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A SUPPORTING EVIDENCE FOR (2 + 2) CYCLOADDITION OLIGOMERIZATION OF PHENYLACETYLENE

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Abstract

The polymerization of phenylacetylene by chromium hexacarbonyl in toluene was studied in detail. Since ladder compounds containing fused cyclobutane rings were isolated, the proposed (2 + 2) -cycloaddition mechanism for oligomerization was corroborated.

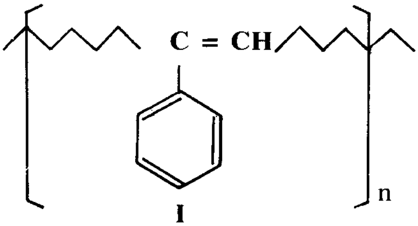
Although phenylacetylene has long been known to polymerize by anionic and cationic as well as fre radical process[1], coordinated metal acetylide [2,3] and, recently, metal carbene mechanisms[4] have also been presented. Catalysts based on carbonyl complexes of group VIB metals have been proposed to promote another type of mechanism, a (2 + 2) -cycloaddition polymerization [5-7]. With the aid of the organometallic complex, the reaction initially proceeds by the coupling of two molecules of alkynes leading to a cyclobutadiene, Dewarbenzene and a ladder compound containing fused cyclobutane rings[5]. The compound reacts with further alkynes to give finally linear polyphenylacetylene, phenylacetylene[6] and triphenylbenzene derivatives [7].

Normally, organomolybdenum complexes are superior catalysts to analogous chromium or tungsten complexes for the polymerization of alkynes in the production of high molecular weight linear polymer[6]. In this study, however, the system of chromium hexacarbonyl in toluene is selected because of its milder property as a catalyst for polymerization. It is hoped that the toluenechromium tricarbonyl complex produced in situ will catalyze the polymerization reaction but can be stopped at initial stages and ladder oligomers may be isolated. These oligomers will serve as evidence in support of the (2 + 2) -cycloaddition mechanism we have proposed[5]. Other systems (Table) have also been studied for comparison of products and yeilds.

The polymerization reactions were carried out under nitrogen atmosphere by refluxing phenylacetylene, chromium hexacarbonyl or tungsten hexachloride in different solvents for 15-20, according to Table. The crude products were separated by preparative thin layer chromatography on alumina to two major portions (Band PO, Table) when toluene was used as an elvent. The upper part was colorless but strongly fluorescent under ultraviolet light and identified as cyclotrimerization products of benzene derivatives. This (from run number 1, 0.15 g, 10.5 %) was further purified by fractional crystallization in cyclohexane and cold acetic acid to give 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene in the ratio of 33 : 67 [8,9]. The lower part was identified as oligomerization products as described below.

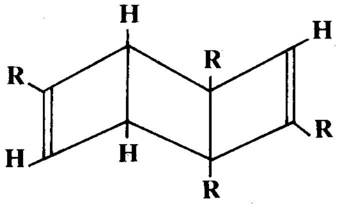
When cyclohexane was used as an eluent for preparative thin layer chromatography (tlc), crude products were separated into five bands. They were recovered as summarized in Table. The first (uppermost) band which was fluorescent under ultraviolet light was ascertained as benzene derivatives [8,9]. The lower four bands were yellow and identified as linear and ladder oligophenylacetylenes as described below.

The semisolid recovered from the fifth (lowest) band was identified by comparison of infrared nuclear magnetic resonance (ir) and (nmr) spectra with those reported[10] as oligophenyl-acetylene (I; 0.10 g, 5.5 %). The mass spectral data was m/e 408, 306 and 204 indicated than n $\geqslant$ 4. The fourth band was similarly indentified as linear oligophenylacetylene with n $\geqslant$ 3 (m/e 306, 204; 0.11 g, 5.9 %)

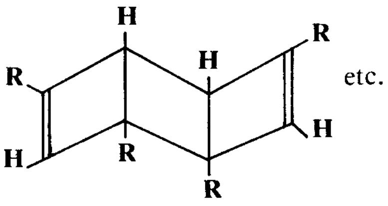


I

The third band isolated was a yellw semisolid exhibiting aromatic-olefinic ir C-H stretching at 3010 cm^{-1} and an aliphatic ν(C-H) band at 2900 cm^{-1}.The mass spectral data showed a parent ion at m/e 408 ($C_{32}H_{24}^{+}$, P^{+}) and major fragments at 306 ($C_{24}H_{18}^{+}$ or P^{+}-C_8H_6) and 204 ($C_{16}H_{12}^{+}$ or P^{+}-$(C_8H_6)_2$). The nmr spectrum exhibited signals at δ1.25 and δ7.8-6.6 ppm (integrated intensities 1:11). Based upon these information and discussions presented before[5], the semisolid isolated from the third band was identified as isomeric mixtures of tetraphenyltricyclo (4.2.0.$0^{2,5}$) octa-3,7-dienes (II and III etc.; 0.04 g, 2.1 %)



II



III

$R = C_6H_5$

Total ≒ 12 isomers

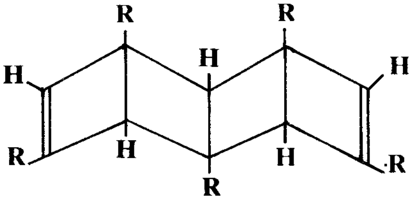
TABLE CONDITIONS AND PRODUCTS SEPARATED BY TLC TECHNIQUES

No.	Catalyst		Phen Acet mmol	Solvent ml	Polymer product, %								B /PO
					I	II	III	IV	V	B	PO	Total	
1	$Cr(CO)_6$,	0.45	18	tol,50						10.5	17.5	28	0.6
2	$Cr(CO)_6$,	0.27	0.27	tol, 3	11.8	2.7	2.1	5.9	5.5	10.4	17.6	28	0.59
3	-		18	tol,50			-			2	3.4	5.4	0.57
4	$Cr(CO)_6$	0.45	18	hep,50			-			5.4	2.6	8.1	2.1
5	$Cr(CO)_6$	0.27	hep, 3		8.5	2.4	3.3	4.6	4.1	15.5	7.4	22.9	2.1
6	-		18	hep,50			-			0.4	0.3	0.7	1.3
7	$Cr(CO)_6$,	0.27	0.27	cy, 3	26.1	11.6	3.7	6.8	7.1	43.4	11.9	55.3	3.7
8	-		18	cy, 3			-			1.0	1.9	2.9	0.53
9	$Cr(CO)_6$,	0.27	ch, 3		38.7	4.9	2.9	6.8	13.4	49.5	17.2	66.7	2.9
10	WCl_6,	0.1	18	ch, 10			-			20.4	26.3	46.7	0.78
11	WCl_6,	0.15	0.27	et:ch,1:3	11.4	7.9	5.1	9.5	12.8	20.4	26.3	46.7	0.77
12	-		18	ch, 3			-			2.3	5.1	7.4	0.45

Phen Acet = Phenylacetylene; tol = toluene, hep = heptane, cy = cyclohexane; ch = chlorobenzene,
et:ch = ethanol : chlorobenzene; I-V represents bands separated on tlc plates; B = benzene derivatives, PO = phenylacetylene linear oligoners; B/PO = benzene derivatives/linear oligomers ratio

The formation of compounds containing fused cyclobutane rings mentioned above could be accounted for via a series of (2 + 2) -cycloaddition as shown for production of five isomers of triphenyl Dewarbenzene[5]. With the addition of another molecule of phenylacetylene to each of these Dewarbenzene isomers, 16 out of the 20 possible tetraphenytricyclo $(4.2.0.0^{2,5})$ octa-3,7 -dienes were isolated. The nmr spectrum of the isomeric mixture showed a relative intensity between aliphatic to aromatic-olefinic protons of 1:11. The expected ratio for the proposed structures is 2:22.

The second bad was also a yellow semisolid having ir, nmr and mass spectral data showing resemblance to the third band. Likewise, the compounds were identified as pentaphenyltetracyclo $(4.4.0.0^{2,5}0^{7,10})$ deca-3, 8-diene isomers (IV; 0.05 g, 2.7 %).



$R = C_6H_5$

IV

Total = 28 isomers

By analogy to the previous discussion, after an addition of another phenylacetylene to all three-ring ladder compounds, 72 out of the 80 possible pentaphenyltetracyclo $(4.4.0.0^{2,5}0^{7,10})$ deca-3, 8-dienes contain a relative intensity of 1:9 (aliphatic:aromatic-olefinic protons). The expected ratio for the proposed structures is 3:27.

Products from other runs qualitatively showed similar sequence and distribution pattern of bands as run number 1 and 2 but chemical identifications have not been characterized.

Among possible mechanisms for alkyne polymerization, only the (2 + 2) -cycloaddition could produce products which contain aliphatic protons. These protons are located at bridges between adjacent cyclobutane rings of the ladder oligomers. Since compounds of this nature have isolated in this work, the proposed (2 + 2) -cycloaddition oligomerization of phenylacetylene is thence corroborated.

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บทคัดย่อ

การแยกสารประกอบแลดเดอร์ ซึ่งประกอบด้วยวงไซโคลบิวเทนที่เชื่อมต่อกันได้จากปฏิกิริยาโพลิเมอไรเซชันของเฟนนีลอะเซทีลีนด้วยโครเมียมเฮกซะคาร์บอนีลในโทลูอีน เป็นการสนับสนุนกลไก 2 + 2 ไซโคลแอดดิชันสำหรับปฏิกิริยาเมอไรเซชันของอัลไคน์