passing through the minimum point C. It may say, therefore, that this photoirradiation is apparently equivalent to the replacement of the aqueous solution of pH 7.5 (a in Figure 1) by that of pH 7.8 (b′) in the dark. Triarylmethane leucohydroxide derivatives are known to dissociate into ion pairs under ultraviolet light irradiation with production of a hydroxide ion[19] (eq 2 in Scheme II). Changes in the UV-visible absorption spectrum of the rose-PGA membrane effected by light irradiation could be correlated with the photodissociation of the rose moiety, yielding a hydroxide ion and the corresponding dye. This suggests that the pH value in the membrane can be controlled by light irradiation via the photodissociation of the rose side chains. In addition, Figure 1 shows that the conformations of the rose-PGA membrane at pH 7.5 are very sensitive to small increase in pH. These results imply that the photoinduced α-helix formation can be explained in terms of the cooperative effect between the photodissociation of the rose moiety with production of a hydroxide ion and the induced acid dissociation of L-glutamic acid moieties accompanied by the increase in pH in the membrane phase on UV irradiation (eq 3 in Scheme II). One additional important aspect should be noted; i.e., after removal of the light, CD bands at 222 and 208 nm gradually decreased again and returned to the initial value after 100 min in the dark at 25 °C, thus confirming the reversibility of the change. It was also found that the photoinduced conformational transitions of the rose-PGA membrane depend on the rose group content and pH value of the aqueous solution at which irradiation is carried out. The study of the detailed photoresponsiveness of the rose-PGA membrane is in progress.

Acknowledgment. This work was partly supported by the Grant-in-Aid from Japanese Ministry of Education, Science & Culture (No. 6075082 in 1985).

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First Two-Step 1,3-Dipolar Cycloadditions: Nonstereospecificity†

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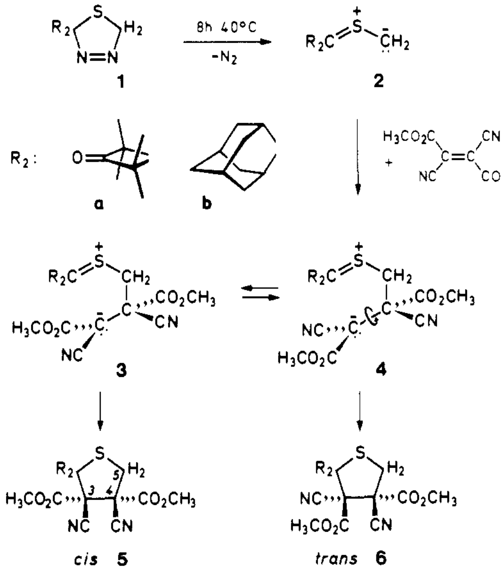
All mechanistic criteria point to the concertedness of 1,3-dipolar cycloadditions.[1] An alleged violation of stereospecificity for an azomethine imine[2] is an artifact.[3] We report on the first nonstereospecific (3 + 2) cycloadditions.

Sustmann's PMO model of concerted cycloadditions[4] envisions *two* cases in which the stepwise mechanism might compete with the concerted one. Two similar HO–LU interaction energies correspond to a minimum of rate, and a *diradical* pathway is expected, if stabilizing substituents are present.

A second limiting case is foreseen when the interaction HO-(1,3-dipole)–LU(dipolarophile) is strongly dominant in the transition state. The higher the difference in π-MO energies of reactants, the lower would be the energy contribution by the second HO–LU interaction; in the extreme it should no longer outweigh the additional entropy requirements of the concerted process. A unilateral electron flow should result, establishing *one* bond between the reactants, i.e., generation of a *zwitterionic intermediate.*[5]

Sulfur and carbon possess the same electronegativity on the Pauling scale. Absence of the more electronegative O or N atoms brings *thiocarbonyl ylides*[6] close to the high MO energies of the allyl anion, electronic prototype of 1,3-dipoles. An aliphatic thiocarbonyl ylide and an ethylene derivative bearing four electron-attracting substituents offer a reactant pair with extremely different MO energies.

Nitrogen evolution from the spiro-1,3,4-thiadiazoline **1a**[7,8] in THF furnished 2,2,4,4-tetramethylcyclobutan-1-one-3-thione *S*-methylide (**2a**) which combined in situ with dimethyl 2,3-dicyanofumarate to give the *cis,trans-isomeric* cycloadducts **5a** and **6a**;[9] the yield of 94% and the 48:52 ratio were based on ^{1}H NMR analysis. The separated adducts are stable under the reaction conditions indicating kinetic control. At no stage did the solution of 2,3-dicyanofumaric ester[10] show sign of the cis isomer. We consider rotation of the *zwitterionic intermediates* **3a** and **4a** responsible for the nonstereospecific course.



The cis,trans ratio **5a**/**6a** increases with solvent polarity. **5a** (%): CCl_4 37, toluene 36, CS_2 40, THF 48, CH_2Cl_2 47, acetone 60, CH_3CN 62. The small growth is ascribed either to increasing approach to rotational equilibrium, in accord with the steric course of (2 + 2) cycloadditions via zwitterions,[11] or to solvent dependence of the rotamer equilibrium.

The thiadiazoline **1b** eliminates N_2 with a similar half-life as **1a** (33 min vs. 25 min, xylene, 45 °C), and adamantanethione *S*-methylide (**2b**) is an active 1,3-dipole.[12] Its in situ reaction with dimethyl dicyanofumarate in THF provided the cis,trans cycloadducts **5b** and **6b**, 90%, 41:59 (57:43 in the more polar acetonitrile). Each adduct, isolated crystalline, results from kinetic control.

The cis,trans assignment in the **a** and **b** series was based on solvent dependence of the isomer ratio, higher solubility of cis vs. trans,[13] X-ray analysis of a related cis adduct, and cis,trans in-

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† Dedicated to Professor David Ginsburg on the occasion of his 65th birthday.

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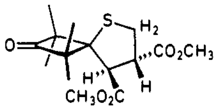
terconversions. Whereas **5b** and **6b** were stable in refluxing acetonitrile, a 44:56 equilibrium was established from both sides in benzonitrile (E_T 42.0) at 139 °C with $k_{cis} + k_{trans} = 2.0\ 10^{-5}$ s^{-1}. Isomerization was 5 times slower in the less polar *o*-dichlorobenzene (E_T 38.1). A 41:59 equilibrium was attained in 2 h at 135 °C in ethereal 2.9 M $LiClO_4$, a medium resembling a salt melt.[14] Only in this medium was a slow cis,trans isomerization of **5a** observed. All this is in harmony with cis,trans isomerization via rotation of the ring-opened zwitterions **3** and **4**. The rate difference between series **a** and **b** parallels solvolysis rates of the corresponding alkyl chlorides.[15]

Cycloaddition of **2a** to dimethyl fumarate in THF was stereospecific and afforded 99% of **7** (^1H NMR analysis); the 500-MHz spectrum did not reveal the methyl signals of **8** (<0.03%). In contrast, reaction of **1a** with dimethyl maleate[16] (3.5 equiv, neat, 8 h 40 °C) furnished 82% of **7** and **8**, 1.1:98.9, accompanied by the thiirane **9**.[8] The cis adduct **8**—alone or in presence of decomposing **1a**[17]—did not noticeably isomerize at 40 °C.



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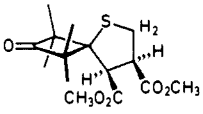

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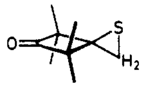

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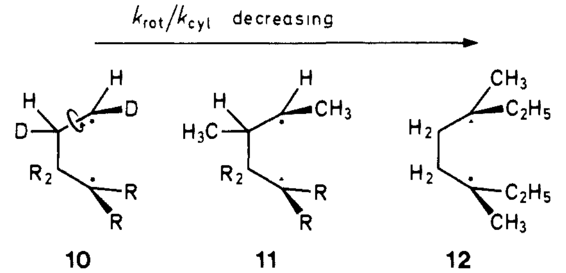
We interpret this result as minor participation of the zwitterionic pathway in the reaction of **2a** with maleic ester and no involvement in the fumaric ester case. Why is this two-step reaction less favored than for dimethyl dicyanofumarate? (1) The π-MO energies of the latter are lower than those of ethylenedicarboxylic esters. (2) *Steric shielding* of one terminus of the thiocarbonyl ylide **2** impairs *concerted* addition of fumaric and maleic esters less than that of the tetrasubstituted ethylene. The two-step mechanism, however, is less affected. The higher activity of dimethyl fumarate vs. maleate in concerted additions (early transition state) is well understood.[1] Rapid concerted addition of **2a** to dimethyl fumarate prevents occurrence of stereochemical leakage.

Is it conceivable that all 1,3-dipolar cycloadditions take the two-step course and that k_{rot}/k_{cycl} is too small as a rule to allow detection of the nonstereospecific portion? A retention of >99.997% was found for the addition of diazomethane to methyl tiglate;[18] $\Delta G_{rot} - \Delta G_{cycl}^{\ddagger} > 6.2$ kcal mol^{-1} is hard to rationalize for an intermediate.



10 **11** **12**

The ratio k_{rot}/k_{cycl} for the related tetramethylene species decreases with terminal substitution: 12 for *cis*- and *trans*-**10**, R = H;[19] large for **10**, R = F;[20] 1.3 and 0.6 for *cis*- and *trars*-**11**, R = H;[21] 4.3 and 2.0 for *cis*- and *trans*-**11**, R = F;[22] and <0.02 for **12**.[23] Thus, the deuterium-labeled methylene rotor offers the highest chance to bring to light an intermediate in cycloadditions. This was why Houk, Firestone, et al.[24] tested addition of 4-nitrobenzonitrile oxide to *cis*- and *trans*-dideuterioethylene; ≥98% retention was observed! In contrast, the nonstereospecific 1,3-cycloadditions described here concern terminally persubstituted intermediates **3** and **4**.[25] The conclusion: *normal* stereospecific 1,3-dipolar cycloadditions follow a *fundamentally different mechanism* involving no intermediates.

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[13] This heuristic criterion for dicarboxylic esters was introduced by A. von Baeyer, the discoverer of cis,trans isomerism in ring compounds: Baeyer, A. *Justus Liebigs Ann. Chem.* **1888**, *245*, 103; **1890**, *258*, 145; **1892**, *269*, 145.

[14] Pocker, Y.; Ellsworth, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 2284 and references cited therein.

[15] k_{solv} in 80% ethanol at 25 °C: 1-Methyl-1-cyclobutyl chloride 6.2 × 10^{-7} s^{-1},[a] 2-methyl-2-adamantyl chloride 6.5 × 10^{-5} s^{-1}.[b] (a) Brown, H. C.; Borkowski, M. *J. Am. Chem. Soc.* **1952**, *74*, 1894. (b) Schleyer, P. v. R.; Harris, M., private communication.

[16] Commercial dimethyl maleate contained 0.34 ± 0.03% fumarate. Fumaric ester content dropped to 0.0037% (i.e., below the analytical limit) after reaction with 12 mol % diphenyldiazomethane at 0 °C and distillation; the percentage is based on a measured competition constant of 36 for fumaric vs. maleic ester. A 0.0037% content of dimethyl fumarate in dimethyl maleate should give rise to 0.011% **7** (negligible), based on a competition constant of 52, determined separately. After the experiment, the fumaric ester content remained below the analytical limit.

[17] Test was necessary because thiocarbonyl ylides are basic; see: Mloston, G.; Huisgen, R. *Tetrahedron Lett.* **1985**, *26*, 1053.

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Carbon-Hydrogen Bond Activation through a Binuclear C-H Bond Complex

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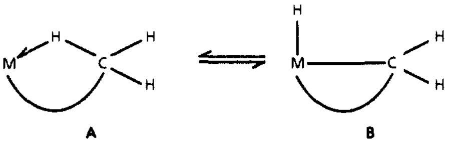
There is increasing interest in agostic interactions between a metal and a carbon-hydrogen bond.[1] This interaction is thought to be especially important in the carbon-hydrogen bond activation process (eq 1).[2] Systems that show such interactions are useful



(1)

as models to provide characteristic reaction types and characteristic spectroscopic features. We were interested in the possibility of such interactions for heteronuclear systems which could be thought of as the simplest models for mixed-metal heterogeneous catalysts[2] and systems that show strong metal-support interactions.

We recently developed an efficient route to heteronuclear μ-methylene complexes $Cp_2TiML_n(\mu\text{-}CH_2)(\mu\text{-}Cl)$.[3] The μ-chloride

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[†] Department of Chemistry, Northwestern University.

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