J. Org. Chem. 1987, 52, 1161–1165

Bis(benzylthio)methane (15). The reaction mixture turned quickly dark red with polymer formation. Filtration and removal of the toluene gave a dark red oil which was separated on a chromatographic column (silica gel; eluent 1:19 mixture of E/P). Two fractions were obtained: (1) a colorless oil which was crystallized from pentane, giving 0.83 g (13%, based on 6.2 g of used thiol) of colorless crystals, **15**,[26] mp 47–49 °C (lit.[24] mp 55 °C), and (2) a red oil which could be crystallized from E/P to give 0.27 g (4%) of slightly yellow crystals identified as **17**,[26] mp 98–100 °C (lit.[25] mp 102.2–103.2° C).

By performing the reaction in the presence of 0.2 g (2 mmol) of CuCl, 0.65 g (10%) of **15** and 80 mg (1%) of **17** were obtained.

Attempted Reaction with Methanol. This reaction has been reported previously[11a] and a repetition with neat methanol at −78 °C applying the experimental set-up used in this work only resulted in polymer formation. The methanol could be quantitatively recovered.

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Registry No. **2**, 622-15-1; **3**, 20278-32-4; **4**, 106712-04-3; **5**, 5780-30-3; **6**, 13749-55-8; **7**, 106712-05-4; **8**, 106712-06-5; **9**, 637-51-4; **10**, 1424-14-2; **13**, 3561-67-9; **14**, 4431-80-5; **15**, 4431-79-2; **16**, 16754-60-2; **17**, 10606-38-9; CS, 2944-05-0; CS_2, 75-15-0; PhSH, 108-98-5; BuSH, 109-79-5; $PhCH_2SH$, 100-53-8; CS (polymer), 69822-67-9; diisopropylamine, 108-18-9; aniline, 62-53-3; benzylamine, 100-46-9; *tert*-octylamine, 107-45-9; morpholine, 110-91-8; dibutylamine, 111-92-2; piperazine, 110-85-0; *p*-nitroaniline, 100-01-6; *N*-methylaniline, 100-61-8; diphenylamine, 122-39-4; pyridine, 110-86-1; triethylamine, 121-44-8; *N*-benzyldithiocarbamic acid benzylammonium salt, 106712-07-6; morpholinomethanedisulfonic acid morpholinium salt, 5327-10-6; methanol, 67-56-1.

Homogeneous Catalysis with a Heterogeneous Pd Catalyst. An Effective Method for the Cyclotrimerization of Alkynes

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Introduction

In 1866, Berthelot discovered the formation of benzene in small yields by high temperature treatment of acetylene.[1] In 1949, Reppe reported that homogeneous nickel complexes can be employed for the preparative cyclization of acetylene to benzene.[2] This key observation was followed by the development of a variety of transition-metal systems for cyclotrimerization of alkynes.[3]

The oligomerization of alkynes has been reviewed.[3,4] In the following we list only a few selected examples demonstrating the diverseness of methods and catalysts developed. Substituted benzenes have been prepared by the cyclotrimerization of alkynes in the presence of metal carbonyls $HgNi(CO)_4$ and $Hg(Co(CO)_4)_2$,[5,6] $Fe(CO)_5$ and $Fe(CO)_4H_2$,[7] $Co_2(CO)_8$,[8,9] trialkyl- and triarylchromium compounds,[10] and Ziegler catalysts.[11] Ziegler catalysts require careful optimization of the ratio of alkylaluminum and transition-metal halide to avoid polymer formation and thereby improve yield of trimers.[11a] High yields of hexaethylbenzene were obtained with optimized ratios of $i\text{-}Bu_3Al$ and $TiCl_4$.[11b] Good yields of hexaethyl-, hexamethyl-, and hexaphenylbenzene were obtained from the corresponding alkyne with $i\text{-}Bu_2AlH$.[12] Monosubstituted alkynes and acetylene itself can be trimerized in moderate to good yields with this Ziegler-type catalyst system.[11,13] Hexaisopropylbenzene, the most hindered benzene prepared to date by alkyne trimerization (see MM2 molecular mechanics calculations below), utilizes Co complexes, apparently the most effective catalysts for alkyne trimerization.[6,9] Careful examinations of such cobalt-mediated trimerizations led to the development of highly efficient and selective syntheses of steroids and other complex molecules.[14]

Bis(acrylonitrile)nickel(0)[15] and bis(benzonitrile)palladium chloride[16] can catalyze trimerization of tolane to give hexaphenylbenzene. Bis(benzonitrile)palladium chloride[17] was found suitable for cyclotrimerization. The reaction with 1-phenylpropyne resulted in a complex mixture which after tedious workup afforded all the three possible isomers.[17a] $NaBH_4$ with $NiCl_2$[18] has also been utilized for the cyclotrimerization of alkynes. The cyclization of 3-hexyne gave reasonable yields of hexaethylbenzene while cyclization of diphenylacetylene afforded poor yields of hexaphenylbenzene using this catalyst.

The use of uncomplexed $PdCl_2$ for the cyclotrimerization of 1-phenylpropyne and 1-phenyl-1-butyne resulted in low yields of unsymmetrical trimer, polymer products, and several complexes.[19] Tantalum and niobium compounds like $Ta_2Cl_6(THT)_3$ and $Nb_2Cl_6(THT)_3$ (THT = tetrahydrothiophene) were found to trimerize terminal alkynes effectively while polymerization predominated with unsymmetrically disubstituted acetylenes.[20] Rhodium complexes were found to effect a low yield trimerization of 3-hexyne and tolane on prolonged heating.[21] Even iron atoms can induce the cyclotrimerization of alkynes.[22]

Many of these methods produce complex reaction mixtures which afford low yields of the desired trimers while all require very stringent reaction conditions. The development of a more convenient method for the trimerization of alkynes is therefore still desirable.

Although the trimerization of alkynes has remained

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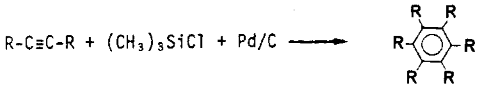
Table I. Trimerization of Alkynes with Me_3SiCl and Pd/C in Refluxing THF as Solvent

starting compounds	reaction time	yield of product (%)
3-hexyne	3 h	1 (100)
5-decyne	6 h	2 (100)
diphenylacetylene	4 days	3 (100)
2-hexyne	48 h	4 (60)
1-phenyl-1-propyne	6 days	5 (20), 6 (80)
tert-butylacetylene	48 h	7 (30), 8 (40)

essentially a homogeneously catalyzed reaction, the formation of benzene on (111) Ni faces has been reported by Bertolini et al. in 1977.[23] Tysoe[24] and Sesselmann[25] reported in 1983 the trimerization of acetylene on low Miller index planes of palladium. It has been found that (111) Pd surfaces are more active than (100) or (110) surfaces.[26] This heterogeneous reaction has also been extended to the formation of pyridine from acetylene and hydrogen cyanide;[27] however, all attempts to achieve trimerization of substituted alkynes on single-crystal surfaces have been unsuccessful.[28] The development of a general heterogeneous method for the trimerization of alkynes still represents a challenging problem.

During the attempted addition of trimethylsilyl chloride to alkynes in the presence of Pd/C, we observed the formation of hexaethylbenzene from 3-hexyne in high yields.



This apparently heterogeneously catalyzed cyclization turned out to be homogeneous upon closer inspection. It is amusing to find a heterogeneous reaction which is actually homogeneous in nature, considering the more common problem of proving that a homogeneous reaction is not in fact heterogeneously catalyzed. Because of the high yield, the ambient reaction conditions and the simplicity of the procedure we have studied this reaction in some detail.

Results and Discussion

A simple new method for the trimerization of alkynes has been developed. The procedure utilizes heterogeneous Pd/C as catalyst in normal atmosphere with refluxing THF as solvent and commercial-grade trimethylsilyl chloride. Most reactions were conducted on a preparative scale to provide several grams of substituted benzene. Scheme I and Table I summarize the results. The reactions were monitored by GC for disappearance of starting material.

Disubstituted Alkynes. 3-Hexyne trimerizes most readily in quantitative yield after only 3 h. High yields of hexaethylbenzene formation have also been reported with $Ta_2Cl_6(THT)_3$ and Ziegler catalyst under more stringent conditions.

5-Decyne trimerizes to hexa-*n*-butylbenzene in quantitative yield but requires a longer reaction time of 6 h.

Diphenylacetylene trimerized in high yield to hexaphenylbenzene with a reaction time of 4 days. The data indicate that the trimerization is not affected by aromatic or straight chain aliphatic substituents. The long reaction time for the diphenylacetylene may point to steric hindrance. Table II lists the results of molecular mechanics calculations. The strain energies for all the hexasubstituted benzenes are similar, about 20 kcal/mol, with the exception of hexaisopropylbenzene and 1,2,4-tri-*tert*-butylbenzene.

Scheme I

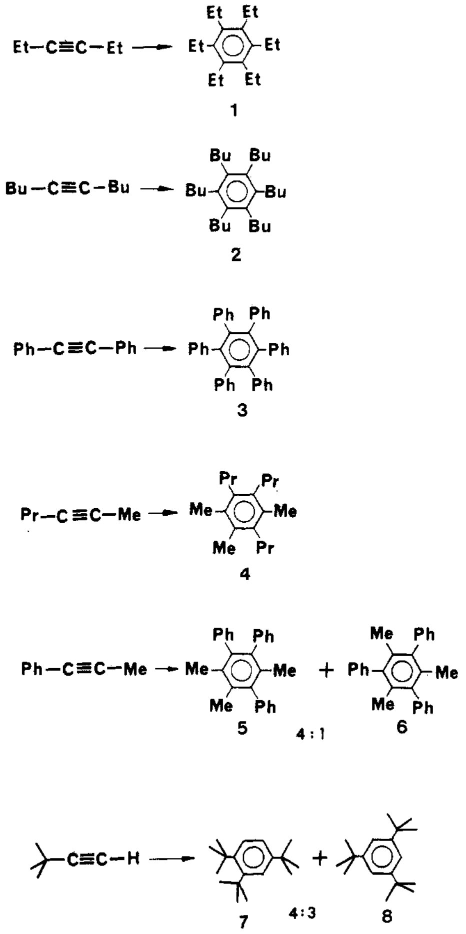


Table II. MMP2[40] Calculations of Alkyne Monomers and the Associated Trimers

compound	H_f (kcal/mol)	strain energy (kcal/mol)
2-hexyne	26.18	0
3-hexyne	27.76	0.22
5-decyne	4.83	0.31
tert-butylacetylene	29.82	0.56
diisopropylacetylene	16.40	0.38
4,4-dimethyl-2-pentyne	20.48	0.56
1-phenylpropyne	180.47	11.86
diphenylacetylene	102.50	19.33
1,2,4-trimethyl-3,5,6-tri-*n*-propylbenzene	−42.53	17.22
1,3,5-trimethyl-2,4,6-tri-*n*-propylbenzene	−42.10	17.65
hexaethylbenzene	−38.99	20.76
hexa-*n*-butylbenzene	110.53	18.27
1,3,5-tri-*tert*-butylbenzene	−42.31	18.20
1,2,4-tri-*tert*-butylbenzene	−29.39	31.13
1,3,5-tri-*tert*-butyl-2,4,6-trimethylbenzene	−33.15	45.36
1,3,5-trimethyl-2,4,6-triphenylbenzene	86.56	47.14
1,2,4-trimethyl-3,5,6-triphenylbenzene	87.34	48.19
hexaisopropylbenzene	−31.93	62.35
hexaphenylbenzene[a]	166.02	20.13

[a] Hexaethylbenzene was calculated with the MMP2 program from Molecular Design.

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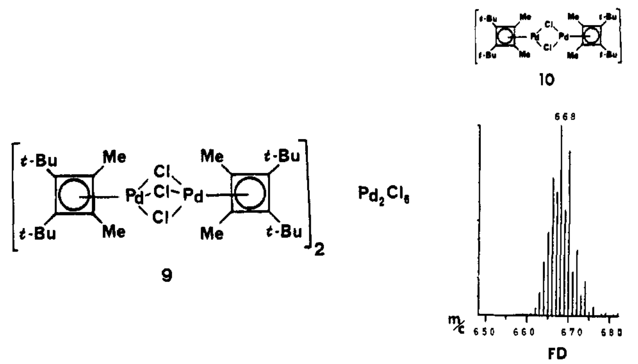

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Figure 1. Proposed structure **9** for the isolated Pd complex and its field desorption spectrum (FD).

Trimerization of the unsymmetrical 2-hexyne produced the asymmetric trimer 1,2,4-trimethyl-3,5,6-tripropylbenzene in about 90% yield. The structure of this new compound could be assigned unequivocally by the spectroscopic data. Such a clear preference for the formation of the less stable trimer indicates kinetic product formation.

1-Phenylpropyne, previously trimerized with Ziegler catalysts[12] and i-Bu$_2$AlH,[17a] also formed the asymmetric 1,2,4-trimethyl-3,5,6-triphenylbenzene to a larger extent; however, the symmetric isomer could also be isolated.

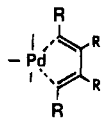
Attempts to trimerize the more hindered 2,5-dimethyl-3-hexyne and 4,4-dimethyl-2-pentyne were unsuccessful. No trimer was detectable even after 7 days of reaction time by GC-MS. In the case of the diisopropylacetylene, an unidentified dimer was obtained.

Small amounts of an insoluble palladium complex could be isolated by crystallization from the reaction of 4,4-dimethyl-2-pentyne. This Pd complex was found to be very active for the trimerization of 3-hexyne, indicating that such complexes might represent the actual catalyst formed in the Pd/C and Me_3SiCl mixture. Attempted mass spectroscopy by electron impact analysis was unsuccessful. Fast atom bombardment (FAB) produced four major ions: m/z 703 (dimer **10** + Cl), m/z 667 (dimer **10** + 1), m/z 633 (dimer **10** − Cl), and m/z 333 (monomer). In addition, m/z 191, the alkyne dimer − 1, is a rather strong signal, indicating the presence of cyclobutadiene complexes. Field desorption (FD, see below) shows only the correct isotope pattern for $(t\text{-BuC}{=}\text{CMe})_4\text{Pd}_2\text{Cl}_2$ (m/z 667) in the molecular ion region. IR lacks any triple-bond resonance. Combustion analysis shows the total composition to be $(\text{4,4-dimethyl-2-pentyne})_4\text{Pd}_3\text{Cl}_6$, which is identical with $[\text{Pd}_2\text{Cl}_3(\text{C}_4\text{-}t\text{-Bu}_2\text{Me}_2)_2]_2[\text{Pd}_2\text{Cl}_6]$, a highly insoluble compound reported by Kelly et al.[29] shown below (**9**). Although the data provided are strong evidence that the isolated Pd complex is identical with **9**, the lack of spectroscopic data in the original literature did not allow unequivocal assignment.

Terminal Alkynes. The trimerization of acetylene to benzene was accomplished at 0 °C. All attempts to trimerize 1-hexyne resulted in the formation of polymeric material along with small amounts of tetramers (GC-MS). No indication of trimer formation was obtained. Ni(0) complexes selectively trimerize phenylacetylene to the 1,2,4-triphenylbenzene.[30] Attempts to trimerize phenylacetylene with the Pd/C method resulted in the formation of a mixture of unidentified tetramers which, based on ^{1}H NMR and high resolution MS, appeared to be a mixture of tetraphenylcyclooctatetraenes. No trace of trimer could be detected by GC-MS of the crude product mixture.

The trimerization of 3,3-dimethyl-1-butyne (*tert*-butylacetylene) was selected to probe the sensitivity of the reaction to steric effects. The unsymmetrical 1,2,4-trimer has been synthesized by classical procedures in 18% yield[31] and in about 25% yield by trimerization of *tert*-butylacetylene with $\text{Co}_2(\text{CO})_8$ catalyst as the first benzene derivative containing two *o*-*tert*-butyl groups.[32] The molecular mechanics calculations, which predict an energy difference of 13 kcal/mol between the symmetrical and the unsymmetrical trimer, are in reasonable agreement with the experimental energy difference of 16.8 ± 1.7 kcal/mol.[5]

The reaction was carried out under reflux conditions and monitored for disappearance of starting material. We obtained a complex product mixture which was separated by preparative TLC. The major products could be identified as the unsymmetrical 1,2,4- and the symmetrical 1,3,5-tri-*tert*-butylbenzene, which had formed to about 40% and 30%, respectively (GC data). The example shows that even a strain energy difference of 13 kcal/mol in the products is not sufficient to override the formation of the less stable isomer. Since the stepwise mechanisms of this alkyne trimerization on Pd has already been demonstrated,[33] the preferred formation of the unsymmetrical trimer can be readily traced to a steric effect during the coupling of the first C–C bond (intermediate **11**). Such an intermediate is also consistent with the exclusive formation of head-to-head dimers in cyclobutadiene Pd complexes formed from alkynes.[34]



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These results indicate that the more reactive terminal alkynes undergo oligomerization much more readily than disubstituted alkynes. The predominant formation of the less stable isomer can be rationalized by the usual stepwise trimerization mechanism in which the first C–C bond formation connects the more substituted alkynes, resulting in the less hindered metallocyclopentadiene (**11**).

Mechanistic Studies. In order to obtain more insight into the mechanism of this reaction, additional studies were conducted with 3-hexyne and 5-decyne as substrates. The reaction was carried out with varying amounts of trimethylsilyl chloride and the yield of trimer was found to be highest in the presence of equimolar or larger amounts. The only other byproducts were hexamethyldisiloxane and traces of hexamethyldisilane as identified by GC-MS. Trimerization of 3-hexyne with varying amounts of Pd/C indicated first-order dependence on the amount of catalyst (trimerization of the same amount of 3-hexyne required 3 days with 50 mg of Pd/C and 3 h with 1 g Pd/C). No indication of solvent effects could be obtained by the cyclotrimerization of 3-hexyne in methanol and methylene chloride. Most curious was the function of the trimethylsilyl chloride in this reaction. The hypothesis that trace amounts of HCl, formed during the

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reaction from the moisture present on the carbon support, is the actual catalyst, was tested. 3-Hexyne was subjected to cyclization with Pd/C and THF in the presence of hydrochloric acid (1% and 10%) and *p*-toluenesulfonic acid (1% and 10%) respectively. It was found that cycloaddition of 3-hexyne occurred with HCl (1%, 10%) to **1** in low yields (20%) while *p*-toluenesulfonic acid failed to give any detectable quantity of trimer. The formation of the byproduct hexamethyldisilane mentioned can also not be rationalized by a simple acid-promoted mechanism.

A purely acid-catalyzed mechanism bypassing the Pd could be excluded by the complete lack of trimerization product in a reaction of 3-hexyne with equivalent amounts of trimethylsilyl chloride in the absence of Pd/C. No trimerization with Pd/C in the absence of trimethylsilyl chloride confirmed the importance of both the Pd/C and the Me_3SiCl as precursors or part of the catalytic site. When the Pd/C was treated with trimethylsilyl chloride in refluxing THF for 3 h, filtered, and centrifuged, the mother liquor was found to be active for the 3-hexyne trimerization as well as for 1-octene hydrogenation, evidence for a homogeneous catalyst system. More evidence for the formation of homogeneous complexes was obtained from atomic absorption spectroscopy of the mother liquor obtained from the workup of reaction mixture of diphenylacetylene trimerization which indicated considerable amounts of dissolved Pd. During the workup of a 2-hexyne, trimerization the heterogeneous catalyst was separated by suction filtration and the mother liquor subjected to distillation. After removal of the solvent, the formation of an intensive Pd mirror was observed on the distillation flask, indicating the presence of considerable amounts of homogeneous or colloidal Pd in the reaction mixture. This palladium mirror was found to be active for the hydrogenation of 1-octene, confirming its nature.

The formation of hexamethyldisilane suggests that Pd may react with the trimethylsilyl chloride to form $PdCl_2$ and disilane. The presence of some highly dispersed Pd particles on the Pd/C may provide the driving force to overcome the otherwise poor thermochemistry of such a reaction. The activity of $PdCl_2$ as a catalyst for cyclotrimerization of alkynes has been described in the past.[17,19] Indeed, when we subjected 3-hexyne to $PdCl_2$ in refluxing THF, trimerization occurred in reasonable yields. 5-Decyne, however, under identical conditions, did not produce any trimer but tarry polymer confirming earlier reports on the polymerization of alkynes in the presence of $PdCl_2$.[19] When the trimerization of 5-decyne was attempted with a mixture of $PdCl_2$ and trimethylsilyl chloride, an excellent yield of the trimer was obtained, suggesting that trimethylsilyl chloride somehow solubilizes the $PdCl_2$ and interacts to form a soluble homogeneous complex that catalyzes the cyclization. Although this observation does not prove that the catalytic species obtained from Pd/C and from $PdCl_2$ with Me_3SiCl are identical, their effectiveness for alkyne trimerization is comparable. Considering the ease of trimerization under many reaction conditions, as shown in the introduction, it is not clear that there is only one catalytically active species.

Conclusion. A simple and general procedure for the trimerization of alkynes has been developed. Contrary to previous procedures, this method utilizes a heterogeneous Pd catalyst and does not require special precautions with respect to reaction conditions. It represents the most simple procedure for alkyne trimerization yet and can be recommended for medium scale synthesis.

More important than the development of a new experimental technique for the trimerization of alkynes, however, is the observation that effective homogeneous catalysis has been achieved with the use of a heterogeneous catalyst. Such a procedure seems very attractive for preparative applications considering the difference in cost per metal atom between heterogeneous catalysts and defined complexes. It may not only lead to practical applications in all areas of catalysis, it also acts as a drastic example for homogeneous catalysis obtained with a heterogeneous catalysts. It clearly raises the question on the true heterogeneity of heterogeneously catalyzed reactions, especially when conducted under drastic reaction conditions like high temperature or in strongly acidic or basic solvents.

Experimental Section

All solvents and reagents were used as obtained. The melting points are uncorrected. The infrared and UV spectra were recorded on Perkin-Elmer 297 and IBM 9430 spectrophotometers, respectively. ^1H NMR and ^{13}C NMR were obtained on a UCB 200 MHz instrument. GC was performed with a Shimadzu Model equipped with FID, a Hewlett-Packard 3390 A integrator, and a 50-m SE30 capillary column. A Hewlett Packard 5790A/5970A GC-MS system equipped with a 59970A workstation and a 50-m capillary column (HP Ultra No. 1 cross-linked methyl silicone) was used to analyze product mixtures. The Pd catalyst was the commercial 10% Pd/C catalyst from Aldrich.

General Procedure for the Cyclotrimerization of Alkynes to Substituted Benzenes. A 50-mL, round-bottomed flask equipped with a reflux condenser is charged with alkyne (0.1 mol), 1 g of Pd/C (10%), trimethylsilyl chloride (0.1 mol), and THF. The resulting suspension is refluxed for 3 h to a few days to obtain the desired substituted benzene. The progress of the reaction is monitored by GC or GC-MS. After complete disappearance of the starting material, the reaction mixture is filtered while hot and the solvent is evaporated. The residue is distilled under reduced pressure to yield crude compounds as solid residues or liquids which are purified by recrystallization and/or preparative TLC.

Hexaethylbenzene (1). A solution of 4.5 mL (39.8 mmol) of 3-hexyne, 4.5 mL (35.5 mmol) of trimethylsilyl chloride, and 1 g of Pd/C (10%) in 15 mL of THF was refluxed for 3 h. The resulting reaction mixture was filtered and evaporated under reduced pressure to yield 3.3 g of **1** (100%) as a colorless liquid (bp 50 °C, 20 mm) which subsequently solidified. **1** was purified by recrystallization from heptane to give white needles: mp 130 °C (lit. mp 126 °C,[31] 129[35]). ^1H NMR ($CDCl_3$) δ 1.2 (t, 18), 2.7 (q, 12, six CH_2); ^{13}C NMR ($CDCl_3$) δ 15.609 (q), 22.037 (t), 137.702 (s); MS (relative intensity) *m/z* (relative intensity) 246.30 (M^+ 53), 231.60 ($M^+ - CH_3$, 100). Anal. Calcd for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 88.01; H, 12.27.

Hexa-*n*-butylbenzene (2). To a solution of 4 mL of 5-decyne (26 mmol) in 15 mL of THF were added 4 mL of trimethylsilyl chloride (31 mmol) and 1.0 g of Pd/C (10%). The resulting mixture was refluxed for 6 h and filtered. The filtrate on concentration afforded 3.6 g of a yellow solid which on recrystallization from heptane provided **2** as colorless crystals, mp 59–60 °C (lit.[35] mp 56.5–57.5 °C); ^1H NMR ($CDCl_3$) δ 1.2 (t, 18, six methyl), 1.75 (m, 24, 12 methylene), 2.75 (t, 12, six benzylic methylene); ^{13}C NMR ($CDCl_3$) 13.788 (q), 23.604 (t), 29.294 (t), 33.637 (t), 136.526 (s); GC-MS, *m/z* (relative intensity) 414.55 (M^+, 100). Anal. Calcd for $C_{30}H_{54}$: C, 86.89; H, 13.12. Found: C, 87.01; H, 13.14.

Hexaphenylbenzene (3). Pd/C (1.01 g) and 2 mL of trimethylsilyl chloride (16 mmol) were added to a solution of 5 g of diphenylacetylene (28 mmol) in 15 mL of THF. The resulting mixture was heated under reflux for 4 days and then filtered. The solution was distilled under reduced pressure to leave a yellow brown solid which was recrystallized from benzene/chloroform, yielding white crystals of 4.8 g of **3** (80%), mp 478 °C (lit.[36] mp 454 °C; ^1H NMR ($CDCl_3$) δ 6.8 (s); ^{13}C NMR was in agreement with literature data.[37]

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1,2,4-Trimethyl-3,5,6-tri-*n*-propylbenzene (4). Trimethylsilyl chloride (7 mL, 55.2 mmol) and 1.08 g of Pd/C (10%) were added to a solution of 4.38 g of 2-hexyne (53, 4 mmol) in 15 mL of THF. The resulting suspension was refluxed for 2 days and then filtered. The removal of solvent from filtrate left 4.5 g of a yellow liquid (GC purity 65%). This on purification by preparative TLC (silica gel, cyclohexane) gave **4** as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.12 (t, 9, CH_3), 1.55 (m, 6, CH_2), 2.33 (s, 6, CH_3), 2.38 (s, 3, CH_3), 2.72 (d, t, 9, aromatic CH_3); ^{13}C NMR ($CDCl_3$) δ 14.71 (C-5 or C-6 CH_3), 14.84 (C-5 or C-6 CH_3), 15.58 (C-3 CH_3), 16.28 (C-3 CH_2), 22.85 (C-5 or C-6 CH_2), 22.93 (C-5 or C-6 CH_2), 23.92 (C-1 or C-2 CH_3), 23.10 (C-1 or C-2 CH_3), 29.16 (C-4 CH_3), 32.02 (C-3 benzylic methylene), 32.65 (C-5 or C-6 benzylic methylene), 32.71 (C-5 or C-6 benzylic methylene), 132.16 (C-1 or C-2), 132.32 (C-1 or C-2), 133.21 (C-4), 136.42 (C-3), 137.18 (C-5 or C-6), 137.25 (C-5 or C-6). Anal. Calcd for $C_{15}H_{24}$; C, 87.73; H, 12.27. Found: C, 87.74; H, 12.25.

1,3,5-Trimethyl-2,4,6-triphenylbenzene (5) and 1,2,4-Trimethyl-3,5,6-triphenylbenzene (6). 1-Phenyl-1-propyne (5.2 mL, 41 mmol), 5.2 mL of trimethylsilyl chloride (0.0410 mol), 1 g of Pd/C (10%), and 15 mL of THF were refluxed for 6 days. The resulting reaction mixture after filtration and distilled to remove the solvent and impurities. The brown solid so obtained was recrystallized from $CHCl_3$/methanol to give 3.8 g of brown crystals of **6** (80%): mp 221 °C (lit.[17a] mp 223 °C); ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3, C-4 CH_3), 2.1 (s, 6, C-1 CH_3 and C-2 CH_3), 6.9–7.6 (m, 15, three C_6H_5); ^{13}C NMR ($CDCl_3$) δ 18.02 (C_3), 18.21 (CH_3), 19.37 (CH_3), 125.58, 125.63, 126.36, 127.21, 128.32, 128.37, 129.29, 130.20, 131.10, 131.79, 133.84, 139.11, 139.71, 140.52, 141.53, 142.04, 142.35. Anal. Calcd for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 92.99; H, 6.77.

The colorless crystals obtained on filtration were recrystallized from $CHCl_3$/benzene/methanol to yield white crystals of **5** (20%): mp 327–380 °C (lit.[17a] mp 320 °C); ^{1}H NMR ($CDCl_3$) δ 1.8 (s, 9, three methyl), 7.2–7.6 (m, 15, three phenyl); ^{13}C NMR ($CDCl_3$) δ 19.31 (C-1, C-3, and C-5 methyls), 127.18, 128.31, 129.26, 130.18, 131.48 (C-1, C-3 and C-5), 142.01 (C-2, C-4, and C-6); GCMS, *m/z* (relative intensity) 348.15 (M^+, 100). Anal. Calcd for $C_{27}H_{24}$; C, 93.06; H, 6.94. Found: C, 92.89; H, 6.77.

1,3,5-Tri-*tert*-butylbenzene (7) and 1,2,4-Tri-*tert*-butylbenzene (8). A mixture of 6 mL of *tert*-butylacetylene (49 mmol), 6 mL of trimethylsilyl chloride (47 mmol), and 1 g of Pd/C (10%) in 15 mL of THF was heated to reflux for 2 days after which the solution was filtered. The solution was concentrated on a rotary evaporator to a yellow liquid which was separated on preparative TLC (silica gel, petroleum ether) to give 1.2 g of **7** (30%), mp 74–75 °C (lit.[41] mp 75 °C), and 1.6 g of **8** (40%), liquid oil (lit.[31] mp 46 °C). The characteristics of **7** are as follows: ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 27, three *tert*-butyl), 6.55 (s, 3, aromatic H); ^{13}C NMR ($CDCl_3$) δ 28.72 (*tert*-butylmethyl), 39.12 (quaternary carbon), 117.76 (C-2, C-4, and C-6), 147.88 (C-1, C-3, and C-5).

The properties of **8** are as follows: ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 9, *t*-Bu), 1.32 (s, 9, *t*-Bu), 1.37 (s, 9, *t*-Bu), 6.15 (dd, H-5 and H-6), 6.61 (d, 1, H-3); ^{13}C NMR was in agreement with literature data.[38]

Oligomerization of Phenylacetylene. Phenylacetylene (4 mL, 0.0364 mol) was added to a mixture of 4 mL (0.0315 mol) of trimethylsilyl chloride, 1.0336 g of Pd/C (10%), and 16 mL of THF and heated to reflux for 60 h. The mixture was filtered and distilled to afford a red sticky mass. This on recrystallization from alcohol gave red crystals of tetramers, believed to be cyclooctatetraenes (5 g, 100%): mp 164–167 °C; ^{1}H NMR ($CDCl_3$) δ 7–7.5 (m); ^{13}C NMR ($CDCl_3$) δ 126, 126.50, 127.50, 128, 128.50, 129, 130, 137, 144.50, 148; MS, *m/z* (relative intensity) 408 (M^+, 100).

Diisopropylacetylene was prepared by following the procedure of Nicholas and Siegel.[39]

Reaction of Diisopropylacetylene. Diisopropylacetylene (0.36 g, 33 mmol) in 25 mL of THF was heated to reflux with 1.2 mL (9.5 mmol) of trimethylsilyl chloride and 0.5 g of 10% Pd/C. After 7 days, the solution was filtered and distilled to yield 0.4 g of a green residue. The material was recrystallized from a benzene–acetone mixture followed by ether and ethanol to give white crystals of dimer **9** (0.010 g), mp 194–195 °C, along with a yellow liquid. Attempts to crystallize the yellow liquid were unsuccessful. TLC (benzene:acetone, 3:1) showed it to be homogeneous and GC-MS indicated one major compound (90%): UV_{max} (MeOH) 218, 221, 227, 273 nm; IR (neat) 3025, 2900, 2850, 1950, 1875, 1800, 1600, 1585, 1485, 1440, 1305–1365 (br), 1180, 1150, 1060, 1020, 900, 740, 690; GC-MS, *m/z* (relative intensity) 220 (M^+, 29), 205 (100).

Reaction of 4,4-Dimethyl-2-pentyne with Trimethylsilyl Chloride and 10% Pd/C (Cyclobutadiene–$PdCl_2$ Complex) (9). Trimethylsilyl chloride (5 mL, 0.0394 mol) was added to a suspension of 3.6 g (37 mmol) of 4,4-dimethyl-2-pentyne and 1 g of 10% Pd/C in 15 mL of THF. The resulting mixture was refluxed for 3 days and filtered. The solid obtained on recrystallization from benzene/chloroform yielded orange needles of a highly insoluble complex (**9**): mp 223–224 °C; IR (KBr) 3050, 2925, 1960, 1880, 1810, 1600 (d), 1495, 1450, 1310–1370 (br), 1185, 1160, 1065, 1030, 908, 820, 750, 700 cm. Anal. Calcd for $(C_7H_{12})_4Pd_3Cl_6$: C, 36.69; H, 5.28; Cl, 23.21; Pd, 34.83. Found: C, 36.67; H, 5.24; Cl, 23.25.

Oligomerization of Acetylene Catalyzed by Pd/C and Trimethylsilyl Chloride (Formation of Benzene). A 25-mL three-necked flask equipped with a gas inlet attachment, water condenser, magnetic stirrer, and stopcock was charged with 0.8 g of Pd/C (10%), 4 mL (32 mmol) of trimethylsilyl chloride, and 5 mL of THF. The contents were stirred and cooled to −60 °C when acetylene was introduced. The temperature gradually increased but ws maintained below 10 °C by external cooling. The reaction was monitored by GC and GCMS and the supply of acetylene was terminated after 2.30 h when extensive formation of benzene was observed. The mixture was filtered and the solvent removed. The remaining liquid on fractionation yielded about 2 mL of benzene: GCMS, *m/z* (relative intensity) 78 (M^+, 100).

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Supercritical Carbon Dioxide. 3.[1] The Decomposition of Phenylazotriphenylmethane in Supercritical Carbon Dioxide

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Introduction

Phenylazotriphenylmethane (PAT) is a one-bond initiator (see Scheme I) that decomposes at a convenient rate near the critical temperature of carbon dioxide. Since the formation of the initial caged radical pair is reversible, k_{obsd} is sensitive to the viscosity of the medium,[2,3] though by no

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