addition of the reactive α-methoxystyrene **13**[17] (2.5 equiv) by syringe drive over 30 h to a methanolic solution of DNP salt **12** at 40 °C and stirring for a further 10 h gave cycloadduct **14** (90%). The adduct was hydrolyzed by acid and then immediately aromatized[18] with strong alkali and the resultant aldehyde oxidized to naphthoic acid **15** (82% from **14**) by Jones reagent. DPPA rearrangement of **15** in dry toluene with added benzyl alcohol[9] afforded benzyl urethane **16**, which was reduced by $LiAlH_4$ and formylated with chloral[19] to give **17** indistinguishable from authentic material (36% overall from **15**).

The foregoing examples help to define the scope of isoquinolinium cycloadditions and validate their potential in natural products synthesis. Further studies leading to cis-fused benzophenanthridines[20] and other classes of natural products are in progress.

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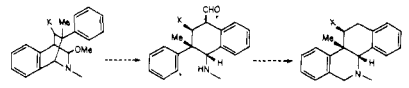
Registry No. 2, 84133-48-2; **4**, 84133-49-3; (±)-**6**, 84133-41-5; (±)-**7**, 84133-42-6; (±)-**8**, 84173-74-0; (±)-**9**, 84173-67-1; (±)-**10**, 84133-46-0; (±)-**11**, 83607-67-4; **12**, 83379-65-1; **13**, 84133-47-1; (±)-**14**, 84133-43-7; **15**, 84133-44-8; **16**, 84133-45-9; **17**, 84143-15-7.

Supplementary Material Available: Physical data for **2–7**, **9**, **10**, **13–15**, and **17** (2 pages). Ordering information is given on any current masthead page.

(17) Obtained as a colorless oil from 2,3,4-trimethoxyacetophenone by the following method: Loudon, G. M.; Smith, C. K.; Zimmerman, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 465.
(18) Manna, S.; Falck, J. R.; Mioskowski, C. *J. Org. Chem.* **1982**, *47*, 5021.
(19) Blicke, F. F.; Lu, C.-J. *J. Am. Chem. Soc.* **1952**, *74*, 3933–3934.
(20) Reversal of the regiospecificity observed with α-substituted styrenes offers, in principle, an expeditious route to cis-fused benzophenanthridines by incorporating the original isoquinoline nitrogen into ring C (eq i).



(i)

Cation Radical Catalyzed Olefin Cyclodimerization

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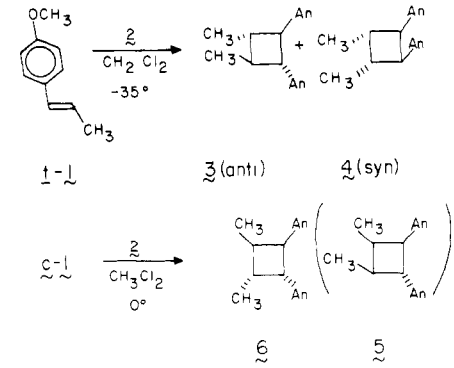
The cyclodimerization of *N*-vinylcarbazole giving *trans*-1,2-bis(*N*-carbazolyl)cyclobutane via a cation radical chain reaction, observed by Ledwith in 1969, in potentially one of the pioneering observations in cation radical pericyclic chemistry.[1] The mechanistic details of the cation radical cycloaddition step have not yet been clarified, but Ledwith and others have apparently assumed it occurs in stepwise fashion.[2,3] The fundamental interest in this question is enhanced by the recent observation of an apparently concerted path for the cation radical catalyzed Diels–Alder reaction.[4] A stereochemical study of the cation radical catalyzed dimerizations of *cis*- and *trans*-anethole (**1**, Scheme I) has now been carried out, which established these dimerizations as stereospecific. An MNDO theoretical reaction path study of the prototype cycloaddition of ethene cation radical and ethene, assisted by STO-3G ab initio calculations on the key intermediate, suggests a novel mechanism for such cycloadditions that is in full accord with the experimental determination of stereospecificity. Further, a synthetically attractive new procedure for olefin cyclodimerization, involving catalysis by tris(*p*-bromophenyl)-aminium hexachloroantimonate (**2**) in methylene chloride solution, is developed. The first cation radical cycloadditions of nonequivalent olefinic components are also reported.

Scheme I



The dimerization of *trans*- and *cis*-anethole (**1**) illustrates the new synthetic procedure and also illuminates the reaction stereochemistry. When added to a methylene chloride solution containing 5 mol% of **2** at 0 °C, *trans*-**1** is converted, in less than 10 min, to the head-to-head *trans,anti,trans*-cyclobutane dimer **3** in 45% yield. The reaction appears to be completely (>99%) stereoselective, and as is customarily observed in cation radical processes catalyzed by **2**, the only noteworthy competing reaction is polymerization of **1**. Of somewhat greater mechanistic interest is the observation that dimerization of *trans*-**1** at −35 °C produces, instead of pure **3**, a 52:48 mixture of **3** and a second dimer (**4**), the latter being the same head-to-head *trans,syn,trans*-cyclobutane dimer produced in the direct photodimerization of 1.[5] Both **3** and the thermodynamically much less stable **4** are formed in reactions that are formally $[{}_{\pi}2_s + {}_{\pi}1_s]$ cycloadditions, i.e., with complete retention of the stereochemistry of *trans*-**1**, thus providing the first experimental suggestion of a possible stereospecific reaction. This premise was further examined by studying the cycloreversion of **4** to **1**, which occurs smoothly at 0 °C in methylene chloride solutions of **2**. GC/MS was used to analyze samples of the reaction quenched by methoxide/methanol at various stages of reaction, including times as short as 5 s. Even at the shortest reaction times, under conditions in which *cis*-**1** would have been readily detectable, the cycloreversion of **4** produces *trans*-**1** with complete (>99%) stereoselection. The subsequent dimerization of *trans*-**1** generates only **3** and, again, no other dimer. The cycloreversion of **4** is thus also a doubly suprafacial process, formally $[{}_{\pi}2_s + {}_{\pi}1_s]$, as would behoove a concerted cycloreversion, and is not accompanied by isomerization to any of the other possible cyclobutane dimers.

The dimerization of *cis*-anethole, which in theory should provide the most direct test of stereospecificity, was complex stereochemically, yielding (at 0 °C) **3**, **5**, and **6**, instead of pure **6** as expected for a selective $[{}_{\pi}2_s + {}_{\pi}1_s]$ cycloaddition. However, GC/MS analysis of the unreacted **1** revealed that the isomerization of *cis*-**1** to *trans*-**1** was occurring at a rate competitive with cycloaddition. Statistical treatment of product composition–time data (5–60 s) obtained by GC/MS analysis gave an extrapolated value for the percentage of **3** in the dimer mixture at zero time (no isomerization) of 0.0%. The dimerization *cis*-**1** thus yields none of the thermodynamically most stable dimer, within experimental error. These data strongly suggest that the dimerization

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(2) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.
(3) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.
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(5) Nozaki, H.; Noyori, R.; Kawanisi, M. *Tetrahedron* **1968**, *24*, 2183.

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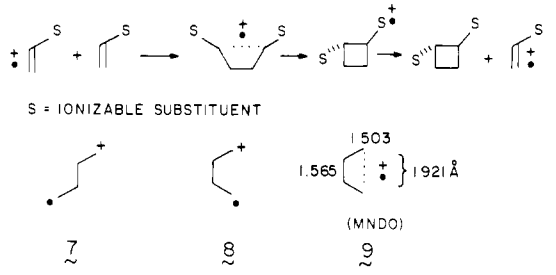
Scheme II



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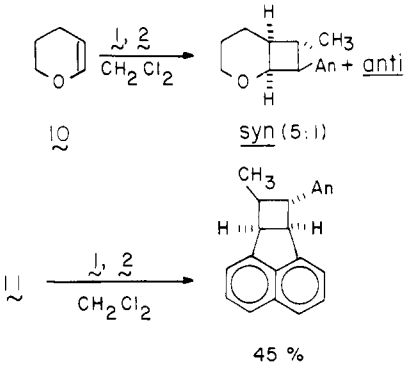
of *cis*-**1** is stereoselectively $[_\pi 2_s + _\pi 1_s]$, as was found for the dimerization of *trans*-**1** at 0 and −35 °C and the cycloreversion of **4** at 0 °C. It is therefore concluded that the cyclodimerization of **1** is inherently stereospecific.

For a reaction that has been regarded as stepwise, the stereospecificity of the anethole cycloaddition is mildly surprising. A stepwise mechanism involving an open *s-trans*-cation radical intermediate (**7**, Scheme II) seems clearly to be ruled out. The involvement of an open, *s-cis*-cation radical intermediate (**8**) cannot be rigorously eliminated, since cyclization could be more rapid than the relevant rotations in such an intermediate. However, this possibility is regarded as remote. A theoretical study of the prototype [2 + 1] cycloaddition suggests a novel modification of this latter mechanism that is in excellent accord with the stereochemical results (Scheme II). The key observation is that the cyclobutane cation radical structural minimum occurs, according to both MNDO and optimized STO-3G calculations, at a long (one-electron) bond structure (**9**) similar to those found for the ethane and other alkane cation radicals.[6] A long bond dissociation energy comparable to that of the one-electron bond in the ethane cation radical (38 kcal/mol) should easily be sufficient to preserve configurational stability in **9**. Direct experimental evidence for stable long-bond structures is available form CIDNP studies on the *cis*- and *trans*-1,2-diphenylcyclopropane cation radicals.[7] These cation radicals have a long 1,2 bond and are configurationally stable. Subsequent closure of the long-bond cyclobutane to a "normal" cyclobutane structure appears feasible only when relatively ionizable (usually π or n) substituents are present upon which to localize the cation radical site in the fully cyclized cyclobutane adduct. The MNDO reaction path calculation reveals the powerful effect of the cation radical "hole" in lowering the barrier to cycloaddition. The activation energy for the formation of **9** from ethene and ethene cation radical is merely 1.3 kcal/mol.[8]

The chemical cyclodimerization[9] procedures reported by Ledwith were apparently limited to vinylcarbazoles and a few extremely electron-rich alkenes (e.g., 1,1-bis(*p*-(dimethylamino)-phenyl)ethene).[2] The new catalyst system therefore extends the reaction scope modestly, to include double bonds activated by anisyl substituents. Nevertheless, simple olefins and olefins activated only by phenyl groups remain unreactive or are polymerized by **2**. Within its very considerable limitations, the new proceudre is rapid and convenient, and it has proved capable of effecting the first reported [2 + 1] cycloadditions of nonequivalent olefins. The additions of *trans*-**1** to dihydropyran (**10**) and acenaphthylene (**11**) illustrate this capability (Scheme III). The former reaction (53% yield based on **1** consumed; 11% conversion) is highly regiospecific, but forms syn:anti isomers in the ratio 5:1. The yield of adduct from **9** is 45% at complete conversion (syn:anti = 1:10).

Scheme III



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Work designed to further extend the scope of the cyclodimerization is in progress.

Acknowledgment. We thank the Robert A. Welch Foundation (F-149) for support of this research and the NSF for a Minority Graduate Student Fellowship to R.P.

(6) Bellville, D. .; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 5700.

(7) Roth, H. D.; Mannion, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 7210.

(8) The transition state was refined and verified by using Professor M. J. S. Dewar's NDTS60B and NDFORB programs. Full details of the reaction path calculation are included in a full paper submitted to this journal.

(9) A photosensitized version that has somewhat greater scope has evolved from Ledwith's work, e.g.: Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677.

Red Shifts in the Optical Spectra of Porphyrin Schiff Bases upon Protonation

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In a number of metalloporphyrin- and metallochlorin-containing proteins, there is an opportunity for modulation of the physical and chemical properties of the ring system by interactions between its peripheral substituents and nearby amino acid side chains. Such effects, for example, have been postulated for the vinyl groups of protoheme in hemoglobin and in cytochrome b_5,[1] for the formyl group of heme *a* in cytochrome oxidase,[2] and for the keto and formyl groups of various chlorophyll species.[3] A Schiff's base linkage between a substituent carbonyl group and a protein amino group donor is especially attractive in this role owing to the fact that both formation of the linkage and its subsequent protonation may be subject to functional control. Recent work on the linear polyene aldehyde retinal and its Schiff's bases has demonstrated the strong dependence of the optical properties of the chromophore upon the chemistry that occurs at the CHO group;[4] moreover, protonation/deprotonation reactions of the retinal Schiff's base species in situ in rhodopsin[5] and in bacteriorhodopsin[6] have been

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