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Supplementary Material Available: Observed and calculated structure factor amplitudes, atomic coordinates (Table I), and anisotropic temperature factors (Table II) (19 pages). Ordering information is given on any current masthead page.

Models for Asymmetric [2 + 2] Cycloadditions

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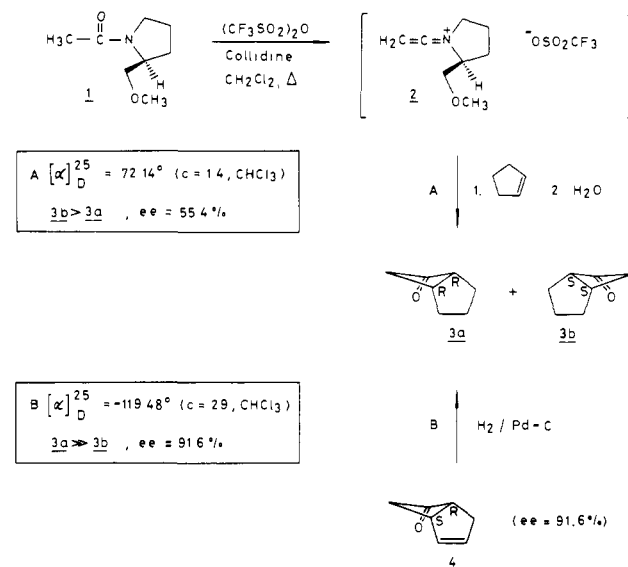
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Strained molecules have become valuable and often used intermediates in organic synthesis.¹ Thus, in the vicinal alkylation of olefins,² the key step involves the formation of a cyclobutanone by [2 + 2] cycloaddition of an olefin to a ketene or a ketene iminium salt. Then, the energy-rich four-membered ring is cleaved to give a product that is the net result of the regio- and stereoselective attachment of two carbon-chains to an olefinic double bond. Obviously, the availability of asymmetric [2 + 2] cycloadditions would considerably enhance the usefulness of this methodology. Here we report our preliminary studies on models for asymmetric [2 + 2] cycloadditions to olefins.

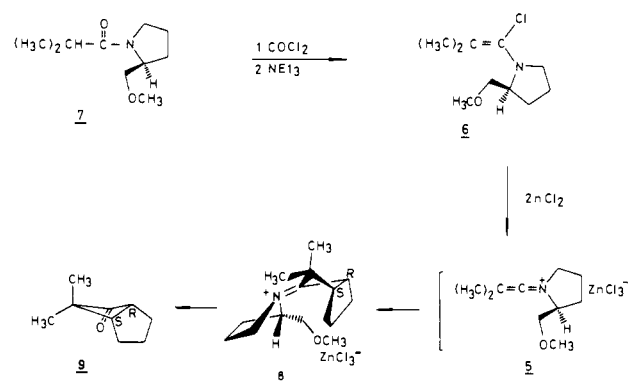
We have examined a ketene equivalent bearing the chiral inductor on the carbon atom where bonding is expected to be the most advanced in the transition state of the cycloaddition. In principle, keteneiminium salts derived from chiral amines meet the above stated structural specifications.

1-Acetyl-2-(methoxymethyl)pyrrolidine³ (**1**) ($[\alpha]_D^{25} -82.15^\circ$, c 2.0, CH_2Cl_2) was converted into the corresponding ketene iminium triflate **2** by treatment with an equivalent amount of triflic anhydride (added over a period of 6 h, CH_2Cl_2 , reflux) in the presence of collidine (1.2 equiv) according to our recently described procedure for the preparation of aldoketene iminium salts.⁴ **2** was trapped in situ by cyclopentene (~5 equiv) to give, after hydrolysis (H_2O , overnight), a 30% yield of adduct **3**: ν (CHCl_3) 1765 cm^{-1} , $[\alpha]_D^{25} +72.14^\circ$, c 1.4, CHCl_3 , (Scheme I). The use of a chiral shift reagent, $\text{Eu}(\text{hfc})_3$, at various concentrations gave complex spectra even at 200 MHz. The enantiomeric excess was determined by comparing the optical rotation of adduct **3** with that of an authentic sample of (1*R*,5*R*)-bicyclo[3.2.0]heptan-6-one

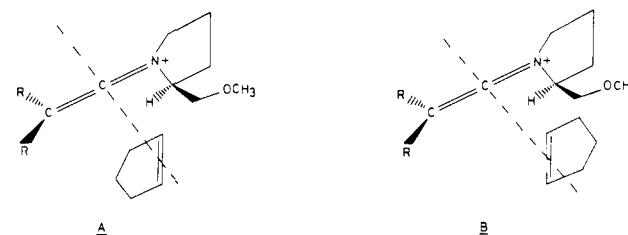
Scheme I



Scheme II



Scheme III



prepared by hydrogenation of **4** (ee = 91.6%).⁵ The enantiomeric excess in the adduct **3** was 55.4% in favor of the (1*S*,5*S*) isomer **3b**.

The diastereoselectivity was even higher for the reaction of cyclopentene with the β -disubstituted ketene iminium salt **5** (Scheme II). The precursor, α -chlorenamine **6**, was obtained from amide **7**³ according to the standard procedure.⁶ Compound **6** (~8 mM) was dissolved in dichloromethane (15 mL) and reacted with zinc chloride (14 mM) and cyclopentene (22 mM) for 16 h at 20 °C. Hydrolysis (3 N NaOH, 3 h) of the crude iminium salt **8** yielded **9** [bulb-to-bulb 145 °C (20 torr); 70% from **7**; $[\alpha]_D^{20} -170.3^\circ$, c 2.1, CHCl_3 ; $\nu_{\text{C=O}}$ 1760 cm^{-1} in CH_2Cl_2]. Cyclobutanone **9** showed a single set of NMR signals (200 MHz) in the presence of $\text{Eu}(\text{hfc})_3$, thus indicating almost (>97%) complete asymmetric induction. The nonequivalence of the two diastereoisomeric complexes with the chiral shift reagent would

(5) We thank Dr. A. H. Wadsworth and Dr. S. M. Roberts (Glaxo) for a generous gift of chiral **4**.

(6) Haveaux, B.; Dekoker, A.; Rens, M.; Sidani, A. R.; Toye, J.; Ghosez, L. *Org. Synth.* 1980, 59, 26.

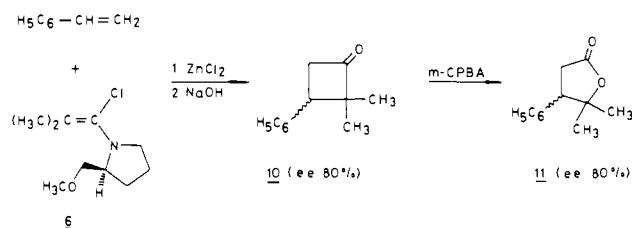
(1) For instance: (a) Ghosez, L. In "Medicinal Chemistry, V. Proceedings of the 5th International Symposium on Medicinal Chemistry"; Mathieu J., Ed.; Elsevier Scientific Publishing Company: New York, 1977. (b) Nakamura, E.; Kuwajima, I.; *J. Am. Chem. Soc.* 1977, 99, 7360. (c) Gilgen, P.; Heimgartner, H.; Schmid, H.; Hansen, M. *J. Heterocycles* 1977, 6, 143. (d) Danishefsky, S. *Acc. Chem. Res.* 1979, 12, 66. (e) Schmitz, E. *Adv. Heterocyclic Chem.* 1979, 24, 63. (f) L'Abbé, G. *Angew. Chem., Int. Ed. Engl.* 1980, 4, 276. (g) Newton, R. F.; Roberts, S. M. *Tetrahedron* 1980, 36, 2163.

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(3) Both **1** and **7** were obtained from the corresponding acyl chloride and (2*S*)-(methoxymethyl)pyrrolidine. The latter was prepared according to the described procedure: Enders, D.; Eichenauer, H. *Chem. Ber.* 1979, 112, 2933. Seebach, D.; Kalinowski, H. O.; Bastani, B.; Crass, G.; Daum, H.; Dörr, H.; Dupreez, N. P.; Ehrig, V.; Langer, W.; Nüssler, C.; Oei, H. A.; Schmidt, M. *Helv. Chim. Acta* 1977, 35, 301.

(4) Falmagne, J. B.; Escudero, J.; Sahraoui-Taleb, S.; Ghosez, L. *Angew. Chem., Int. Ed. Engl.* 1981, 93, 926.

Scheme IV



have been revealed as demonstrated by the spectrum of racemic **9** in the presence of $\text{Eu}(\text{hfc})_3$.

The structure and configuration of the adduct was established by an X-ray diffraction analysis of **8**, recrystallized ($\text{CHCl}_3\text{-Et}_2\text{O}$) as a perchlorate.⁷ The absolute configuration of **8** followed from the known chirality of the inductor, and the configuration at the ring fusion was found to be (1*R*,5*S*). Thus, in addition to providing a much higher enantiomeric excess (>97% vs. 55.4%), the reaction of cyclopentene with the β -disubstituted ketene iminium salt **5** also produces an adduct that is of *opposite configuration*⁸ to that formed from the unsubstituted ketene iminium salt **2**.

These differences are readily understood when one considers steric interactions in the two possible perpendicular approaches (Scheme III).⁹ Transition state A leads to the 1*S*,5*S* configuration in the adduct and is favored when $\text{R} = \text{H}$. When the β -hydrogen substituents of the ketene iminium salt are replaced by bulkier groups ($\text{R} = \text{CH}_3$), transition state A becomes highly hindered. The product results exclusively from transition state B and has then 1*R*,5*S* configuration at the ring junction. Moreover, from the absolute configuration of **8** it could be inferred that in transition state B the methoxymethyl group was directed toward the olefin. This suggests a stabilizing interaction between the oxygen lone pair and the developing positive charge on the olefinic carbon atoms.¹⁰

Although the mechanistic discussion presented here can only be considered tentative, the examples represent useful models for designing chiral partners for [2 + 2] cycloaddition reactions with olefins.¹¹ Preliminary studies on the reaction of **5** with acyclic olefins were quite promising (Scheme IV). Thus, cycloaddition of **5** (**6** + ZnCl_2) to styrene gave, after hydrolysis (0.1 N NaOH), cyclobutanone **10** [55% from **7**, bulb-to-bulb 125 °C (0.1 torr,

(7) The structure was solved by MULTAN 80 (Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declercq, J. P. "MULTAN 80: A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; York, England, Louvain-La-Neuve, Belgium, 1980) and refined by the SHELX 76 program (Sheldrick, G. M. "SHELX 76: Program for Crystal Structure Determination"; University of Cambridge, England, 1976) on the basis of 1111 observed reflections for which $I > 2.5\sigma(I)$. Incident radiation was $\text{Mo K}\alpha$ ($\lambda = 0.71069 \text{ \AA}$). The final R value is 0.070. Crystal data: $\text{C}_{15}\text{H}_{26}\text{O}_2\text{ClN}$; orthorhombic space group $P2_12_12_1$; cell dimensions $a = 7.178$ (2), $b = 14.035$ (4), $c = 17.331$ (6) Å ; $V = 1746.0$ (9) Å^3 ; $Z = 4$. Coordinates and molecular dimensions are available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

(8) From the sequencing rule it follows that bicyclo[3.2.0]heptan-6-ones **3a** and **9** of the same absolute configuration are described as 1*R*,5*R* for the 7-unsubstituted compound **3a** and 1*R*,5*S* for the 7-dimethyl derivative **9**.

(9) Ghosez, L.; O'Donnell, M. J. In "Pericyclic Reactions", Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 2, pp 79.

(10) (a) Meyers, A. I. *Acc. Chem. Res.* **1978**, *11*, 375. (b) Enders, D.; Eichenauer, H. *Chem. Ber.* **1979**, *112*, 2933. (c) Mukaiyama, T.; Soai, K.; Sato, T.; Shimizu, H.; Suzuki, K. *J. Am. Chem. Soc.* **1979**, *101*, 1455. (d) Kolb, M.; Barth, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 725.

(11) For earlier examples of asymmetric [2 + 2] cycloadditions to olefinic double bonds, (a) Sulfene + enamines: Paquette L. A.; Freeman, J. P.; Maiorana, S. *Tetrahedron* **1971**, *27*, 2599. (b) Allene + acrylonitrile: Baldwin, J. E.; Roy, U. V. *J. Chem. Soc., Chem. Commun.* **1969**, 1225. Baldwin, J. E.; Fleming, R. H. *Fortschr. Chem. Fortsch.* **1970**, *15*, 281. (c) Allene + ketenes: Bertrand, M.; Le Gras, J.; Goré, J. *Tetrahedron Lett.* **1972**, 2499; Ducan, W. G.; Weyler, W., Jr.; Moore, H. W. *Tetrahedron Lett.* **1973**, 4391. Bamfield, H. A.; Brook, P. R. *J. Chem. Soc., Chem. Commun.* **1974**, 171. Bamfield, H. A.; Brook, P. R.; Mc Donald, W. S. *Ibid.* **1975**, 132. (d) Allene dimerizations: Moore, W. R.; Bach, R. D.; Ozretich, T. M. *J. Am. Chem. Soc.* **1969**, *91*, 5918. (e) Olefin dimerizations: Elgavi, A.; Green, B. S.; Schmidt, G. M. *J. Ibid.* **1973**, *95*, 2058. Green, B. S.; Rabinsohn, Y.; Rejtö, M. *J. Chem. Soc., Chem. Commun.* **1975**, 313. Green B. S.; Hagler, A. T.; Rabinsohn, Y.; Rejtö, M. *Isr. J. Chem.* **1976/1977**, *15*, 124.

$[\alpha]_{\text{D}}^{25} -33.6^\circ$, c 2.3, CHCl_3 , ee = 80% by NMR, 200 MHz, CDCl_3 + $(\text{Eu}(\text{hfc})_3)$. Bayer-Villiger oxidation (*m*-CPBA, NaHCO_3) of **10**, provided a quantitative yield of the chiral lactone **11** ($[\alpha]_{\text{D}}^{20} -63.03^\circ$, c 3.3, CH_2Cl_2 , ee = 80%).

Work is now in progress to develop reagents for the asymmetric alkylation of olefins and for the enantioselective synthesis of β -lactams by [2 + 2] cycloadditions to imines.

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Registry No. **1**, 81390-99-0; **2**, 81391-01-7; **3a**, 81444-96-4; **3b**, 81444-97-5; **4**, 71155-04-9; **5**, 81391-03-9; **6**, 81391-04-0; **7**, 81391-05-1; **8**, 81391-07-3; **9**, 81444-98-6; **10**, 81391-08-4; **11**, 81391-09-5; cyclopentene, 142-29-0; styrene, 100-42-5.

Supplementary Material Available: Crystallographic data for compound **8** (2 pages). Ordering information is given on any current masthead page.

Intersystem Crossing in Styrene and Styrene Derivatives

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We report experimental results disproving the common idea that the quantum yield of intersystem crossing is extremely low for styrene and styrene derivatives. This assumption, which appears in nearly every paper dealing with photophysics of styrenes,¹ is founded on the inefficiency of large-size phenylcycloalkenes to sensitize the phosphorescence of biacetyl.² It was reinforced by the failure of several attempts to observe the phosphorescence of styrenic compounds.^{3,4} It is now obvious that the method of the sensitized phosphorescence of biacetyl is totally unsuitable for measuring ϕ_{is} in 1-phenylcyclohexene (PC6) and other large-size phenylcycloalkenes since the only metastable triplet of these compounds is a perpendicular triplet nearly degenerate in energy with the ground state of the same geometry⁵ and thus unable to sensitize the biacetyl triplet.

Observation by laser-flash photolysis of a triplet-triplet (T-T) absorption of styrenic compounds allowed us to measure ϕ_{is} by the following sequence: (a) measurements of the T-T absorption following direct excitation, (b) evaluation of the number of excited molecules from the amount of excitation energy absorbed, and (c) determination of the extinction coefficient for the T-T transition.

Styrenes, in argon-flushed cyclohexane, were excited at 249 nm by an excimer laser pulse (Lambda-Physik EMG 500, KrF, pulse characteristics: 30-100 mJ, 15-20 ns). The transient T-T absorption was measured at 325 nm, using a crossed-beam arrangement and an He-Cd laser (Liconix 4050-UV) as monitoring light source. Thus the detection system (monochromator and photomultiplier) could be placed several meters away from the sample cell in order to suppress the effects of the strong fluorescence emitted by the solution.

The decay times of the transient absorptions observed under these conditions for a number of styrenes are identical, within experimental uncertainty, with lifetimes measured by triplet

(1) See for instance ref 3b, 4, 5a, and 10.

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(3) (a) Crosby, P. M.; Dyke, J. M.; Metcalfe, J.; Rest, A. J.; Salisbury, K.; Sodeau, J. R. *J. Chem. Soc., Perkin, Trans 2* **1977**, 182-185. (b) Lyons, A. L.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *100*, 3177-3181.

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