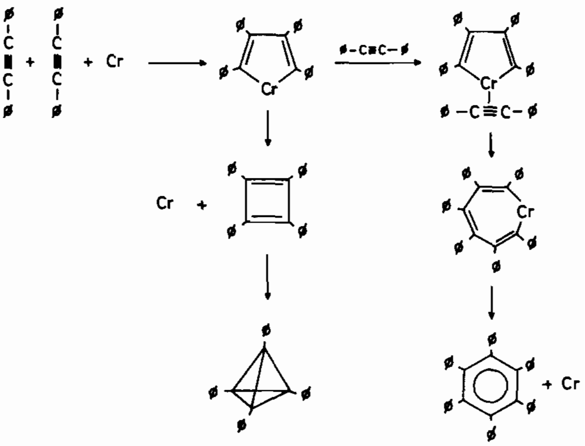
The mixture of organic products was repeatedly chromatographed on Al_2O_3. The trimer of bisphenylacetylene(hexaphenylbenzene) was isolated and then identified by MS and NMR. The ^1H NMR spectrum has a singlet at 6.81 ppm. The mass spectrum has a parent peak at m/e = 534. The reddish-orange dimer-(tetraphenylcyclobutadiene) was not isolated as a pure compound. However, the mass spectrum exhibits m/e, 336(M), 279(M − C_6H_5), 202(M − $2C_6H_5$), 126(M − $3C_6H_5$) and confirms the existence of the compound.

Method B

Chromium (0.6 g) was evaporated over 2 hours and condensed with diphenylacetylene vapor (10 g) at −196 °C by introducing the latter simultaneously through a heatable inlet (+50 °C). After removing the excess unreacted diphenylacetylene, the residue was analyzed by mass spectroscopy. Only the dimer and trimer could be found in the reaction products.

The reddish-orange dimer, tetraphenylcyclobutadiene, may have been isomerized to an air stable colorless compound of tetraphenyltetrahedrane, identified from its mass spectrum, and is similar to the report [7] that tetra-tert-butylcyclobutadiene can be converted to tetra-tert-butyltetrahedrane.

On the basis of mass spectroscopic product analysis, a possible mechanism for a generalized oligomerization scheme is proposed and shown below.



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