Tetrahedron Letters No.46, pp. 5779-5782, 1966. Pergamon Press Ltd.
Printed in Great Britain.

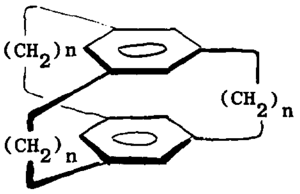
SYNTHESIS OF A NOVEL CLASS OF MONOBENZENOID-CAGE COMPOUNDS

A. J. Hubert and M. Hubert

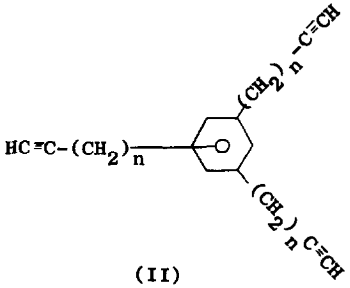
Union Carbide European Research Associates, S.A.
95 Rue Gatti de Gamond
Brussels 18, Belgium

(Received 3 September 1966)

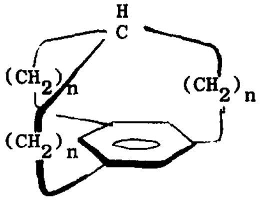
A series of dibenzenoid cage compounds (I) has been synthesized recently by internal cyclotrimerization of aromatic triynes (II) (1). We want now to report the synthesis of a novel class of monobenzenoid-cage compounds (III) which is obtained by internal cyclotrimerization of the triynes (IV) on a Ziegler catalyst (1).



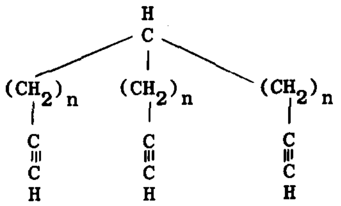
(I) (n = 3,4,5,6,7,8,9)



(II)



(III) (n = 4,5,6)



(IV)

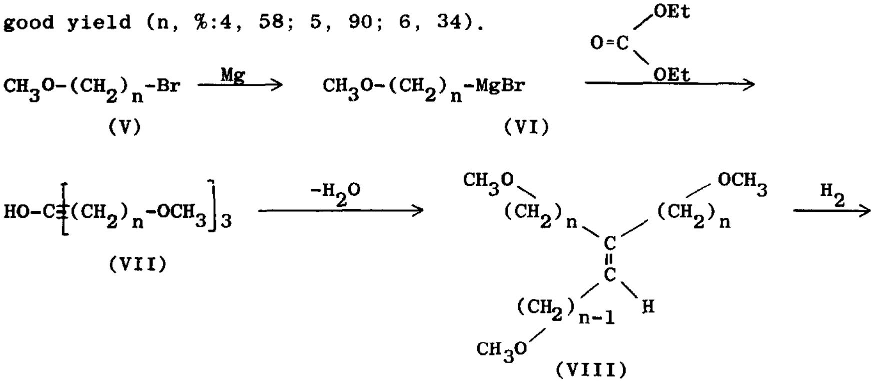
The triynes (IV) were prepared by the following steps:

The ω-methoxyalkyl bromides (V) were prepared by the reaction of the corresponding ω-methoxyalkanol with PBr_3 (2) or, better, by the reaction of sodium methoxide with the α,ω-dibromoalkanes (3).

Reaction of the ω-methoxyalkylbromides (V) with Mg according to the standard procedure gave the corresponding Grignard reagent (VI) which was treated with one equivalent (1/3 mole) of diethyl carbonate. The carbinols (VII) were obtained in good yield (~50%) and dehydrated on alumina at 250°C. In some attempts the dehydration occurred directly during the distillation of the carbinols and the olefins (VIII) were obtained without further treatment. The yield of olefin was at least 65%. Catalytic reduction in the presence of Pt at 100°C. under pressure of hydrogen (>100 Kg) gave the tris(ω-methoxyalkyl)-methane (IX). Reaction of (IX) with a saturated solution of hydrogen bromide in acetic acid gave the tris(ω-bromoalkyl-) methane (X) in good yield (90%).

The tribromides (X) were shaken with a solution of monosodium acetylide in ammonia in an autoclave at room temperature.

The tris(ω-alkynyl-) methanes (IV) were obtained in good yield (n, %:4, 58; 5, 90; 6, 34).



$$\underset{(IX)}{H\text{-}C\left[\text{-}(CH_2)_n\text{-}OCH_3\right]} \xrightarrow{HBr} \underset{(X)}{H\text{-}C\left[\text{-}(CH_2)_n\text{-}Br\right]_3} \xrightarrow{NaC\equiv CH} IV.$$

Cyclotrimerization under high dilution (1) gave the cage-compounds (III) (Table I) as a mixture of isomers.

TABLE I

n	Yield % Mixture of Isomers	Yield % Pure 1,3,5 Isomer	bp °/mm	mp(1,3,5) °C
4	14	~ 8*	160-185/0.001	liq.
5	40	22*	160-180/0.001	155
6	17	8**	180-190/0.001	64

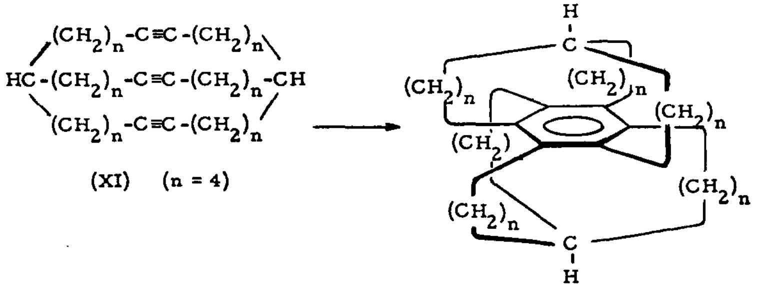
---

* measured by G.L.C.

** isolated by crystallization.

The cage compounds (IV) were identified by analysis, molecular weight determination, IR spectra (particularly strong absorption at 6.25 μ typical for a 1,3,5-trisubstituted benzene ring) and UV spectra. Typical absorption occurs at 268 mμ, ε $\simeq$ 300, in the case of n = 4, the absorption is weaker and the resolution is very poor : there is a shoulder at 264 mμ, ε $\simeq$ 230 : this indicates probably a deformation of the benzene ring (4).

Condensation of the trisodium salt of the triyne (IV) (n=4) with the tribromide (X) (n=4) gave a novel type of macrocyclic triyne (XI) which was isolated by distillation (bp 220-260°/ 0.001 mm).



(XI) (n = 4)

Recrystallization in hexane gave crystals (2.3%) melting at 176°. We hope that internal trimerization of the triyne (XI) will give a novel kind of cage compound (XII) ; this is being investigated.

Cage compounds similar to (III) but with polymethylene chains of different lengths are now being synthesized : Reaction of ω-methoxyalkyl magnesium bromide (VI) containing n methylene groups in the chain with ethyl formate gives a secondary alcohol which is oxidized to the ketone by CrO_3 in acetone. Reaction with another ω-methoxyalkyl magnesium bromide containing $m \neq n$ methylene units gives a carbinol (VII) containing (m, n, n) polymethylene chains. The other steps are identical to those described above. The triyne (IV) ($m = 5$, $n = 4$, $n = 4$) has been prepared by this procedure. Others are under preparation and will be trimerized. The spectra and the chemical properties of these compounds will be investigated.

REFERENCES.

(1) A. J. Hubert, Chemical Society Anniversary Meeting, Glasgow (1965), J. Chem. Soc. 1966, 000.

(2) L. I. Smith, J. A. Sprung, J. Amer. Chem. Soc. 1943, 65, 1279.

(3) H. T. Clarke, J. Chem. Soc. 1913, 103, 1703.

(4) D. J. Cram and Counkers, J. Amer. Chem. Soc. 1959, 81, 5971.
1964, 86, 5722.