Effects of Neighboring Nonconjugated Double Bonds in the Diels–Alder Reaction

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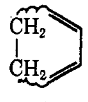
Abstract: *cis*-Hexahydro- and *cis*-tetrahydronaphthalenes (**1** and **2**) and in one case, *cis*-dihydronaphthalene (**3**), were treated with diethyl fumarate, tetracyanoethylene, and 4-phenyl-1,2,4-triazoline-3,5-dione to examine the effects of the additional double bonds on the stereoselectivity of the Diels–Alder reaction. Attack on the less hindered face was preferred in all cases, but the margin of preference decreased as the number of double bonds increased, a result best interpreted as a steric effect, with the π orbital showing itself to be of smaller size than the pair of hydrogens it replaces. A secondary orbital interaction did not appear to be consistent with the results. The additional double bonds also strongly suppressed the surprising participation of the parent system **1** in an ene reaction. The latter reaction was the first reported case in which tetracyanoethylene behaved as an enophile toward a relatively unhindered, cis-fixed diene. Facile photosensitized ring closure of several of the Diels–Alder adducts produced some new cage systems.

The sources of stereochemical control in the Diels–Alder reaction have been a topic of inquiry since the principle of cis addition was laid down.[1] While the reasons for cis addition are no longer subjects of investigation, most other facets of Diels–Alder stereochemistry have remained controversial. In the matter of Alder's endo rule,[1b] proposals for the intervention of electrostatic (charge tranfer) forces,[2] secondary bonding forces,[3] steric repulsions,[4] dipole induction and dispersion forces,[5] secondary orbital interactions,[6] and overlap geometry as influenced by steric considerations[7] have been offered as explanations of observed stereochemistry.

Secondary orbital interactions of one sort or another have become the commonest such explanation,[8] but, in general, only the interactions of substituents directly conjugated with the bond-forming orbitals have been considered, either experimentally or in calculations. It would be of interest to see whether such interactions could be extended to substituents geometrically close to but not conjugated with the reacting bonds. For example, as a first approximation, the approach of a dienophile to the diene moiety of B should be perturbed, as far as orbital symmetry is concerned, in a repulsive manner compared with the approach to A. No such symmetry engendered repulsion should appear with C. Whether there would in fact be a lower barrier to reaction with C than to reaction with A cannot be determined by such a simple analysis.



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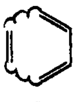
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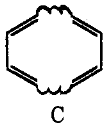
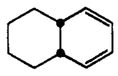

C

A set of compounds that might provide a test of all the parts of this reasoning consists of diene, triene, and tetraene, **1**, **2**, and **3**. Although the isolated double bond in **2** and the second diene system in **3** are not held in rigid alignment with the other half of the molecule, models indicate that in the conformations likely to be stablest, the π systems are held close to one another (3–4 Å), and more nearly parallel than not. The ratio of exo to endo addition in the reactions of **1** (Figure 1) would serve as the unperturbed case to which the reactions of **2** and **3** would be compared.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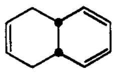
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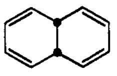
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Results

Although compounds **1**, **2**, and **3** are all known,[9] the literature syntheses of the first two are laborious, low-yield procedures. An alternate pair of syntheses were devised (Scheme I), and though yields are modest, all reactants are readily available and no purification is required until after the final reaction. Only the cis-fused rings are produced. A sample of trans-fused diketone[10] was carried through the same steps to yield **4**. Analysis (glpc) showed that no detectable amount of **4** was present among the products in the synthesis of **1**.

Choice of Dienophiles. Besides the exo and endo approaches with reference to the second ring (Figure 1), an unsymmetrical dienophile could give both exo and endo products with reference to the reacting diene moiety.[11] Since it would be easier to separate two

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[1] (a) K. Alder and G. Stein, *Angew. Chem.*, **47**, 837 (1934); (b) *ibid.*, **50**, 510 (1937).

[2] R. B. Woodward and H. Baer, *J. Amer. Chem. Soc.*, **66**, 645 (1944).

[3] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[4] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[5] A. Wassermann, "The Diels-Alder Reaction," Elsevier, Amsterdam, 1965, p 86.

[6] (a) R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, **87**, 4388 (1965); (b) L. Salem, *ibid.*, **90**, 543, 553 (1968).

[7] W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, 3095 (1967).

[8] (a) K. L. Williamson, Y.-F. Hsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, **91**, 6129 (1969); (b) C. G. Cardenas, *Chem. Commun.*, 134 (1970); (c) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970).

[9] (a) Diene **1**: W. Hückel and W. Kraus, *Justus Liebigs Ann. Chem.*, **654**, 49 (1962); (b) triene **2**: E. E. van Tamelen and B. C. T. Pappas, *J. Amer. Chem. Soc.*, **93**, 6111 (1971); (c) tetraene **3**: E. E. van Tamelen and B. C. T. Pappas, *ibid.*, **85**, 3296 (1963); W. v. E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

[10] H. B. Henbest, M. Smith, and A. Thomas, *J. Chem. Soc.*, 3293 (1958).

[11] To avoid confusion, references hereafter to exo or endo adduct will be taken with the configuration of the second ring (Figure 1) in mind and not the configuration dependent on dienophile symmetry.

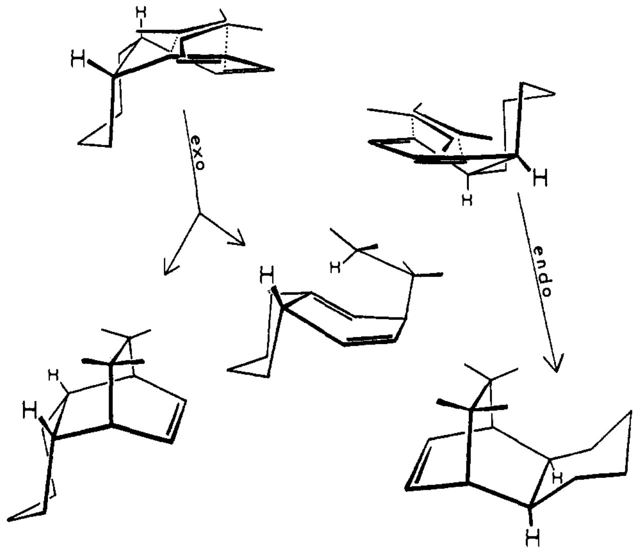
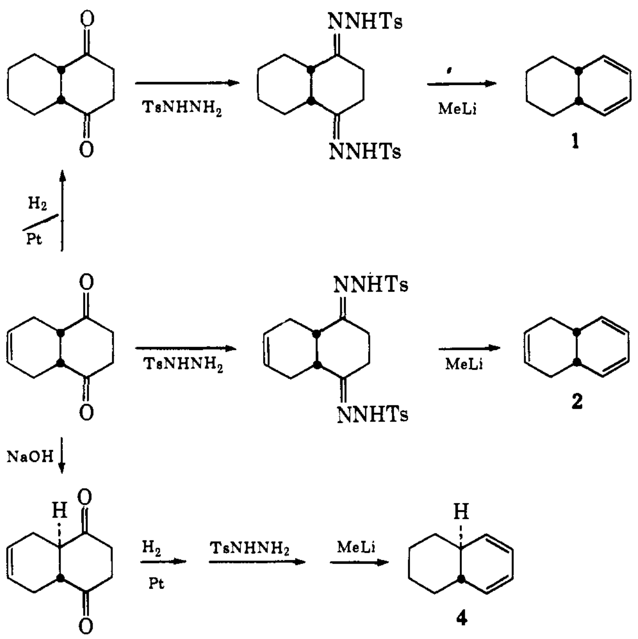
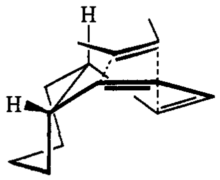


Figure 1. Exo and endo approaches to 1.

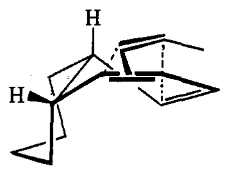
Scheme I



rather than four adducts, and easier to assign their structures, the first dienophiles used were of symmetries that could yield only two Diels–Alder adducts.



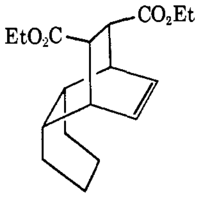
exo
exo



exo
endo

Dimethyl acetylenedicarboxylate reacted with 1 slowly at 80°. However, the products underwent a second reaction, cleavage to dimethyl phthalate and cyclohexene, at a comparable rate. Because of this complication, the ratio of exo to endo product could not be determined, and this dienophile was abandoned.

Diethyl fumarate reacted with 1 at somewhat higher temperatures to give primarily exo adduct 5. The remaining material, homogenous by tlc but showing a shoulder (and unfortunately indications of decomposition as well) on glpc, appeared to be the ene product 7, rather than endo adduct. Triene 2 gave adducts 6 and 8 in a similar manner (see Table I).



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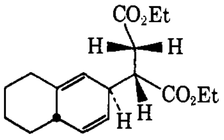

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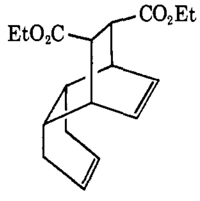

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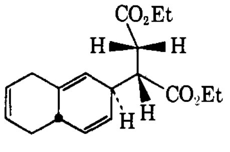

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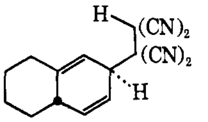
Table I. Products from the Reactions of 1 and 2 with Diethyl Fumarate and with Tetracyanoethylene

Olefin	Dienophile	Temp, °C	% exo adduct	% ene adduct[b]
1	Fumarate	120	85[a]	15[a]
2	Fumarate	120	97[a]	3[a]
1	TCNE	44	35[c]	65[c]
2	TCNE	37	78[c]	22[c]

[a] Determined by glpc and isolation, values range over ±2% from run to run. [b] May contain small amounts of endo adduct. [c] Determined by nmr integration, values range over ±3% from run to run.

It was also clear from the temperature needed to effect reaction (>100°) that 3 would not survive long enough to yield any adducts;[12] a more reactive dienophile would be required.

Tetracyanoethylene was found to consume 1 in a few hours at room temperature. The major product was the unstable ene adduct 9 which decomposed on standing overnight, or on brief heating in refluxing chloroform, to yield a tar from which small amounts of tetralin and tetracyanoethane could be isolated. The exo adduct 10 was stable. 2 gave similar results, with the exo adduct 11 now predominating (Table I). In both cases, the decomposition of the ene product[13] made the search for endo adduct difficult. None was isolated but small amounts could certainly have escaped notice.



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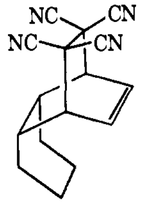

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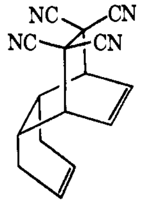

11

It was apparent that the common symmetric dieno-

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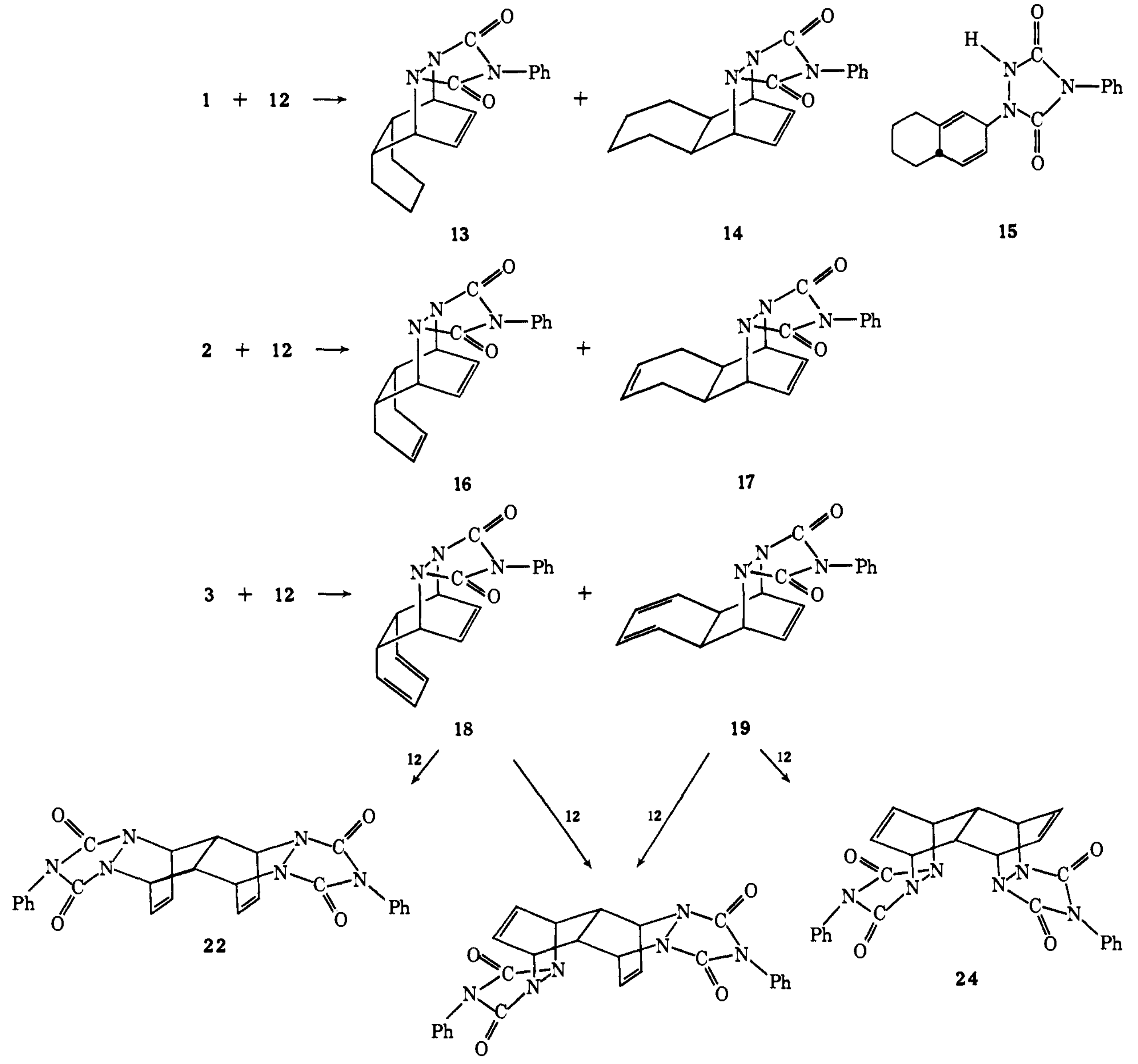
(12) W. v. E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **89**, 4534 (1967).

(13) A. L. Andrews, R. C. Fort, and P. W. Le Quesne, *J. Org. Chem.*, **36**, 83 (1971).

Scheme II



philes would not suffice for this work; it would be necessary to risk formation of more than two Diels–Alder adducts in order to suppress the ene reaction and do so at a temperature compatible with survival of **3**. 4-Phenyl-1,2,4-triazoline-3,5-dione (**12**) proved to be a satisfactory dienophile; it reacted instantly at room temperature with all three substrates (Scheme II), and supression of the ene reaction was almost complete (Table II). The tetraene **3** was more ticklish to work with than expected. Attempts to purify it by preparative glpc yielded material containing 10 to 20% of triene **20** and naphthalene (formed from the disproportionation[12] of **3**). Since **20** was about as reactive as **3**, it had to be eliminated at all cost, but it was found that **20** was being produced in the chromatograph detector and upon condensation in the trap, especially when large amounts were being collected. However, reinvestigation of the pyrolysis of bullvalene by which **3** was synthesized[9c] showed that at very low conversions of bullvalene (3–5%) no **20** could be detected. Furthermore, neither the other minor products[14] nor bullvalene itself reacted with **12** at room temperature. The Diels–Alder reaction could therefore be run on the crude pyrolysate after only a single trap-to-trap distillation at room temperature (to eliminate polymeric material). As a precaution, a small amount of **20** was isolated and allowed to react with **12**. Addition yielded **21** as the only detectable product by nmr. It (**21**) was absent from the crude products of **3** and **12**. An additional complication was introduced because the 1 : 1 adduct **18** (and probably **19** as well) was more

Table II. Products from the Reaction of **1**, **2**, and **3** with 4-Phenyl-1,2,4-triazoline-3,5-dione

Olefin	% exo adduct[a]	% endo adduct[a]	% ene adduct	(ene + exo)/endo
1	86	5	9[a]	19
2	88	12	*b*	7
3	80	20	*c*	4

[a] Determined by nmr integration and isolation. [b] None detected, estimated limits of detection 2%. [c] None detected, estimated limits of detection 5%.

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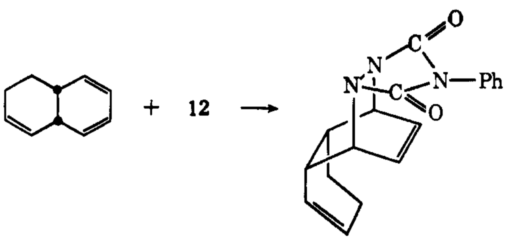
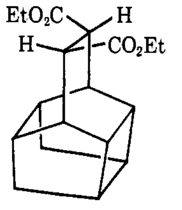
[14] The major impurity was found to be 1,4-dihydronaphthalene with traces of naphthalene the next largest material.



20 **21**

reactive toward **12** than was **3**. Precisely because the relative reactivities of **18** and **19** were unknown, formation of the 2:1 adducts **22**, **23**, and **24** had to be suppressed to ensure accurate determination of the ratio of **18** to **19**. By adding the dienophile to a 20- to 30-fold excess of **3**, 2:1 adduct formation could be kept to less than 3% of the amount of **18**. Fortunately, the 2:1 adducts are also extremely insoluble in most solvents, and for preparative purposes, lower ratios of **3** to **12** could be used and the 2:1 adduct filtered out. This very limited solubility did make characterization of the 2:1 adduct difficult and the exact proportions **22**:**23**:**24** remain unknown. It was shown that **22** did predominate by a large margin (*vide infra*).

Identification of the Adducts. All the major adducts could be obtained pure by fractional crystallization. Nmr data for the Diels–Alder adducts showed the expected ratios of phenyl, vinyl, bridgehead, and methylene hydrogens but were not conclusive with regard to exo or endo stereochemistry. Assignment of configuration was founded upon recognition that exo adducts **6**, **16**, and **22** should undergo photochemical-ring closure to cage compounds **25**, **26**, and **27**, respectively, whereas endo adducts such as **17** could not. Irradiation of the solutions of **6**, **16**, and **22** in acetone did give high yields of the expected cage structures, while **17** was stable to brief irradiation and decomposed to undetermined but still unsaturated products if irradiation was prolonged.



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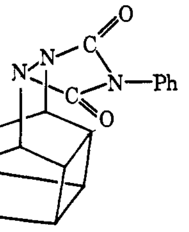

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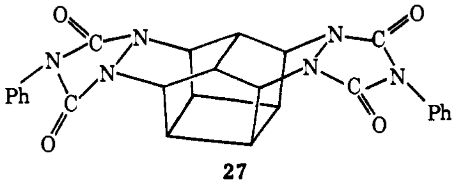

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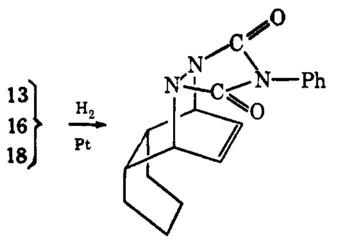
By crystallization the minor adducts could only be obtained with 30–50% contaminating major adduct. However, brief irradiation of such a mixture of **16** and **17** converted **16** to **26**, after which pure **17** could be separated. A 50:50 mixture of **18** and **19** or of **13** and **14** upon hydrogenation produced a mixture of **28** and **29** which could be separated by crystallization. Ene product **15** was isolated by extraction with base, its solubility therein being further indication of its structure.



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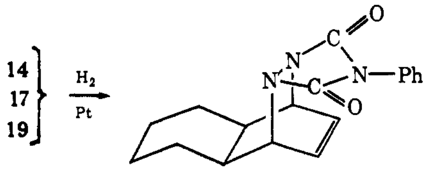

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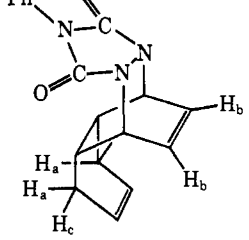
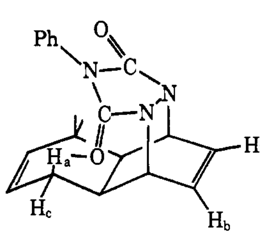
The failure of **17** to close to a cage structure constituted only negative evidence for structure assignment. Furthermore, the ring closure reaction does not rule out structure **16a** in place of **16**. Here, however, the nmr data were sufficient to choose **16** and **17** over **16a** and **17a**. The adducts are clearly so paired because the chemical shift of hydrogens H_b is the same in both compounds (δ 6.50), and this would not be likely if the triazole ring were removed from the vicinity of these hydrogens in only one adduct. Models also show that **17a** is almost impossibly crowded, with at least one of the methylene hydrogens H_a virtually immersed in the carbonyls, regardless of conformation, yet all the methylene nmr signals H_a and H_c for **17** come quite close together, much more so than even in **16**. Hydrogenation of any of the adducts also causes the phenyl signal (a singlet) to disperse to a multiplet. At least in **16a**, the phenyl signal ought not to be so sensitive to changes in distant parts of the molecule. Aside from nmr evidence, one would also make the same structural assignments based on secondary orbital interactions between the carbonyls and the diene moiety of **2**. Hydrogenations of **16** and **17** to **28** and **29** serve to relate the products from the three dienes, completing the assignments.



16a



17a

The stable TCNE adducts, **10** and **11**, were assigned the exo configuration on the basis of their nmr spectra, the latter being markedly more similar to those of the corresponding exo triazolinedione adducts than to the endo ones.

Discussion

Geometric constraints require that the ene products, if formed in a concerted process,[15] arise only by exo approach of the dienophile (Figure 1). If the yields of ene product and exo adduct are lumped together or

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[15] H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

even if the former is ignored, the exo:endo ratio decreases uniformly in the reactions of **1**, **2**, and **3** with **12** (Table II, last column). This is inconsistent with a predominant role for interactions based on orbital symmetry (*vide supra*) but is explainable by simple steric arguments.

π orbitals themselves occupy a certain volume of space. If it is assumed that the additional double bonds in **2** and **3** are repulsive to the approaching dienophile at all points of the reaction path before the transition state, *but less so than the hydrogens they have replaced*, then the observed product ratios become understandable. Quick comparison of the van der Waals radius of a methylene group (2.0 Å)[16] with the "bulk" of a double bond (estimated as the "half thickness" of a typical aromatic molecule (1.7 Å)[16] indicates that the methylene is clearly larger. The Diels–Alder results then follow from the gradually decreasing steric interference in the series **1**, **2**, **3**.

Somewhat more complicated explanations are certainly possible. It is conceivable that at early points along the reaction path the dienophile will be at a distance from the diene for which a van der Waals interaction with the isolated double bonds in **2** and **3** is in fact attractive rather than repulsive. Since the second diene system in **3** should be more polarizable than the one double bond in **2**, and the latter more polarizable than the hydrogens in **1**, the attraction would increase in the same order as the observed increase in endo addition. However, in **3** the closest substituents to the incoming dienophile (that are not in the plane of the reacting diene moiety) are the π orbitals of the second diene system. If the van der Waals interaction with these orbitals were indeed attractive, it would be expected that endo addition predominate over exo. Since this is not the case, this interaction in **3** must be repulsive. (Conceivably the more distant π orbital in **2** is attractive to the dienophile, but exo addition still predominates because of the repulsion by the β-methylene groups. The latter, of course, are absent in **3**.)

Still another explanation is to assume that the approach of the dienophile to the isolated double bond of **2** is analogous to an AX 2 + 2 cycloaddition[17] which would have a stabilizing s + s component. But for such a component to be significant, the charge transfer nature of the interaction must be large.[17] Since the olefinic portion of the donor molecule in the supposed AX pair is a simple cyclohexene, and therefore not a particularly good donor, it is questionable whether any charge transfer interaction would be large. In the absence of precise information about the ionization potentials and $\pi - \pi^*$ transitions of these molecules, the possibility of an s + s attraction should not be dismissed,[18] but a steric or van der Waals force argument would appear to be more reasonable. This is bolstered by one further consideration. Although it is experimentally aggravating that neither TCNE nor diethyl fumarate showed signs of yielding any endo adducts, it is not surprising, since, unlike the triazolinedione, these two dienophiles possess bulky groups on both sides of the double bond and thus have much greater steric requirements in cycloaddition. On the other hand, were the AX 2 + 2 stabilization a dominant factor in the results, TCNE, being an extremely good charge transfer acceptor, should still have afforded appreciable endo adduct with **2** despite its bulk. Clearly, steric factors outweigh electronic ones in this case.

These results also imply that when dienophilic behavior of pairs of molecules, such as cyclopentene and cyclopentadiene, are compared,[8c] the effects of decreased size must be superimposed on any secondary orbital interactions present. Differences in the behavior of the two molecules should not be ascribed entirely to the latter interaction.

The presence of significant ene reaction was unexpected, particularly of the magnitude found using TCNE. Very few cases of TCNE undergoing an ene reaction with a cisoid diene have been reported[13,19] and in those instances, steric hindrance on both faces of the diene was considered extreme, thus preventing a Diels–Alder reaction. That is not the case here, nor can the increasing possibility of endo attack in the series **1**, **2**, **3** account for the drop in ene product, since this drop is far more precipitous than the increase in endo product. There also appears to be not a whit of difference sterically, on the exo face, among **1**, **2**, and **3**. Further investigation of competing ene and Diels–Alder reactions in this and other systems appears called for.

Experimental Section[20]

***cis*-Decalin-1,4-dione Bis(*p*-toluenesulfonylhydrazone).** Δ^6-*cis*-Octalin-1,4-dione[21] (18 g) was placed in 55 ml of benzene with 60 mg of PtO_2 in a 200-ml round-bottom flask and stirred magnetically. The air in the flask was replaced with hydrogen (two freeze–pump–thaw cycles) and the mixture stirred vigorously until hydrogen uptake slackened. The starting material, only partly soluble in this volume of benzene, dissolved as the reaction proceeded. The solvent was removed on a rotary evaporator after filtration to remove the platinum. *p*-Toluenesulfonylhydrazide (41 g) and 100 ml of 95% ethanol were added and the mixture was swirled on the steam bath until all solids had dissolved. Gentle heating was continued for 4 hr during which time the bishydrazone precipitated. After a further 24 hr standing at room temperature, the solid was collected, washed with ethanol, and air-dried to yield 49.5 g (90%), mp 188–191° dec. The hydrazone is insoluble in all neutral solvents: nmr (CF_3COOH) δ 7.3–8.0 (m, 8), 2.5 (s, 6), 1.0–2.8 (m, 14).

Δ^6-*cis*-Octalin-1,4-dione Bis(*p*-toluenesulfonylhydrazone). Δ^6-*cis*-Octalin-1,4-dione (16 g) was dissolved in 95% ethanol (100 ml). *p*-Toluenesulfonylhydrazide (35 g) was added and the mixture swirled on the steam bath until dissolution was complete. Gentle heating was continued for several hours during which time the bishydrazone precipitated. After standing 24 hr, the product was collected, washed with ethanol, and air-dried to yield 49 g (97%) of white crystals: mp 181–182° dec; nmr (CF_3COOH) δ 7.3–8.0 (m, 8), 5.7 (m, 2), 2.6–3.2 (m, 10), 2.5 (s, 6).

***trans*-Decalin-1,4-dione Bis(*p*-toluenesulfonylhydrazone).** Δ^6-*trans*-Octalin-1,4-dione[10] (20 g) was hydrogenated and treated with *p*-toluenesulfonylhydrazide in the same manner as the cis isomer to yield 50 g (81%) of the bishydrazone: mp 185–188° dec; nmr (CF_3COOH) identical with that of the cis isomer.

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[16] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 226, 257–264.

[17] N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972).

[18] I wish to thank one of the referees for bringing this possibility to my attention.

[19] (a) A. M. Lautzenheiser and P. W. Le Quesne, *Tetrahedron Lett.*, 207 (1969); (b) K. D. Bingham, G. D. Meakins, and J. Wicha, *J. Chem. Soc. C*, 671 (1969).

[20] Melting points are uncorrected. Nmr spectra were obtained on a Perkin-Elmer R-12 spectrometer or Varian A-56/60A spectrometer equipped with a C-1024 time averaging computer. Elemental analyses were performed by Elek Microanalytical Laboratories, Harbor City, Calif. 90710.

[21] (a) L. F. Fieser, *J. Amer. Chem. Soc.*, 70, 3165 (1948); (b) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *ibid.*, **83**, 606 (1961).

***cis*-1,2,3,4,9,10-Hexahydronaphthalene (1).** *cis*-Decalin-1,4-dione bis(*p*-toluenesulfonylhydrazone) (50.5 g, 0.1 mol) was placed with 200 ml of benzene in a 1-l., three-necked flask equipped with a gas inlet tube, mechanical stirrer (Ace Trubore), and still head. Benzene was distilled from the flask until the distillate was clear and then an additional 50 ml was distilled out. The still head was replaced with a dry dropping funnel; the air in the system was pumped out and replaced with argon. A mercury bubbler exit tube was attached to the system. Next, 260 ml of methyllithium in diethyl ether (1.66 *M*, 0.43 mol, Alfa Inorganics) was transferred to the funnel by a siphon under argon pressure. The flask was cooled with an ice bath and the methyllithium introduced over a 10-min period with stirring. The ice bath was removed and stirring continued for 10–15 hr by which time almost all the hydrazone had dissolved. The ice bath was again placed around the flask and water was added slowly. The first few milliliters brought about precipitation of a solid which redissolved after addition of another 300–400 ml of water. The organic phase was removed, washed twice with water (100 ml) and once with saturated NaCl solution, dried over anhydrous K_2CO_3, and filtered. The bulk of the solvent was distilled away rapidly through a 6-in. column of steel mesh. The residue of 30–50 ml was transferred to a smaller flask and the distillation continued through the same column at reduced pressure to yield 5.8 g of colorless liquid, bp 58–61° (9 mm). Analysis by glpc showed only two products (83 and 17%). Preparative glpc (20 ft × $^3/_8$ in. of 20% Apiezon J on 60–80 mesh Chromosorb P) gave 4.3 g of **1**: nmr (CCl_4) δ 5.5–6.0 (m, 4), 2.25 (m, 2), 1.4 (m, 8); uv max (95% ethanol) 262 nm (ϵ 4100). Hydrogenation over Pt yielded only *cis*-decalin. The other product isolated by glpc was tentatively identified as 1,2,3,4,7,10-hexahydronaphthalene: nmr (CCl_4) δ 5.5 (m, 2), 5.25 (m, 1), 2.4–2.7 (m, 3), 0.9–2.3 (m, 8); uv end absorption only.

***cis*-1,4,9,10-Tetrahydronaphthalene (2).** The procedure was identical with that used for the hexahydro material. Starting from 50 g of the corresponding bishydrazone yielded 4.8 g of liquid, bp 62–64° (8 mm). Glpc analysis showed two major products (85:15) and traces of several others. Preparative glpc yielded 4.1 g of **2** (30% yield): nmr (CCl_4) δ 5.5–5.9 (m, 6), 2.2–2.6 (m, 2), 1.9–2.2 (m, 4); uv max (95% ethanol) 262 nm (ϵ 3800). Hydrogenation over Pt yielded only *cis*-decalin. Spectra of **2** matched those of a sample of **2** prepared by the method of van Tamelen.[9b]

***trans*-1,2,3,4,9,10-Hexahydronaphthalene (4).** The trans bishydrazone (32 g) was treated by the same procedure as the cis isomer to yield 4.5 g of liquid, bp 55–56° (10 mm), yield 50%. Glpc showed a single product, **4**: nmr (CCl_4) 5.5–5.9 (m, 4), 1.1–2.2 (m, 10). Hydrogenation of a sample over Pt yielded only *trans*-decalin.

Handling of Dienes. Hydrocarbons **1, 2, 3, 4**, and **20**, and cycloadducts **18** and **19** are all somewhat air sensitive. Samples of **1** and **2** stored exposed to air for 1 month at 0° in the dark were found to have been 30% converted to tetralin and 1,4-dihydronaphthalene, respectively, as well as being *heavily contaminated with peroxides.* These materials should be kept under an inert atmosphere as much as possible.

Reaction of 1 with Diethyl Fumarate. **1** (3.1 g, 0.023 mol), freshly purified by glpc, and 5.0 g (0.029 mol) of diethyl fumarate were placed in a 15 × 150 mm test tube. The mixture was degassed by two freeze–pump–thaw cycles and sealed *in vacuo.* It was then placed in an oil bath and held at 120–125° for 24 hr. After cooling, the tube was opened. Glpc (9 ft × $^1/_8$ in. 10% Apiezon J on 60–80 Chromosorb W) showed two peaks in 85:15 ratio, the smaller being broadened and trailing as if decomposing, plus unreacted diene (*ca.* 25%) and excess fumarate. The reaction mixture deposited crystals on standing (refrigerated) which were collected and recrystallized from methanol to yield 3.6 g of **5**: mp 83–83.5°; nmr (CCl_4) δ 6.25 (quint, 2), 4.1 (two overlapping q, 4, J = 7 Hz), 3.15 (d of doublets, 1, J = 2 Hz, 6 Hz), 2.75 (m, 3), 0.8–1.9 (envelope plus two overlapping t at 1.2, J = 7 Hz, total 16). *Anal.* Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55; O, 20.89. Found: C, 70.38; H, 8.45.

The mother liquor and washings were combined and heated at 60° (0.05 mm) to remove unreacted diene and excess fumarate (0.3 g of **1** recovered). The residue (2.2 g) was chromatographed on Florisil: first eluent 80% petroleum ether, 20% ethyl ether until **5** (1.4 g) had eluted, then 70% petroleum ether, 30% ethyl ether to elute **7** (0.6 g). The latter was isolated as a colorless oil: nmr (CCl_4) δ 5.5–5.9 (m, 2), 5.25 (m, 1), 4.2 (two overlapping q, 4, J = 7 Hz), 3.3 (m, 1), 2.2–3.1 (m, 2), 0.9–3.0 (many m plus two overlapping q, J = 7 Hz at 1.25, 16). *Anal.* Found: C, 70.19; H, 8.20. After prolonged heating in air, small amounts of tetralin could be isolated from decomposing **7**; combined yield of **5** + **7** based on diene consumed, 80%.

Reaction of 2 with Diethyl Fumarate. Glpc purified **2** (1.58 g, 0.012 mol) and 4.5 g (0.026 mol) of diethyl fumarate were placed in a 15 × 150 mm test tube. The mixture was degassed by two freeze–pump–thaw cycles and sealed *in vacuo.* The tube was placed in an oil bath and held at 120–125° for 36 hr. After cooling, the tube was opened and glpc analysis showed that all the triene had been consumed. Only two significant peaks of long retention time were present, their ratio being 97:3. Crystals were deposited over a period of hours as the cooled reaction mixture stood. Filtration and washing with methanol gave 1.17 g of **6**: mp 75–76°; nmr (CCl_4) δ 6.2 (quintet of doublets, 2), 5.7 (m, 2), 4.1 (two overlapping q, 4, J = 7 Hz), 3.2 (doublet of doublets, 1, J = 2 Hz, 5 Hz), 2.7–2.9 (m, 3), 1.5–2.3 (m, 6), 1.2 (two overlapping triplets, 6, J = 7 Hz). *Anal.* Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95; O, 21.02. Found: C, 71.18; H, 8.05.

After the bulk of the excess diethyl fumarate had been distilled away (60° (0.05 mm)), trituration of the residue with methanol yielded a second crop of 0.8 g of **6**. Chromatography of the residue after evaporation of the mother liquor and washings (eluent: 80% petroleum ether, 20% ethyl ether) yielded a final 0.4 g of **6** (overall yield 65%) and *ca.* 50 mg of an oil identified as **8**, contaminated with traces of diethyl fumarate: nmr (CCl_4) δ 5.2–5.9 (m, 5), 4.1 (two overlapping quartets, 4, J = 7 Hz), 3.3 (m, 1), 2.5–3.1 (m, 4), 1.7–2.5 (m, 4), 1.2 (two overlapping triplets, 6, J = 7 Hz).

Hydrogenation of 5. Recrystallized **5** (280 mg) in 3 ml of 95% ethanol was hydrogenated over PtO_2 catalyst (6 mg). Hydrogen (23 ml) was taken up (calcd for one double bond plus catalyst reduction, 24 ml). The solution was filtered twice and heated to boiling, and water was added until the turbidity remained. A few drops of ethanol were added and on cooling 250 mg of crystals was deposited: mp 50–52°; nmr (CCl_4) δ 4.1 (q, 4, J = 7 Hz), 3.0 (broad s, 2), 1.0–2.0 (m, plus an overlapping t at 1.2, J = 7 Hz, total 22). *Anal.* Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15; O, 20.75. Found: C, 69.87; H, 9.03.

Hydrogenation of 6. **6** (90 mg) in 2 ml of 95% ethanol was hydrogenated over 5 mg of PtO_2. Hydrogen (15 ml) was taken up (calcd for two double bonds, 16 ml). The solution was treated as in the hydrogenation of **5**. The product was identical with the product from **5** by nmr, melting point, and mixture melting point.

Photosensitized Ring Closure of 6. **6** (0.53 g) (recrystallized from ethanol–water) was placed in 350 ml of acetone in a Pyrex irradiation apparatus. Nitrogen was bubbled through the solution while irradiation proceeded (450-W Hanovia medium-pressure mercury lamp). After a few hours, no starting material remained. Removal of the solvent on a rotary evaporator and recrystallization of the residue from ethanol–water yielded 0.41 g (80%) of **25**: mp 79–80°; nmr (CCl_4) δ 4.20 (two overlapping q, 4, J = 7 Hz), 3.4 (doublet of doublets, 1, J = 3 Hz, 6.5 Hz), 3.1 (doublet of doublets, 1, J = 3 Hz, 6.5 Hz), 2.1–2.9 (m, 6), 1.6–1.9 (m, 4), 1.2 (two overlapping t, 6, J = 7 Hz), 0.8–1.1 (broad doublet, 2, J = 12 Hz). *Anal.* Found: C, 70.95; H, 7.97.

Reaction of 1 with Tetracyanoethylene. **1** (0.93 g, 6.9 mmol) (freshly purified by glpc) and 0.87 g (6.8 mmol) of TCNE were mixed in 5 ml of tetrahydrofuran (distilled from $LiAlH_4$) under nitrogen with the immediate appearance of a dark purple color. During 2 hr of magnetic stirring, the color gradually faded to yellow and crystals precipitated. The stoppered flask was placed in the freezer for a few hours; the crystals were collected and washed with cold (−78°) acetone to yield **10**: mp 226–227° (sublimes); nmr (acetone-d_6) δ 6.7 (doublet of doublets, 2, J = 3 Hz, 5 Hz), 3.7 (m, 2), 2.35 (m, 2), 0.9–1.8 (m, 8). *Anal.* Calcd for $C_{16}H_{14}N_4$: C, 73.26; H, 5.38; N, 21.36. Found: C, 73.29; H, 5.44; N, 21.17.

The mother liquor, after evaporation, yielded a brown solid which upon attempted recrystallization from $CHCl_3$ gave white crystals, mp 180–185° dec, nmr (acetone-d_6) δ 5.9 (s), probably tetracyanoethane. The $CHCl_3$ solution from the "recrystallization" showed nmr signals for tetralin.

The reaction was repeated with 183 mg of **1** and 180 mg of TCNE in 1 ml of THF in a sealed degassed nmr tube. Reaction was allowed to proceed in the spectrometer (probe temperature 44°). Peaks above δ 4 were obscured by the solvent, but observation of the vinyl region showed reaction to be complete in 1 hr. Besides the signal for **10**, signals were observed at δ 7.1 (s, tetralin?), 6.0–6.3 (m), 5.6–5.9 (m), 5.4–5.6 (m) (the last three in 1:1:1 ratio), and 5.7 (s, tetracyanoethane?). After standing overnight at room temperature, the nmr tube was found to be filled with a heavy precipitate and dark brown liquid. Assuming structure **9** was responsible for the multiplets, the ratios **9**:**10**:tetralin were 57:35:8.

Reaction of 2 with TCNE. **2** (85 mg) (freshly purified by glpc) and 84 mg of TCNE were mixed in 0.5 ml of THF in a nmr tube to give a red-orange solution. After 2 hr at 37° the color had faded to yellow and white crystals had precipitated. Additional THF was added to dissolve the solid. Nmr signals in the vinyl region were present at δ 6.7 (doublet of doublets, J = 3 Hz, 5 Hz), 5.9 (m), and 5.7 (m) in a ratio of 1:1:0.29. The solution was partly evaporated under nitrogen to yield white crystals of **11** (filtered and washed with cold THF): mp 227–228° (sublimes); nmr ($CDCl_3$) δ 6.7 (doublet of doublets, 2, J = 5 Hz, 3.5 Hz), 5.9 (m, 2), 3.4 (m, 2), 2.6 (m, 2), 1.5–2.3 (m, 4). *Anal.* Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.59; H, 4.72; N, 21.48.

The minor product, though somewhat stabler than **9** had been, still decomposed on standing a few days and could not be obtained pure.

Reaction of 1 and 12. To 1.05 g of (freshly purified by glpc) **1** in 5 ml of dry ethyl acetate under nitrogen was added a solution (EtOAc) of **12** (freshly sublimed) until the color of th edienophile persisted. A water bath was used to keep the mixture at room temperature since the reaction was quite exothermic. Sufficient hot $CHCl_3$ was added to dissolve the precipitated product, and a sample of the hot clear solution was withdrawn. The solvent was removed from this smaller sample and replaced with $CDCl_3$, and the nmr spectrum recorded with repeated integrations. The sample was then returned to the main body of material. Recrystallizations yielded three crops of crystals, the first two from ethyl acetate and the third from CCl_4. The first crop, 1.55 g, was pure **13**: mp 217–219° dec; nmr ($CDCl_3$) δ 7.45 (s, 5), 6.50 (t, 2, J = 4 Hz), 4.75 (m, 2), 2.3 (m, 2), 0.8–1.9 (m, 8). *Anal.* Calcd for $C_{18}H_{18}N_3O_3$: C, 69.88; H, 6.19; N, 13.58; O, 10.34. Found: C, 69.38; H, 6.20; N, 13.74.

The second crop (0.47 g) consisted of 87% **13** and 13% **15**. The third crop (74 mg) was a 1:1 mixture of **13** and **15**. Extraction of the third crop with cold 20% NaOH followed by neutralization (HCl) of the hydroxide solution afforded 30 mg of white ene product **15**: mp 208–209°; nmr ($CDCl_3$) δ 7.5 (s, 5), 5.5–6.1 (m, 2), 5.2–5.5 (m, 2), 1.0–2.8 (m, 9). *Anal.* Found: C, 70.21; H, 6.33; N, 14.05.

The recrystallization from CCl_4 also separated out a totally insoluble material (0.15 g) thought to be a decomposition product of **12** (only aromatic nmr absorbances). The yellow-white residue (210 mg) appeared to be a 30:70 mixture of **13** and **14**, respectively. Further recrystallizations from acetone and CCl_4 failed to free **14** completely from **13**; nmr signals for **14**: δ 7.45 (s, 5), 6.50 (t, 2, J = 4 Hz), 4.65 (m, 2), 1.0–2.1 (m, 10). *Anal.* (of the 30:70 mixture) Found: C, 69.45; H, 6.12; N, 13.74.

Hydrogenation of the 30:70 mixture over PtO_2 did allow separation of the two products (*vide infra*); overall yield of isolated adducts 96%.

Reaction of 2 with 12. The procedure for reaction and determination of adduct distribution was the same as for **1**. From 1.21 g of **2**, three crops of crystals were obtained. The first, 1.80 g, was pure **16**: mp 222–224° dec; nmr ($CDCl_3$) δ 7.45 (s, 5), 6.50 (t, 2, J = 4 Hz), 5.9 (m, 2), 4.7 (m, 2), 1.4–2.8 (m, 6). *Anal.* Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67; O, 10.41. Found: C, 70.45; H, 5.53; N, 14.03.

The second crop, 0.58 g, was greater than 96% **16**, the remainder being **17**. The third crop, 0.35 g, was a 26:74 mixture of **16** and **17**. The residue, 0.11 g, appeared to be a mixture of **16**, **17**, and decomposed dienophile.

Photosensitized Ring Closure of 16. Isolation of 17. **16** (0.41 g) (recrystallized from EtOAc) was placed in a photolysis well with 350 ml of acetone. N_2 was bubbled through the solution while irradiation with a 450-W Hanovia medium-pressure mercury lamp proceeded (irradiation time 1 hr). Removal of the solvent and recrystallization of the residue from ethanol–water afforded 0.34 g (83%) of **26**: mp 225–228° dec; nmr ($CDCl_3$) δ 7.2–7.7 (m, 5), 4.15 (s, 2), 2.7–3.0 (m, 4), 2.5–2.7 (m, 2), 1.8 (d, 2, J = 12 Hz), 0.9–1.3 (d, 2, J = 12 Hz). *Anal.* Found: C, 70.45; H, 5.60; N, 13.77.

The reaction was repeated with 96 mg of a 26:74 mixture of **16** and **17** in 50 ml of acetone (irradiation time 30 min). Recrystallization of the residue from ethyl acetate now afforded 56 mg of recovered **17** free of **16**. A second crop of 35 mg consisted of **26** and **17** in roughly equal amounts; for **17**: mp 171–173°; nmr ($CDCl_3$) δ 7.45 (s, 5), 6.50 (t, 2, J = 4 Hz), 6.05 (m, 2), 4.60 (m, 2), 1.8–2.5 (m, 6). *Anal.* Found: C, 70.13; H, 5.64; N, 13.62.

Reaction of 3 with 12. A solution of **3** (*ca.* 200 mg in 100 ml of ethyl ether) was prepared by pyrolysis of bullvalene at 360° (less than 5% conversion), filtration of the ethereal pyrolysate at −78° (to remove the bulk of the unreacted bullvalene), and trap-to-trap distillation of the solution at room temperature (0.05 mm). The amount of **3** present was estimated very roughly by glpc using the bullvalene still in the solution as an internal standard. The solution was kept under nitrogen at all times.

Approximately 0.04 mol equiv of **12** (10 mg) in ethyl acetate was dripped into the vigorously stirred solution of **3**. The clear solution was then distilled a second time (as above) leaving a residue of cycloadducts (18 mg). The residue was taken up in $CDCl_3$ and showed nmr peaks for **18** and **19** in a 79:21 ratio.

The reaction sequence was repeated twice using $^1/_6$th equiv of **12** and adding a filtration step before trap-to-trap distillation to remove the highly insoluble 2:1 adducts. Finally, the tetraene still remaining was treated with **12** until the dienophile color persisted, and the 2:1 adduct was then collected. The combined 1:1 adducts (150 mg) were recrystallized from CCl_4 to afford 40 mg of white **18**: mp 217–220° dec; nmr ($CDCl_3$) δ 7.45 (s, 5), 6.65 (t, 2, J = 4 Hz), 5.6 (m, 4), 4.9 (m, 2), 3.5 (s, 2). Further recrystallizations of the residue from acetone yielded, on the fourth crop, 22 mg of a 1:1 mixture of **18** and **19**; nmr signals for **19** ($CDCl_3$) δ 7.45 (s, 5), 6.45 (t, 2, J = 4 Hz), 5.6? (m, 4), 5.1 (m, 2), 2.6 (s, 2).

A sample of the 2:1 adduct as filtered out was dissolved in $CDCl_3$ (saturation solution *ca.* 2 mg/ml), and a nmr spectrum was obtained by time averaging (250 sweeps). Signals for **22**: δ 7.5 (s, 10), 6.2 (t, 4, J = 4 Hz), 5.0 (m, 4), 3.3 (m, 2). *Anal.* Calcd for $C_{26}H_{20}N_6O_4$: C, 64.99; H, 4.20; N, 17.49; O, 13.32. Found (mixture of 2:1 adducts): C, 64.72; H, 4.24; N, 16.97.

Photosensitized Ring Closure of 22. A 100-ml portion of a saturated solution of **22** (52 mg of crude adducts) in acetone was irradiated by the usual procedure for 25 min. The acetone was evaporated and the white residue washed with 3 ml each of acetone, $CHCl_3$, and CCl_4 to yield 44 mg of crude **27**, which did not melt upon heating to over 380°. The nmr spectrum again required time averaging: δ 7.5 (s, 10), 4.5 (m, 4), 3.25 (m, 4), 2.3 (m, 2). *Anal.* Found: C, 65.02; H, 4.31; N, 17.53.

Reaction of 20 with 12. **20** (70 mg), isolated by glpc from a sample of **3** heated to 100° for a time,[12] was dissolved in 3 ml of ethyl acetate and a solution of **12** (EtOAc) was added until the red color persisted. The solvent was evaporated to yield 182 mg of raw adduct. A nmr spectrum showed predominantly (≥95%) one product but traces of others were visible by tlc. Recrystallization from ethyl acetate yielded pure **21**: mp 194–196°; nmr ($CDCl_3$) δ 7.45 (s, 5), 6.5 (t, 2, J = 4 Hz), 5.9 (m, 1), 5.6 (m, 1), 4.9 (m, 2), 2.9 (m, 2), 1.9 (m, 4). (The latter two peaks were absent from the nmr of the crude adducts of **3** and **12**.) *Anal.* Calcd, see for **16**. Found: C, 69.90; H, 5.80; N, 13.31.

Hydrogenation of Adducts 13, 16, 18, and 21. A 50-mg sample of adduct in 2 ml of ethyl acetate was hydrogenated over 2 mg of PtO_2 until the calculated volume of hydrogen was taken up. Filtration to remove the Pt, evaporation of the solvent, and recrystallization from ethanol–water yielded in every case the same material, **28**: mp (and mmp) 147–149°; nmr ($CDCl_3$) δ 7.5 (m, 5), 4.2 (s, 2), 1.2–2.4 (m, 14). *Anal.* Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.49; O, 10.28. Found: C, 68.95; H, 6.72; N, 13.65.

Hydrogenation of 17. **17** (50 mg) in 2 ml of EtOAc with 2 mg of PtO_2 absorbed 7.5 ml of hydrogen (calcd 8.0). After filtration and removal of solvent, recrystallization from acetone yielded 35 mg of **29**: mp 190–192°; nmr ($CDCl_3$) δ 7.5 (m, 5), 4.15 (s, 2), 1.2–2.2 (m, 14). *Anal.* Found: C, 69.24; H, 6.80; N, 13.36.

Hydrogenation of a Mixture of 13 and 14. A 30:70 mixture of **13**:**14** (20 mg) was hydrogenated in 1 ml of EtOAc over 1 mg of PtO_2. Filtration, evaporation, and recrystallization (Craig tube) from acetone yielded 10 mg of solid, mp 189–191°. A mixture melting point with **29** produced from **17** showed no further depression.

Hydrogenation of a Mixture of 18 and 19. A 1:1 mixture of **18** and **19** (10 mg) was hydrogenated in 1 ml of EtOAc over 1 mg of PtO_2. Filtration and evaporation yielded a solid whose nmr ($CDCl_3$) matched the nmr of a 1:1 mixture of **28** and **29**. Recrystallization from acetone (Craig tube) yielded 1 mg of material which, when mixed with 1 mg of **29**, showed no melting point depression.

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