refrigerated for 4 h. The clear solution was decanted off from the precipitated $KClO_4$ and stored in the refrigerator.

**Cyanohydrin Formation.** The formation of the cyanohydrin was studied in 80% dioxane. The procedure was essentially that of Lapworth and Manske.[27] The dissociation constant ($K_D$) was computed by using the eq 1, where $a$ is the initial [selenone], $b$

$$K_D = (a - x)(b - x)/x \qquad (1)$$

is the initial [HCN], and $x$ is the equilibrium [cyanohydrin]. Each experiment was repeated three times, and the consistency of various determinations of $K_D$ is illustrated by the values obtained with *r*-2,*cis*-6-diphenyl-4-selenanone (**3**): $10^3K_D$ = 8.75, 8.79, and 8.74 (mean 8.77 ± 0.02).

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**Registry No. 1a**, 621-98-7; **1b**, 14164-67-1; **1c**, 63114-78-3; **1d**, 55901-61-6; **2a**, 74966-31-7; **2b**, 74966-32-8; **2c**, 74966-33-9; **2d**, 74966-34-0; **3**, 54232-38-1; **4**, 74966-35-1; **6a**, 74966-36-2; **6b**, 74966-37-3; **6c**, 74966-38-4; **6d**, 74966-39-5; **6e**, 74966-40-8; **6f**, 74966-41-9; **6g**, 74966-42-0; **7a**, 74985-55-0; **7b**, 74985-56-1; **7c**, 74985-57-2; **7d**, 74966-43-1; **7e**, 74985-58-3; **7f**, 74985-59-4; **7g**, 74985-60-7.

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(27) A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 2335 (1928); 1976 (1930).

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# Pressure Effects on Azocumene Decomposition Rates, Efficiencies of Radical Production, and Semibenzene Dimers[1,2]

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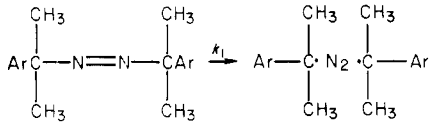
*Received March 17, 1980*

Rates of thermal decomposition of azocumene (**1a**) and *p,p'*-dimethylazocumene (**1b**) in cumene or chlorobenzene are decreased by pressure with decomposition activation volumes of +5 $cm^3$/mol (**1a**, cumene), +4.3 $cm^3$/mol (**1a**, chlorobenzene), and +4.6 $cm^3$/mol (**1b**, cumene). Efficiencies (*f*) of radical production, with di-*tert*-butyl nitroxide (DBNO) or thiophenol as scavengers, decrease with pressure; however, the pressure dependence of *f* with DBNO is anomalous. This is explained by the formation of semibenzene dimers as cage products, which subsequently decompose to give cumyl radicals. The corresponding α-ortho semibenzene dimers of cumyl radicals are formed from both **1a** and **1b**. The α-para semibenzene dimer from decomposition of **1a** in chlorobenzene appears to rearrange to give *p*-cumylcumene. No such rearrangement appears to occur from the α-ortho dimers nor is it likely that any α-para dimer is formed from **1b** decomposition. An apparent activation volume for thermal decomposition of the α-ortho semibenzene dimer in cyclohexane at 20 °C is ca. +6 $cm^3$/mol. Pressure favors disproportionation over coupling for geminate cumyl radicals.

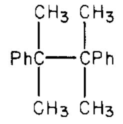
Azocumene (**1a**) thermally decomposes to give two cumyl radicals and a molecule of nitrogen in the primary scission step (eq 1).[5] The resulting radicals combine,



$$\mathrm{Ar}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}N{=}N{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{Ar} \xrightarrow{k_1} \mathrm{Ar{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{\cdot\ N_2\ \cdot}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}Ar} \qquad (1)$$

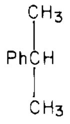
**1a**, Ar = phenyl
**b**, Ar = *p*-methylphenyl

disproportionate, or diffuse apart. It had been thought that the sole reaction products in an inert medium were bicumyl (**2**) from combination and cumene (**3**) and α-methylstyrene (**4**) from disproportionation. However, Bartlett obtained evidence which led him to suggest that the semibenzene **5a** was also a combination product.[5]



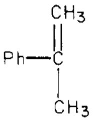
$$\mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{Ph}$$

**2**



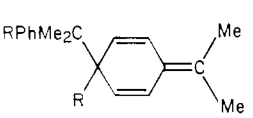
$$\mathrm{Ph}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{H}$$

**3**

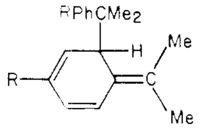


$$\mathrm{Ph{-}}\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_3}}{\overset{\|}{\mathrm{C}}}}$$

**4**



**5a**, R = H
**b**, R = $CH_3$



**6a**, R = H
**b**, R = $CH_3$

Subsequently, McBride concluded that both **5a** and **6a** are formed from cumyl radical combination.[6] These semibenzenes are unstable and can revert to cumyl radicals under conditions used to thermally decompose azocumene. However, they have been generated and studied spectrally by photolyzing azocumene at low temperatures.

Several years ago, as part of a continuing study of radical initiators,[7,8] we investigated effects of pressure on the rates,

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(1) High-Pressure Studies. 23. Part 22: R. C. Neuman, Jr., and C. T. Berge, *Tetrahedron Lett.*, 1709 (1978).

(2) Support by the National Science Foundation through Grants GP-8670 and GP-23968 is gratefully acknowledged.

(3) To whom correspondence should be addressed.

(4) Taken from the Ph.D. Dissertation of Michael J. Amrich, Jr., University of California, Riverside, CA, Dec 1971.

(5) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, 88, 137 (1966).

(6) K. J. Skinner, H. S. Hochster, and J. M. McBride, *J. Am. Chem. Soc.*, 96, 4301 (1974).

0022-3263/80/1945-4629$01.00/0

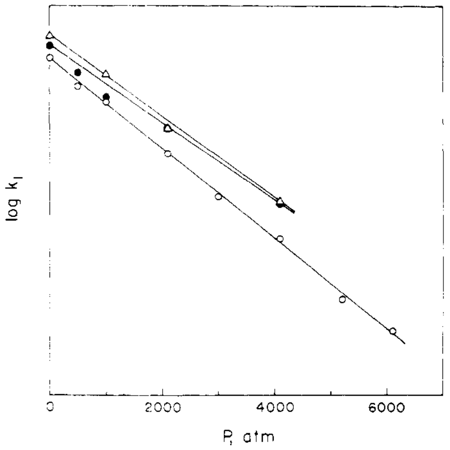


**Figure 1.** Pressure dependence of the decomposition rate constants for azocumene (**1a**) in cumene (○) and chlorobenzene (●) and for dimethylazocumene (**1b**) in cumene (△) at 55 °C (see Table I).

efficiencies of radical production, and products of thermal decomposition of azocumene (**1a**) and *p,p'*-dimethylazocumene (**1b**). The rate data were reported in a preliminary communication,[9] but the efficiency and product data have not been published.

In this manuscript we report the complete results of our studies on the azocumenes **1a** and **1b**. The rate data clearly confirm a two-bond scission mechanism, while the efficiency and product data demonstrate that pressure retards separative diffusion of the geminate radicals as we have observed in other systems.[7,8] These data also suggest that pressure alters the ratios of products arising from geminate reactions of radical pairs and that the presence of the semibenzene products leads to unusual pressure effects on the apparent efficiency of radical production.

## Results and Discussion

**Rates of Thermal Decomposition.** Pressure decreased the thermal decomposition rates of both **1a** and **1b** (Table I, Figure 1). The resulting activation volumes ($\Delta V^*$) calculated from the slopes of the plots in Figure 1 ($-\Delta V^*/2.303RT = \Delta \log k_1/\Delta P$) are +5.0 cm$^3$/mol (**1a**, cumene), +4.3 cm$^3$/mol (**1a**, chlorobenzene), and +4.6 cm$^3$/mol (**1b**, cumene).

Rate constants were determined by using samples both with and without added radical scavenger. There was no effect of the scavengers on the rates within experimental error. However, the data show that values of $k_1$ with chlorobenzene as the solvent were slightly greater than those obtained with cumene.

The absolute values of the rate constants at atmospheric pressure for both **1a** and **1b** are slightly lower than previous values. Bartlett determined a rate constant of $9.28 \times 10^{-5}$ s$^{-1}$ for **1a** in toluene (55.34 °C),[5] while the activation parameter data of Shelton[10] gave a rate constant of $9.9 \times 10^{-5}$ s$^{-1}$ for **1b** in toluene (55.0 °C). Bartlett's rates were determined by monitoring gas evolution, while Shelton used the UV absorbance of the azo linkage.

Azo compounds can decompose either by one-bond or by simultaneous two-bond scission (Scheme I). The apparent activation volume for decomposition of an azo initiator ($\Delta V^*_{\text{obsd}} = RT\, \partial ln\, k_{\text{obsd}}/\partial P$) can provide a basis for distinguishing between the two mechanisms.[7] For two-bond scission azo initiators, $\Delta V^*_{\text{obsd}}$ depends only on the pressure dependence of $k_{1'}$ (eq 2) because the radicals do

$$\Delta V^*_{\text{obsd}} = \Delta V^*_{1'} \qquad (2)$$

not recombine with nitrogen to regenerate the azo compound. However, for one-bond scission azo initiators, $\Delta V^*_{\text{obsd}}$ also depends on the competition between the various reactions available to the initial pair $\overline{\text{RN=N}\cdot\text{R}\cdot}$ (eq 3). Since separative diffusion of radical pairs ($k_d$) should

$$\Delta V^*_{\text{obsd}} = \Delta V^*_1 + RT\partial ln\ [1 + k_{-1}/(k_\beta + k_d)]/\partial P \qquad (3)$$

be strongly retarded by increased pressure as a result of a viscosity increase of the medium, the differential term in eq 3 is expected to be positive, and $\Delta V^*_{\text{obsd}}$ should be larger for the one-bond mechanism.[7]

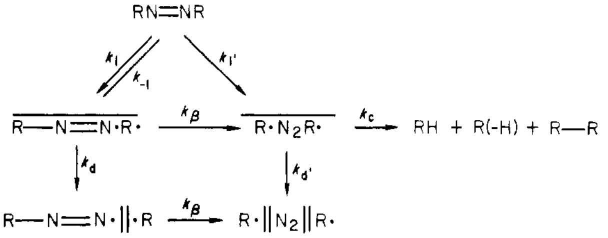
The activation volumes for **1a** and **1b** of ca. +5 cm$^3$/mol compared to those for other azo compounds (Table II) support this contention. They are comparable to values obtained for decomposition of azobis(isobutyronitrile)[11] and di-*tert*-butyl hyponitrite,[12] both two-bond initiators, but are much smaller than values for [(*p*-nitrophenyl)azo]triphenylmethane,[9] a system most certainly decom-

**Table I. Rate Constants for Thermal Decomposition of Azocumene (1a) and Dimethylazocumene (1b) in Cumene and Chlorobenzene at 55 °C[a]**

| | $10^5k_1$, s$^{-1}$ | | |
|---|---|---|---|
| *P*, atm | 1a in cumene | 1a in chlorobenzene | 1b in cumene |
| 1 | 8.10 ± 0.05[b]<br>8.10 ± 0.22 | 8.50 ± 0.10[b]<br>8.52 ± 0.30[c] | 8.86 ± 0.06[b] |
| 500 | 7.20 ± 0.24 | 7.61 ± 0.12 | |
| 1000 | 6.75 ± 0.10 | 6.88 ± 0.10<br>7.28 ± 0.30[c] | 7.54 ± 0.17 |
| 2050 | 5.45 ± 0.04 | 6.03 ± 0.08<br>6.10 ± 0.20[c] | 6.02 ± 0.27 |
| 3000 | 4.56 ± 0.10 | | |
| 4100 | 3.83 ± 0.10 | 4.42 ± 0.12 | 4.47 ± 0.06 |
| 5200 | 2.98 ± 0.11 | | |
| 6100 | 2.62 ± 0.07 | | |

[a] Determined by UV analysis of the azo absorption unless otherwise indicated. All rate constants for 1a are averages of individual rate constants separately determined with DBNO present and absent. DBNO was present in all runs of 1b. The uncertainties represent the larger value of a rate constant standard deviation or an average of standard deviations where rate constants were combined. The solutions were degassed and the samples prepared under argon or nitrogen and decomposed in sealed Teflon tubes (see Experimental Section). [b] Sealed glass tubes were used for these runs. [c] Sample contains 0.17 M thiophenol; rate determined by NMR (see Experimental Section).

**Scheme I**



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[7] R. C. Neuman, Jr., *Acc. Chem. Res.*, **5**, 381 (1972), and references therein.

[8] (a) R. C. Neuman, Jr., and R. P. Pankratz, *J. Am. Chem. Soc.*, **95**, 8372 (1973); (b) R. C. Neuman, Jr., and E. Ertley, *ibid.*, **97**, 3130 (1975). (c) R. C. Neuman, Jr., and R. Wolfe, *J. Org. Chem.*, **40**, 3147 (1975).

[9] R. C. Neuman, Jr., G. D. Lockyer, Jr., and M. J. Amrich, *Tetrahedron Lett.*, 1221 (1972).

[10] J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Am. Chem. Soc.*, **90**, 354 (1968).

[11] A. H. Ewald, *Discuss. Faraday Soc.*, **22**, 138 (1956).

[12] R. C. Neuman, Jr., and R. J. Bussey, *J. Am. Chem. Soc.*, **92**, 2440 (1970).

Table II. Activation Volumes for Decomposition of Azo Initiators (RN=NR′)

| R | R′ | $T$, °C | solvent | $\Delta V^*$, cm$^3$/mol |
|---|---|---|---|---|
| $Me_2C(CN)$ | $Me_2C(CN)$ | 70 | toluene | +4[a] |
| $Me_2C(Ph)$ | $Me_2C(Ph)$ | 55 | cumene | +5.0[b] |
| | | | chlorobenzene | +4.3[b] |
| $Me_2C$(*p*-MePh) | $Me_2C$(*p*-MePh) | 55 | cumene | +4[b] |
| $Me_3CO$ | $Me_3CO$ | 55 | *n*-octane | +4.3[c] |
| $PhCHCH_2CH_2CHPh$ | | 60 | toluene | +5.5[d] |
| $PhCHCH_2CH_2CH_2CHPh$ | | 65 | toluene | +5.5[d] |
| $Ph_3C$ | *p*-$NO_2Ph$ | 60 | cumene | +20[b] |
| | | | *n*-octane | +18[b] |
| | | | *tert*-butylbenzene | +21[b] |

[a] A. H. Ewald, *Discuss. Faraday Soc.*, 22, 138 (1956). [b] R. C. Neuman, Jr., G. D. Lockyer, Jr., and M. J. Amrich, *Tetrahedron Lett.*, 1221 (1972). [c] R. C. Neuman, Jr., and R. J. Bussey, *J. Am. Chem. Soc.*, 92, 2440 (1970). [d] Cyclic azo compounds: R. C. Neuman, Jr., and E. W. Ertley, *J. Am. Chem. Soc.*, 97, 3130 (1975).

Table III. Pressure Dependence of Decomposition Rate Constants for an Intermediate from Azocumene Photolysis in Cyclohexane at 20 °C[a]

| $P$, atm | $10^4 k_{obsd}$, s$^{-1}$ | $P$, atm | $10^4 k_{obsd}$, s$^{-1}$ |
|---|---|---|---|
| 333 | 1.13 | 830 | 0.96 |
| | 1.04 | 1000 | 0.80 |
| 571 | 0.96 | 1497 | 0.86 |

[a] Determined by UV analysis on degassed samples. The $\lambda_{max}$ for the intermediate is at 330 nm.

Table IV. Products from Decomposition of Azocumene (1a) in Chlorobenzene (55 °C) with Thiophenol (0.16 M) as Analyzed by NMR[a]

| $P$, atm | **3** | **2** | **8** | **1a**[b] |
|---|---|---|---|---|
| 1 | 3.52 | 0.52 | 0.12 | 1.88 |
| 1000 | 2.02 | 0.43 | 0.29 | 1.81 |
| 2050 | 1.82 | 0.37 | 0.25 | 1.53 |
| 4100 | 1.68 | 0.45 | 0.22 | 1.50 |
| 4100[c] | (0.22) | (0.79) | (0.31) | 1.16 |
| 5000 | 1.37 | 0.33 | 0.22 | 1.14 |

[a] Product yields in units of (mol/L) × $10^2$. [b] Amount of azocumene decomposed (M × $10^2$). [c] No thiophenol present; the yields are based on the assumption that **2**, **3**, and **8** are the only products (see text).

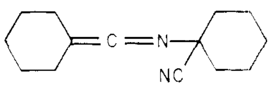
posing via one-bond scission.

**Formation and Decomposition of an Intermediate.** Samples of azocumene, and of dimethylazocumene, decomposed in cumene under pressure with no scavenger present and analyzed by UV early in the kinetic runs, showed the azo absorption at 370 nm, an additional moderate absorption band at about 330 nm, and an intense band below 310 nm. The band at 330 nm disappeared over the course of 1 h at the ambient temperature (28 °C) of the UV spectrometer cell compartment. From these spectra, first-order rate constants of approximately $4.4 \times 10^{-4}$ s$^{-1}$ and $1.6 \times 10^{-4}$ s$^{-1}$ were calculated for decomposition of the intermediates from azocumene (**1a**) and dimethylazocumene (**1b**), respectively.

A more careful study was carried out in which degassed samples of azocumene (**1a**) in cyclohexane were photolyzed in a high-pressure optical cell, and, after photolysis, the loss of the intermediate was monitored at different pressures at 20 °C. The first-order rate constants obtained in these experiments (Table III) give an apparent decomposition activation volume of ca. +6 cm$^3$/mol.

We suggest that these transient intermediates are the $\alpha$-ortho semibenzenes **6a** and **6b**, respectively. They have the same UV spectral characteristics as reported by McBride for **6a** and similar $\alpha$-ortho semibenzenes,[6] and their atmospheric pressure decomposition rate constants are comparable to that rate constant obtained by Bartlett for loss of an intermediate with the same spectral features formed from decomposition of **1a** in cyclohexane ($2.4 \times 10^{-4}$ s$^{-1}$ at 26 °C).[5]

The apparent activation volume of ca. +6 cm$^3$/mol is consistent with a one-bond scission initiator such as **6a** or **6b** decomposing in the *absence* of a radical scavenger. Activation volumes for one-bond scission azo initiators are much larger than those for multibond scission azo initiators[7-9] (vide supra) presumably because the initial cage $\overline{\text{RN=N·R·}}$ does not re-form after separative diffusion ($k_d$) of the radicals due to the instability of the diazenyl radical. This is not the case here; the decomposition of **6a** in cyclohexane is analogous mechanistically to the decomposition of the one-bond scission initiator *N*-(1-cyanocyclohexyl)pentamethyleneketenimine (**7**), whose decomposition activation volume in the absence of a scavenger is +5 cm$^3$/mol.[13]



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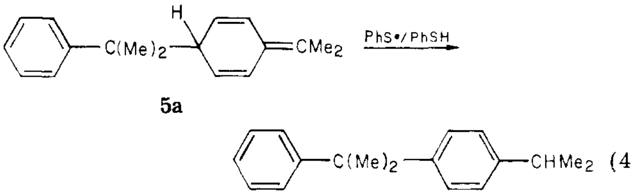
We have no *direct* evidence for the formation of the $\alpha$-para semibenzenes (**5**). McBride estimates that the relative yields of bicumyl (**2**), $\alpha$-ortho semibenzene **6a**, and $\alpha$-para semibenzene **5a** are 1.0/0.1/0.2 (or 77, 8, and 15%), respectively, from low-temperature photolysis of azocumene (**1a**) in several solvents.[6] Since **6a** has been detected by us, we expect that **5a** was also a reaction product. In addition, we shall present evidence below that *p*-cumylcumene (**8**) is a stable reaction product formed when azocumene is decomposed in chlorobenzene in the presence of the scavenger thiophenol. We propose that it is formed from **5a** by a rearrangement reaction (eq 4) catalyzed by



5a

8

(4)

PhS· radicals for which there is precedent in the literature.[14] The relative yields of bicumyl and **8** at atmospheric pressure are 1.0 and 0.23, remarkably close to McBride's ratio of 1.0:0.2 for bicumyl and **5a**.[6]

**Products.** Samples of azocumene, partially decomposed at various pressures in chlorobenzene containing 0.16 M thiophenol, were analyzed by NMR.[15] The spectra showed that cumene and bicumyl as well as unreacted azocumene were present, but $\alpha$-methylstyrene was not observed. The methyl protons of azocumene gave a singlet at $\delta$ 1.46, those of cumene gave a doublet at $\delta$ 1.09 and 1.20, and those of bicumyl gave a singlet which overlapped the higher field resonance of the cumene doublet ($\delta$ 1.20).

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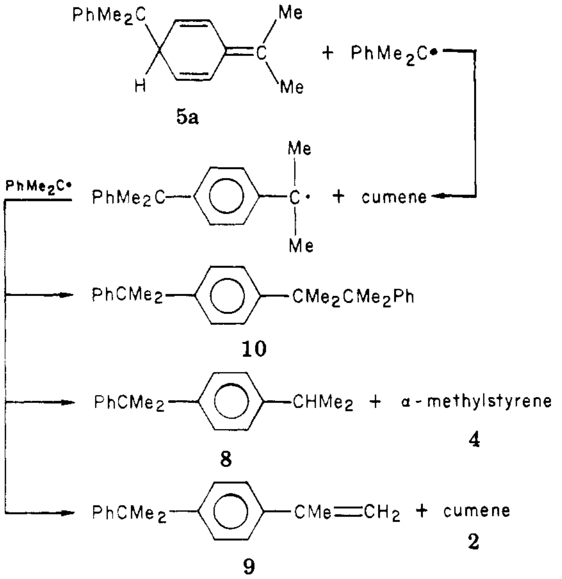
(13) R. C. Neuman, Jr., and M. J. Amrich, *J. Am. Chem. Soc.*, **94**, 2730 (1972).

(14) E. S. Lewis and M. M. Butler, *J. Org. Chem.*, **36**, 2582 (1971).

(15) See S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

Scheme II



A sharp singlet at $\delta$ 1.58 was also observed,[16] identical with that due to the *gem*-diphenyl methyl groups in an authentic sample of *p*-cumylcumene (**8**) in chlorobenzene. In addition to this singlet at $\delta$ 1.58, the NMR spectrum of **8** in chlorobenzene shows a methyl doublet at $\delta$ 1.09 and 1.20 identical with that observed for cumene. Combination of a chlorobenzene solution of **8** with one of the decomposed high-pressure reaction mixtures caused the resonances at $\delta$ 1.09, 1.20, and 1.58 to increase relative to the methyl resonance of unreacted azocumene. The concentrations of the products (Table IV) were calculated by assuming the formation of **8** as a product.

We have proposed that *p*-cumylcumene (**8**) is formed by a PhS· radical catalyzed rearrangement of the $\alpha$-para semibenzene dimer **5a** (eq 4). But the $\delta$ 1.58 resonance signal was also observed in spectra of a chlorobenzene reaction mixture of **1a** decomposed at 4100 atm with no thiophenol present. While a source of **8** under these conditions might be from rearrangement of **5a** by adventitious acid, it is also possible that **8** and other products which spectrally mimic **8** are formed by another radical mechanism.

When thiophenol is not present, cumyl radicals could react with the $\alpha$-para dimer as shown in Scheme II. This could lead to **8** and two new compounds **9** and **10**. Since the isopropyl resonance of **8** has a chemical shift identical with that for cumene, it would not be surprising for the $\delta$ 1.58 resonance to be observed in both **9** and **10** and to directly overlap that for **8**. In fact, an examination of **8–10** suggests that a mixture of them could give an NMR spectrum essentially identical with that of a mixture of cumene, bicumyl, $\alpha$-methylstyrene, and *p*-cumylcumene.

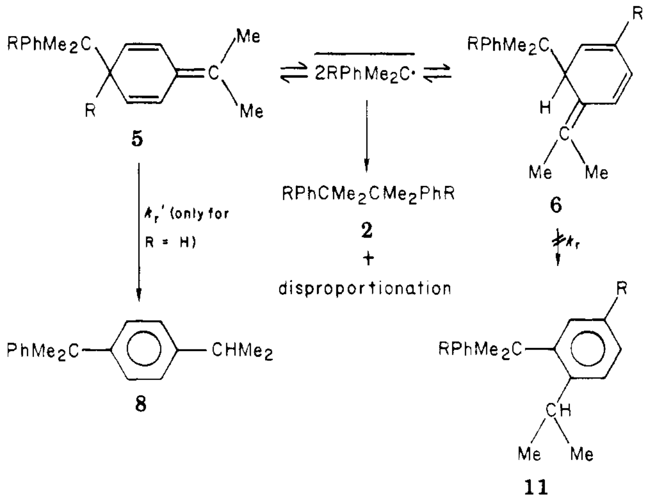
Products from **1a** decomposition in chlorobenzene without thiophenol have also been analyzed by GLC (Table V). In the absence of a scavenger, yields of cumene and $\alpha$-methylstyrene should be equal since they are the products of disproportionation of two cumyl radicals. In practice, $\alpha$-methylstyrene yields from azocumene decomposition are often low and this is generally attributed to polymerization reactions. This may be the case here, but it is conceivable that the higher yields of cumene are partly the result of the incursion of the reactions shown in Scheme II. Cumene is a primary product of the sequence in which **5a** reacts with cumyl radicals.

Table V. Products from Decomposition of Azocumene (1a) in Chlorobenzene (55 °C) as Analyzed by GLC[a,b]

| P, atm | 3 | 4 | 2 | yield,[c] % | 3/2 | 4/2 |
|---|---|---|---|---|---|---|
| 1 | 0.20 | 0.07 | 2.06 | 113 | 0.10 | 0.03 |
| 1000 | 0.26 | 0.18 | 1.43 | 85 | 0.18 | 0.13 |
| 3100 | 0.38 | 0.22 | 1.23 | 81 | 0.31 | 0.18 |
| 6000 | 0.46 | 0.18 | 0.97 | 72 | 0.47 | 0.19 |

[a] Initial azocumene concentration $2.0 \times 10^{-2}$ M. [b] Product yields in units of (mol/L) $\times 10^2$; toluene present is as an internal standard. [c] (**2** + **3**)/(azocumene).

Scheme III



The data are not good enough to provide a definitive conclusion. The high overall yield at atmospheric pressure indicates calibration errors. However, substantially lower yields at the higher pressures seem significant because unidentified GLC peaks were observed with retention times longer than that for bicumyl. This could be explained by the formation of **8–10**.

Samples of dimethylazocumene (**1b**) were also decomposed in chlorobenzene in the presence of 0.16 M thiophenol at 1 and 5000 atm. NMR spectra showed the presence of the corresponding *p,p'*-dimethylbicumyl, *p*-methylcumene, and unreacted azo compound, but no resonance comparable to that for **8** ($\delta$ 1.58) was observed. This is consistent with our prediction that the formation of the $\alpha$-para semibenzene dimer **5b** (R = $CH_3$) would be expected to be very unfavorable because of the presence of the methyl group at the site of attack on the aromatic ring (see Scheme III), and also, it is impossible for any rearrangement to occur ($k_r' = 0$) even if **5b** was formed.

In contrast, there should be no major difference in the ease of formation of **6a** or **6b** (Scheme III). However, it seems unlikely that either of these compounds would easily aromatize ($k_r$). Steric interference between the ortho cumyl and isopropyl substituents in the resulting compounds **11** should be severe. While the absence of a proton signal at $\delta$ 1.58 in the dimethylazocumene/chlorobenzene/thiophenol system does not preclude the presence of **11**, it is additional evidence that it was not formed.

We have previously noted that increasing pressure favors disproportionation reactions of two radicals over combination when these processes compete.[7,13] This competition for cumyl radicals is reflected by the ratio of $\alpha$-methylstyrene to bicumyl and the data (Table V) indicate that this trend continues. It is probably due to viscosity effects on rotational diffusion[17] and has been observed for vis-

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[16] The methyl resonance of cumyl hydroperoxide is at $\delta$ 1.48 under these conditions, and it was not observed as a product.

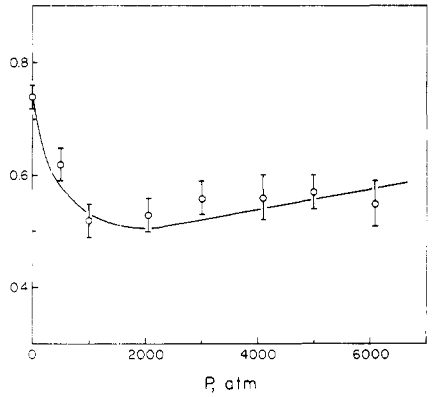

**Figure 2.** Pressure dependence of the efficiency of radical production (*f*) from azocumene (**1a**) in cumene at 55 °C with DBNO as radical scavenger (see Table VI).

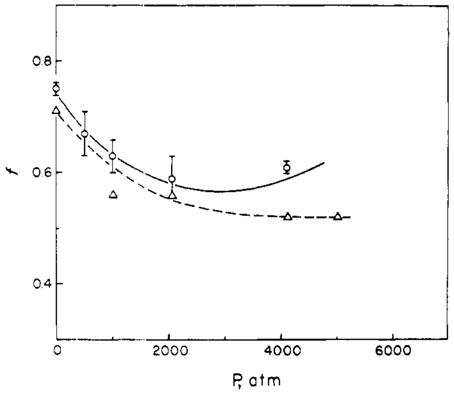

**Figure 3.** Pressure dependence of the efficiency of radical production (*f*) from azocumene (**1a**) in chlorobenzene at 55 °C: DBNO radical scavenger (○) (see Table VI); thiophenol radical scavenger (△) (see Table VII).

cosity increases induced by temperature and medium changes[18] as well as pressure. The cumene/bicumyl ratio increases much more dramatically with pressure (Table V), but the possibility that cumene can arise by reactions other than disproportionation (Scheme II) obviates any definitive conclusion from these latter ratios.

**Efficiency of Radical Production.** The efficiency (*f*) of radical production from an initiator is the fraction of the initially formed radicals which escape the solvent cage [$f = k_d/(k_c + k_d)$; see Scheme I]. Determinations of efficiencies from decomposition of **1a** or **1b** at different pressures and in different solvents were attempted by using the radical scavengers di-*tert*-butyl nitroxide (DBNO) and thiophenol (RSH). Both scavengers were present in excess concentration compared to the azo compound.

With DBNO, previously used in studies of azocumene at atmospheric pressure,[15] efficiencies were determined at various times during initiator decomposition by comparing the relative amounts of DBNO and initiator which had reacted. One molecule of DBNO reacts with one radical so that the efficiency (*f*) should be given by the formula shown in eq 5 where $(\mathrm{DBNO})_t$ and $(\mathrm{azo})_t$ are the amounts of DBNO and azo initiator which *react* in time *t*.

$$f = (\mathrm{DBNO})_t/2(\mathrm{azo})_t \qquad (5)$$

The effects of pressure on *f* for **1a** in cumene and chlorobenzene and for **1b** in cumene (Table VI and Figures 2–4) appear to be anomalous. We have typically observed in other systems that efficiencies decrease continuously with increasing pressure.[7-9] The data here show, however, that after initial decreases, values of *f* tend to level off and then appear to increase slightly. At relatively low pressures it *appears* that a further increase in pressure no longer retards the separative diffusion of geminate radical pairs. This seems unlikely in view of the expected continuous increase in solvent viscosity with increasing pressure.[19]

**Table VI. Apparent Efficiencies (*f*) of Radical Production from Azocumene (1a) and Dimethylazocumene (1b) with the Scavenger DBNO at 55 °C**[a]

| *P*, atm | 1a in cumene | 1a in chlorobenzene | 1b in cumene |
|---|---|---|---|
| 1 | 0.74 ± 0.02 | 0.75 ± 0.01 | 0.76 ± 0.01 |
| 500 | 0.62 ± 0.03 | 0.67 ± 0.04 | |
| 1000 | 0.52 ± 0.03 | 0.63 ± 0.03 | 0.61 ± 0.02 |
| 2050 | 0.53 ± 0.03 | 0.59 ± 0.04 | 0.46 ± 0.03 |
| 3000 | 0.56 ± 0.03 | | |
| 4100 | 0.56 ± 0.04 | 0.61 ± 0.01 | 0.45 ± 0.01 |
| 5000 | 0.57 ± 0.03 | | 0.41 ± 0.01 |
| 6100 | 0.55 ± 0.04 | | |

[a] Calculated from the equation $f = (\mathrm{DBNO})_t/2(\mathrm{azo})_t$, where $(\mathrm{DBNO})_t$ and $(\mathrm{azo})_t$ are the amounts of these materials which react in time *t*. [b] Errors are least-squares values determined by using data at various times.

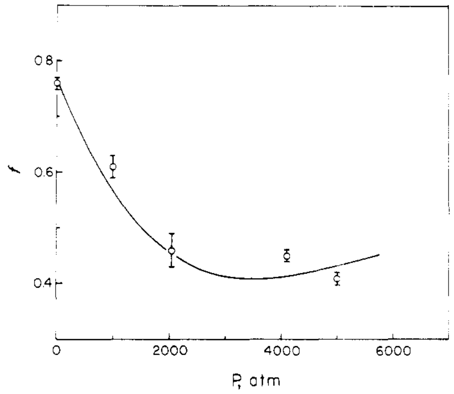

**Figure 4.** Pressure dependence of the efficiency of radical production (*f*) from dimethylazocumene (**1b**) in cumene at 55 °C with DBNO as radical scavenger (see Table VI).

We suggest that these results are due to the semibenzene dimers. They are cage products and should increase in absolute yield with pressure, and they are also subsequent sources of cumyl radicals. If the cumyl radical pairs formed from their decomposition return more often to **5a** and/or **6a** rather than bicumyl, in contrast to the behavior of the more separated cumyl radical pairs from azocumene decomposition, then the apparent leveling off in efficiency would be an artifact of these cumyl radical sinks. The cumyl radicals arising from the semibenzenes could counterbalance the decrease in scavengable radicals from the initial cages formed from azocumene.

Since **5b** is an unlikely product from dimerization of *p*-methylcumyl radicals (from **1b**) the leveling-off effect should not be as marked with dimethylazocumene, and this is apparent in the data. Although *f* values from **1b** do level off with pressure, they do so at higher pressures and lower efficiencies (contrast Figures 2 and 4).

In principle, it is also possible to calculate efficiencies from the product yields obtained for decomposition of

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[17] See A. B. Jaffe, K. J. Skinner, and J. M. McBride, *J. Am. Chem. Soc.*, **94**, 8510 (1972).

[18] See also: (a) C.-M. Backman, Inaugural Dissertation, Uppsala University, Sweden, 1976; (b) H. Schuh and H. Fischer, *Int. J. Chem. Kinetics*, 8, 341 (1976).

[19] P. W. Bridgeman, "Collected Experimental Papers", Vol. IV, Harvard University Press, Cambridge, MA, 1964, pp 2043–2085.

Table VII. Calculated Product Distribution from Decomposition of Azocumene (**1a**) in Chlorobenzene (55 °C) with Thiophenol as Scavenger[a,b]

| | | % yield | | | | |
|---|---|---|---|---|---|---|
| | | 3 | | | | |
| P, atm | 3/2[c] | cage[d] | scavenge[e] | 2 | 8 | f[f] |
| 1 | 0.03 | <1 | 73 | 22 | 5 | 0.73 |
| 1000 | 0.13 | 3 | 56 | 24 | 16 | 0.56 |
| 2050 | 0.16 | 4 | 56 | 24 | 16 | 0.56 |
| 4100 | 0.18 | 5 | 52 | 29 | 14 | 0.52 |
| 5000 | 0.19 | 5 | 52 | 26 | 17 | 0.52 |

[a] Product yields in percent normalized to a total of 100%. [b] Calculated from yields in Table IV. [c] Calculated ratios from a plot of the values for 4/2 in Table V vs. pressure. [d] From concentration values calculated by using the equation (cumene)/(bicumyl) × (bicumyl) (see text). [e] From the difference between total cumene concentration (Table IV) and cage cumene concentration. [f] Efficiency of radical production.

azocumene (**1a**) in chlorobenzene with added thiophenol (Table IV). In order to do this, however, one must identify the products arising from cage and noncage reactions. With thiophenol as a scavenger, cumyl radicals which escape the initial cage should abstract hydrogen to give cumene (eq 6).[15]

$$\mathrm{Ph\dot{C}Me_2 + PhSH \rightarrow PhCHMe_2 + PhS\cdot} \qquad (6)$$

Thus, the yields of cumene reported in Table IV arise both from cage disproportionation of two cumyl radicals and from noncage hydrogen abstraction (eq 6).[20] Bicumyl is a product which can only come from cage coupling of two cumyl radicals. We have proposed that *p*-cumylcumene (**8**) is a product and that it arises from rearrangement of the α-para semibenzene **5a** (eq 4) which is formed, like bicumyl, from coupling of two cumyl radicals in the initial cage. Thus, the combined yields of bicumyl and *p*-cumylcumene (**8**) reflect the cage effect.

The molar yields of the various products from Table IV have been converted into percentages, normalized to 100%, and these are given in Table VII. The percentages of "cage" cumene and "scavenge" cumene were calculated by comparing the data in Tables IV and V as described below.

In the absence of a scavenger, it has been generally assumed that cumene arises only by disproportionation of two cumyl radicals. If this were the case, the cumene/bicumyl ratios without a scavenger (Table V) should be a good approximation to the ratios of "cage" cumene to bicumyl when a scavenger such as thiophenol is present. Unfortunately, we suspect that in the unscavenged chlorobenzene reaction system, cumene may also be formed by reaction of cumyl radicals with the α-para semibenzene dimer (Scheme II). Therefore, we have made use of the α-methylstyrene/bicumyl ratios from the unscavenged experiments (Table V) to estimate the "cage" cumene/bicumyl ratios in the thiophenol-scavenged systems. Since data were obtained at different pressures in the presence (Table IV) and absence (Table V) of thiophenol, the predicted $[(\text{cumene})/(\text{bicumyl})]_{\text{cage}}$ ratios for the pressures in Table IV were calculated from a graph of the α-methylstyrene/bicumyl data in Table V, and these are listed in Table VII. These ratios were multiplied by the corresponding yields of bicumyl (Table IV) to obtain molar yields of "cage" cumene; yields of "scavenge" cumene were then calculated as the difference between total cumene (Table IV) and "cage" cumene yields.

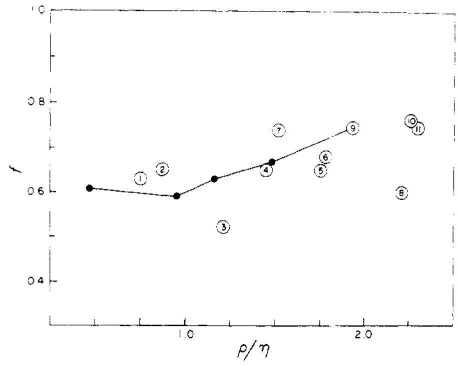

**Figure 5.** Kinematic viscosity dependence of the efficiency of radical production (*f*) from azocumene (**1a**) in chlorobenzene at various pressures (55 °C), solid points and line, and in various solvents at atmospheric pressure (Bartlett,[15] 62.5 °C except as noted): 1, *n*-dodecane; 2, tetralin; 3, nitrobenzene; 4, cyclohexane; 5, methylcyclohexane; 6, cumene; 7, cumene (our data, 55 °C); 8, chlorobenzene; 9, chlorobenzene (our data, 55 °C); 10, benzene; 11, toluene.

The percent yields of "scavenge" cumene directly give the efficiency of radical production *f*, and these values are tabulated in the last column of Table VII. These efficiencies appear to decrease "more normally" than when DBNO is the scavenger (see Figure 3), and we suggest that this is because the intermediate **5a** is trapped by rearrangement to **8** and properly counted as a cage product.[21]

Bartlett examined the effect of solvent variation on efficiencies for azocumene decomposition (numbered points in Figure 5). Because the efficiency data showed a great deal of scatter when plotted against kinematic viscosity, he concluded that other solvent properties such as specific solvation were important in determining the cage effect.[15]

Application of pressure to a medium is an alternate way to change viscosity. We have taken our DBNO efficiency data for azocumene in chlorobenzene at 55 °C (Table II) and also plotted these in Figure 5 vs. the kinematic viscosity of chlorobenzene at the various pressures utilized. These viscosity values were obtained from the data of Bridgeman.[19,22] It is interesting to note that with the exception of Bartlett's points 3 and 8, the general trend in his data is parallel to that in ours.

This suggests that factors related to viscosity, and not specific solvation effects, are of major importance in determining efficiencies. In our case, viscosity changes occur in the same solvent due to changes in pressure, while viscosity changes in Bartlett's study are produced by solvent variations. The highly deviant points 3 and 8 correspond to atmospheric pressure data obtained by Bartlett using nitrobenzene and chlorobenzene, respectively. While we have not obtained data in nitrobenzene, our results for chlorobenzene at atmospheric pressure give a substantially greater efficiency (point 9) which is more consistent with the other data.[23]

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(20) One mole of cumene from cage disproportionation corresponds to 1 mol of azocumene; however, 1 mol of cumene from thiophenol scavenging corresponds to 0.5 mol of azocumene.

(21) If the cumene/bicumyl ratios from Table V are used for these calculations, rather than the α-methylstyrene/bicumyl ratios from the same table, the efficiency values obtained are 0.71 (1 atm), 0.55 (1000 atm), 0.55 (2050 atm), 0.48 (4100 atm), and 0.47 (5000 atm), rather than those reported in Table VII. These values appear to be even "more normal" than those in Table VII, but they are subject to the uncertainty discussed in the text.

(22) (a) Kinematic viscosity is equal to $\eta/\rho$, where $\rho$ is the density of a liquid with viscosity $\eta$. At each pressure, Bridgeman's viscosity[21] and compressibility data [22b] for chlorobenzene were used to calculate values of $\eta/\rho$ at 55 °C. (b) Reference 21, pp 3915–3931.

## Experimental Section[24]

**Solvents.** Cumene (Matheson Coleman and Bell) was stirred over concentrated sulfuric acid, washed, and dried. It was then distilled under an atmosphere of nitrogen and stored in a dark bottle under an atmosphere of nitrogen or argon. Chlorobenzene (Matheson Coleman and Bell) was purified as described for cumene and stored over molecular sieves.

**Di-*tert*-butyl nitroxide (DBNO)** was synthesized from 2-nitro-2-methylpropane[25] and sodium metal by following the procedure of Hoffmann et al.[26] After careful washing of the resultant product with 0.2 N hydrochloric acid, drying, and vacuum distillation a cherry-red liquid was obtained which was identified as DBNO: bp 64–65 °C (4.5 mm) [lit.[26] bp 60 °C (11 mm)]; UV (*n*-hexane) $\epsilon_{465\text{nm}}$ 9.0 $M^{-1}$ $cm^{-1}$ (lit.[26] 8.9 $M^{-1}$ $cm^{-1}$), $\epsilon_{238\text{nm}}$ $2.25 \times 10^3$ $M^{-1}$ $cm^{-1}$ (lit.[26] $2.14 \times 10^3$ $M^{-1}$ $cm^{-1}$).

**Azocumene (1a)** was synthesized by treatment of cumylamine (vide infra) with iodine pentafluoride (Matheson Coleman and Bell).[5] Recrystallization from pentane gave crystals with a melting point of 87.7–88.0 °C dec (lit.[5] mp 86.9–88.7 °C dec); UV (cyclohexane) $\lambda_{max}$ 252, 258, 265 and 367 nm with $\epsilon$ 664, 612, 412 and 47 $M^{-1}$ $cm^{-1}$, respectively (lit.[5] $\epsilon$ 660, 598, 374 and 44 $M^{-1}$ $cm^{-1}$, respectively); NMR ($CCl_4$) $\delta$ 1.51 (s), 7.33 (aromatic m) (area ratio 6:5) (lit.[5] $\delta$ 1.49 and 7.21).

**Cumylamine** was obtained by the following route. Benzyl cyanide (Matheson Coleman and Bell) was methylated with iodomethane[27] to give cumyl cyanide. This was hydrolyzed to the corresponding amide[27] which was then converted via the Hofmann degradation to cumylamine:[27] bp 75–76 °C (6 mm) [lit.[27] bp 72–73 °C (8 mm)]; IR 2.9–3.0 μm (NH stretch).

***p,p*′-Dimethylazocumene (1b)** was a gift from Professor G. S. Hammond. The yellow powder (mp dec 89–90 °C) was recrystallized from pentane to give pale yellow-green needles: mp dec 93.5–94.5 °C (lit.[28] mp 92–95 °C); UV (cyclohexane) $\lambda_{max}$ 367 nm, $\epsilon$ 47 $M^{-1}$ $cm^{-1}$ (lit.[28] $\epsilon$ 49.5 $M^{-1}$ $cm^{-1}$).

**Bicumyl (2)** was prepared by decomposition of *tert*-butyl peroxide in cumene[29] and recrystallized from 95% ethanol; mp 116.5–117.5 °C (lit.[30] mp 116–117 °C).

***p*-Cumylcumene (3).** Cumene was brominated with *N*-bromosuccinimide, and the reaction mixture was filtered to remove unreacted NBS and succinimide and then treated with anhydrous ferric chloride. Vacuum distillation yielded a yellow fraction at 139–150 °C (1.3–1.4 mm) whose infrared spectrum was identical with that of *p*-cumylcumene[31] [lit.[31] bp 118 °C (0.3 mm)]. This fraction was further purified by preparative GLC using a $^1/_4$ in. × 12 ft SE-30 column at 200 °C to give a few milligrams of a colorless liquid whose infrared spectrum was again the same as that of *p*-cumylcumene: NMR (neat liquid, capillary tube, $Me_4Si/CCl_4$ external reference) $\delta$ 1.15 and 1.26 (methyl d), 1.66 (methyl s), 2.84 (septet), 7.02–7.18 (aromatic m). Integration of the NMR signals was relatively unsatisfactory due to the small amount of sample available; the approximate signal areas were 4:6:1:8, respectively, while the theoretical relative areas for *p*-cumylcumene are 6:6:1:9.

A sample of this material in chlorobenzene gave NMR signals at $\delta$ 1.09 and 1.20 (methyl d) and at $\delta$ 1.58 (methyl s) which corresponded exactly, as shown by mixing samples, to NMR signals observed in a partially decomposed high-pressure sample of azocumene in chlorobenzene containing thiophenol.

**Rates of Thermal Decomposition of 1a and 1b.** Master solutions were prepared by dissolving weighed amounts of **1a** or **1b** and scavenger (if used) in cumene or chlorobenzene under a nitrogen or argon atmosphere. Azo compound concentrations ranged from $2.0 \times 10^{-2}$ to $3.0 \times 10^{-2}$ M, and scavenger concentrations were in excess of those for **1a** or **1b**; concentrations of DBNO were (5.0–7.0) $\times 10^{-2}$ M, and those of thiophenol were 0.10–0.20 M. These solutions were vacuum degassed or bubbled with argon, opened only in a glovebag under an inert atmosphere, and stored in a refrigerator when not in use.

Samples which were decomposed at pressures greater than atmospheric were contained in capped Teflon tubes which had been filled in a glovebag under nitrogen or argon atmosphere and then sealed in three consecutive polyethylene bags. These prepared and "triply bagged" tubes were stored in a brown bottle in a freezer prior to use. Some atmospheric pressure samples were run in bagged Teflon tubes, but others were decomposed in evacuated sealed-glass ampules following normal sealed-tube procedures. Glass ampules, after being filled and sealed, were stored in a freezer prior to use.

Samples in the bagged Teflon tubes were decomposed under high pressure as previously described.[32] At least six samples were decomposed for various times spanning at least 2 half-lifes in any kinetic run in addition to zero- and infinite-time samples. All rate constants reported in Table I are averages of at least two independent kinetic runs. The samples were analyzed as described below immediately after each kinetic run.

Decomposed solutions of **1a** or **1b** in cumene with or without DBNO and in chlorobenzene without thiophenol were analyzed by UV over the spectral range 320–650 nm. Loss of the azo compound was monitored at 370 nm, and the resulting spectral data were used to construct first-order rate plots. Appropriate control experiments were performed to correct for base-line drift and minor overlap of the DBNO absorption band. No Beer's law deviations were observed over the experimental concentration ranges for any of the absorption bands used in this study.

Decomposed solutions of **1a** in chlorobenzene containing thiophenol were analyzed by monitoring the change in area of the NMR resonance signal corresponding to the methyl groups of azocumene. All samples from a given kinetic run were analyzed at the same time, and the methyl resonance areas were taken as the average of two separate traces for each sample.

**Efficiency of Radical Production. DBNO.** The partially decomposed samples of **1a** or **1b** in cumene or chlorobenzene containing DBNO used to determine decomposition rates (vide supra) were also used for the efficiency experiments. The decrease in the DBNO absorption band at approximately 465 nm was monitored to determine the change in concentration of DBNO compared to that for **1a** or **1b**. The error bars (Figures 2–4) represent the range of values for $f$ at different times during initiator decomposition. These values for a given set of reaction conditions were relatively constant with time. However, for high-pressure samples, values of $f$ at "infinite time" (most of the azo compound decomposed) were consistently smaller than values of $f$ at shorter times. Bartlett observed that fully decomposed samples of azocumene containing excess DBNO seemed to regenerate previously reacted DBNO (which should make efficiencies look lower) after exposure to air.[15] While all of our samples were deoxygenated, those used in the pressure experiments had a greater opportunity for trace oxygen contamination. Thus, in view of the possibility that some extraneous reaction path exists for regenerating reacted DBNO after long reaction times, we chose to exclude infinite time samples in calculating values of $f$.

**Product Yields. NMR.** Fully decomposed samples of azocumene in chlorobenzene containing 0.16 M thiophenol and $1.4 \times 10^{-2}$ M toluene as an internal standard were analyzed by NMR Corrections were necessary because the methyl resonance of bicumyl exactly overlaps with the lower field member of the cumene methyl doublet. These were accomplished by preparing and analyzing by NMR a series of calibration solutions containing varying amounts of cumene and bicumyl.

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[23] The difference in temperature between our results (55 °C) and those of Bartlett (62.5 °C) is the reason that points 6 and 7 and points 8 and 9 are displaced from each other on the $\rho/\eta$ axis in Figure 5.

[24] Detailed experimental procedures are fully outlined in the Ph.D. Dissertation of M. J. Amrich, Jr., University of California, Riverside, CA, Dec 1971.

[25] N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Am. Chem. Soc.*, 78, 4003 (1956).

[26] A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Am. Chem. Soc.*, 86, 639 (1964).

[27] A. Cope, T. Foster, and P. Towles, *J. Am. Chem. Soc.*, 71, 3932 (1949).

[28] J. R. Shelton, J. F. Gormish, C. K. Liang, P. L. Samuel, and P. Kovacic, *Can. J. Chem.*, 1149 (1968).

[29] J. V. Behar, Ph.D. Dissertation, University of California, Riverside, CA, 1969.

[30] C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, 81, 1137 (1959).

[31] P. Kovacic, C. Wu, and R. W. Stewart, *J. Am. Chem. Soc.*, 82, 1917 (1960).

[32] R. C. Neuman, Jr., and J. V. Behar, *J. Am. Chem. Soc.*, 91, 6024 (1969).

**GLC.** Fully decomposed samples of azocumene in chlorobenzene without thiophenol but containing toluene as an internal standard were analyzed by GLC using an F&M Model 700 dual-column thermal conductivity gas chromatograph containing a pair of matched 6 ft × $^1/_8$ in., 10% UC-W98, stainless-steel columns. Operating conditions were as follows: injection port, 215 °C; detector, 250 °C; oven, isothermal at 70 °C for 7 min and then programmed at 10 °C/min to 220 °C; helium flow rate, 31.1 mL/min. Samples of 2 $\mu$L were injected with a Hamilton automatic syringe. Appropriate calibration curves relating concentrations to peak areas were prepared and utilized to analyze the samples.

**Rates of Thermal Decomposition of an Intermediate.** Partially decomposed high-pressure samples of **1a** or **1b** in cumene with no scavenger showed a moderate absorption at 330 nm and an intense absorption below 310 nm. The loss of the longer wavelength band was monitored at 320 nm in a Cary UV spectrometer at ambient cell compartment temperature (ca. 28 °C). Corrections were necessary for end azo absorption at that wavelength.

In a separate study the effect of pressure on the decomposition rate of the intermediate absorbing at 315 nm from decomposition of **1a** in cyclohexane was monitored by UV spectroscopy using a high-pressure optical cell previously described.[33] A $1 \times 10^{-2}$ M master solution of **1a** in cyclohexane (Mallinckrodt, spectrophotometric grade) was prepared, carefully deoxygenated by utilizing procedures described above, and stored in a refrigerator, in the dark, under a nitrogen atmosphere. Samples of this solution were placed in the high-pressure optical cell under an inert atmosphere and photolyzed at various pressures for periods from 30 to 90 min by using a Hanovia 100-W high-pressure quartz mercury-vapor lamp in conjunction with a Corning 737 filter to provide light primarily at 366 nm. The cell was thermostated at 20 °C, and UV spectra were repeatedly scanned from 450 to 300 nm as a function of time. Disappearance of the intermediate was monitored at 316 nm. Decomposition was usually followed for 2 or 3 half-lives, and an "infinite time" trace was obtained after at least 20 h of decomposition.

**Acknowledgment.** The authors are grateful for support from the National Science Foundation and also wish to thank Professors J. M. Bride and E. G. Janzen for helpful discussions.

**Registry No. 1a**, 5676-79-9; **1b**, 18344-79-1; **2**, 1889-67-4; **3**, 98-82-8; **4**, 98-83-9; **8**, 62545-70-4; 2-nitro-2-methylpropane, 75-64-9; di-*tert*-butyl nitroxide, 2406-25-9; cumylamine, 585-32-0; benzyl cyanide, 140-29-4; iodomethane, 74-88-4; azobis(isobutyronitrile), 78-67-1; di-*tert*-butyl hyponitrite, 14976-54-6; 3,4,5,6-tetrahydro-3,6-diphenylpyridazine, 66090-52-6; 4,5,6,7-tetrahydro-3,7-diphenyl-3*H*-1,2-diazepine, 7433-52-5; [(*p*-nitrophenyl)azo]triphenylmethane, 16186-97-3.

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[33] (33) G. D. Lockyer, Jr., Ph.D. Dissertation, University of California, Riverside, CA, 1971.

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# Generation of 2-Chloronaphthalene-1,3-diyl

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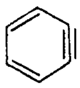
Reaction of 1-bromo-3,4-benzo-6,6-dichlorobicyclo[3.1.0]hexane with potassium *tert*-butoxide in tetrahydrofuran yields 2-chloronaphthalene along with nine other naphthalenes which result from solvent incorporation or reaction with nucleophile (Br$^-$, Cl$^-$, *t*-BuO$^-$). Use of tetrahydrofuran-$d_8$ as the solvent leads to the incorporation of two deuterium atoms into the chloronaphthalene. This result is interpreted in terms of a 1,3-dehydronaphthalene opening to the diradical, followed by abstraction of deuterium atoms from the solvent. The products which result from incorporation of solvent would then arise by dimerization of radical pairs. The remaining products are thought to arise from nucleophilic addition to the closed form of the dehydronaphthalene.

Although *o*-benzyne has been generated, trapped, and characterized spectroscopically as 1,[1,2] evidence for the para and meta isomers rests primarily on trapping experiments. Two different approaches to *p*-benzyne led to reactive intermediates possessing quite different properties. Pyrolysis of *cis*-1,2-diethynylethylene yielded products derived from diradical **2**,[3] whereas treatment of 1-chlorobicyclo[2.2.0]hexadiene with lithium diethylamide gave polyene **3**,[4] which was trapped in situ by addition of the base across the central bond. The vigorous conditions required to generate **3** suggest that this intermediate does not experience significant resonance stabilization.



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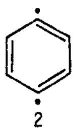
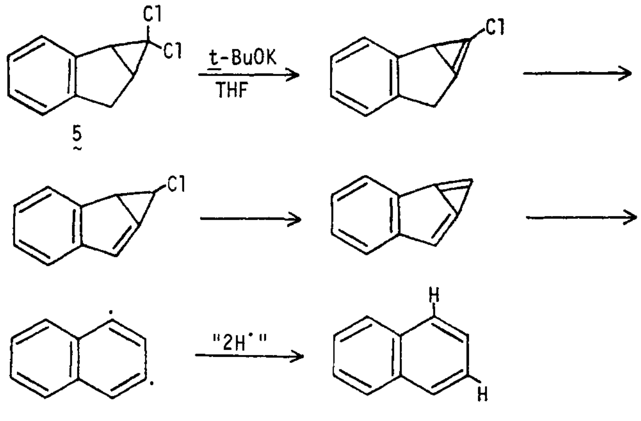


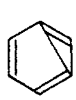
2

3

Scheme I



Washburn and his co-workers used *exo*,*exo*-4,6-dibromobicyclo[3.1.0]hexane as a precursor to *m*-benzyne (**4**).[5] When the bicyclic dibromide was treated with several



4

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