any of these conditions was <1%.

(8) A study involving asymmetric alkylation of aldehydes via their chiral imines has been performed and appears to depend upon different parameters than that reported here [A. I. Meyers, G. S. Poindexter, and Z. Brich, *J. Org. Chem.*, **43**, 892 (1978)].

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Novel Oligomers of Propyne: Tetramethylcyclooctatetraenes and (*Z*)-2,4-Dimethyl-1,3-heptadien-5-yne

Summary: Propyne has been catalytically oligomerized to produce novel cyclic tetramers, a linear trimer, and cyclic trimers.

Sir: Numerous organometallic compounds are known to catalyze the oligomerization of propyne to mixtures of 1,2,4- and 1,3,5-trimethylbenzene.[1] We wish to report that the black, nickel-containing substances prepared by the co-condensation[2] of nickel atoms and alkynes are active, homogeneous catalysts for the oligomerization of terminal acetylenes under very mild conditions, in some cases producing novel oligomers.[3] In the case of propyne, the new oligomers are: 1,3,5,7-tetramethylcyclooctatetraene (I), 1,2,4,6-tetramethylcyclooctatetraene (II), 1,2,4,7-tetramethylcyclooctatetraene (III), and (*Z*)-2,4-dimethyl-1,3-heptadien-5-yne (IV), a linear trimer; the first named compound was prepared earlier by photolysis of 2,4-dimethylcoumalin.[7]

For the purpose of this study, oligomerization reactions were conducted in sealed tubes at 60 °C in dioxane solvent in the presence of 10 g of liquid propyne employing the soluble, black Ni–propyne co-condensation product as catalyst. Propyne and other alkynes such as acetylene, phenylacetylene, and 2-methyl-3-butyn-2-ol can also be cyclotetramerized at room temperature and 1 atm pressure. In a typical sealed tube reaction, 0.1 g of nickel catalyst dissolved in 5 mL of dry, air-free dioxane will oligomerize 4–6 g of propyne monomer in 20 h. The distribution of products is given in Table I.

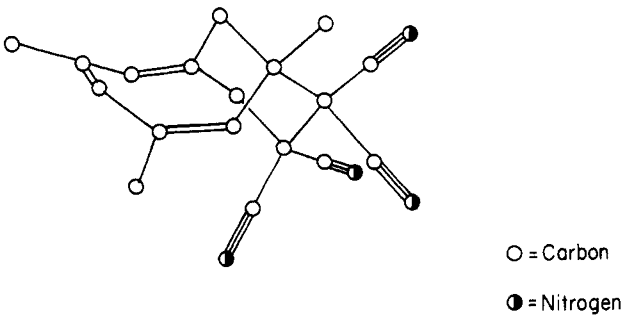
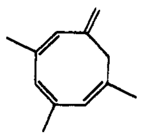


Figure 1. Perspective view of 3,5,7-trimethyl-8,8,9,9-tetracyanobicyclo[5.3.1]undeca-1,3,5-triene (hydrogen atoms omitted for clarity).

For the purpose of structural characterization of particular isomers, the oligomer mixture was reacted with tetracyanoethylene (TCNE) in ether–dioxane solution at 18 °C under nitrogen, using TCNE as the limiting reagent, giving a brown-red solution which becomes almost colorless in about 3 min. Removal of solvent and unreacted oligomers under vacuum at room temperature and sublimation of the white residue at 75 °C (10^{-2} Torr) yields two products, a tetramer–TCNE adduct (*m/e* 288) and a trimer–TCNE adduct (*m/e* 248). The adducts can be separated by vacuum thermal gradient sublimation, yielding a white tetramer–TCNE adduct (mp 184–186 °C dec) (V) and a white trimer–TCNE adduct (mp 86–87 °C) (VI).

Definitive structural information about V was obtained from an X-ray crystal structure analysis on crystals grown from ether solution. The structure of V is shown in Figure 1.[4]

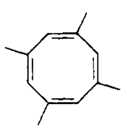
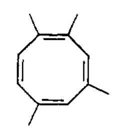
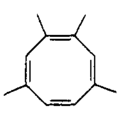
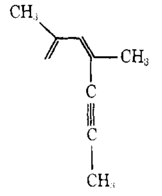
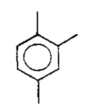
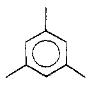


VII

Consideration of the structure of V reveals it to be the 8 + 2 cycloaddition product of TCNE with the hydrocarbon (VII), an exocyclic methylene isomer of 1,3,5,7-tetramethylcyclooctatetraene (I). We believe that VII arises from I during the course of the reaction by means of an isomerization of I mediated by TCNE radical anion[5] and the inherent stability of the radical cation of I compared to radical cations of other isomers of tetramethylcyclooctatetraene.[6] Other information supporting the presence of I rather than VII in the oligomer mixture includes: (1) the absence of *exo*-methylene and allylic methylene resonances in ^{1}H and ^{13}C NMR spectra of tetramer mixtures; (2) the presence of ^{13}C NMR resonances attributable to I at 23.9, 125.7, and 140.8 ppm vs. Me$_4$Si in DCCl$_3$ from tetramer mixtures distilled from the trimer; (3) the decrease of a sharp ^{1}H NMR methyl resonance at δ 1.66 from within the methyl resonance envelope after reaction with TCNE, compared to the methyl resonance of δ 1.68 reported for pure I;[7] (4) in reactions requiring 40 h at 20 °C Criegee et al.[8] prepared TCNE adducts of three isomeric tetramethylcyclooctatetraenes (none of which was I). All adducts were 4 + 2 cycloaddition products of the bicyclo form of the olefin. Because our adduct is formed in 3 min, we believe a route other than that observed by Criegee is involved.

After reaction with TCNE, unreacted tetramer eluted from 10% AgNO$_3$ on silica gel with 20:1 pentane–ether proved to

Table I. Oligomers of Propyne

oligomer						
	I	II	III	IV		
mol % oligomer produced	10[a]	30[a]	15[a]	34[b]	6[b]	5[b]

[a] Integration of ^{1}H NMR shows 55% tetramer; amounts of individual isomers are estimated from GC/MS data. Tetramer mixtures show an asymmetric vinyl resonance centered at δ 5.40 and asymmetric methyl resonances centered at δ 1.70 vs. Me$_4$Si in CS$_2$ solution. [b] Integration of ^{1}H NMR.

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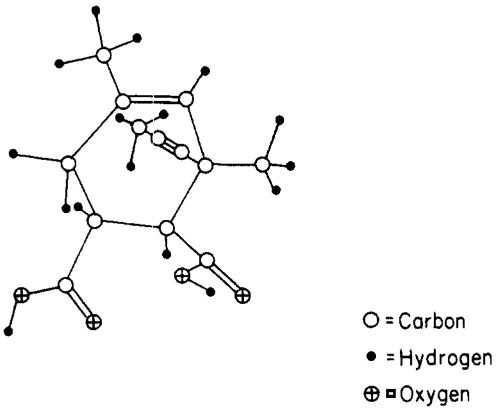

Figure 2. Perspective view of 3,5-dimethyl-*trans*-3-(1-propynyl)-4-cyclohexene-*cis*-1,2-dicarboxylic acid.

be primarily one isomer, assigned structure II based on ^{13}C NMR resonances at 21.7, 21.9, 23.5, 23.7, 125.9, 126.2, 128.4, 128.5, 138.4, 139.1, 140.6, and 141.2 ppm. Material not chromatographed from $AgNO_3$ proved to be a mixture of primarily two isomers, compound II and another isomer, assigned structure III based on ^{13}C NMR resonances at 21.6, 23.9, 125.8, 128.8, 138.7, and 140.7 ppm.

Repeated attempts to obtain crystals of the trimer–TCNE adduct (VI) suitable for X-ray analysis proved fruitless. Thus, reaction of trimer mixtures with excess maleic anhydride in dioxane–acetone for 4 h at 60 °C produces a trimer–maleic anhydride adduct (VIII) (*m/e* 218) almost quantitatively. After thermal gradient vacuum sublimation to separate excess maleic anhydride, VIII unfortunately proved to be a colorless, viscous liquid which could not be crystallized. Treatment of VIII with H_2O at 80 °C for 30 min produced an almost quantitative yield of the trimer–"maleic acid" adduct (IX) (*m/e* 236) which after sublimation at 125 °C (10^{-2} Torr) and recrystallization from ether–hexane gave white crystals (mp 197–198 °C) suitable for X-ray analysis.

The results of the X-ray structural analysis of IX are shown in Figure 2.[9]

Analysis of this adduct by standard Woodward–Hoffmann rules for Diels–Alder adducts[10,11] shows the trimer to be (*Z*)-2,4-dimethyl-1,3-heptadien-5-yne (IV) rather than the other possible isomeric arrangement about the 4 position. Compound IV exhibits the following NMR spectra: ^{1}H in dioxane, slightly broad vinyl resonances at δ 6.05, 5.01, and 4.87, and sharp methyl resonances at δ 1.92 and 1.87, with relative areas 1:1:1:6:3; ^{13}C, in $DCCl_3$, sp^3 resonances at 4.5, 21.2, and 26.0, sp resonances at 80.6 and 92.2, sp^2 resonances at 116.6, 117.6, 136.1, and 142.5 ppm vs. Me_4Si. The other trimers, 1,2,4- and 1,3,5-trimethylbenzene, were identified from reference ^{1}H and ^{13}C NMR spectra.

Additionally, the same nickel catalysts used for propyne oligomerization will reduce benzene to cyclohexane and methyl benzoate to methyl cyclohexylcarboxylate at room temperature and 2 atm hydrogen pressure in ether solution.

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