Tetrahedron Letters No.49, pp. 5129-5130, 1968. Pergamon Press. Printed in Great Britain.

## OLIGOMERIZATION CATALYSTS - IV.

## FORMATION OF BENZENE DERIVATIVES BY CATALYTIC REACTION BETWEEN NORBORNADIENE AND ACETYLENIC HYDROCARBONS: A CASE OF CATALYZED INVERSE DIELS-ALDER REACTION.

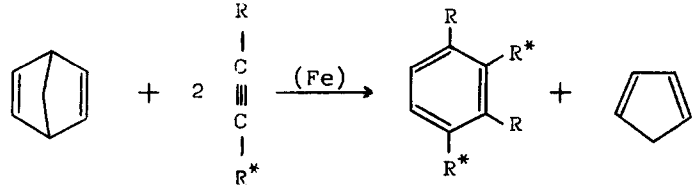
A. Carbonaro, A. Greco, G. Dall'Asta
Centro Ricerche Milano, Montecatini Edison S.p.A., Milano - Italy

(Received in UK 15 August 1968; accepted for publication 9 September 1968)

In previous papers we described the cooligomerization between conjugated dienes and alkenes or alkynes catalyzed by organometallic iron compounds (1, 2). Now we wish to describe the reaction of norbornadiene(bicyclo[2,2,1]hepta-2,5-diene) with mono- or disubstituted acetylenic hydrocarbons in the presence of the same catalysts.

By reacting norbornadiene with alkyl or aryl substituted acetylenic hydrocarbons in the presence of organometallic iron catalysts the main products were neither the homooligomers nor the expected cooligomers but aromatic compounds, in which only four ring carbon atoms stem from the acetylenic compound used, according to scheme (A):

(A)



($R = CH_3$ or $C_6H_5$; $R^* = H$ or R; (Fe) = iron catalyst).

This reaction occurs in a catalytic manner. It was checked in the case of propyne, 2-butyne, phenylacetylene, and diphenylacetylene. The main products were respectively m-xylene, 1,2,3,4-tetramethylbenzene, m-terphenyl, and 1,2,3,4-tetraphenylbenzene. The reactions were carried out in the 20-130°C temperature range using bis(cyclooctatetraene)iron [$Fe(C_8H_8)_2$ (1)] or $FeCl_3/(iC_3H_7)MgCl$ in diethylether as catalyst. The yields (100 moles aromatic compound/moles norbornadiene introduced) were in the 20-40% range. The selectivity is generally high.

A typical run is the following: 50 mg $Fe(C_8H_8)_2$, 1.4 ml 2-butyne, and 0.6 ml norbornadiene were introduced under nitrogen in a glass vial cooled to -78°C. The vial was hot sealed and maintained for 18 hrs at 60°C. The product (0,25 g) boiling at 75-77°C/7 mm Hg, isolated from the reaction crude, was found to be 1,2,3,4-tetramethylbenzene (ir, nmr, and mass spectroscopic analysis). Yield about 30%. Among the reaction products, in addition to the two unreacted starting hydrocarbons, the gaschromatography revealed the presence of dicyclopentadiene and of cyclooctatetraene, the latter deriving from the catalyst.

Among the by-products of the reaction between norbornadiene and diphenylacetylene we singled out two mixed dimers (about 25% referred to tetraphenylbenzene), the mixture of them has a mass spectroscopic molecular weight of 270, corresponding to 1:1-codimers.

Analogous cooligomerization products were not observed in the reaction of norbornadiene with the other mentioned acetylenic hydrocarbons.

The formation of aromatic compounds according to reaction (A) does not seem to have been ever reported in literature. This reaction is stereospecific, e.g. leading only to m-derivatives starting from monosubstituted acetylenes.

The mechanism of reaction (A) is not completely understood. Likely, the reaction is initiated by a coordination of one molecule of norbornadiene and of two molecules of acetylenic compound to the zerovalent iron compound. Coordination compounds of norbornadiene, in which both double bonds are coordinated to zerovalent iron are known (3). Also coordination compounds of tolane to zerovalent iron were recently found by us (4).

Presumably, the transition step between the coordination complex and the aromatization reaction is a cycloaddition product of the two acetylenic hydrocarbons to one norbornadiene double bond. The driving force for the supposed ring opening reaction, which leads to cyclopentadiene and substituted benzenes, most likely is the energy gain in the aromatization of the cyclohexadiene ring and in the release of the strain of the norbornadiene ring.

This reaction may be considered as an inverse case of the catalyzed Diels-Alder type reaction that we have recently described (2).

## REFERENCES

1. A. Carbonaro, A. Greco, and G. Dall'Asta, Tetrahedron Lett. 22, 2037 (1967).
2. A. Carbonaro, A. Greco, and G. Dall'Asta, J. Organic Chem., in press.
3. M.L.H. Green, L. Pratt, and G. Wilkinson, J. Chem. Soc. 989 (1960).
4. Our unpublished results.