We believe that this is due to a high-chain "melting" temperature. The side chains melt at a temperature above that necessary to cause columns consisting of benzene cores to unstack. However, cyclohexane cores unstack at a higher temperature, so a mesophase is observed with this core.

The enthaply change for the crystal-mesophase transition of the branched compounds is lower than that for the *n*-alkanoyloxy compounds. As predicted by this model, the enthalpy change for the mesophase-isotropic transition is not reduced by branching.

These observations can be explained by the following arguments. Branches close to the core at C-2 interfere sterically with efficient stacking. Stacked benzene cores in the discotic phase are separated by an average distance of 4.6 Å.[9] The depression of melting point by branching in the middle of the side chains might be due to steric crowding with neighboring chains, and an increase in the conformational disorder about the branch. Branching at C-7 of the octanoate chain has little effect because at this distance from the cores the chains are not crowded by their neighbors and the region of the branch point is already disordered to a high degree prior to melting of the crystal phase (vida supra).

These data fit the model of separate side chain "melting" points and core "unstacking" temperatures for discotic liquid crystals. By varying the side-chain structure of discogens we are able to control the temperature range over which the discotic phase is stable. Work is in progress to further control the mesophase range of disklike molecules.

Acknowledgment. This work was supported by a grant from the Materials Research Laboratory at the University of Massachusetts.

Supplementary Material Available: ΔH and ΔS values for thermal transitions of all compounds (2 pages). Ordering information is given on any current masthead page.

Reduction of Azoalkanes by Benzhydryl Radicals

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Abstract: Benzhydryl radicals donate a hydrogen atom rapidly to the less hindered nitrogen atom of aliphatic and aromatic azo compounds, leading to the corresponding hydrazines. When the initially formed hydrazyl radical possesses a weak β-bond, it undergoes scission before receiving a second hydrogen atom. Thermolysis of benzpinacol with azocyclopropane causes a complex rearrangement to 1,5-diazaoct-5-en-1-yne (**21**).

Attempted triplet sensitization by aromatic ketones in the presence of a hydrogen donor can lead to complications due to the participation of ketyl radicals, a phenomenon commonly called chemical sensitization.[1] Recently, it was discovered in this laboratory that irradiation of xanthone with azocyclopropane (ACP) and thiophenol afforded propanal cyclopropylhydrazone (**6**) and propanal azine (**7**).[2] The mechanism in Scheme **I**, involving hydrogen transfer from xanthydryl radical (**1**) to the ground-state azo linkage, was proposed to explain the formation of these products (s = syn, a = anti).

Although the reducing properties of hydroxyalkyl radicals are well known[3-6] and the azo linkage is readily attacked by radicals,[7] the only azo compounds reported to react with ketyl radicals are azo dyes.[8-11] In order to test the above mechanism, we studied the reduction of azoalkanes by thermally generated benzhydryl radicals.[12]

I. Results

The photoreaction of benzophenone with triethylamine produces a near quantitative yield of benzhydryl radical,[13] but irradiation of this solution in the presence of ACP caused rapid destruction of starting azoalkane and formation of a complex mixture. In contrast, azo-*tert*-butane (ATB) was reduced to 1,2-di-*tert*-butylhydrazine (**8**) under the same conditions. To confirm the participation of the benzhydryl radical, this species was produced independently in the presence of ATB by thermolysis of benzpinacol,[14] leading cleanly to **8**. Further investigation of the thermal reaction using the azoalkanes listed in Table I showed reduction to be general.

All of the aliphatic hydrazines were identified by comparing their ^{1}H and/or ^{13}C NMR spectra (cf. Table II) with those from the literature[15] or from authentic samples made by catalytic hydrogenation[16] of the corresponding azoalkane. The structures of the arylhydrazines are supported by the similarity of their ^{13}C chemical shifts to those of hydrazobenzene. Products **21**, **25**, **27**, and **29** were identified by comparison with independently synthesized samples.[17] The reduction products of **36** were confirmed by NMR comparison with a mixture of acetone azine and acetic acid.

Thermolysis of benzpinacol proceeds at low enough temperature (130 °C) that competing decomposition of the azoalkanes selected

(1) Engel, P. S.; Monroe, B. M. *Advan. Photochem.* **1971**, *8*, 262 and references therein.
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(3) Rubin, M. B.; Ben-Bassat, J. M. *Mol. Photochem.* **1971**, *3*, 155.
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(6) Rubin, M. B.; Ben-Bassat, J. M. *Tetrahedron Lett.* **1971**, *3403*.
(7) Dacey, J. R.; Mann, R. F.; Pritchard, G. O. *Can. J. Chem.* **1965**, *43*, 3215. Roberts, B. P.; Winter, J. N. *Tetrahedron Lett.* **1979**, 3575. Strausz, O. P.; Berkley, R. E.; Gunning, H. E. *Can. J. Chem.* **1969**, *47*, 3470. Beckwith, A. E.; Wang, S.; Warkentin, J. *J. Am. Chem. Soc.* **1987**, *109*, 5289.
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(9) Heijkoop, G.; van Beek, H. C. A. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 83.
(10) van Beek, H. C. A.; Heertjes, P. M.; Schaafsma, K. *J. Soc. Dyers. Colour.* **1971**, *87*, 342.
(11) van Beek, H. C. A.; Heertjes, P. M.; Visscher, F. M. *J. Soc. Dyers Colour.* **1965**, *82*, 400.
(12) Schenck, G. O.; Matthias, G.; Pape, M.; Cziesla, M.; van Bunau, G. *Justus Liebigs Ann. Chem.* **1968**, *719*, 80.
(13) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419. Parola, A. H.; Cohen, S. G. *J. Photochem.* **1980**, *12*, 41.
(14) Weiner, S. A. *J. Am. Chem. Soc.* **1971**, *93*, 6978.
(15) NMR data for ethylhydrazines are given: Condon, F. E. *Org. Magn. Reson.* **1972**, *6*, 517.
(16) Stowell, J. C. *J. Org. Chem.* **1967**, *32*, 2360.
(17) Authentic **27** and **29** were made by Y.-Q. Chen in this laboratory.

0002-7863/89/1511-1830$01.50/0

Scheme I

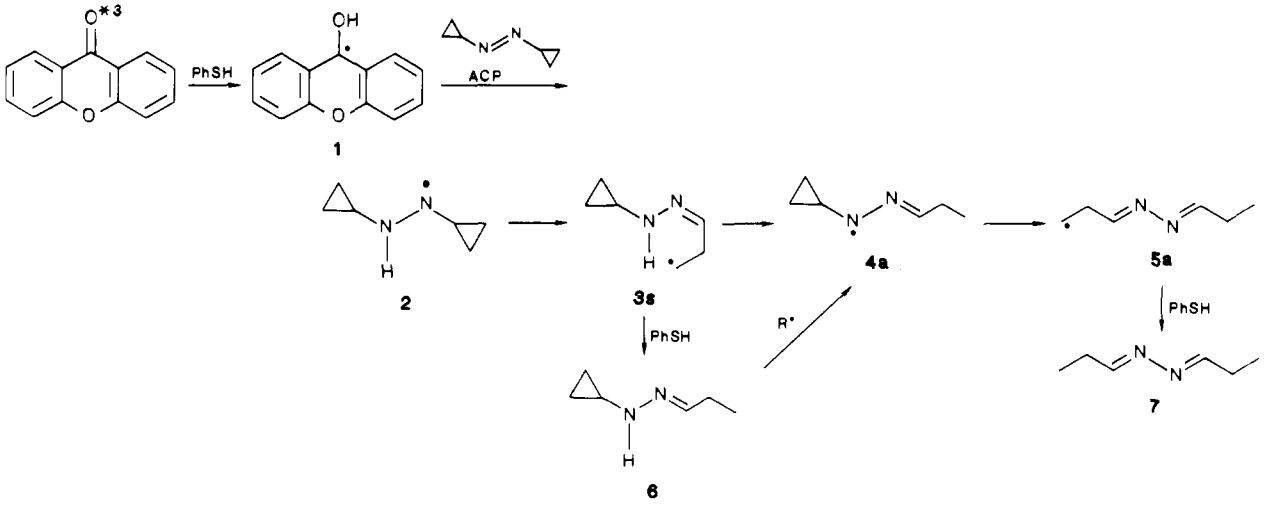
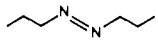
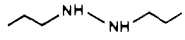
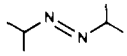
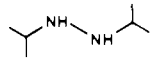
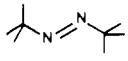
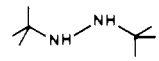
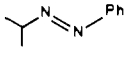
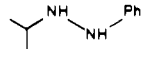
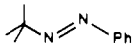
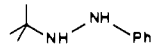
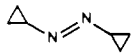
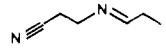
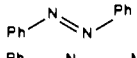
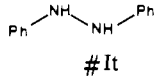
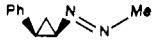
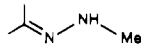
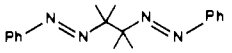
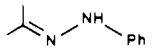
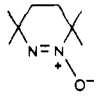
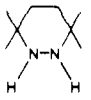
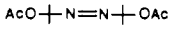
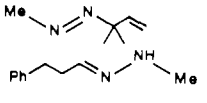
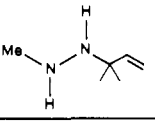
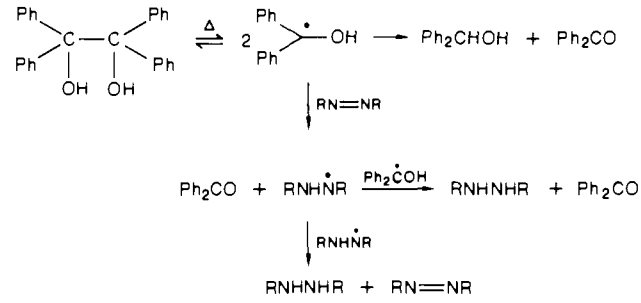


Table I. Products from Thermolysis of Benzpinacol in the Presence of Azoalkanes

	azoalkane		product
9		**10**	
11		**12**	
ATB		**8**	
13		**14**	
15		**16**	
17		**18**	
19		**20**	
ACP		**21**	
22		**23**	
24		**25**	#It
26		**27**	
28		**29**	
30	azo-1-adamantane	**31**	1,2-di-1-adamantylhydrazine
32		**33**	
34		**35**	
36			acetone azine + acetic acid
37		**38**	

was generally not a problem. The observed overall rate constant ($k = 1.1 \times 10^{-3}$ s^{-1} at 130 °C), calculated from the time-dependent decrease of the ^{1}H NMR peak area of benzpinacol's OH signal relative to that of the internal reference, hexamethyldisiloxane, in the presence of **9** or **11**, agrees very closely with the rate constant reported[14] for thermolysis of benzpinacol in the presence of scavengers. Flash-photolysis experiments indicated that ATB quenched the benzhydryl radical with a rate constant greater than 10^8 M^{-1} s^{-1}.

Scheme II



II. Discussion

Two possible mechanisms come to mind for the benzhydryl-induced reduction of azoalkanes: hydrogen atom transfer, or single-electron transfer (SET) followed by rapid protonation of the azoalkane radical anion. SET can be ruled out on the basis of one electron redox potentials (versus SCE) in acetonitrile, a solvent which favors electron transfer: benzhydryl radical, estimated $E^0(\text{ox})_{1/2} = -0.7$ V,[18] azobenzene, $E^0(\text{red})_{1/2} = -1.37$ V.[19] The free energy change for SET to azobenzene is substantially positive ($\Delta G^0 = 15.5$ kcal/mol) and is expected to be still more endothermic for azoalkanes.[20] Since it is impossible to reconcile the observed large interaction rate constant ($>10^8$ M^{-1} s^{-1}) with such endothermic electron transfer, we suggest that hydrogen transfer from the benzhydryl radical to the azo linkage is the first step of the reduction, as shown Scheme II.

Many reducible organic compounds quench benzhydryl radicals by what is proposed to be the SET mechanism.[21] In the case of acridine, however, SET is more endothermic than in azobenzene,[22] yet the interaction rate constant is still 2×10^7 M^{-1} s^{-1}.[23] Initial hydrogen atom transfer is therefore the preferred mechanism for both acridine and azo compounds.

Once the hydrazyl radical has formed, another H• is required to generate the product. The second hydrogen probably does not come from induced decomposition of benzpinacol since no rate acceleration is seen over that reported in the literature.[14] Therefore

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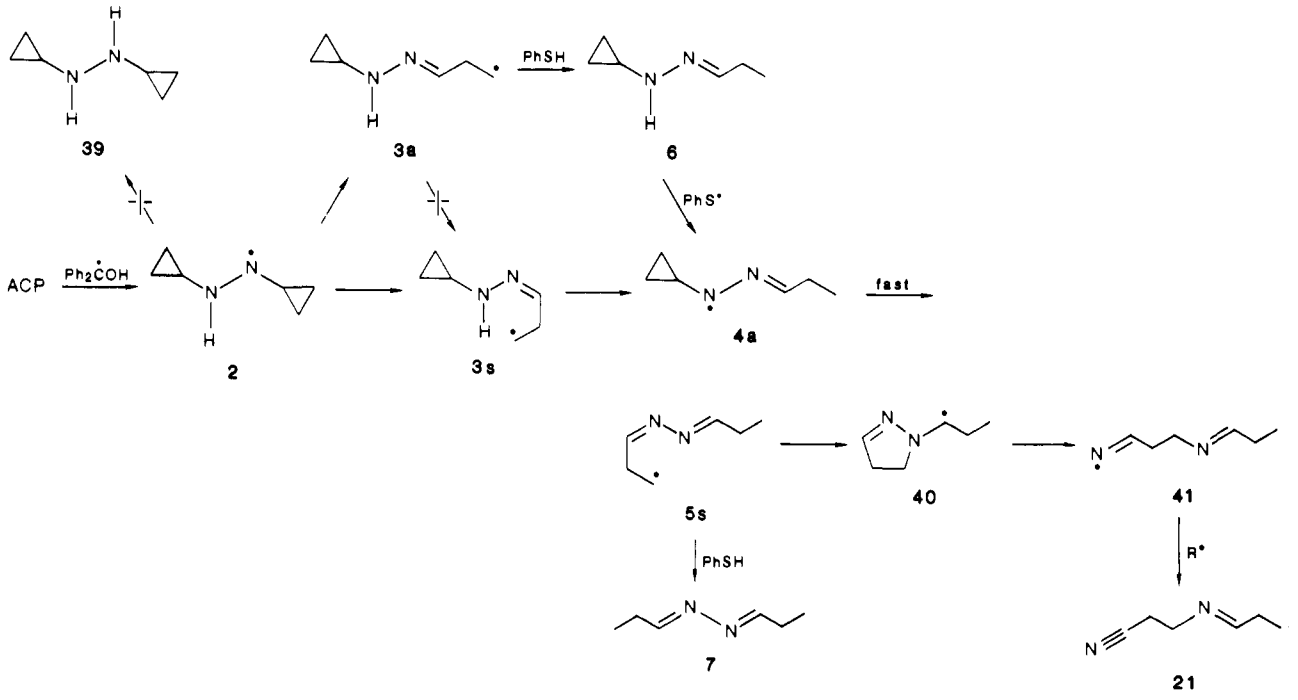
(19) Rao, P. S.; Hayon, E. *Anal. Chem.* **1976**, *48*, 564.
(20) Azoalkane anions are known, however. Krynitz, U.; Gerson, F.; Wiberg, N.; Veith, M. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 755. Sustmann, R.; Sauer, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1248.
(21) Kemp, T. J.; Martins, L. J. A. *J. Chem. Soc., Perkin Trans. 2*, **1980**, 1708.
(22) Tabner, B. J.; Yandle, J. R. *J. Chem. Soc. A* **1968**, 381.
(23) Donckt, E. V.; Porter, G. *J. Chem. Phys.* **1967**, *46*, 1173.

Table II. NMR Data for the Products

product	proton[a]	carbon 13[b]
8	2.2 (br s, 2 H), 1.04 (s, 18 H)	52.31, 27.71
10	2.57 (t, 4 H, J = 7.04), 2.17 (br s, 2 H), 1.40 (m, 4 H), 0.86 (t, 6 H, J = 7.41)	53.61, 21.89, 11.98
12	2.74 (sep, 2 H, J = 6.21), 2.3 (br s, 2 H), 0.98 (d, 12 H, J = 6.22)	50.84, 21.55
14	3.14 (s, 2 H), 3.04 (br s, 2 H), 1.26 (s, 2 H), AB (1.23, 1.16, 4 H, J = 9.32)	56.49, 39.18[c]
16	3.08 (br s, 2 H), 2.54 (s, 2 H), AB (1.55, 1.42, 8 H, J = 7.8)	45.14, 26.52
18	7.18 (m, 2 H, Ar), 6.85 (d, 2 H, Ar), 6.77 (t, 1 H, Ar), 4.47 (br s, 1 H), 2.75 (br s, 1 H), 2.63 (sep, 1 H, J = 6.22), 0.83 (d, 6 H, J = 6.22)	150.81, 129.22, 118.71, 112.87, 51.13, 20.87
20	7.22 (m, 2 H, Ar), 6.96 (d, 2 H, Ar), 6.79 (t, 1 H, Ar), 4.58 (br s, 1 H), 2.52 (br s, 1 H), 0.88 (s, 9 H)	151.54, 130.17, 118.64, 113.06, 53.47, 27.10
21	7.12 (t, 1 H, J = 4.08), 2.84 (t, 2 H, J = 6.45), 1.91 (dq, 2 H, J = 4.21, 7.36)[d], 1.76 (t, 2 H, J = 6.50), 0.87 (t, 3 H, J = 7.47)	167.55, 118.17, 56.02, 29.02, 19.04, 9.82
23	7.08 (t, 4 H, Ar), 6.75 (t, 2 H, Ar), 6.61 (d, 4 H, Ar), 4.70 (br s, 2 H)	149.29, 129.44, 119.85, 112.54
25	7.10 (m, 5 H, Ar), 6.44 (t, 1 H, J = 5.04), 4.55 (br s, 1 H) 2.70 (t, 2 H, J = 7.78), 2.46 (m, 5 H)[e]	142.03, 136.73, 128.75, 128.60, 126.10, 35.12, 34.56, 33.97
27	3.90 (br s, 1 H), 2.83 (s, 3 H), 1.77 (s, 3 H), 1.23 (s, 3 H)	142.94, 25.02, 14.80
29	7.20 (m, 4 H, Ar), 6.82 (m, 1 H, Ar), 6.59 (br s, 1 H), 1.78 (s, 3 H), 1.13 (s, 3 H)	146.68, 142.34, 119.71, 129.40, 113.35, 24.98, 14.59
31	2.25 (br s, 2 H), 2.05 (br s, 6 H), 1.65 (br s, 24 H)	52.29, 41.87, 37.40, 30.02
33	3.49 (br s, 2 H), 1.30 (s, 2 H), 0.98 (s, 12 H)	63.58, 55.89, 28.36
35	2.38 (br s, 2 H), 1.21 (s, 4 H), 0.91 (s, 12 H)	48.75, 33.51[f]
38	5.71 (m, 1 H), 4.97 (m, 2 H), 3.07 (br s, 2 H), 2.40 (s, 3 H), 1.11 (s, 6 H)	146.09, 112.01, 56.94, 40.46, 25.50
39	3.27 (br s, 2 H), 3.22 (m, 2 H), 0.38 (m, 4 H), 0.28 (m, 4 H)	31.69, 6.08
45	7.17 (m, 5 H, Ar), 3.23 (br s, 2 H), 2.42 (m, 1 H), 2.11 (s, 3 H), 1.77 (m, 1 H), 0.75 (m, 2 H)	
46	6.97 (m, 8 H, Ar), 4.80 (s, 2 H), 3.33 (br s, 2 H)	
48	3.53 (s, 3 H), 2.40 (s, 3 H), 1.20 (s, 6 H), 1.18 (s, 6 H)	
50	1.13 (s, 12 H), 1.11 (s, 4 H)	

[a] ^{1}H chemical shifts are reported in ppm on the δ scale with either solvent signal (C_6D_6 δ 7.15) or internal hexamethyldisiloxane (δ 0.11) as reference. [b] C_6D_6 (δ 128.00) was used as internal standard. [c] All carbons except bridgehead. [d] Decoupling experiments clearly showed that this double quartet is coupled with the triplet at 7.12 and the triplet at 0.87. [e] $NHCH_3$ and $CH_2CH{=}N$. [f] Methyl and methylene carbons.

Scheme III



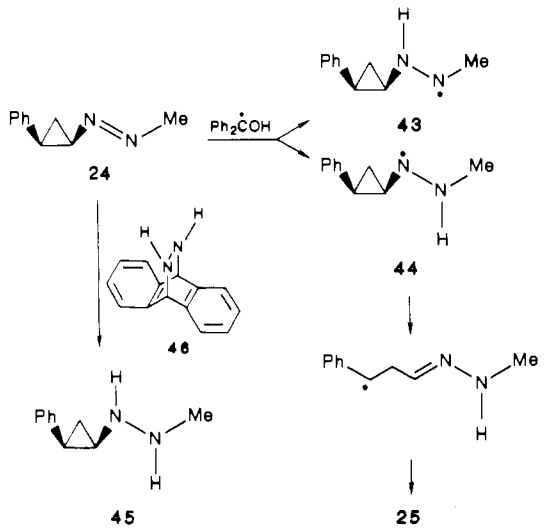
this H· must be transferred from a second benzyhydryl radical or from a second hydrazyl radical, whose disproportionation is known.[24]

The reaction of ACP with thermally produced benzyhydryl radicals did not give 1,2-dicyclopropylhydrazine (**39**), as shown by NMR comparison with authentic **39**, generated by diimide reduction[25] of ACP. Instead the most prominent peaks in the complex NMR spectrum of the reaction mixture were shown by comparison with that of independently synthesized material to arise from **21**, a drastically rearranged isomer of ACP. This unusual product must derive from a scavengeable radical, for it was found among the products of the irradiation of benzophenone with triethylamine and ACP but was absent both in the xanthone–thiophenol–ACP photoreaction[2] and in the benzpinacol–ACP thermolysis with added thiophenol. The major product (>80%) of the latter experiment was azine **7**, but heating 0.10 M ACP with 0.24 M thiophenol in C_6D_6 at 130 °C for 15 min gave no reaction. Since **7** must have arisen by scavenging of a radical on the pathway to **21**, we propose that the reaction of ACP with benzhydryl radicals proceeds as shown in Scheme III.

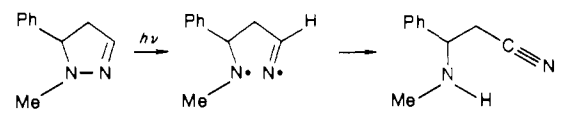
(24) For an example of this disproportionation, see: Holt, P. F.; Hughes, B. P. *J. Chem. Soc.* **1955**, 98.

(25) Although diimide has been used frequently to reduce azobenzene, we are unaware of its use in the aliphatic series. See: Hünig, S.; Müller, H. R.; Thier, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 271.

Scheme IV

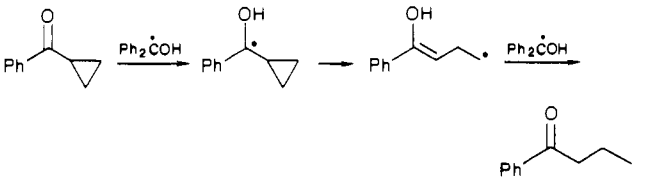


The rearrangement of **2** to **3s** and of **4a** to **5s** (cf. Scheme III) resembles the rapid ring opening of cyclopropylaminyl radicals[26] while cyclization of **5s** to **40** finds analogy in radical attack at imine nitrogen.[27] The cyclization rate of **5s** is apparently slow enough to allow scavenging so that **7** becomes the product when thiophenol is added. The absence of hydrazone **6** in the benzpinacol–thiophenol reaction is surprising since **2** should open to a mixture of **3s** and its anti isomer **3a**, which should be trapped by PhSH. Although one might speculate that **3a** at 130 °C undergoes thermal inversion to **3s** faster than it is trapped, the activation barrier for inversion[28] is too high for such an explanation. Radical **3a** may reclose to **2** faster than it is trapped, or perhaps any **6** that forms is converted by phenylthiyl radicals to **4a**. Similarly, **4a** should open to both **5s** and its anti isomer, **5a**. In the absence of PhSH, **5a** apparently recloses to **4a** and may also be responsible for some of the unidentified products of the unscavenged reaction. The main route to **4a** is proposed to be intramolecular hydrogen abstraction in **3s** followed by facile isomerization of the initial *syn*-hydrazonyl radical to **4a**.[29] Conversion of **41** to product **21** requires disproportionation with another radical R•. Although recombination is the usual fate of disubstituted iminyl radicals,[30] an intramolecular analogy for our last step is found in the photolysis of pyrazoline **42**.[31] Furthermore, phenylmethanimine radicals (PhCH=N•) disproportionate to benzonitrile,[32,33] while the hydrazone $H_2C{=}NNHCH_3$ decomposes to HCN and CH_3NH_2 in the pyrolysis of $(CH_3)_2NN_3$.[34]



Reaction of another azocyclopropane (**24**)[31] with benzhydryl radicals could lead initially to two hydrazyl radicals, **43** or **44** (cf. Scheme IV). Since **43** cannot undergo cyclopropylcarbinyl rearrangement, it should lead to hydrazine **45**. However, **45** was not formed in this reduction, the observed product **25** arising exclusively from **44**. The following control experiment showed that the absence of **45** was not due to its instability under the reaction conditions. A mixture of **24**, benzpinacol, and the anthracene adduct of diimide **46**[35] in a 1:1:2 molar ratio was degassed and sealed in an NMR tube. This source of diimide, which undergoes thermolysis at 50–90 °C, was selected to avoid introduction of potentially reactive substances and to allow clean generation of the air-sensitive hydrazine. After the reduction of **24** to **45** was nearly complete, the temperature was raised to 130 °C to decompose benzpinacol. Hydrazine **45** was unchanged but the residual azoalkane **24** proceeded as usual to **25**.

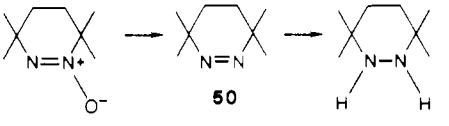
Another possible reason for the absence of **45** during benzhydryl radical reduction of **24** is that **43** transferred H• back to a benzhydryl radical, regenerating **24**. However this process would lead to benzhydrol, which was not observed in the reaction. We conclude that **43** does not form and that hydrogen transfer to **24** occurs only at the least hindered nitrogen. Intermediate **44** then rearranges exactly as expected from the ACP results. Of course, the absence of a second cyclopropyl ring greatly simplifies the chemistry. The reaction of **24** and the initial steps for ACP are similar to the following reduction of cyclopropyl ketones reported by Neckers and Schaap:[36]



Bisazoalkanes **26** and **28** also behaved unusually upon prolonged exposure to benzhydryl radicals, giving only the hydrazones **27** and **29** (cf. Scheme V). These products of central C–C bond cleavage were observed at a reaction time of 20 min as well; however, the early reduction mixture from **26** showed additional NMR peaks attributed to hydrazine **48**. An authentic sample of **48** was generated for spectral comparison by catalytic half-hydrogenation of **26**. On the basis of the conclusions from **24** (see above), we suggest that hydrogen is delivered selectively to the less hindered end of the azo group of **26** and **28** and not to the neopentyl-like nitrogen. The resulting hydrazyl radical, **47**, undergoes rapid β-scission when R = phenyl because the released radical has additional resonance stabilization.[37] On the other hand, **47** (R = Me), which cleaves less readily, reacts as expected with benzhydryl radicals to give **48**. Since **48** is still an azoalkane, it can be reduced by benzhydryl radicals to **49**, perhaps accounting for the absence of **48** at longer reaction times.

Despite the fact that thermolysis of **37** at 120 °C was only 2.4 times slower than that of benzpinacol, we were able to determine that the sole reduction product was the simple hydrazine **38**. No evidence was found for delivery of H• to the olefin, intramolecular attack of the intermediate hydrazyl on the olefin, or free-radical rearrangements.[38]

Reduction of azoxyalkane **34** by 2 equiv of benzpinacol gave exclusively the expected hydrazine (**35**). According to NMR, the intermediate azoalkane, **50**, reached a maximum concentration



of about 10% of the mixture in 5 minutes, when 60% of **34** remained and 30% of **35** was formed. One equivalent of benzpinacol is known to reduce azoxybenzene to azobenzene[5] but we did not

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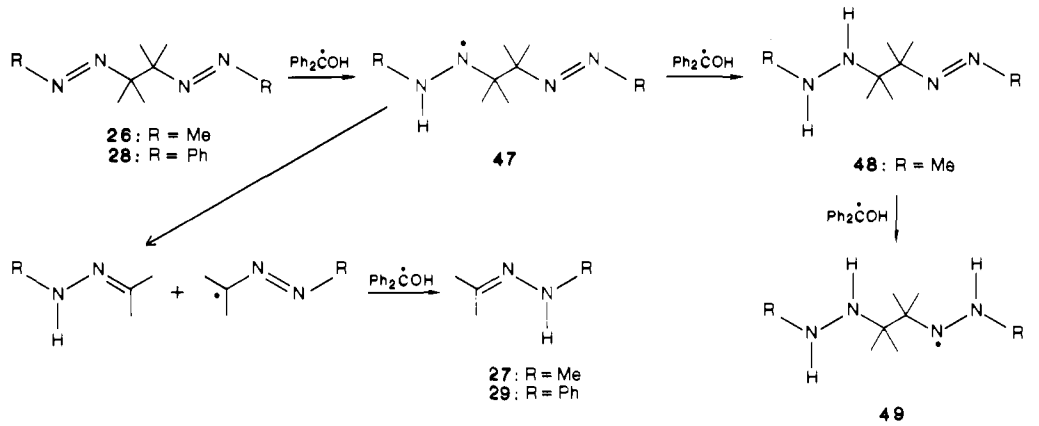
Scheme V



try to reduce **34** with equimolar benzpinacol. Even if reduction of aliphatic azoxy compounds cannot be stopped cleanly at the azoalkane stage, the reaction is a potentially useful synthesis of azoalkanes from azoxyalkanes[2,39] since hydrazines are easily reoxidized to azoalkanes.

Azoalkane **36** also behaved abnormally on reduction with benzhydryl radicals, the products being exclusively acetone azine and acetic acid. Following initial H• transfer to the azo linkage, loss of acetoxy radical may generate a hydrazone that loses acetic acid. Alternately, the diacetoxyhydrazine could form as usual but then lose acetic acid.

By way of historical perspective, Monroe and Wamser[5] obtained some secondary products from the reduction of azoxybenzene with photochemically produced acetophenone ketyl radical. Those products were postulated to arise from further reduction of azobenzenes by acetophenone ketyl radical. Hashimoto et al.[40] also noted the possibility of chemical sensitization in their work on photoreduction of azobenzene. Our reduction of azobenzene (**22**) nicely confirms their hypotheses.

In summary, we have found that thermolysis of benzpinacol in the presence of azoalkanes provides a clean method to generate air-sensitive hydrazines.[41,42] The mechanism begins with rapid hydrogen atom transfer from benzhydryl radical to the least hindered nitrogen of the azo linkage. When a weak bond is situated β to the initially formed hydrazyl radical as in azocyclopropanes or vicinal bisazoalkanes, cleavage of this bond leads to hydrazones by rational mechanisms.

III. Experimental

General Procedures. NMR spectra were obtained on an IBM AF-300 spectrometer in C_6D_6. Analytical GC was carried out on a Hewlett-Packard 5890 instrument equipped with a data system while preparative GC employed an Antek 300 TC chromatograph.

Compounds. Before use, **9**,[43] **11**,[43] **17**,[44] and **29**[44] were purified from stock samples by preparative GC on an OV-17 column. Compounds **13**[45] and **15**[46] were purified by sublimation while **22** was recrystallized from ethanol. Relatively pure ATB,[43] **19**,[47] ACP,[2] **26**,[44] **28**,[44] **30**,[48] **32**,[49] **34**,[50] **36**,[51] and **37**[52] were used without further purification. A 0.1 M solution of **24** in C_6D_6, prepared by G. A. Bodager,[2] was used without isolation. Benzpinacol was prepared by irradiating benzophenone in isopropanol.[53] The hexane solvent used for flash photolysis was B & J Chrompure (American Scientific Products). Phenylbenzoin was prepared and purified as described in the literature,[54] benzophenone was recrystallized from methanol, and triethylamine was refluxed and distilled from potassium hydroxide pellets. Authentic samples of **8**, **14**, **16**, **31**, **33**, **35**, and **48** were prepared by catalytic hydrogenation of the appropriate azoalkanes at 1 atm in methanol or ether over 10% Pd/C.

1,5-Diazaoct-5-en-1-yne (21). To 0.5 mL of C_6D_6 containing 14 mg (0.2 mmol) of 3-aminopropanenitrile[55] in an ice bath was added dropwise with stirring a cold solution of 11.6 mg (0.2 mmol) of distilled propionaldehyde in 0.5 mL of C_6D_6. The mixture was stirred at room temperature for a few minutes and dried over anhydrous Na_2SO_4 for 2 h with frequent shaking. ^1H and ^{13}C NMR of the solution showed that the major peaks coincided with those found in the reduction of ACP. Attempted large-scale preparation and purification were not successful due to the instability of the product. Thus the NMR solution described above decomposed to a complex mixture after standing for 26 days in the freezer.

3-Phenylpropanal *N*-methylhydrazone (25) was prepared according the literature procedure.[56] The pure hydrazone underwent air oxidation, presumably to the peroxide, on standing at room temperature for a few hours.

Benzhydryl Reduction of Azoalkanes. All reactions were run in sealed NMR tubes in C_6D_6 (Cambridge Isotope Laboratories, 99.6%) degassed by three freeze–thaw cycles. The concentrations of benzpinacol and azoalkane were typically 0.1 M. The tubes were immersed in an oil bath at 130 ± 0.1 °C and were removed periodically for NMR analysis. GC analysis of the reduction mixture from ACP showed benzophenone, benzhydrol, and **21**, whose retention times matched those of authentic materials. GC conditions: Supelcowax 30-m capillary column (column, 150 °C; injector, 150 °C; detector, 250 °C).

^1H and ^{13}C NMR of the reduction of **24** showed that the major peaks coincided with those in the authentic sample of **25**. Both the reduction product and the authentic samples contained a small amount of *Z* isomer.[57] The reduction mixture of **24** showed a GC peak with the same retention time as that of **25** on a 25-m SE-54 capillary column (column, 160 °C; injector, 200 °C; detector, 250 °C). 9,10-Biiminoanthracene (**46**) was prepared according to the published procedure[35] escept that hydrolysis of the dicarbamate required 7 days. The biimine was mixed in C_6D_6 with **24** and benzpinacol in a 1:1:2 ratio in an NMR tube. Reduction of **24** to **45** began even while the solution was being vacuum degassed and the remainder of **46** was decomposed by heating at 70 °C for 10 min. While the major product was **45**, some azoalkane remained, probably because the diimide was not consumed with 100% efficiency.

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After heating of the sealed NMR tube at 130 °C for 10 min, all of the **24** had gone to **25** and the hydrazine **45** remained unchanged, even after an additional 2 h at 130 °C.

Heating **26** with benzpinacol for 20 min afforded products **27** and **48** in the 5:1 ratio according to ^{1}H NMR. The amount of **48** decreased on longer heating, reaching an undetectable level after 10 h. In contrast, bis(azoalkane) **28** showed **29** as the only product, even when thermolysis was interrupted after 20 min.

Flash Photolysis. The rate constant for quenching of benzhydryl radicals by ATB was determined by laser flash photolysis using 540-nm light to monitor the radical. A nitrogen-purged solution of 3.35×10^{-5} M benzophenone and 0.066 M triethylamine[13] in hexane and a solution of 2.83×10^{-4} M phenylbenzoin[18] was irradiated at 266 nm. Similarly, a 5×10^{-3} M solution of phenylbenzoin was irradiated at 355 nm. Addition of ATB shortened the decay lifetime, although vaporization of the quencher during purging causing scatter in the calculated k_q values. It was clear, however, that k_q was at least 10^8 M^{-1} s^{-1}.

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Statistical Analysis of Some Structural Properties of Solid Hydrocarbons

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Abstract: The crystal structures of 391 hydrocarbon molecules, comprising 18 249 atoms, retrieved from the Cambridge Structural Database, have been examined. Centrosymmetric space groups occur more frequently than in general organic compounds. Tables of atomic volume and surface increments are given. Averages of various packing indices are calculated. Molecular size is correlated to the packing energy, as computed by empirical potentials; methods to estimate accurately sublimation energies are developed, and trends in groups of compounds are discussed in terms of molecular structural properties. These trends survive changes in the potential energy parameters. It is found that flat, rigid, unsaturated molecules have the best chances to form a compact crystal, while alkyl substituents are strong perturbing factors. Bulk moduli and thermal conductivities are estimated, and it is found that the modulus is a convenient index of packing efficiency and correlates to molecular shape and symmetry effects. A principal-component analysis reveals three main factors, which can be interpreted as size, packing score, and packing "failure" coordinates; the shape effect cannot yet be deconvoluted from these factors. The analysis of the distribution of atomic contributions to the cohesion energy allows a verification of the homomeric principle and reveals the intramolecular screening factors that diminish the cohesion at certain atoms, as opposed to the effects of irregular molecular shape, which diminish the cohesion more uniformly at all atoms. Cylindric molecules pack in such a way that their elongation axes are very nearly parallel in the solid state. Future uses of the packing analysis hydrocarbon files are sketched.

X-ray crystallography has been, in the last 30 years or so, at the forefront of organic physical chemistry, providing an invaluable help in understanding chemical properties in terms of structure. As a result of this massive effort, all the basic information a chemist may need on molecular geometry is by now, or will be in the next few years, stored in the Cambridge Structural Database[1a,b] (CSD), from which exhaustive catalogs of molecular dimensions have already been produced.[1c]

It has been less widely recognized, let alone exploited, that another kind of expertise is made available by X-ray studies of organic crystals, that is, a detailed knowledge of the molecular packing. This intermolecular information is stored in the CSD as well, and, although so far considered as a fringe benefit of crystal studies, it is now very much in demand for use in materials science and drug design. It appears then well worth trying to tap this source of chemical knowledge; among the previous efforts in this direction we may mention studies of H bonding[2a-b] and of

Table I. Geometrical Rules for Automatic Classification of C Atom Types and Assignment of Hydrogen Atoms[a]

no. of bonds to other C atoms	test procedure	classification (H atoms assigned)
3	$R_1 + R_2 + R_3 < 4.44$	aromatic (none)
	>4.44	aliphatic (one, methine)
2	$R_1 + R_2 < 2.65$	acetylenic or allenic (none)
	$2.65 < R_1 + R_2 < 2.96$	aromatic (one H atom)
	$R_1 + R_2 > 2.96$	methylenic (two H atoms)
1	$R < 1.48$	ad hoc procedures
	$R > 1.48$	methylic (three H atoms)

[a] R_i's are the distances (Å) from other C atoms.

(1) (a) Data were retrieved from the 1986 release. Programs used are described in: Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, G. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. J.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331. (b) *Molecular Structures and Dimensions*; Kennard, O., Watson, D. G., Allen, F. H., Bellard, S. A., Eds.; Reidel: Dordrecht, The Netherlands, 1984; Vol. 15, and continuing series. (c) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

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