

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: $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 $\text{C}_{15}\text{H}_{24}$: 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (CDCl_3) δ 18.02 (C₃), 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 $\text{C}_{27}\text{H}_{24}$: 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); $^1\text{H NMR}$ (CDCl_3) δ 1.8 (s, 9, three methyl), 7.2–7.6 (m, 15, three phenyl); $^{13}\text{C NMR}$ (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 $\text{C}_{27}\text{H}_{24}$: 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: $^1\text{H NMR}$ (CDCl_3) δ 1.24 (s, 27, three *tert*-butyl), 6.55 (s, 3, aromatic H); $^{13}\text{C NMR}$ (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: $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ 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; $^1\text{H NMR}$ (CDCl_3) δ 7–7.5 (m); $^{13}\text{C NMR}$ (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–PdCl₂ 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 $(\text{C}_7\text{H}_{12})_4\text{Pd}_3\text{Cl}_6$: 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 was 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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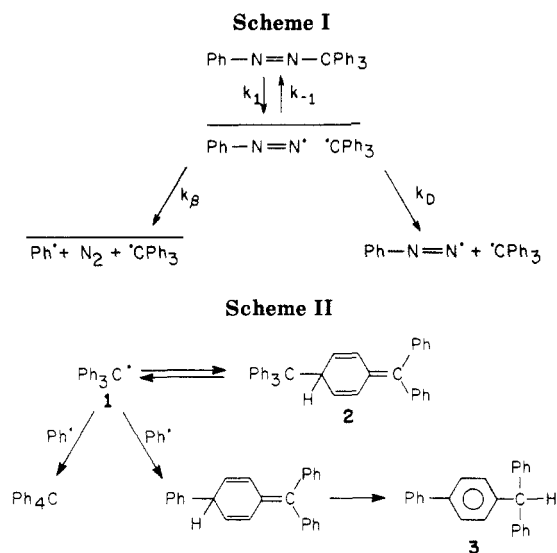
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means completely determined by that parameter.² A probable reason for the dependence of k_{obsd} on the type of solvent, rather than solely on the viscosity, is that solvation of the phenyldiazanyl radical changes k_{β} .

The products in conventional solvents include tetraphenylmethane, *p*-xenyldiphenylmethane (3), triphenylmethane, and substances derived from the solvent. The phenyl moiety has been trapped in nearly quantitative yield by I_2^4 and by trimethyl phosphite.⁵ Trityl radical (1) and its dimer 2 (Scheme II) are among the products in ligroin; substantial amounts of the trityl moiety have been trapped as the peroxide⁶ in the presence of O_2 . In trimethyl phosphite the trityl moiety is recovered mainly as triphenylethane and partly as triphenylmethane.⁵

Results

Products in Supercritical CO_2 . Most product studies of the decomposition of PAT reveal substantial involvement of the solvent, since radicals add to solvent molecules or abstract hydrogen. Since radicals have never been shown to add to CO_2 and since CO_2 has no hydrogen atoms to abstract, our initial assumption was that the products from PAT in CO_2 would be simple and the material balance high. These assumptions proved to be incorrect.

Major Products. During runs in the optical cell, as the absorption bands due to PAT decay, trityl radical bands⁷ at about 510 and 340 nm grow in and then partly decay. An apparent isobestic point early in the runs is lost later on. The stronger trityl band, at 340 nm, is still detectable at the end of the reaction, although partly obscured by other products. At low CO_2 densities a deposit of tetraphenylmethane sometimes formed on the windows. The appearance of the spectrum at the end of the run also varies from run to run, indicating considerable differences in the composition of the later, secondary reaction products.

The decomposition of PAT in CO_2 with minimal adventitious oxygen, initial PAT concentrations of 10^{-3} to 10^{-4} M, temperature at 55 °C, and CO_2 densities near 0.8 g/mL gave three identifiable major products besides trityl and its dimer: tetraphenylmethane (14 mol %), its isomer

p-xenyldiphenylmethane (3) (10%), and triphenylmethane (4) (12%). Although trityl radical has abstracted hydrogen to give 4, none of the phenyl radicals were recovered as benzene or as biphenyl. Products corresponding to the addition of radicals to CO_2 were also absent.

Because the remaining trityl radical and its dimer 2 form peroxides when the bomb is opened at the end of the run, oxygen-containing products are seen by gas chromatography even in runs with minimum adventitious O_2 . The peroxides formed at this point and pyrolyzed during gas chromatography account for the triphenylcarbinol (ca. 6%), benzophenone (ca. 4%), and phenol (ca. 4%). The amount of trityl and its dimer remaining at the end of the run is therefore about 10% of the initial trityl moiety.

In runs in which the pressure vessel was not thoroughly evacuated before the run, the yields of oxygenated products increased. In these runs the phenol yields ranged upwards to 35%, the benzophenone yields to 16%, and the triphenylcarbinol yields to 15%, while the nonoxygenated products were still present in small amounts (ca. 1%). Since the phenol yields exceeded the yields of benzophenone, some of the phenol must have been formed from trapped phenyl radicals rather than from decomposition of trityl peroxides.

Larger amounts of oxygen could be introduced by flooding the evacuated vessel with a slight positive pressure of O_2 before pumping in the CO_2 . Under these conditions, yields of phenol up to 41%, benzophenone up to 20%, and triphenylcarbinol up to 24% were obtained. It is significant that in these runs tetraphenylmethane and its isomer *p*-xenyldiphenylmethane (3), presumed to be geminate products in conventional solvents, were still detectable. For comparison, the yields of the geminate products in trimethyl phosphite solution were about 0.5 mol %.⁵ Although oxygen is not the best scavenger for phenyl radicals,⁸ this result suggests that some geminate recombination of trityl and phenyl radicals occurs even in CO_2 .

A run using the same excess oxygen technique but with added pyrogallol to act as a hydrogen donor was used to trap trityl radicals as the hydroperoxide. Titratable peroxide, calculated on the basis that it is entirely trityl hydroperoxide rather than ditryl peroxide, was obtained in 106 mol % yield. After reduction of the peroxide, triphenylcarbinol was found in 74 mol % yield. A similar experiment using thiophenol as the hydrogen source gave triphenylmethane in 62% yield, triphenylcarbinol 3%, benzophenone 13%, and phenol 7%.

Kinetics. If k_D and k_{β} are small enough compared to k_{-1} , geminate recombination of trityl and phenyldiazanyl radicals could also occur, causing k_{obsd} to depend on the viscosity of the supercritical CO_2 . Unfortunately, the kinetic runs by the spectrophotometric method (our only practicable choice) suffered from unpredictable interferences. The variation in the profile of the spectrum at the end of the runs, and the occasional precipitation of tetraphenylmethane on the windows, have already been mentioned. Although the fit to first-order kinetics within a given run was usually satisfactory, the k_{obsd} values varied erratically between runs.

The rates were measured in a large number of runs at CO_2 densities ranging from 0.31 to 0.94 g/mL, π^* from -0.61 to -0.12 , viscosities from 0.25 to 1.02 mP, and temperatures from 34 to 60 °C. Since temperature was clearly the most important variable, deviation from the Arrhenius equation was used as a criterion for dropping the worst

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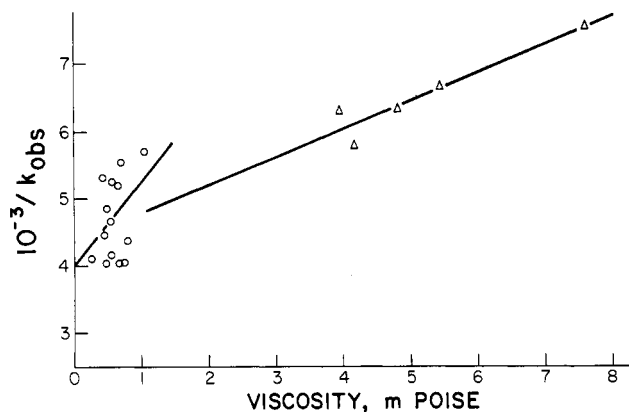


Figure 1. Plot of $10^{-3}/k_{\text{obsd}}$ against viscosity. The line is the least-squares line for the conventional solvents (Δ).

runs, some of which deviated by more than 100%. The activation energy from the complete set of runs was 27.99 kcal/mol and the correlation coefficient 0.867. The activation energy after dropping about half of the runs was 27.3 kcal/mol and the correlation coefficient 0.967. This activation energy is close to that reported for benzene, 24.4 kcal/mol.⁹

The 27.3 kcal/mol activation energy was used to adjust the rate constants of the remaining runs to a common temperature of 50 °C, giving a mean value of $2.16 \times 10^{-4} \text{ s}^{-1}$ and a standard deviation of 0.27×10^{-4} . The small variation remaining in this set of adjusted rate constants was then tested for correlations with solvent parameters.

The regression of $10^{-3}/k_{\text{obsd}}$ against the viscosity (the range of viscosity was from 0.25 to 1.02 mP) had a slope of 1.21 and a correlation coefficient of only 0.37, indicating a very small and not significant association of higher rate constants with lower viscosities. Neuman's data² for a very different range of viscosities (3.95–7.58 mP), for octane and four aromatic solvents, gave a slope of 0.42 and a correlation coefficient of 0.94. As shown in Figure 1, this regression line, extended toward lower viscosities, passes through the group of CO_2 points. Regression of the combined data sets gives a slope of 0.40 and $r = 0.87$. It should be noted that correlations of rates with functions of the viscosity have been reported to break down for viscosities below about 7 mP.¹⁰

Regression of $\log_{10} k_{\text{obsd}}$ against CO_2 π^* values (which ranged from -0.12 to -0.61)¹¹ gave a slope of -0.12 and a correlation coefficient of only -0.28 . Neuman's data for octane and four aromatic solvents ($\pi^* -0.08$ to $+0.59$) also showed no significant correlation with π^* . The combined data sets had a slope of -0.18 and $r = -0.73$.

Conclusions. The correlation of the rates in supercritical CO_2 with the viscosity has to be very slight and may not be real. This means that geminate recombination of phenyldiazanyl and trityl radicals cannot be very important in CO_2 . If so, k_{obsd} should be greater than the k_{obsd} values for more viscous nonpolar media, in which geminate recombination is important. The rate constants reported for some conventional solvents compare with our k_{obsd} at 50 °C as shown in Table I.

In the limit of no geminate recombination of trityl and phenyldiazanyl radicals, k_{obsd} should be equal to k_1 . The value predicted by Neuman and Lockyer from their vis-

Table I

solvent	$10^4 K, \text{ s}^{-1}$	solvent	$10^4 K, \text{ s}^{-1}$
CO_2	2.17 ± 0.27	benzene ²	1.37 ± 0.01
octane ²	1.59 ± 0.04	benzene ⁹	1.24 ^a
toluene ²	1.73 ± 0.01	cyclohexane ⁹	0.96 ^a

^a At 49.9 °C.

cosity studies^{2,12} was $10.0 \times 10^{-4} \text{ s}^{-1}$ at 60 °C. Our k_{obsd} , adjusted to that temperature, is somewhat smaller, $7.69 \times 10^{-4} \text{ s}^{-1}$.¹³

Experimental Section

Phenylazotriphenylmethane (PAT). PAT,¹⁴ mp 110–111 °C, was stored in an evacuated desiccator and protected from light.

Kinetics. The high-pressure optical cell and the method of pressurizing it with CO_2 have been described previously.¹ A known amount of PAT was put in the cell as a solution in CH_2Cl_2 and the solvent evaporated in a stream of nitrogen. The cell was then connected to the gage block assembly, evacuated to 25 μm , and filled with CO_2 . The pressure at room temperature was set at a value that would give the desired pressure when the temperature was raised. The cell was heated by a metal jacket with two 80-W cartridge heaters. The temperature was monitored by a linear temperature probe and controlled by a thermocouple. The contents of the cell were mixed by the motion of a glass bead kept in a recess out of the light path during the optical density measurements. The disappearance of PAT was followed by the decrease in optical density at 460 nm.

Products. A 10–15-mg sample of PAT was weighed a small vial and the vial placed in a 21-mL stainless steel Parr reaction vessel. This vessel was evacuated to 25 μm and CO_2 pumped in to a pressure at room temperature that would give the desired pressure at the reaction temperature. Stirring was accomplished by the movement of a glass bead or of a magnetic stirring bar. The bomb was immersed in a heated oil bath. After the reaction, the bomb was cooled to 0 °C and vented through a cold trap containing CH_2Cl_2 . The bomb was then warmed to room temperature and opened, and the contents were washed out with CH_2Cl_2 . The two CH_2Cl_2 solutions were analyzed separately by GLC on a 0.25-mm quartz capillary column containing a nonpolar bonded phase, DB 1710.

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Crystal Structure of a Highly Strained Substituted Prismane

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Prismane¹ and a few substituted prismanes have been synthesized, but detailed structural data on these highly

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