Organic and Biological Chemistry

"Stretched Benzene." A Kinetic Analysis of Possible Pseudoaromaticity Resulting from (2 + 2 + 1 + 1) Partitioning of a Neutral Six-Orbital Six-Electron System

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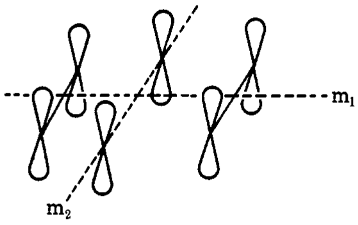
Abstract: The cycloaddition of cyclobutadiene and benzocyclobutadiene to 3,6-disubstituted *s*-tetrazines gives rise in a single manipulation to derivatives of the *exo,exo*-11,12-diazatetracyclo$[4.4.2.0^{2,5}.0^{7,10}]$dodeca-3,8,11-triene system. The kinetics of the thermal decomposition of these azo compounds have been determined in an effort to assess the possibility of pseudoaromatic stabilization in the resulting diradicals which can be considered to be "stretched benzenes." Also, the products of these thermochemical processes, together with those derived from photoinduced decompositions, have been investigated in order to determine if the azo compounds may also serve as potential precursors to substituted cyclodecapentaenes. Mechanistic interpretations of the various transformations are presented.

The key role which the benzene ring has played in the development of organic chemistry needs no elaboration. The recognition by Hückel over two decades ago[1] that all monocyclic, fully conjugated polyenes endowed with $(4n + 2)$ π electrons should possess "aromatic character" has encouraged the synthesis and detailed examination of such hydrocarbons with values of n from 0 to 7. Although a number of variations on the original Hückel theme have recently made their appearance (*e.g.*, homoaromaticity,[2] spiroconjugation,[3] effects of spanning alkyl moieties,[4] bicycloaromaticity,[5] and dehydro derivatives[6]), considerably less attention has been given to the extension of classical aromaticity to pseudoaromaticity. A neutral pseudoaromatic molecule is herein considered to be one in which $(4n + 2)$ p orbitals, consisting of olefinic and radical components, are coupled in relatively strain-free fashion with the resultant stabilization in excess of that available in the absence of interaction. In an uncharged six-electron system, the partitioning may take one of the following forms: $5 + 1, 4 + 2, 4 + 1 + 1, 3 + 3, 3 + 2 + 1, 3 + 1 + 1 + 1, 2 + 2 + 2, 2 + 2 + 1 + 1, 2 + 1 + 1 + 1 + 1$, and $1 + 1 + 1 + 1 + 1 + 1$.[7] Partition $4 + 2$ is representative of the transition state of the Diels–Alder reaction, $2 + 2 + 2$ is benzene, and $3 + 3$ can be viewed as the transition state of the Cope rearrangement. The symmetry considerations relating to these latter partitions have been reviewed previously.[8]

At the present time, we wish to focus attention on the $2 + 2 + 1 + 1$ partition with an interacting orbital pattern as shown in **1**. Theoretical calculations reveal



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that an orbital arrangement as in **1** possesses potential overlaps, and thus binding stabilization, which might surpass that in benzene, providing, of course, that the atomic centers are sufficiently proximate. The difficulty arises in designing a model in which geometrical constraints to the attainment of the necessary overlap are not prohibitive. Clearly, if the four components of **1** are not mutually insulated by a similar number of noninteracting centers, benzene is obtained. The simplest possible candidate, therefore, is one in which the benzene ring has been "stretched" to accommodate four intervening insulators.

The possibility has been considered that the structural rigidity in **3** would make this ring system an unusually favorable model for use in probing the geometrical and spatial requirements for conjugative stabilization in a "stretched benzene." *exo,exo*-11,12-Diazatetracyclo$[4.4.2.0^{2,5}.0^{7,10}]$dodeca-3,8,11-triene (**2**) seemed a logical precursor to **3** since azo compounds are recognized to decompose *via* free-radical intermediates.[9] Additional interest in **2** arises because this molecule contains an azo linkage and ten appropriately disposed

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[1] E. Hückel, "Grundzüge der Theorie ungesättiger und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

[2] S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 1 (1967).

[3] H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

[4] E. Vogel, *Chem. Soc., Spec. Publ.*, No. 21, 113 (1967); V. Boekelheide and W. Pepperdine, *J. Amer. Chem. Soc.*, **92**, 3684 (1970), and the many earlier papers in this series.

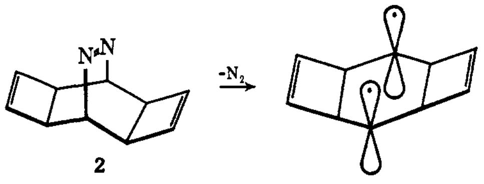
[5] M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

[6] F. Sondheimer and Y. Gaoni, *ibid.*, **82**, 5765 (1960); F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *ibid.*, **84**, 4595 (1962).

[7] We wish to acknowledge an enlightening discussion and exchange of information with Professor R. Hoffmann on this subject.

[8] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[9] (a) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969), and references cited therein; (b) J. W. Timberlake and M. L. Hodges, *Tetrahedron Lett.*, 4147 (1970).



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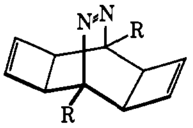
3

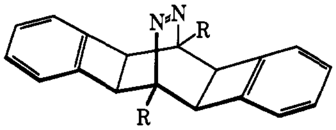
(CH) units; it is, therefore, also an attractive potential precursor of [10]annulene.[10] Such a synthetic entry to cyclodecapentaenes was deemed worthy of scrutiny because it represents a substantial departure from the time-worn alternative approaches.[11]

Results

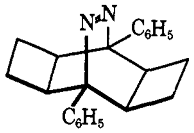
To shed light on the above questions, we have studied the rates of thermal decomposition of the 1,6-diphenyl derivative **4a**, its dibenzolog **5a**, and tetrahydro derivative **6**. For the purpose of resolving certain points



4a, R = C_6H_5
b, R = CH_3



5a, R = C_6H_5
b, R = CH_3



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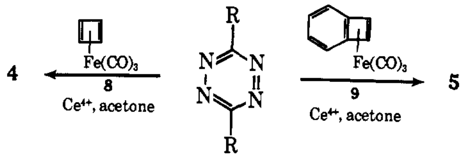
relating to the influence of the attached phenyl groups on product distribution, the methyl-substituted compounds **4b** and **5b** were also synthesized. We have noted that the phenyl groups are of value not only in guaranteeing that the developing free-radical centers be as sp^2 hybridized as possible but also in reducing the temperatures required for nitrogen extrusion to a level (165–185°) where reliable kinetic measurements could be obtained.

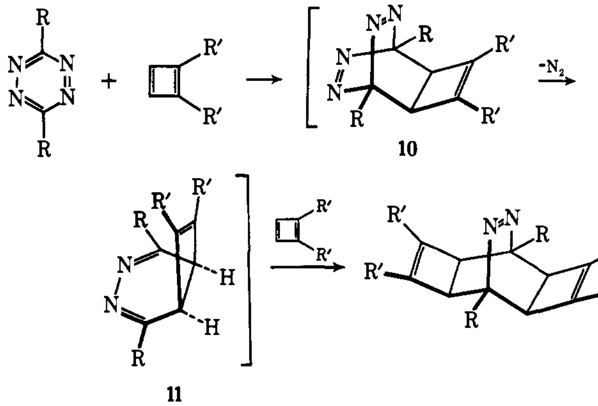
If the interactions arising in **3** and its dibenzo derivative are indeed conjugative and stabilizing, the development of such favorable resonance delocalization in the transition state would be expected to give rise to observable rate enhancements. The transition state for the decomposition of **6** cannot partake of orbital interaction and therefore its rate of nitrogen loss can be considered as that realizable in the absence of those factors responsible for enhanced stabilization. The possibility exists that the loss of nitrogen from such systems could take place concertedly with the rupture of an internal cyclobutene σ bond. Because of stereochemical features (see Discussion), however, this was not considered likely. Accordingly, the direct relevance of the rates of decomposition within this series to available stabilization originating from pseudoaromatic interactions appeared well grounded.

Synthesis. The azo compounds of interest were prepared in one step from the reaction of 3,6-disubstituted *s*-tetrazines[12] with cyclobutadiene or benzocyclobutadiene. These highly reactive dienophiles were generated *in situ* by oxidation of their iron tricarbonyl complexes (**8** and **9**, respectively) with ceric or ferric ion. The success of this remarkably facile synthesis can be attributed in large part to the apparent high level of reactivity inherent in the presumed 3,4-diazabicyclo[4.2.0]-octatriene intermediates, **11**. Such bicyclic valence tautomers of 1,2-diazocine are reasoned to be the result of initial (4 + 2) cycloaddition of the cyclobutadienes to **7** and facile loss of nitrogen from **10**.[13] The addition of a second mole of cyclobutadiene to **11** is evidently much faster than to the *s*-tetrazine since **4** and **5** are the only products formed, irrespective of the relative proportion of *s*-tetrazine present (Scheme I).



7a, R = C_6H_5
b, R = CH_3

Scheme I



The exo,exo configurations of **4a** and **4b**, assigned to conform with symmetry-controlled secondary orbital interactions operative in the transition state for cycloaddition to **11**,[14] were supported by their nmr spectra which fully substantiated the highly symmetrical structures (see Experimental Section). Because the steric bulk of the cyclobutene ring in **11** opposes the approach of cyclobutadiene from the top surface, this four-membered ring necessarily becomes cis to the developing azo linkage. The endo,exo isomer of **4** (**12**) would be expected to exhibit an nmr spectrum displaying two separate cyclobutene regions, by analogy to the spectral properties of **13**;[15] exo,exo isomer **14**, like **4**, shows a

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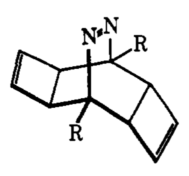
(10) L. A. Paquette and J. F. Kelly, *Tetrahedron Lett.*, 4509 (1969).

(11) T. L. Burkoth and E. E. van Tamelen, "Nonbenzenoid Aromatics," Vol. I, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, p 63; S. Masamune, R. T. Seidner, H. Zenda, M. Weisel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, 90, 5286 (1968); S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969).

(12) R. A. Carboni and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81**, 4342 (1959).

(13) Ready loss of nitrogen from related tetraazanorbornadienes has been previously observed: (a) ref 12; (b) M. Avram, I. G. Dinulescu, E. Marica, and C. D. Nenitzescu, *Chem. Ber.*, **95**, 2248 (1962); (c) J. Sauer and G. Heinrichs, *Tetrahedron Lett.*, 4979 (1966); (d) M. A. Battiste and T. J. Barton, *ibid.*, 1227 (1967); (e) A. Steigel and J. Sauer, *ibid.*, 3357 (1970); (f) W. S. Wilson and R. Warrener, *ibid.*, 4787 (1970).

(14) Such effects are known to be particularly influential in cyclobutadiene additions irrespective of whether this hydrocarbon plays the role of (a) dienophile [L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970); **93**, 5128 (1971)] or (b) diene [L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **88**, 623 (1966)].



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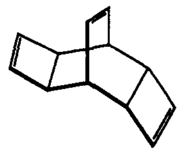

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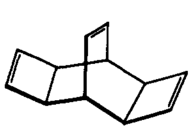

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highly symmetrical spectrum.[15] The stereochemical assignments to **5a** and **5b** depend upon similar considerations.

Reduction of **4a** with a 20-fold molar excess of diimide afforded **6** in 63% yield.

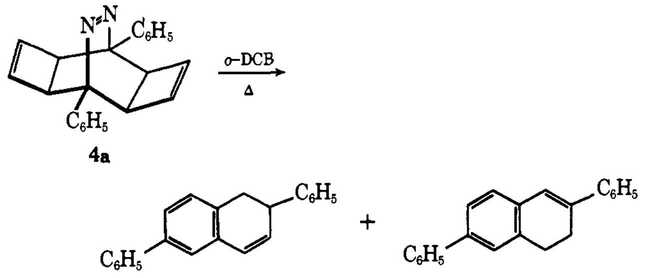
Kinetic Studies. The rates of decomposition of **4a**, **5a**, and **6** (Table I) were monitored by measuring nitrogen evolution using a constant-volume variable-pressure kinetic apparatus.[16] All of the decompositions were conducted in diphenyl ether solution and good first-order kinetics were obtained through at least three half-lives in each instance. The activation parameters were calculated from rate constants determined at least in duplicate at the three indicated temperatures.[17]

Table I. Rate Constants and Activation Parameters for Decomposition of Azo Compounds

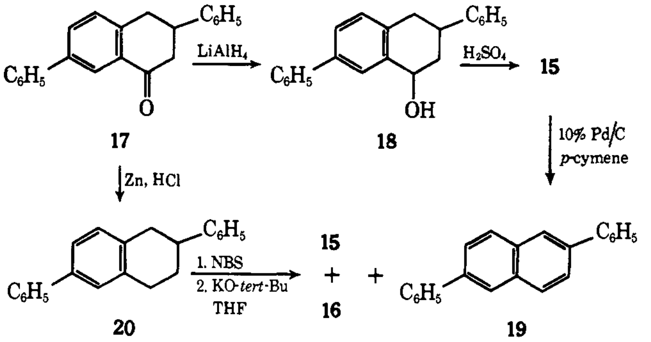
Compd	Temp, °C	$k \times 10^4$, sec^{-1}	E_{act}, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
4a	165.0	1.84			
	175.1	6.81	43.8	42.9	+21.6
	184.0	14.8			
6	165.0	3.94			
	175.4	8.86	30.9	29.9	−6.5
	184.4	17.7			
5a	165.0	1.51			
	175.4	4.62	36.7	35.8	+5.0
	184.4	10.2			

No significant rate differences were seen in the results obtained for **4a** and **5a**. It was particularly interesting to find, however, that the rates of decomposition of **4a** and **6** differ only be a factor of 2, *with* **6** *exhibiting the greater reactivity*. Clearly, no assistance to diradical formation is provided by the presence of sites of unsaturation at C_3–C_4 and C_8–C_9. Since the relatively large energies of activation for C–N bond homolysis in these symmetrical azo compounds (compare azocumene[9b,18]) support the two-bond cleavage mechanism to diradical intermediates, the lack of acceleration in **4a** and **5a** would appear to be a reflection of the absence of stabilizing electronic interaction in the respective transition states for nitrogen loss. In these considerations, compensation has not been made for the small existing differences in the ground-state energies of **4a** and **6**. Notwithstanding, an assessment of the stabilities of the free radicals produced in these thermal decompositions is possible and these clearly do not parallel the anticipated order of pseudoaromatic interaction.

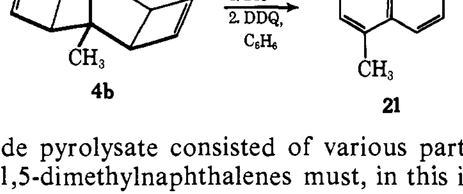
Thermal Decompositions. Preparative scale thermolysis of **4a** in refluxing *o*-dichlorobenzene for 30 min led to the production of **15** and **16** in yields of 78.5 and 8%, respectively. The structures of these hydrocarbons were secured on the basis of their ultraviolet spectra (see Experimental Section) and unequivocal synthesis from 2,6-diphenyl-5-tetralone (**17**, Scheme II). Control experiments have established that interconversion of **15** and **16** was not operative under the reaction conditions. However, prolonged heating of the mixture did result in partial air oxidation of both **15** and **16** to 2,6-diphenylnaphthalene (**19**).



Scheme II



Pyrolysis of **4b** under analogous conditions did not eventuate in measurable reaction within reasonable time limits. Accordingly, this azo compound was heated without solvent in a sealed tube at 240° for 7 hr. Gas chromatographic analysis indicated the formation of seven products. No attempt was made to identify these substances; rather, the mixture was dehydrogenated directly with DDQ in refluxing benzene. Such treatment gave rise to a single compound identified as 1,5-dimethylnaphthalene (**21**). The conclusion that the crude pyrolysate consisted of various partially reduced 1,5-dimethylnaphthalenes must, in this instance, be tempered somewhat by the realization that the overall yield for the formation of **21** from **4b** was only 11%. However, we consider it mechanistically significant that the various other dimethylnaphthalenes were not seen. In our hands, the level of detectability of the isomeric possibilities (vpc techniques) was better than 0.5%.



Tetrahydro derivative **6**, being slightly more reactive than **4a**, could also be satisfactorily decomposed in re-

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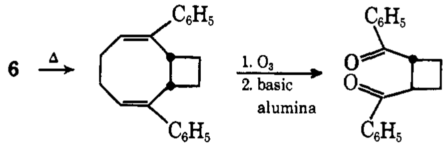
(15) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 4159 (1969); *J. Amer. Chem. Soc.*, **93**, 5735 (1971).

(16) J. C. Martin and J. W. Timberlake, *ibid.*, **92**, 978 (1970). We thank Professor Timberlake for detailed instructions on the construction of such an apparatus.

(17) D. F. Detar in "Computer Programs for Chemistry," Vol. III. D. F. Detar, Ed., W. A. Benjamin, New York, N. Y., 1969.

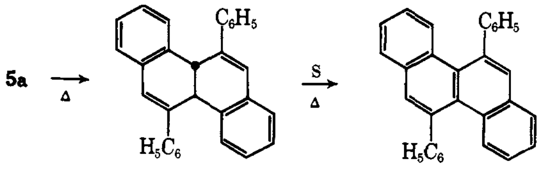
(18) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).

fluxing *o*-dichlorobenzene. At this temperature, nitrogen evolution was rapid and a single hydrocarbon was formed. The uv and nmr spectra of this substance suggested it to be *cis*-2,7-diphenylbicyclo[6.2.0]deca-2,6-diene (**22**) and its identity was confirmed by ozonolysis and subsequent epimerization of the cis diketone so produced on basic alumina. The infrared spectrum and melting point of **23** correspond to those reported for authentic *trans*-1,2-dibenzoylcyclobutane,[19] and its nmr spectrum is entirely consistent with this assignment.



22 **23**

The dibenzo derivative **5a** likewise underwent ready loss of nitrogen and skeletal bond reorganization under these conditions to afford dihydrochrysene derivative **24** in essentially quantitative yield. Dehydrogenation of **24** proceeded rapidly in the presence of sulfur and gave rise to 6,12-diphenylchrysene (**25**). The spectral properties of **24** entirely support the assigned structure but are not confirmatory for the trans ring fusion which must therefore be considered tentative. The ease with which **26** is transformed into **24** does, however, provide some measure of support for the stereochemical assignment (see below). It should be noted that because structure **24** enjoys point symmetry and its cis counterpart a C_2 axis of symmetry, the capability of distinguishing these isomers on the basis of possible molecular dissymmetry does not exist.

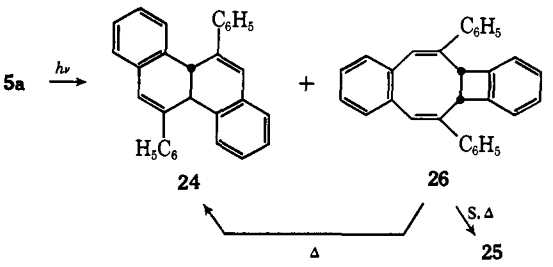


24 **25**

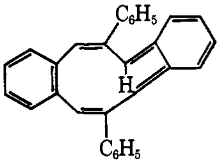
As with **4b**, **5b** could be recovered unchanged after refluxing in *o*-dichlorobenzene. At 250° in a sealed tube without solvent, **5b** does decompose smoothly, but we have been unable so far to isolate a pure substance from this reaction.

Photolysis Experiments. With the exception of **5a**, the photolyses of *exo,exo*-11,12-diazatetracyclo[4.4.2.$0^{2,5}$.$0^{7,10}$]dodeca-3,8,11-trienes appear to be exceptionally complex. In general, polymer formation dominates and monomeric compounds are either totally intractable (if present) or isolated only in low yields. A case in point is **4a** which upon photolysis in tetrahydrofuran affords 3,6-diphenylnaphthalene (**19**) in 17% yield as the only characterizable product. Variations in the lamp source, solvent, and filter did not lead to noticeable improvement of this conversion.

In striking contrast, irradiation of **5a** affected ready conversion to **24** and **26** in yields of 53.9 and 41.5%, respectively. Photoproduct **26** displayed an nmr spectrum suggestive of a symmetrical molecule; in particular, it showed a multiplet of area 2 due to the olefinic protons centered at δ 6.30 and a singlet of equal weight at 4.32 assignable to the methine hydrogens. This hydrocarbon could not be satisfactorily degraded by ozonolysis or other oxidative methods. On the other hand, **26** was found to rearrange readily to **24** when heated to 150°. Not unexpectedly, therefore, when **26** was heated with sulfur at 280°, 6,12-diphenylchrysene (**25**) was the only dehydrogenation product to result.



The quantitative stereospecific conversion of **26** to **24** may have its origins in orbital symmetry control. Clearly, the weakest bond in **26** is the internal cyclobutene bond; should this rupture with conrotatory motion, the unstable dibenzo-*cis*^{4},*trans*-cyclodecapentaene (**27**) would result. Subsequent cyclization of this thermodynamically unstable species in a disrotatory mode to give a dihydrochrysene provides access uniquely to trans-fused product. In this respect, the behavior of **26** parallels that of its simpler analog **28** which has similarly been quantitatively isomerized to *trans*-9,10-dihydronaphthalene at modest temperatures.[20] A major distinction between **26** and **28** is the requirement in **26** that the aromatic character of one benzene ring be temporarily interrupted (*cf.* **27**), a feature which is directly reflected in the somewhat more elevated temperatures required to promote the rearrangement. Despite this thermodynamic disadvantage, benzocyclobutenes have previously been recognized to undergo stereospecific thermal conrotatory ring openings.[21]



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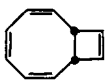

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Discussion

Concerning the Absence of Pseudoaromaticity. Our kinetic results can only be reconciled with the conclusion that the alignment of p orbitals in a rigid matrix as found in **3** does not provide the optimum geometry to achieve pseudoaromatic stabilization. The question at issue is whether or not the pericyclic stabilization inherent in benzene can be interrupted at the four sites indicated in **1** to generate a neutral diradical endowed with experimentally detectable stabilization. Our response is presently affirmative, although we recognize that the topology of such an entity would have to be one which improves on that of **3** and that a more sensitive measure of enhanced orbital interaction is perhaps needed for such diradicals.

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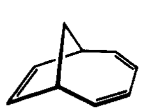
[19] F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, 3251 (1957).

[20] S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, 89, 4804 (1967).

[21] R. Huisgen and H. Seidl, *Tetrahedron Lett.*, 3381 (1964); G. Quinkert, K. Opitz, W. W. Wiersdorff, and M. Finke, *ibid.*, 3009 (1965).

In this regard, it is relevant that enhancement of stabilization in neutral, incompletely conjugated polyenes has thus far been observed only in examples with exceptionally favorable geometrical features.[22] For example, although the cycloheptatriene ring system, which contains one site of interruption, shows some π-orbital interaction,[23] molecules such as **29** and **30**, in which the makeup of the benzene MO has been "stretched" to accommodate two and three insulating methylene groups, respectively, exhibit no evidence of pseudoaromatic stabilization.[24,25]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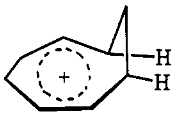
In rather dramatic contrast, related *charged* systems exhibit a greater tendency for extended conjugative overlap despite the presence of interrupting segments. Cations of the homotropylium (**31**),[26] 1,3- (**32**),[27] and 1,4-bishomotropylium (**33**) types,[28] as well as anions such as **34**[29] and **35**,[30] are currently well-recognized homoaromatic entities. In the present instance, although demonstration of similar pseudoaromatic delocalization in a *neutral diradical* was not achieved, the approach which has been utilized will perhaps provide the basis for continuing discussion and the design of new sophisticated experiments.



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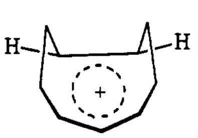

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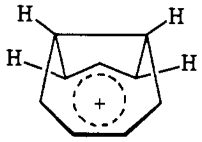

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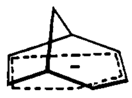

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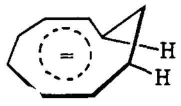

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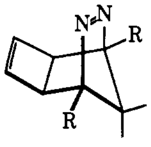
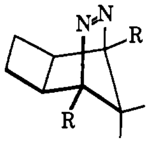
Thermally Induced Bond Reorganizations. In considering now the pyrogenic behavior of **4a** and **4b**, we call attention to the interesting abrupt change in positional selectivity shown by the phenyl and methyl substituents, respectively, in the products of these reactions (**15**, **16**, and **21**). An important initial consideration relates to the possible loss of nitrogen in concert with cleavage of an internal cyclobutene σ bond in an allowed (${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$) mode. By virtue of the stereochemical arrangement present in **4**, the two cyclobutene rings reside cis to the azo group. The same structural features are found in **36**[14a] and its dihydro derivative **37**;[31] the chemical and kinetic behavior of these molecules supports the position that their thermochemical decomposition proceeds through diradical intermediates.[32] There is no reason for **4** not to follow the same mechanistic pattern.



36



37

Once the diradicals are produced, several reaction pathways would appear *a priori* available to them. Firstly, the collapse of such intermediates with generation of a new σ bond is not only energetically unlikely, but also symmetry forbidden.[7] Alternatively, insertion of the odd-electron centers into one of the remote cyclobutene double bonds in analogy with earlier observations on the diphenyl derivative of **36**[14a] could lead to the attractive quadricyclane **38** (Scheme III). Thermal cleavage of **38** in well-precedented fashion[35] would

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(22) This point has recently been discussed in most of its ramifications by M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(23) R. B. Turner, W. R. Meador, W. E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *ibid.*, **79**, 4127 (1957).

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(25) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).

(26) (a) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962); (b) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); (c) S. Winstein, C.G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966); (d) L. A. Paquette, J. R. Malpass, and T. J. Barton, *ibid.*, **91**, 4714 (1969); (e) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970), and references cited in these last two papers.

(27) (a) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971); L. A. Paquette and M. J. Broadhurst, to be published.

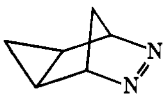
(28) (a) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2146 (1970); (b) M. Roberts, H. Hamberger, and S. Winstein, *ibid.*, **92**, 6346 (1970); (c) H.-P. Löffler and G. Schröder, *Tetrahedron Lett.*, 2119 (1970); (d) G. Schröder, U. Prange, N. S. Bowman, and J. F. M. Oth, *ibid.*, 3251 (1970).

(29) (a) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965); (b) *ibid.*, 638 (1967); (c) *J. Chem. Soc. B*, 411 (1968); (d) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967).

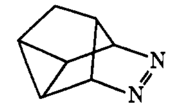
(30) (a) M. Ogliaruso, R. Rieke, and S. Winstein, *ibid.*, **88**, 4731 (1966); (b) M. Ogliaruso and S. Winstein, *ibid.*, **89**, 5290 (1967); (c) M. A. Ogliaruso, *ibid.*, **92**, 7490 (1970).

(31) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **93**, 4922 (1971).

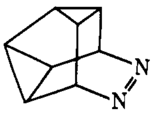
(32) Irrespective of stereochemistry, an edge cyclobutene or cyclobutane bond does not appear to be inherently capable of providing anchimeric assistance to the departure of nitrogen in such systems and in this sense differs appreciably from the cyclopropane ring [see L. A. Paquette and M. J. Epstein, *J. Amer. Chem. Soc.*, **93**, 5936 (1971)].



i

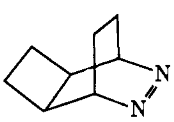


ii

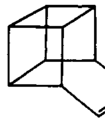


iii

In i-iii, for example, participation by the internal cyclopropyl bonding electrons at the transition state clearly reveals itself in the significantly higher reactivity of these molecules.[33] Such behavior is not paralleled by the closely related homologs iv and v.[34]



iv

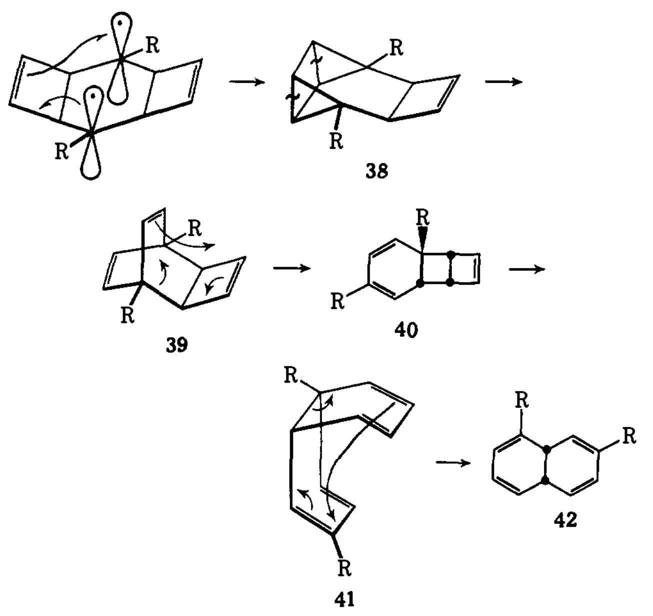

v

(33) (a) M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969); (b) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Amer. Chem. Soc.*, **91**, 3382 (1969); (c) L. A. Paquette, *ibid.*, **92**, 5765 (1970); (d) E. L. Allred and A. L. Johnson, *ibid.*, **93**, 1300 (1971); (e) See also H. Tanida and S. Teratake, *Tetrahedron Lett.*, 4991 (1970).

(34) (a) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *ibid.*, 5345 (1969); (b) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969); (c) J. P. Snyder, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1965; *Diss. Abstr.*, **26**, 5728 (1966).

(35) S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, **80**, 1950 (1958); W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961); P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968).

Scheme III



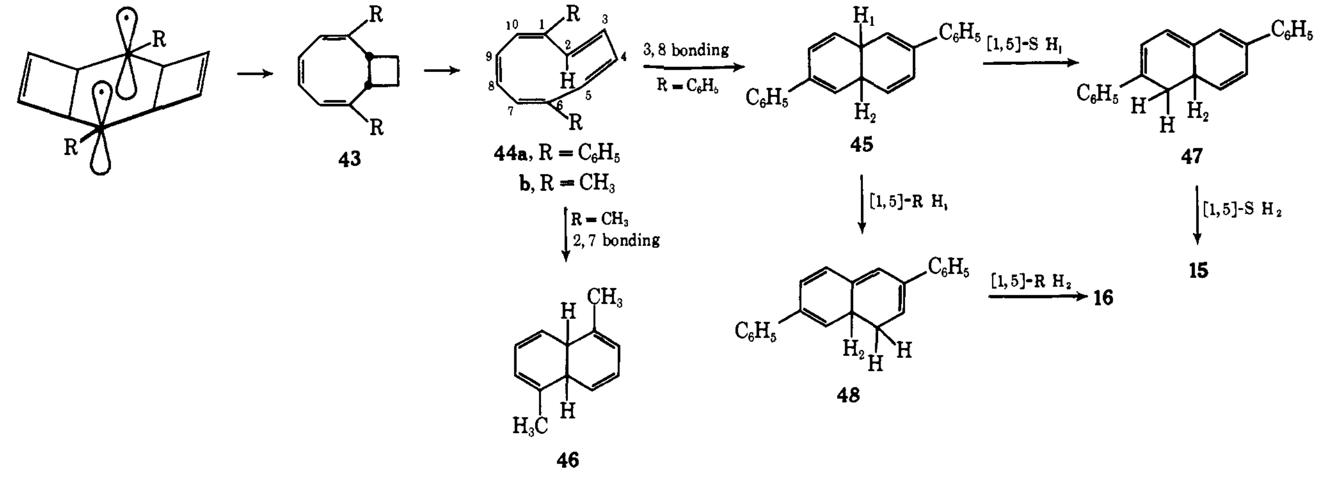
provide access to a derivative of Nenitzescu's hydrocarbon (**39**), Cope rearrangement of which[36] would give rise to **40** and thence to *cis*-9,10-dihydronaphthalene (**41**). In **41**, however, the substituents lie only four atoms apart and there exists no reasonable way (*cf.*, for, example, the [3,3] sigmatropic shift relating **41** to **42**) in which to transform such a structure into **15**, **16**, or **21** where the groups are disposed in a 1,6 relationship. As a result, this pathway must be considered nonoperative.

Contrariwise, all of the results are reasonably accommodated by a mechanistic interpretation based upon initial homolytic cleavage of a proximate cyclobutene σ bond to give **43** (Scheme IV). This step is not only well precedented,[14a,31,34] but is also encountered in the pyrolysis of **6**. Conrotatory opening[20] of **43** serves to provide access to disubstituted cyclodecapentaene **44**, a transient species whose intermediacy is suggested by the substitution patterns in **15**, **16**, and **21**. More specifically, in passing from **4** to products, the attached groups must not only maintain their 1,6 bonding relationship, but the $(CH)_{10}$ framework must also be ultimately free to generate dihydro derivatives of 1,5-dimethyl- and 2,6-diphenylnaphthalene by appropriate bond relocation. In this regard, the direction of ring closure in **44** appears to be dependent on the nature of R. In the diphenyl example, 3,6 bonding operates exclusively, while, when R = CH_3, 2,7 bonding is seen. The causative factors underlying this mechanistic dichotomy are not understood but probably find their origin in the added stabilization provided by the phenyl groups to **44**, and particularly to the transition state leading from **44** to **45**.

Isolation of less conjugated dihydronaphthalene **15** as the major product from **4a** (ratio of **15**/**16** = 9.8) demonstrates that the subsequent rearrangement of **45** is not controlled by the relative stabilities of these two unsaturated hydrocarbons. This result is rationalizable, however, in terms of differing rates for the two competitive suprafacial [1,5] sigmatropic hydrogen shifts open to **45**. Whereas movement in the counterclockwise direction (herein termed a [1,5]-*S* shift) leads to **47**, [1,5]-*R* shift affords **48**. Such competitive processes would be expected to be controlled by stabilization factors in **47** and **48** if the respective transition states reside close to product. Since **47** is more extensively conjugated than **48**, its rate of production would be faster in view of the anticipated differences in activation energies for the two rearrangements. Further progress along these two reaction coordinates requires that H_2 migrate in the same sense as H_1 in each instance, if benzenoid character in **15** and **16** is to be established.

The precise stereochemistries of **45** and **46** are, of course, not known. Nevertheless, the arguments concerning the [1,5] hydrogen shifts are not strictly dependent upon the cis or trans nature of the C_9C_{10} ring fusion. What is required is simply that the sigmatropic shifts occur more rapidly than hydrogen transfer.[37] Since only **15** and **16**, but no 2,6-diphenylnaphthalene (**19**), was observed after short reaction times, this speculation is considerably strengthened. Similar considerations apply to dimethyl derivative **46**, but with less control as expected.

Scheme IV



Experimental Section

***exo,exo*-1,6-Diphenyl-11,12-diazatetracyclo$[4.4.2.0^{2,5}.0^{7,10}]$dodeca-3,8,11-triene (4a).** To an ice-cold stirred solution of 1.0 g (4.2

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(36) H. H. Westberg, E. N. Cain, and S. Masamune, *J. Amer. Chem. Soc.*, 91, 7512 (1969).

(37) See W. von E. Doering and J. W. Rosenthal, *ibid.*, 89, 4534 (1967).

mmol) of 3,6-diphenyl-*s*-tetrazine (**7a**)[12] and 2.0 g (10.4 mmol) of cyclobutadieneiron tricarbonyl (**8**)[38] in 400 ml of acetone was added 30 g of ceric ammonium nitrate in small portions during 30 min. The solution was then poured into 1.5 l. of ice water and filtered. The residue was dried and recrystallized from ethyl acetate (75 ml) to give 1.0 g (76%) of **4a** as colorless crystals: mp 216–216.5° dec; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.40–7.95 (m, 10, aryl), 5.91 (s, 4, olefinic), and 3.45 (s, 4, allylic).

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85. Found: C, 84.66; H, 5.78.

exo,exo-**1,6-Dimethyl-11,12-diazatetracyclo[4.4.2.0^{2,5}.0^{7,10}]dodeca-3,8,11-triene (4b).** A cold solution of 1.87 g (17.0 mmol) of 3,6-dimethyl-*s*-tetrazine (**7b**)[12] and 6.74 g (35 mmol) of cyclobutadieneiron tricarbonyl in 500 ml of acetone was treated while stirring with small portions of ceric ammonium nitrate (95 g) during 20 min. The solution was poured into 1.5 l. of ice water and extracted with ether (ten 100-ml portions). The combined ether washings were dried, filtered, and evaporated. The residue was chromatographed on alumina (elution with hexane–ether 9:1) to give 680 mg (21.5%) of **4b**, mp 125–130°. Recrystallization of this material from hexane furnished pure azo compound: mp 131–132.5°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.97 (s, 4, olefinic), 2.85 (s, 4, allylic), and 1.69 (s, 6, methyl).

Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58. Found: C, 77.09; H, 7.61.

4b,5,5a,9b,10,10a-Hexahydro-5,10-diphenyl-5,10-azobenzo[3,4]cyclobuta[1,2-*b*]biphenylene (5a). To a well-stirred 0° solution of 0.5 g (2.0 mmol) of benzocyclobutadieneiron tricarbonyl (**9**)[39] and 0.26 g (1.0 mmol) of **7a** in 50 ml of acetone was added 15 g of Fe(NO_3)$_3$·9H_2O in small portions during 20 min. The mixture was stirred for an additional 15 min and then poured into 300 ml of cold water. The deposited crystals were filtered and dried to give 0.42 g (100%) of crude **5a**. This material was purified further by extraction with boiling tetrahydrofuran (~600 ml) and cooling: yield 0.37 g (85%); mp 244° dec; $\delta_{\mathrm{TMS}}^{\mathrm{TFA}\text{-}d}$ 6.80–8.15 (m, 18, aryl), and 4.86 (s, 4, olefinic); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 260 (ϵ 38,200), 267 (44,600), 273 (47,100), 312 (920), and 390 nm (80).

Anal. Calcd for $C_{30}H_{22}N_2$: C, 87.77; H, 5.40. Found: C, 87.59; H, 5.48.

4b,5,5a,9b,10,10a-Hexahydro-5,10-dimethyl-5,10-azobenzo[3,4]cyclobuta[1,2-*b*]biphenylene (5b). Treatment of 140 mg (1.25 mmol) of **7b** and 610 mg (2.5 mmol) of **9** in 50 ml of acetone with 15 g of ferric nitrate nonahydrate as described above afforded 220 mg (62.9%) of **5b**: mp 225–226° (from hexane); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.08 (s, 8, aryl), 2.45 (s, 4, allyl), and 2.11 (s, 6, methyl); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 253 (ϵ 26,800), 258 (39,300), 265 (51,800), 272 (51,800), and 380 nm (65).

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34. Found: C, 84.14; H, 6.30.

exo,exo-**1,6-Diphenyl-11,12-diazatetracyclo[4.4.2.0^{2,5}.0^{7,10}]dodec-11-ene (6).** A solution of 1.0 g (3.22 mmol) of **4a** in 50 ml of tetrahydrofuran was mixed with 12.5 g (64.5 mmol) of potassium azodicarboxylate and the mixture was cooled to 0°. With stirring, acetic acid was added in 1-ml portions until the mixture turned white. The precipitated solid was removed by filtration and washed with additional tetrahydrofuran. The combined solutions were evaporated and the residue was recrystallized from ethyl acetate to give 638 mg (63%) of **6**: mp 210–211° dec; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.75–8.20 (m, 4, aryl), 7.20–7.70 (m, 6, aryl), 2.70–3.20 (m, 4), and 1.40–2.00 (m, 6).

Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05. Found: C, 83.66; H, 7.06.

Kinetic Studies. The kinetic experiments were performed in the constant-volume, variable-pressure apparatus which has been diagrammed by Martin and Timberlake.[16] In a typical run, a sample (*ca.* 0.2 mmol) was weighed into the reaction flask and 6.0 ml of diphenyl ether was added. The flask was introduced into the preheated, thermostated oil bath for 180 sec and connected to the apparatus, and the stirrer was started. This procedure was necessary because of the low solubility of the azo compounds in biphenyl ether at room temperature. After the reaction flask was connected, additional volume expansion was observed and hence the starting volume was taken when the automatic buret stopped for the first time. Rate constants were calculated by a least-squares treatment weighting pressure values in proportion to their difference from P^{∞}. The calculated standard deviations for the rate constants were generally ±0.5%. For any one temperature setting, the reproducibility for several runs was within the limits of the calculated error.

Thermolysis of 4a. A solution of 200 mg (0.645 mmol) of **4a** in 20 ml of *o*-dichlorobenzene was refluxed until nitrogen evolution ceased and for an additional 10 min. After cooling, the solvent was distilled *in vacuo* and the solid residue was triturated with 20 ml of hot methanol. The residue was recrystallized from acetone to give 15 mg (8.1%) of **16**: mp 211–212°; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 260 (ϵ 30,800) and 317 nm (33,700); too insoluble for nmr determination.

Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.51; H, 6.17.

The methanol filtrate was evaporated and the residue was chromatographed on silica gel impregnated with 15% silver nitrate (2 × 30 cm column). Elution with hexane–ether (97:3) gave the major product **15**, recrystallization of which from methanol afforded 145 mg (78.5%) of white crystals which decomposed above 100°; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 248 nm (ϵ 56,100).

Anal. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.35; H, 6.53.

2,6-Diphenyl-4-tetralone (17). The procedural details of Price and Tomiser[40] were followed with the exception of the following changes in the work-up. With stirring, ice (25 g) was added to the reaction mixture followed by 25 ml of concentrated hydrochloric acid. The resulting mixture was warmed until all of the carbon disulfide had evaporated. The crude product was separated by filtration and dried. Recrystallization of this material from ether–hexane led to a 70% yield of **17**, mp 143–144°.

2,6-Diphenyl-4-tetralol (18). A solution of 3.0 g (0.01 mol) of **17** in 75 ml of anhydrous ether was added dropwise to a stirred slurry of 760 mg (0.02 mol) of lithium aluminum hydride in 25 ml of the same solvent. The mixture was stirred for 2 hr at 30° and excess hydride was decomposed by the slow addition of 1 ml of water and 1 ml of 40% aqueous sodium hydroxide solution. The precipitated salts were filtered and washed well with ether. The combined filtrates were evaporated and the residue was recrystallized from ether–hexane to furnish 1.9 g (66%) of **18**: mp 128–129°; $\nu_{\max}^{\mathrm{KBr}}$ 3335 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.75–7.85 (m, 1, aryl), 6.95–7.65 (m, 12, aryl), 4.70–5.15 (m, 1, $>CHOH$), 2.85–3.10 (m, 3, benzylic), and 1.85–2.65 (m, 2, remaining CH_2).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.69; H, 6.69.

Independent Synthesis of 15. A suspension of 600 mg of **18** in 15 ml of concentrated sulfuric acid was stirred at room temperature for 2 hr and 25 ml of water was added. The mixture was cooled and the precipitated solid was filtered. Chromatography of this material on silica gel impregnated with 15% silver nitrate (elution with 3% ether–hexane) afforded 440 mg (78.5%) of 1,2-dihydro-2,6-diphenylnaphthalene (**15**), mp >100°.

2,6-Diphenylnaphthalene (19). To a solution of 100 mg of **15** in 25 ml of *p*-cymene was added 100 mg of 10% palladium/carbon and the mixture was refluxed for 15 hr while a slow stream of carbon dioxide was bubbled through. The residue was recrystallized from methanol to give 59 mg (59.4%) of **19**: mp 235–236° (lit.[41] 233–234°); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 260 (ϵ 42,200) and 306 nm (13,900); $\delta_{\mathrm{TMS}}^{\mathrm{CS_2}}$ 7.20–8.00 (m, aryl).

2,6-Diphenyl-1,2,3,4-tetrahydronaphthalene (20). To 20 g of zinc amalgam was added 75 ml of concentrated hydrochloric acid and 600 mg (2.0 mmol) of **17**. The mixture was refluxed for 4 hr with vigorous stirring and cooled to room temperature. The aqueous phase was extracted with ether (four 25-ml portions), the combined ether layers were dried and evaporated, and the crude **20** was recrystallized from methanol. There was obtained 380 mg (67.3%) of white crystals; mp 117–118°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.90–7.65 (m, 13, aryl), 2.75–3.10 (m, 5, benzylic), and 1.90–2.20 (m, 2, methylene).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.73; H, 7.20.

Independent Synthesis of 16. To a solution of 280 mg (1.0 mmol) of **20** in 30 ml of carbon tetrachloride was added 180 mg (1.0 mmol) of *N*-bromosuccinimide and 50 mg of benzoyl peroxide. After being refluxed for 3 hr, the mixture was cooled, the succinimide was filtered, and the filtrate was evaporated. The residue was dissolved in 20 ml of anhydrous tetrahydrofuran and a suspension of 220 mg (2.0 mmol) of potassium *tert*-butoxide in 10 ml of tetrahydrofuran was added slowly at 0°. The mixture was stirred for 30 min at 25° and the solvent was evaporated. The

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[38] (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965); (b) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).

[39] G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1967); W. Merk and R. Pettit, *ibid.*, **89**, 4787 (1967).

[40] C. C. Price and A. J. Tomiser, *ibid.*, **65**, 439 (1943); *J. Org. Chem.*, **7**, 517 (1942).

[41] E. S. Pokrovskaya and T. G. Stepantseva, *J. Gen. Chem. USSR*, **9**, 1953 (1939); *Chem. Abstr.*, 34, 4731 (1940).

residue was stirred with 25 ml of water for 15 min; the insoluble solid was separated by filtration, dried, and heated with 15 ml of methanol. The insoluble material (a mixture of **16** and **19**) was fractionally recrystallized from acetone to give 25 mg (8%) of **16**, identical with the sample obtained from the pyrolysis of **4a**. Processing of the filtrate by chromatography on silica gel-silver nitrate led to the isolation of 60 mg (23.5%) of **15**.

Pyrolysis of 4b. A 200-mg sample of **4b** was placed in a sealed tube and heated at 240° for 7 hr. The tube was cooled and opened, and the contents were dissolved in a small amount of methylene chloride. Analysis by vpc showed the almost total decomposition of **4a** and the formation of seven products. This mixture was oxidized directly with DDQ (500 mg) in refluxing benzene (18 ml) during 16 hr. The solution was cooled, filtered, and chromatographed on activity I alumina (hexane elution). The several early fractions were combined, evaporated, and analyzed by vpc. Only one product was seen and this was identified as 1,5-dimethylnaphthalene (**21**), mp 80–82° (19 mg, 11%), identical in all respects with an authentic sample.

Pyrolysis of 6. A solution of 586 mg of **6** in 50 ml of *o*-dichlorobenzene was heated to reflux and nitrogen was rapidly evolved (complete in 45 min). The solvent was removed *in vacuo*. The residue was chromatographed on silica gel and the resulting viscous oil (475 mg) was subjected to two molecular distillations. The **22** so produced was found to be oxidized rapidly in air, a property which precluded elemental analysis: *m/e* calcd for $C_{22}H_{22}$, 286.1721; found, 286.1729; δ 6.90–7.52 (m, 10, aryl), 5.44–5.90 (m, 2, olefinic), 3.72–4.17 (m, 2, methine), and 1.16–2.88 (br m, 8, methylene); $\lambda_{\max}^{\text{isooctane}}$ 238 nm and end absorption (ϵ unreliable because of air oxidation).

Ozonolysis of 22. Into a solution of 200 mg (0.70 mmol) of **22** in 150 ml of dichloromethane cooled to −70° was bubbled a slow stream of ozone until a blue color persisted. The solution was flushed with oxygen for 20 min, removed from the cooling bath, and treated with 2 g of potassium iodide, 10 ml of methanol, and 1 ml of acetic acid while stirring. The mixture was stirred for 2 hr while being allowed to warm to room temperature. The iodine color was discharged by the slow addition of sodium thiosulfate solution, water (500 ml) was added, and the solution was rendered basic with potassium carbonate. Extraction with methylene chloride (three 100-ml portions) followed by chromatography of the residue remaining from evaporation of the combined organic layers on a small column of alumina afforded 55 mg of **23**: mp 96.5–97.5° (from ether at −20°) (lit.[19] mp 97.5–98.5°); δ 7.89–8.08 (m, 4, aryl), 7.28–7.64 (m, 6, aryl), 4.40–4.73 (m, 2, >*CH*CO–), and 2.27–2.54 (m, 4, methylene).

Pyrolysis of 5a. Heating at reflux a solution of 205 mg (0.50 mmol) of **5a** in 15 ml of *o*-dichlorobenzene as above led after evaporation of the solvent and recrystallization of the residue from acetone to the isolation of 180 mg (94.2%) of **24**: mp 249–250°; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.90–7.90 (m, 20, aryl and olefinic) and 4.33 (s, 2, methine); $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 233 (ϵ 55,200), 300 sh (56,200), 312 (58,200), and 340 sh nm (33,300).

Anal. Calcd for $C_{30}H_{22}$: C, 94.13; H, 5.87. Found: C, 93.86; H, 6.17.

6,12-Diphenylchrysene (25). An intimate mixture of sulfur (30 mg) and **24** (100 mg) was heated at 280° for 1 hr. Chromatography of the mixture on alumina gave 76 mg (76%) of **25**: mp 183–184° (from hexane); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.80–7.90 (m, aryl); $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 234 (ϵ 44,600), 252 (27,200), 284 (64,600), 308 (15,000), 321 (10,900), and 334 nm (9770).

When **24** was heated with sulfur under these conditions, **25** was again the only identifiable product.

Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.77; H, 5.63.

Photolysis of 4a. A 500-mg sample of **4a** was suspended in 250 ml of tetrahydrofuran and photolyzed with a 200-W medium-pressure lamp through Pyrex. The reaction was monitored by thin-layer chromatography. The solvent was evaporated and the residue was chromatographed on silica (elution with 3% benzene in hexane). The eluted product was digested with a small amount of hexane and filtered to afford 77 mg (17%) of 2,6-diphenylnaphthalene, mp 233–235°.

Photolysis of 5a. A solution of 410 mg (1.0 mmol) of **5a** in 100 ml of tetrahydrofuran was irradiated through Pyrex with a 200-W Hanovia lamp. When nitrogen evolution ceased, the solvent was evaporated and the residue was triturated with warm methanol (two 25-ml portions). The insoluble material was recrystallized from acetone to give 206 mg (53.9%) of **24**, identical in all respects with the thermal product.

The methanol solution was concentrated to 20 ml and cooled to afford 170 mg (41.5%) of **26** as white needles: mp 166–167°; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.70–7.20 (m, 14, aryl), 6.15–6.45 (m, 2, vinyl), and 4.32 (s, 3, methine); $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 258 (ϵ 33,400), 264 (57,800), 271 (68,600), and 300 nm (17,700).

Anal. Calcd for $C_{30}H_{22}$: C, 94.13; H, 5.87. Found: C, 94.06; H, 6.03.

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