

COORDINATION SYNTHESIS ON ORGANOMAGNESIUM CENTERS:
OCTAPHENYLCUBANE

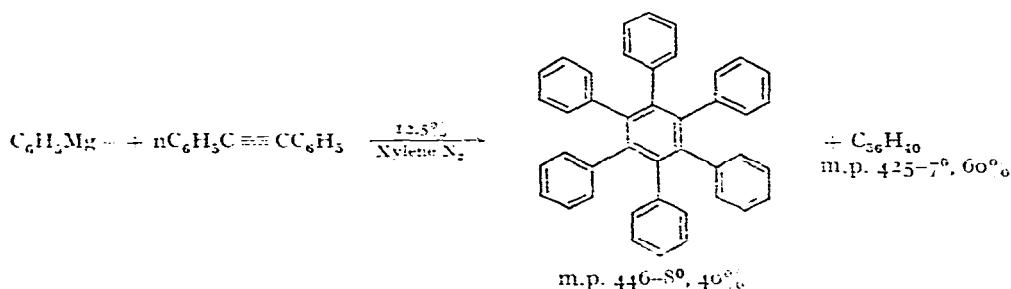
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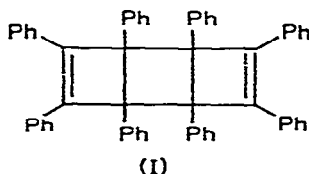
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Initial attempts to synthesize the cyclobutadiene molecule in our laboratory were based on the concept of coordination of acetylenes, *e.g.*, diphenylacetylene, on organonickel centers. This approach stemmed directly from the successful trimerizations of disubstituted acetylenes on alkyl and aryl derivatives of chromium, manganese and cobalt^{1,2}. However, although cyclobutadiene intermediates were proposed to account for the products obtained, the objective of preparing either cyclobutadiene derivatives or their nickel complexes was not realized.

We then turned to organomagnesium reagents whose capacity for coordinating with ethers is well established. By depriving the magnesium centers of ether we hoped to influence these to accept acetylenes as ligands, thereby creating a favorable condition for coordinative synthesis: and in fact this result was obtained. Ether-free phenyl Grignard or diphenylmagnesium in xylene will condense diphenylacetylene to hexaphenylbenzene, a usual cyclic trimer from such reactions, and also to the then unknown, high melting hydrocarbon, C₅₅H₄₀, whose formula showed the compound to be a tetramer of diphenylacetylene. Owing to the sparing solubility

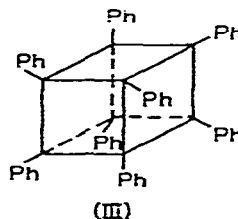
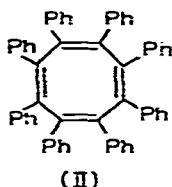


of this 426°-melting substance, chemical evidence for its structure was difficult to obtain. Beyond the several facts of its resistance to hydrogenation, slow absorption of bromine and failure to rearrange thermally to known product, little could be said.



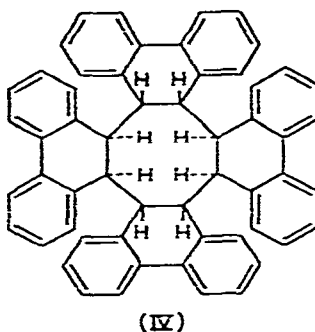
Consequently, although a tricyclic structure (I) arising from an edge-on dimerization of tetraphenylcyclobutadiene was a consideration, it was believed at the time (1959) that the data was insufficient to warrant publication*.

Meanwhile Freedman^{4,5} in the course of a quest for tetraphenylcyclobutadiene has isolated a $C_{56}H_{40}$ hydrocarbon whose properties were the same in all respects as the one in our hands. However, the evidence went much further. On the basis of a crystallographic determination of a four-fold inversion axis in the molecule and the lack of olefinic absorption in its Raman spectrum, Freedman and Petersen⁵ eliminated structure (I). Although octaphenylcyclooctatetraene (II) was considered, they favored the octaphenylcubane structure (III) which could arise from a face-on rather than an edge-on dimerization of tetraphenylcyclobutadiene.



Thermal decomposition of tetraphenylbutadiene derivatives, similar to the method used by Freedman, also produced this hydrocarbon at about the same time for Braye, Hübel and Caplier⁶. Büchi and co-workers⁷ have obtained it from the irradiation of diphenylacetylene in hexane; whereas Maitlis and Stone⁸ have prepared it in 70% yield from tetraphenylcyclobutadienepalladium chloride with triphenylphosphine in refluxing benzene.

The accumulating evidence for the cubane system is compelling. Recent data from the mass spectrograph^{9**} and from oxidations of the hydrocarbon structure support the cubane structure and contradict an alternate (IV) suggested by Cookson and Jones¹⁰. We find that the nitric acid oxidation of the $C_{56}H_{40}$ hydrocarbon gives



p-nitrobenzoic acid in 65% yield to the exclusion of either 4-nitrophthalic acid or its decarboxylation product, *m*-nitrobenzoic acid, expected from an oxidation of struc-

* A former coworker³ has seen fit to publish this data independently together with structure (I).

** We thank the authors for informing us of these results prior to publication.

ture (IV). Final confirmation of the cubane structure now awaits completion of single crystal X-ray examination, although this result may be anticlimatic in view of the identity of the cell dimensions of the hydrocarbon with those of an aluminum-nitrogen system whose cubic structure has been established by Jones and McDonald¹¹.

A more detailed examination of organomagnesium-acetylene systems has revealed the unique character of the phenylmagnesium-diphenylacetylene synthesis of the cubane molecule. With the exception of benzylmagnesium, other organometallic reagents in the list of reagents employed (see Table) are incapable of dimerizing diphenylacetylene under the conditions used successfully with phenylmagnesium. Methyl-, vinyl- and ethynylmagnesium centers fail to tetramerize or trimerize diphenylacetylene. An explanation based solely upon a singular structure for phenylmagnesium is invalidated by the failure of this reagent to tetramerize dimethylacetylene or methylphenylacetylene, although trimerization does occur in these instances. The latter acetylene is converted into a mixture of the two isomeric trimethyl-triphenylbenzenes. Apparently a combination of aromatic-carbon bonding to the acetylene and the proximity of aromatic groups to the magnesium center is essential to cubane synthesis. Even in the exceptional case of benzylmagnesium the separation of the phenyl substituent by one carbon atom from the magnesium center markedly reduces its effectiveness in cubane synthesis. Consideration of such factors as bulk or electronic effects does not appear to lead to a helpful interpretation.

Other organometallic combinations, *e.g.* phenyllithium-diphenylacetylene or dimethylberyllium-diphenylacetylene, do not result in either tetramerization or trimerization. The former pair does produce *trans*-stilbene, a result which coincides with recent attempts by Mulvaney and Gardlund¹² to produce the cubane structure from diphenylacetylene using *n*-butyl- and *tert*-butyllithium.

TABLE I

Organometallic	Reagent + $RC \equiv CR'$	→	Tetramer Cubane	÷ Trimer	÷ Other Products
$(CH_3)_2Mg$	$R, R' = C_6H_5$	—	—	—	—
CH_3MgBr	$R, R' = C_6H_5$	—	—	—	—
$(CH_2=CH)_2Mg$	$R, R' = C_6H_5$	—	—	—	—
$CH_2=CH_2MgBr$	$R, R' = C_6H_5$	—	—	—	—
$(HC \equiv C)_2Mg$	$R, R' = C_6H_5$	—	—	—	—
$HC \equiv CMgBr$	$R, R' = C_6H_5$	—	—	—	—
$(C_6H_5)_2Mg$	$R, R' = C_6H_5$	÷	÷	—	—
C_6H_5MgBr	$R, R' = C_6H_5$	÷	÷	—	—
$C_6H_5CH_2MgCl$	$R, R' = C_6H_5$	÷	÷	—	—
C_6H_5MgBr	$R, R' = CH_3$	—	÷	—	$(C_6H_5)_2$
C_6H_5MgBr	$R = C_6H_5, R' = CH_3$	—	÷	—	resin, $(C_6H_5)_2$
$(CH_3)_2Be$	$R, R' = C_6H_5$	—	—	—	—
C_6H_5Li	$R, R' = C_6H_5$	—	—	—	<i>trans</i> -stilbene

Success or failure in coordinative synthesis as demonstrated in this present work is peculiarly dependent on the structural environment of the metal center at which synthesis is occurring and the nature of the coordinating ligands. A satisfactory termination of the continuing controversy over the structure of Grignard reagents* may

* The recent communication by Rundle¹³ provides an excellent point of reference.

structural problems is of fundamental importance in the rational development of synthetic methods in organometallic chemistry.

EXPERIMENTAL

Experimental conditions consistently employed were the following: reactions were carried out in xylene solution covered by an inert atmosphere (nitrogen or argon) with rigorous exclusion of moisture and oxygen. The organometallic reagents were prepared in diethyl ether or tetrahydrofuran, their titer determined and then freed of ether in part by distillation and finally by heating in boiling xylene. Reaction periods of 4 hours with acetylenes, and 15 hours with those which showed little or no reactivity, were followed by filtration of insoluble products, hydrolysis of the xylene solution with iced water and treatment of the aqueous layer according to the usual ether extraction procedure.

Diphenylacetylene and phenyl Grignard

Diphenylacetylene (3.564 g, 0.02 mole) and phenyl Grignard (0.01 mole) in 37 ml of xylene were refluxed for 4 hours at 130° during which a white crystalline precipitate was formed. This was filtered, washed with dilute hydrochloric acid, water and ether: 0.450 g (12.5% based on the acetylene). Separation and purification was effected by fractionally separating 25 mg of this material with a 3000-fold amount of hot benzene, thereby yielding 15 mg (60%) of an insoluble fraction (1) and 10 mg (40%) of *hexaphenylbenzene*, m.p. 446–448°, which crystallized from the remaining benzene solution. The latter, after recrystallization from benzene was identified by comparison with an authentic sample.

Fraction (1), after 3 recrystallizations from diphenyl ether, reached a constant m.p., 425–427°, and was confirmed crystallographically as *octaphenylcubane* by comparison of its cell constants, $a = 19.54$ and $c = 10.60$ Å, with those reported by Freedman and Petersen², $a = 19.49$ and $c = 10.65$ Å. The crystals are tetragonal* with Space Group $I 4_1/a$.

Diphenylacetylene and benzyl Grignard

Diphenylacetylene (3.564 g, 0.02 mole) and benzyl Grignard (0.01 mole) in 38 ml of xylene were refluxed for 4 hours under nitrogen. After work up as described in the previous experiment 60.5 mg of product (1.7% based on the acetylene) was isolated. Fractional separation of the mixture with benzene gave 8 mg (13%) of octaphenylcubane and 52.5 mg (87%) of hexaphenylbenzene.

Dimethylacetylene and phenyl Grignard

A bomb tube containing 0.006 mole of phenylmagnesium bromide and 0.688 g (0.013 mole) of dimethylacetylene, in 12 ml of xylene was heated in an autoclave at 130° for 4 hours. At the end of this period the reaction contents were hydrolyzed and worked up as described previously. The 370 mg of brown liquid obtained by ether extraction was chromatographed on a column with a 40-fold amount of alumina. Elution with

* Dr. J. J. DALY of these laboratories kindly undertook the task of obtaining this data.

petroleum ether gave 245 mg of a colorless oil from which about equal amounts of *hexamethylbenzene* and *biphenyl* were isolated by preparative gas chromatographic analysis. They were further identified by comparison with authentic specimens.

Methylphenylacetylene and phenyl Grignard

A mixture of the acetylene (2.904 g, 0.025 mole) and 0.0125 mole of phenylmagnesium bromide in 32 ml of xylene were refluxed for 4 hours under argon and then worked up as usual. The viscous product (2.743 g) was chromatographed on alumina from which *ca.* 40 % of the unreacted acetylene was recovered by elution with petroleum ether.

A petroleum ether-benzene mixture eluted crystalline product (8.5 % yield based on the acetylene) which was shown to be a mixture by thin layer chromatography. The mixture was rechromatographed on alumina from which 1.4 % of biphenyl, m.p. 68–70° was eluted with petroleum ether. Further elution with petroleum ether-benzene gave 3.4 % of a crystalline product which after crystallization from methylene dichloride-methanol melted between 216–218°. With the aid of comparative infrared spectra, mixed melting points and thin layer chromatography the material was identified as a mixture of *1,2,4-trimethyl-3,5,6-triphenylbenzene* and *2,4,6-triphenylmesitylene**.

Diphenylacetylene and phenyllithium

The acetylene (3.725 g, 0.021 mole) and phenyllithium (0.010 mole) in 35 ml of xylene were refluxed under argon. Reaction appeared to cease after 5 hours as indicated by the color becoming dark brown. The mixture was hydrolyzed and extracted with ether. The ether layer was then extracted with 2N sodium hydroxide solution. The alkali layer was acidified and reextracted with ether from which a small amount of phenol (*ca.* 1 %) was obtained. The neutral fraction, 4.2 g in the ether layer above, was recovered by removal of solvent and then chromatographed on a 40-fold amount of alumina. By elution with petroleum ether 32 % of unreacted diphenylacetylene was recovered. Further elution with a 9:1 mixture of petroleum ether-benzene gave 38 % yield of a crystalline product m.p. 118–120°, which was identified by comparison as *trans-stilbene*.

Oxidation of C₅₆H₄₀ hydrocarbon with nitric acid

The C₅₆H₄₀-product (451 mg) from the reaction of phenyl Grignard and diphenylacetylene was suspended in 30 ml. of 50 % aqueous nitric acid and refluxed for 72 hours. At the end of the period the hydrocarbon had disappeared giving a yellow solution. This was extracted with ether which in turn was extracted with 2N sodium hydroxide. Acidification of the alkali layer gave 551 mg of crude acidic product. The partly crystalline material, after washing in ether solution, was chromatographed on silica gel, giving a 65 % yield of *p-nitrobenzoic acid*, m.p. 237–239°, identified by mixed melting point and infrared spectral comparison with an authentic sample. The neutral fraction was an amorphous material, 109 mg.

provide an answer to the problem raised here in cubane synthesis. The solution of such

* We are indebted to Dr. W. HÜBEL of European Research Associates, Brussels, for his kindness in supplying samples of these substances.

SUMMARY

Diphenylacetylene is tetramerized uniquely by arylmagnesium to a $C_{56}H_{40}$ hydrocarbon for which the octaphenylcubane structure has been proposed. Synthesis of the cubane ring system cannot be duplicated when methyl or methyl-phenyl substituents are present on acetylene or various other organic groups on magnesium. The singular character of cubane synthesis on magnesium centers is related in a peculiar manner to an environment of aryl groups.

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