

quenched with methanol (1 mL). The solvent was removed (rotavap) and the residue dissolved in methylene chloride, washed with water and saturated brine, and dried (MgSO₄). Evaporation of the solvent and chromatography of the dark brown residue using 4:1 hexanes/methylene chloride as eluent gave 0.14 g (46%) of **24** (X = H) and 0.12 g (28%) of **25**. For **24** (X = H): mp 209–210 °C; ¹H NMR (CDCl₃) δ 1.62 (s, 3 H), 2.11 (s, 3 H), 4.67 (d, 1 H), 4.94 (s, 1 H), 6.14 (d, 1 H), 6.98 (m, 8 H), 7.23 (m, 8 H); ¹³C NMR (CDCl₃) δ 14.30, 15.39, 49.82, 52.71, 53.68, 55.76, 119.96, 120.49, 122.78, 123.40, 124.28, 124.72, 125.07, 140.36, 141.10, 145.51, 145.59, 146.92, 148.36, 150.04; mass spectrum, *m/e* (relative intensity) 470 (1), 468 (4), 433 (3), 256 (3), 217 (11), 215 (12), 192 (100), 191 (28), 178 (30). Anal. Calcd for C₃₄H₂₅Cl: C, 87.10; H, 5.33. Found: C, 86.96; H, 5.30. For **25**: mp >500 °C; ¹H NMR (CDCl₃) δ 3.02 (s, 9 H), 6.73 (s, 3 H), 6.95 (m, 12 H), 7.36 (m, 12 H); ¹³C NMR (CDCl₃) δ 20.19, 48.70, 121.72, 123.48, 125.74, 146.21, 148.30; mass spectrum, *m/e* (relative intensity) 649 (30), 648 (95), 633 (43), 456 (21), 441 (29), 426 (28), 262 (16), 191 (76), 85 (100). Anal. Calcd for C₅₁H₃₆: C, 94.45; H, 5.55. Found: C, 94.33; H, 5.51.

Trimerization of a 3:1 Mixture of 18/19. The procedure is similar to that described for the trimerization of **18**. To 5.1 g (20 mmol) of a 3:1 mixture of **18/19** in 100 mL of THF (argon, -78 °C) was added 8.8 mL (1.1 equiv) of 2.5 M *n*-BuLi in hexanes. The mixture was stirred (1 h), brought to room temperature, heated at reflux (2 h), and worked up as before. Chromatography gave 3.4 g of a mixture of **24–27**. A 0.5-g sample of this mixture was subjected to preparative TLC (silica gel, 1.0 mm) using 4:1 hexanes/methylene chloride as eluent to afford 0.21 g (30%) of **24** (X = H), 0.07 g (10%) of **27** (X = H), and 0.22 g (32%) of a 3:1 mixture of **25/26**. For **27**: mp 259–261 °C; ¹H NMR (CDCl₃) δ 2.14 (s, 3 H), 2.16 (s, 3 H), 4.99 (s, 1 H), 5.66 (d, 1 H), 6.68 (d, 1 H), 6.91 (m, 8 H), 7.20 (m, 8 H); ¹³C NMR (CDCl₃) δ 15.45, 15.66, 50.47, 53.53, 56.26, 58.94, 120.28, 120.69, 123.43, 123.54, 124.57, 124.66, 125.16, 125.49, 141.63, 142.36, 144.72, 146.28, 147.33, 147.78, 147.87, 148.10, 148.72; mass spectrum, *m/e* (relative intensity) same as for **24**. Anal. Calcd for C₃₄H₂₅Cl: C, 87.10; H, 5.33. Found: C, 87.04; H, 5.38. For **26**: ¹H NMR (deduced from the spectrum of the mixture with **25**) δ 2.78 (s, 3 H), 2.79 (s, 3 H), 3.02 (s, 3 H), 6.02 (s, 1 H), 6.08 (s, 1 H), 6.71 (s, 1 H), and peaks in the aromatic region.

11-Chloro-9,10-dimethyl-9,10-etheno-9,10-dihydroanthracene (29). To a solution of 6.1 g (20 mmol) of 11,12-dichloro-9,10-dimethyl-9,10-ethano-9,10-dihydroanthracene (**28**)¹⁰ in 125 mL of THF was added 3.0 g (excess) of potassium *tert*-butoxide. The mixture was heated at reflux for 16 h. The solvent was removed (rotavap), and the residue was taken up in ether, washed with water and saturated sodium chloride solution, and dried (MgSO₄). Evaporation of the solvent and chromatography of the oily residue using hexanes as eluent gave 4.9 g (91%) of **29** as a white solid: mp 106–107 °C; ¹H NMR (CDCl₃) δ 2.08 (s, 3 H), 2.12 (s, 3 H), 6.55 (s, 1 H), 6.99 (m, 4 H), 7.24 (m, 4 H). Anal. Calcd for C₁₈H₁₅Cl:

C, 81.04; H, 5.66. Found: C, 81.05; H, 5.53.

Trapping of Bicycloalkyne 30. To a solution of 0.54 g (2 mmol) of **29** and 0.60 g (2.2 mmol) of 1,3-diphenylisobenzofuran in 25 mL of anhydrous THF at -78 °C under argon was added dropwise 1.0 mL (1.1 equiv) of 2.2 M *n*-butyllithium in hexanes. The mixture was stirred for 2 h, brought to room temperature, and heated at reflux for another 2 h. The cooled reaction mixture was quenched with a small amount of methanol and the solvent was removed. The residue was taken up in methylene chloride, washed with water and saturated sodium chloride solution, and dried (MgSO₄). Evaporation of the solvent and chromatography of the residue using 2:1 hexanes/methylene chloride as eluent gave 190 mg (19%) of **31** as a white solid: mp 306–308 °C; ¹H NMR (CDCl₃) δ 1.82 (s, 6 H), 6.64 (m, 4 H), 6.75 (q, 2 H), 7.11 (m, 4 H), 7.31 (q, 2 H), 7.43 (m, 6 H), 7.73 (m, 4 H); ¹³C NMR (CDCl₃) δ 15.53, 51.49, 66.65, 120.83, 123.12, 124.79, 125.22, 125.41, 129.10, 130.00, 130.93, 135.27, 148.10, 149.59, 150.83; mass spectrum, *m/e* (relative intensity) 501 (2), 500 (6), 396 (5), 395 (15), 365 (8), 194 (10), 270 (100), 105 (35). Anal. Calcd for C₃₈H₂₈O: C, 91.16; H, 5.63. Found: C, 91.11; H, 5.61.

Attempted Trimerization of 29. Formation of Diene 32 and Triene 33. To a solution of 1.35 g (5 mmol) of **29** in 50 mL of anhydrous THF at -78 °C under argon was added dropwise 2.2 mL (1.1 equiv) of 2.5 M *n*-butyllithium in hexanes. The mixture was stirred for 1 h, brought to room temperature, heated at reflux for 2 h, and then cooled, and methanol (1 mL) was added. The solvent was removed (rotavap) and the dark brown residue was taken up in methylene chloride. The methylene chloride solution was washed with water and saturated sodium chloride solution and dried (MgSO₄). Evaporation of the solvent and chromatography of the residue using 3:1 hexanes/methylene chloride gave **32** and **33** as the major products.

For **32** (X = H): 320 mg (26%), mp 263–264 °C; ¹H NMR (CDCl₃) δ 1.38 (s, 3 H), 1.44 (s, 3 H), 2.05 (s, 3 H), 2.09 (s, 3 H), 6.07 (s, 1 H), 7.07 (m, 16 H); ¹³C NMR (CDCl₃) δ 13.90, 14.74, 15.33, 15.83, 49.49, 52.55, 52.64, 119.84, 120.11, 120.60, 124.29, 124.83, 125.20, 142.49, 145.11, 149.48, 150.02, 151.04; mass spectrum, *m/e* (relative intensity) 498 (0.3), 497 (0.3), 496 (0.9), 373 (1.2), 207 (19), 206 (100), 191 (14). Anal. Calcd for C₃₆H₂₉Cl: C, 87.02; H, 5.83. Found: C, 86.95; H, 5.86.

For **33** (X = H): 130 mg (11%), mp 378–380 °C; ¹H NMR (CDCl₃) δ 1.28 (s, 3 H), 1.33 (s, 3 H), 1.51 (s, 3 H), 1.58 (s, 3 H), 1.79 (s, 3 H), 1.82 (s, 3 H), 5.96 (s, 1 H), 6.91 (m, 24 H); ¹³C NMR (CDCl₃) δ 45.38, 47.85, 48.59, 49.81, 50.59, 52.11, 123.17, 123.96, 124.21, 124.67, 125.36, 126.37, 126.66, 127.20, 128.92, 130.75, 140.16, 142.04, 143.37, 144.01, 144.54; no mass spectrum could be obtained. Anal. Calcd for C₅₄H₄₃Cl·H₂O: C, 86.37; H, 5.80. Found: C, 86.28; H, 5.77.

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Allosteric Cooperativity and Transport: Studies in a Circulating System

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Abstract: A model system is used to probe the effects of binding cooperativity on transport. The system involves a crown ether which transports Hg(SCN)₂ through a solvent circulating between two solid phases. It is shown that the positive cooperativity exhibited by the carrier reduces transport effectiveness. This appears to be due to the slower release rate of the cooperative ligand. The model system is contrasted with hemoglobin-mediated O₂ transport.

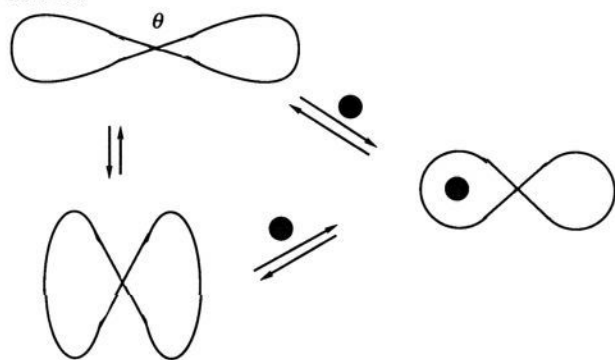
Biochemical systems continue to provide a rich source of inspiration for bioorganic modeling, with good reason. Phenomena such as catalysis, regulation, transport, and recognition are so exotic that they were once believed to be unique properties of

molecules the size of proteins and nucleic acids. Moreover, their names bear little structural information. The model builders have had surprising success in imagining which structural features are required for such behavior. These have been engineered into molecules that are synthetically accessible, and such structures can now perform many of these functions. Regulation—in the form of allostery—is one of the phenomena that has been much

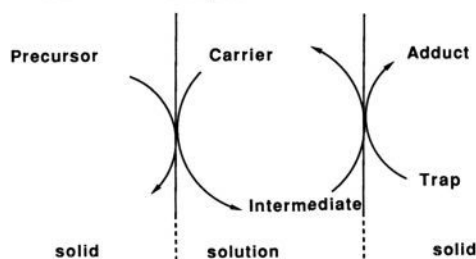
[†]University of Valencia.

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Scheme I

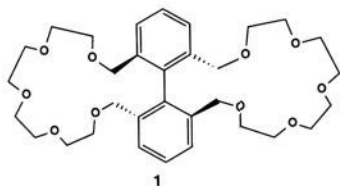


Scheme II. Three-Phase Transport



studied over the last decade in our laboratories.¹ Here, we discuss our findings on allosteric cooperativity and its relation to transport and circulating systems.

Models for allosteric effects that are relevant to oxygen binding and transport have been devised by Tabushi² and Traylor.³ Our own systems have been concerned with cooperativity as an intrinsic phenomenon rather than its expression in hemoglobin, and we introduced a system that showed positive cooperativity using macrocyclic polyethers as the binding sites.⁴ Specifically, structures such as **1**, which feature two symmetrically disposed



binding sites, are connected by a biphenyl unit which transmits conformational information between the sites. Binding of mercuric ions at one site fixes the dihedral angle θ defined by the aromatic ring planes. The rigidity of the biaryl framework ensures this optimal angle is reproduced at the remote site and thereby contributes to the preorganization⁵ of the second site for binding (Scheme I).

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Scheme III

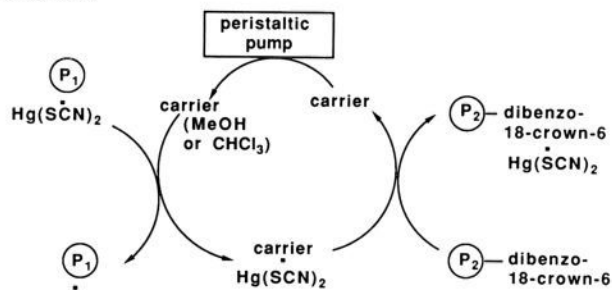


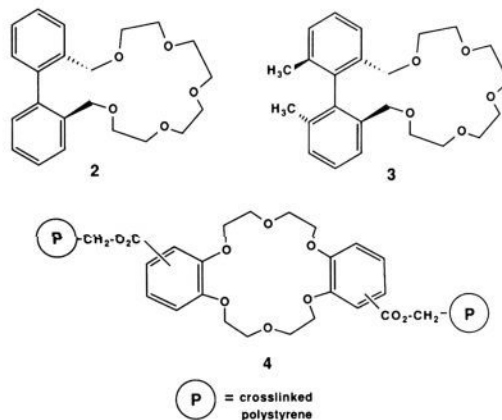
Table I. Intrinsic Association Constants (M^{-1}) for Carriers with $Hg(SCN)_2$ at 24 °C, in CD_3OD

1	$K_1^i = 156, K_2^i = 632$
2	$K_a = 197$
3	$K_a = 172$

Experimental Design

We conceived of transport involving a three-phase system (Scheme II). In some respects this reflects biological systems involving oxygen transport by hemoglobin, wherein air, blood, and solid protein represent the three different phases.⁶ Though our materials and apparatus are so remote from living systems that they may appear unrecognizable, the principles are the same.

The transport phase was a liquid in which the carrier (crown ether) circulates between an insoluble source phase and an insoluble trapping agent. In using this arrangement, we took advantage of our experience with the three-phase test,⁷ updated with the recent developments with polyphasic dynamic reactors (PDR),⁸ for use in circulating systems. The source phase was solid $Hg(SCN)_2$ that was mixed with unfunctionalized, 4% cross-linked polystyrene (Scheme III). For the trapping agent, we prepared a dibenzo derivative of 18-crown-6 and covalently bound it to 2% cross-linked, chloromethylated polystyrene (Merrified resin). The crown ether derivative was prepared as described⁹ and was loaded onto the chloromethylated resin by using typical esterification techniques. The loading level was determined to be ~ 0.44 mequiv/g by titrimetric procedures.



The uptake of mercury salts by the trapping resin could be conveniently monitored by IR. Combustion analysis on a number of partly saturated samples served as a reference to establish a relationship between an IR peak ratio (the SCN band at

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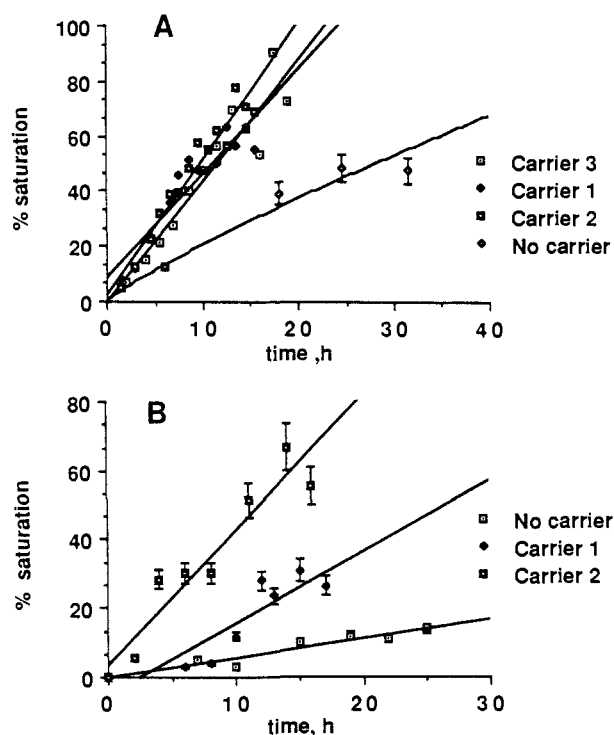


Figure 1. Plots of facilitated transport between solid phases by carriers in a circulating system. Methanol was the solution phase in A and CHCl_3 was the carrier phase in B.

2131–2148 cm^{-1}) and an internal standard band of polystyrene (2778–3122 cm^{-1}). The fractional saturation of the trapping agent was then calculated from the IR peak ratios.

The cooperativity of the carrier toward $\text{Hg}(\text{SCN})_2$ was established by NMR measurements as previously described.^{1b} These were performed under conditions of slow exchange (600 MHz) in the presence of a limited amount of guest. All three crown species, free crown and the 1:1 and 2:1 complexes, can be determined simultaneously by integration.

For the system involving $\text{Hg}(\text{CN})_2$ in organic solvents, the intrinsic association constants for **1** differ by about 1 order of magnitude^{1b} (i.e. $K_1^i = 10 \text{ M}^{-1}$; $K_2^i = 100 \text{ M}^{-1}$). For $\text{Hg}(\text{SCN})_2$ the corresponding values are $K_1^i = 156 \text{ M}^{-1}$ and $K_2^i = 632 \text{ M}^{-1}$ in CD_3OD as a solvent (see Table I). The corresponding value in CD_3OD for **2** was $K_a = 197 \text{ M}^{-1}$ and for **3** $K_a = 172 \text{ M}^{-1}$. Thus, both **2** and **3** adequately reproduce the binding of $\text{Hg}(\text{SCN})_2$ to the first site of **1**, and it appears that nothing unusual is involved in this binding event. The 10–20% reduction of K_1^i compared to that of **2** and **3** was previously noted with $\text{Hg}(\text{CN})_2$ as the guest species. The $\text{Hg}(\text{SCN})_2$ salt was preferred for our current studies (even though the intrinsic cooperativity is less) because it provides a rapid means of detection and quantitation of the binding and transport by IR spectroscopy; $\text{Hg}(\text{CN})_2$ did not show IR bands suitable for such analyses.

In addition to the cooperative carriers we evaluated their single-site counterparts, compounds **2** and **3**, as suitable control systems. These materials provide transport rates comparable to those of the two-site systems (on a per site basis) in the absence of cooperative effects.

The mixture of unfunctionalized polystyrene and mercuric thiocyanate provided a means by which constant dissolution of metal ion could be anticipated during the course of the transport experiments, while circulation was provided by a peristaltic pump. The solvents used were MeOH and CHCl_3 . The former has a relatively high "background" for solubility and transport of $\text{Hg}(\text{SCN})_2$, whereas CHCl_3 as a circulating phase shows very little tendency to transport mercury in the absence of carriers.

Results and Discussion

With CH_3OH as the solution phase and in the absence of crown ether carrier, about 30 h was required for saturation of half of

the sites of the trapping polymer (see Figure 1A). Addition of any of the carriers showed the expected facilitation of transport. However, when the transport rates are adjusted to a per site basis, all carriers appeared to transport at approximately the same efficiency, i.e., the rates were indistinguishable (given the experimental errors). With CHCl_3 (Figure 1B), clear differences with the crown ethers were observed. Remarkably, the cooperative binder proved to be a less effective carrier!

What is the source of this reduced transport efficiency? The cooperativity exhibited by hemoglobin is quite unusual in that individual subunits bind oxygen better than does the "packaged", intact tetramer. From this perspective, the term "cooperativity" as shown by hemoglobin is somewhat misleading, since ligand association *decreases* the intrinsic affinities of the individual subunits. The affinity of the first, second, and third subunits are reduced for O_2 ; only the fourth site has an affinity comparable to that of the monomers.¹⁰ Specifically, K_4/K_1 is approximately 96, while $K_\alpha/K_1 = 238$ and $K_\beta/K_1 = 420$ (K_α and K_β are O_2 association constants for the isolated α and β subunits, respectively).¹¹ The result is that a relatively small drop in partial O_2 pressure triggers the release of several oxygen molecules from the same hemoglobin molecule.

The crown ether system differs from hemoglobin in this critical respect. Its second binding site shows greater affinity and tighter binding than the isolated subunit. The resulting positive cooperativity is expressed in the reduced release rate from the doubly bound crown.¹² It will be interesting to see if this sort of molecular stress can be built into other models for hemoglobin.

Experimental Section

Reagents. The synthesis of carriers 1–3 have been previously described.^{1b} Their respective complexes were prepared by stirring 1 mmol of the appropriate ether in 50 mL of methanol with 1 equiv of $\text{Hg}(\text{SCN})_2$ at room temperature in the absence of light for 6 days, followed by evaporation of the solvent. (For **1**, 2 equiv of the mercury salt was used.) The complex of **1** crystallized from EtOAc and showed the following: mp 168–170 °C; IR 2907, 2133, 1628, 1469, 1348, 1286, 1241, 1095, 1035 cm^{-1} . The complex of **2** crystallized from EtOAc/EtOH: mp 200–210 °C; IR 2905, 2128, 1465, 1350, 1083, 758 cm^{-1} . The complex of **3** crystallized from EtOAc/EtOH: mp 164–166 °C; IR 2918, 2867, 2129, 1456, 1254, 1089, 1026, 757 cm^{-1} .

Association Constants. Binding of $\text{Hg}(\text{SCN})_2$ to the various ethers was determined by NMR.^{1b} For example, a solution of 25.5 mg (0.043 mmol) of **1** and 27.2 mg (0.086 mmol) of $\text{Hg}(\text{SCN})_2$ in 10 mL of CD_3OD showed 28% free **1** (δ 7.50, 7.41), 32.5% of the 1:1 complex (δ 7.61, 7.51, 7.46), and 60.5% of the 2:1 complex (δ 7.63, 7.54). With 15.2 mg (0.048 mmol) of $\text{Hg}(\text{SCN})_2$, the distribution was 51% free and 30% 1:1 and 19% 2:1. For **2** the signal at δ 7.49 (free) and δ 7.56 (bound) was used, and for **3** the signal at δ 7.45 (free) and δ 7.57 (bound) was used. The reproducibility of the NMR integrations was $\pm 6\%$.

Preparation of the Polymer-Bound Trapping Agent, 4. A suspension of 2.5 g of 1% cross-linked, chloromethylated polystyrene resin (2.9 mequiv), 60 mL of Et_3N , and 2.5 g of the dicarboxylic acid derivative⁹ of dibenzo-18-crown-6 was stirred and heated under reflux for 70 h. The resulting resin was filtered, washed with DMF, dioxane, Me_2CO , and CH_2Cl_2 , and then dried in vacuo to give the trapping resin **4**: IR 3026, 2922, 1717, 1601, 1493, 1452, 1269, 1209, 1136, 1059 cm^{-1} . The loading of the diester was determined (saponification) to be 0.44 mmol/g of resin (0.88 mequiv of carboxyl/g). A sample of this resin (0.13 g) and 0.51 g of $\text{Hg}(\text{SCN})_2$ were stirred in 50 mL of acetone at room temperature for 5 days. After filtration, the resin was washed with 1 mL of acetone and 2 mL of CH_2Cl_2 and then dried: IR 3021, 2922, 2121, 1715, 1601, 1493, 1451, 1209, 1140, 1059 cm^{-1} . Combustion analysis showed 7.98% Hg and 1.11% N, indicating a loading at saturation of 0.41 mequiv of mercury salt/g. With several samples the relationship between the fraction saturated and the IR peak intensity ratios was determined to be

$$\% \text{ saturation} = \frac{I_{\text{SCN}}/I_{\text{CH}}}{2.04 \times 10^{-3}}$$

The error is estimated as $\pm 5\%$ based on reproducibility of the IR spectra.

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The solid reservoir of Hg ions was prepared by powdering a mixture of 6 parts Amberlite XE305 (Rohm & Haas Co.) and 4 parts of Hg(S-CN)₂.

Transport Experiments. The polyphasic dynamic reactor used has been previously described.⁸ The appropriate solvent (MeOH or CHCl₃) was introduced with a flow rate of 0.017 mL/s in all experiments. Crown ether **1** was dissolved at 1×10^{-3} M whereas crown ethers **2** and **3** were used as 2×10^{-3} M solutions. Typically 3 g of the reservoir Hg(SCN)₂ source was used and 2 g of the trapping resin **4** was employed. A discussion of transport facilitation and its relationship to experimental pa-

rameters may be found in ref 13.

Acknowledgment. We thank the National Institutes of Health, the joint U.S./Spain Cooperative Program (NSF), and the Dirección General de Investigación Científica y Técnica (Grant PB86-0237) for financial support of this research, and we thank Professor R. Petteer for helpful comments.

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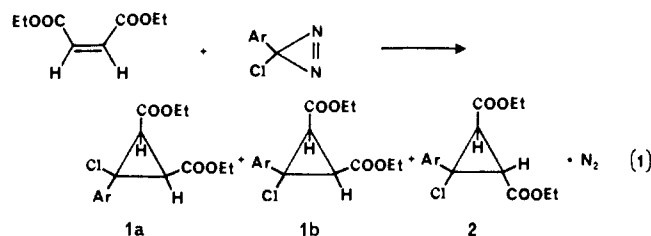
Addition of Arylchlorocarbenes to α,β -Unsaturated Esters. Absolute Rates, Substituent Effects, and Variable Reactivities[†]

N. Soundararajan,^{1a} Matthew S. Platz,^{*,1a} James E. Jackson,^{1a} Michael P. Doyle,^{*,1b} Su-Min Oon,^{1b} Michael T. H. Liu,^{*,1c} and Surinder M. Anand^{1c}

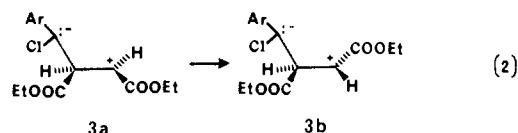
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, Department of Chemistry, Trinity University, San Antonio, Texas 78284, and Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island C1A 4P3, Canada. Received March 14, 1988

Abstract: Addition of arylchlorocarbenes to α,β -unsaturated esters occurs with remarkable facility, even though these carbenes are characterized as electrophilic. Reactions with diethyl maleate, which exhibits isomerization to diethyl fumarate and produces cyclopropanes formally derived from both olefin geometries, are most simply interpreted as concerted additions with isomerization of diethyl maleate resulting from a chemical species generated during decomposition of the reactant diazirine. Absolute rate constants for quenching of a series of para-substituted arylchlorocarbenes with electron-rich and electron-poor alkenes have been obtained. Consistent with concerted addition, diethyl fumarate is more reactive toward cyclopropanation by arylchlorocarbenes than diethyl maleate by factors of more than 20. Absolute rate constants for other alkenes, including *n*-butyl vinyl ether, 1-hexene, and 1-pentene together with the α,β -unsaturated esters ethyl acrylate, ethyl crotonate, and diethyl ethylenemalonate are also reported. Relative reactivities for comparatively electron-rich alkenes are less than those for some electron-poor α,β -unsaturated esters. Increasing solvent polarity has only a moderate influence on the reaction rates of phenylchlorocarbene additions to electron-rich and electron-poor alkenes, and activation parameters do not distinguish between these electronically disparate olefins. Both classifications of alkenes undergo cycloadditions that are dominated by entropy. Hammett correlations have been obtained for reactions of para-substituted arylchlorocarbenes with each alkene substrate, and the resultant positive ρ -values are dependent on the nature of the olefin substituent. Frontier orbital analysis establishes the necessity of including the nucleophilic term in estimating the stabilization energy of the transition state when electron-poor olefins add to reactive carbenes.

We recently reported that arylchlorocarbenes, generated photochemically or thermally from their corresponding diazirines, underwent addition to diethyl maleate (DEM) resulting in the formation of cyclopropane products having both the *cis* and *trans* ester geometries (eq 1).² With diethyl fumarate (DEF) only one



cyclopropane product was produced, and its structure retained the *trans* geometry of the carboxy groups. Isomerization of diethyl maleate to diethyl fumarate accompanied cyclopropane production. These and related observations led Doyle, Liu, and co-workers to propose that arylchlorocarbenes reversibly form a carbene-alkene dipolar adduct (**3**) whose lifetime is sufficiently long that bond rotation can occur (eq 2).^{2b} Results reported from



other laboratories concerning rearrangements that accompany reactions of carbenes with alkenes,³⁻⁵ especially the isomerization of *trans*-cyclooctene to *cis*-cyclooctene during addition of dibromocarbene,⁵ fortified this explanation. However, we are cautioned in this interpretation by the relative ease for conversion of maleate esters to the thermodynamically more stable fumarate

(1) (a) Ohio State University. (b) Trinity University. (c) University of Prince Edward Island.

(2) (a) Doyle, M. P.; Terpstra, J. W.; Winter, C. H. *Tetrahedron Lett.* **1984**, *25*, 901. (b) Doyle, M. P.; Loh, K.-L.; Nishioka, L. I.; McVicker, M. B.; Liu, M. T. H. *Tetrahedron Lett.* **1986**, *27*, 4395.

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(4) Yang, N. C.; Marolewski, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 5654.

(5) (a) Dehmlow, E. V.; Kramer, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 706. (b) Professor Dehmlow has retracted the mechanistic assertion that CBr₂ is responsible for the isomerization of *trans*-cyclooctene. The CBr₂ anion is now postulated as the active species: NATO Conference on Carbenes, Fefor, Norway, September, 1987.

[†] Dedicated to Professor Maitland Jones Jr. on the occasion of his 50th birthday.