Also observed are the stable benzosilacyclobutene **4** (14%), formed from the photochemical insertion of the silylene into the benzylic C–H bond of an ortho isopropyl group,[5] and a small amount of trapping product from the silylene **6** (13%).[10]

In the absence of a trapping agent, thawing[11] of an initially colorless 3-MP glass containing **1** results in the onset of a yellow color at 160 K, which reaches a maximum intensity at 200 K, and then disappears near 250 K. Figure 1 shows the spectroscopic changes during the warmup of the glass when monitored with a 0.1-s acquisition time. The 340-nm band due to **1** decreases with increasing temperature, while a new band due to cyclopropenylsilylene **2** (λ_{max} = 448 nm) grows in.[12] The changes in the absorption spectra follow isosbestic behavior from 170 to 190 K, indicating a clean conversion of **1** to **2**.

The identity of the yellow species is clearly established as **2** by trapping experiments (Scheme II).[13] If a 3-MP glass containing **1** is thawed, allowed to warm to 140 K (solution is colorless), and then quenched with ethanol, only one diastereomeric silacyclobutene **5a** (36%) is obtained. This result shows that silacyclobutadiene **1** is present in solution at this temperature. However, if the thawed glass is allowed to warm to 200 K (maximum yellow coloration) before the ethanol is added, the silylene trapping product **6** (22%) is formed instead. In both cases, a small amount of the insertion compound **4** (~20%) is detected as the only other volatile product.[14]

The thermal transformation of **1** to **2** succinctly shows that **2** is the thermodynamically more stable of the two species. Ab initio calculations on the parent SiC_3H_4 system indicate that cyclopropenylsilylene and silacyclobutadiene are isoenergetic at the 631-G* level.[1c] The greater stability of **2** relative to **1** is therefore likely due to differences in steric interactions between the large peripheral substituents of these species.

The kinetic stability of the cyclopropenylsilylene **2** is remarkable. The silylene is stable in 3-MP solution to 200 K before significant decomposition begins. At 238 K, the "first-order" half-life of **2** is approximately 1 h.[15] Although an ether adduct of an organosilylene has been previously shown to exist in low-temperature solutions,[16] this is the first example of a *free* silylene stable under these conditions.[17] The extreme stability of **2** can be attributed to steric protection by its two bulky substituents. This is consistent with laser flash photolysis studies which show that steric hindrance is a primary factor governing organosilylene half-lives and bimolecular reactivity.[18]

Although the general pathway for the decomposition of organosilylenes in solution involves an initial dimerization to give disilenes ($R_2Si{=}SiR_2$),[6,19] the typical π–π^* absorption band[20] for these species is not observed as the silylene **2** disappears. This implies that either **2** does not decompose through a disilene intermediate or that the disilene, if formed, is extraordinarily reactive. Efforts are currently underway to elucidate the exact mode of decomposition for **2**.

Acknowledgment. We thank the Tulane Committee on Research for support of this work. High resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility (Grant CHE-8620177).

Supplementary Material Available: Complete characterization (^{1}H NMR, GC-MS, IR, and HRMS) of new compounds and electronic absorption spectra showing photochemical generation of **2** from **3** in 3-MP, 77 K; photoisomerization of **2** to **1** in 3-MP, 77 K; and warmup of **2** at $T > 200$ K in 3-MP solution (5 pages). Ordering information is given on any current masthead page.

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(8) Only one diastereomer, **5a**, is formed by the addition of ethanol to **1**. However, under conditions of repetitive photolysis and annealing, **5a** photolyzes to give a photostationary mixture of both **5a** and **5b**.

(9) The silacyclobutenes **5a** and **5b** do not arise from the reaction of EtOH with the silylene **2**. If only 254-nm photolysis is employed, the ratio **6**/**5a**+**5b** is 1.6 as compared to 0.2 if the visible photolysis is also included. Furthermore, photolysis of **3** in 3-MP solution at 253 K gives exclusively the silylene trapped product **6**.

(10) The silylene insertion product likely arises from reaction of the silylene with neighboring ethanol molecules in the matrix, since photobleaching of the silylene is complete before thawing of the matrix.

(11) The softening point of a 3-MP glass is approximately 100 K.

(12) There is a 6-nm shift in the absorption maximum of the silylene in solution versus that of the frozen matrix. This small change may be attributed to either a nonspecific matrix effect or to a slight thermochromism of the silylene.

(13) In a typical trapping experiment, a glass consisting of 6 mg of the trisilane **3** in 9 mL of 3-MP is photolyzed at 254 nm for 45 min, followed by photolysis with visible light (>400 nm) for 60 min. The glass is slowly thawed over liquid nitrogen vapors, and 1.2 mL of anhydrous, degassed, and prechilled ethanol is added via syringe. Temperature measurements are made by a small Pt RTD affixed to the photolysis tube. Photoconversions are approximately 90% based on **3**; absolute yields of products are based on GC-MS and ^{1}H NMR with $(Me_3Si)_4Si$ as an internal standard. Yields are highly reproducible; the average of triplicate experiments are reported.

(14) The slightly lower yield of **4** in those experiments where EtOH is copresent in the glass is attributed to scavanging of the silylene **2** by neighboring EtOH molecules. This depletes the amount of **2** which may undergo further photoreaction to give **4**.

(15) Due to experimental difficulties, we are unable to clearly distinguish between first- and second-order decomposition kinetics at this time. The half-life stated is based on the assumption of first-order decomposition. The concentration of **2** for the kinetics is 9×10^{-3} M.

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(20) Disilene absorptions are generally strong and fall between 300 and 450 nm, ref 6. No new absorption bands between 300 and 800 nm are observed during the decomposition of **2**.

Stereomutation of Optically Active Poly(diphenyl-2-pyridylmethyl methacrylate)

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Polymers which manifest optical activity arising only from helicity have been of particular recent interest.[1] The existence of this phenomenon has recently been reported on several different types of synthetic polymers such as polyisocyanides,[2] polymethacrylates,[3-5] and polychloral.[6]

Optically active poly(triphenylmethyl methacrylate) (PTrMA) and poly(diphenyl-2-pyridylmethyl methacrylate) (PD2PyMA) have the unusual characteristic for vinyl polymers of the ability to maintain extended helical structures in solution.[3,4] These

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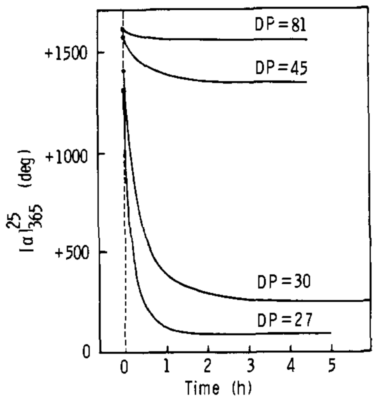
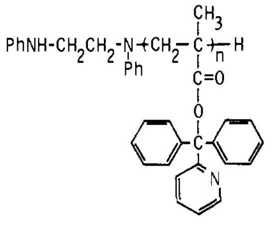


Figure 1. Change of optical rotation of PD2PyMAs of DP = 27, 30, 45, and 81 in chloroform at 60 °C.

polymers when prepared by helix-sense-selective polymerization using chiral anionic initiators exhibit entirely isotactic structures with large optical activities. We have found PD2PyMA to be conformationally less stable than PTrMA. At low degrees of polymerization (DP), in solution at 25 °C,[4b] PD2PyMA shows a slow decrease in optical activity. As has been proposed in the polymethacrylates,[5] this decrease could be ascribed to the uncoiling of the helix, that is, to a helix-coil transition.



PD2PyMA (n = 27, 30, 45, 81)

In the present work, we investigated this change of optical activity with use of PD2PyMA samples with narrow molecular weight distributions[7] and found that the polymer does not undergo a helix-coil transition but rather that a helix-to-helix transition is responsible for the loss of optical activity.

Optically active PD2PyMA was prepared by the asymmetric polymerization of the methacrylate monomer with the complex of (*S*)-(+)-2-(1-pyrrolidinylmethyl)pyrrolidine and *N*,*N*′-diphenylethylenediamine monolithium amide in toluene at −78 °C.[7] Four samples with DP = 27 (Mw/Mn = 1.04, $[\alpha]_{365}^{25}$ +1325° in $CHCl_3$-2,2,2-trifluoroethanol (90/10)), DP = 30 (Mw/Mn = 1.08, $[\alpha]_{365}^{25}$ +1406°), DP = 45 (Mw/Mn = 1.13, $[\alpha]_{365}^{25}$ +1651°), and DP = 81 (Mw/Mn = 1.12, $[\alpha]_{365}^{25}$ +1675°) were used for this work.[8]

Figure 1 shows the change of optical rotation of the four PD2PyMA samples in chloroform at 60 °C. The rotation of the polymers of lower DP changed remarkably, and the final values depended greatly on DP. The polymers of higher DP appear to be far more conformationally stable at 60 °C although some lowering of specific rotation is observed here as well. The GPC analysis of these samples suggests that the polymers of DP = 45 and 81 associate in chloroform.[7] At this time, we are uncertain if their resistance to change of their optical activity is associated with this aggregation.

The polymer (DP = 27) was quickly dissolved in $CDCl_3$ in about 10 min at room temperature, and ^1H NMR (JEOL GX-500, 500 MHz) was measured at 60 °C. The spectra were taken between 3 min and 3 h. No clear difference was observed during this time. The spectra always showed rather sharp peaks at δ 0.49 ppm due to CH_3, at 1.67 and 2.49 ppm due to CH_2, and at 6.1–8.6 ppm due to the aromatic groups.[9] These results offer no conflict to the suggestion that the polymer does not change its conformational properties during the stereomutation.

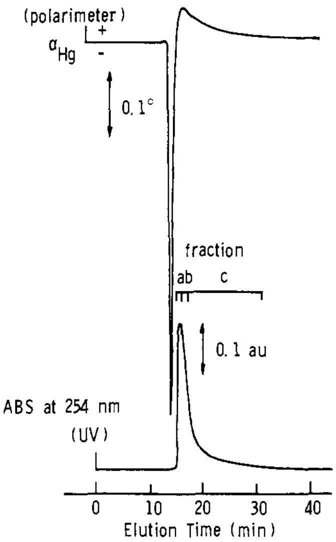


Figure 2. Optical resolution of PD2PyMA (DP = 30, $[\alpha]_{365}^{25}$ +389°) on a (+)-PTrMA column. UV (1.0 mm-cell) and polarimetric (5 × 0.2 (i.d.) cm cell) detectors were connected in series (column, 50 × 0.72 (i.d.) cm; eluent, $CHCl_3$; flow rate, 1.0 mL/min; temperature, 15 °C; amount of sample, 4 mg).

Important information was obtained by chromatographic optical resolution of the polymer (DP = 30) which had undergone stereomutation (Figure 2). Optically active (+)-PTrMA chemically bonded to silica gel was used as the chiral stationary phase for the high performance liquid chromatography (HPLC) experiment.[10] The UV detector showed only one peak, but the polarimetric detector revealed that the initially eluted part was levorotatory and the latter part dextrotatory. When (−)-PTrMA was used as the stationary phase, the order of elution was reversed; dextrotatory polymer eluted first and the levorotatory polymer second. The same results were obtained for the polymer of DP = 27. The polymers eluted from the chiral column were fractionated into three parts as shown in Figure 2. Fraction a showed specific rotation $[\alpha]_{365}^{25}$ −532°, and fraction c $[\alpha]_{365}^{25}$ +1138°. The low resolution of the chromatographic experiment suggests these are not maximum values. The CD spectral patterns of these fractions were similar but not identical with that of the PD2PyMA of higher optical rotation.[11] These results indicate that the PD2PyMA after change of optical activity consisted of (+)- and (−)-PD2PyMAs which had maintained a helical conformation comparable to the original PD2PyMA of high optical rotation. The polymers obtained on chiral chromatography, as described above, changed their optical rotation again; fraction a, which was levorotatory, reached $[\alpha]_{365}^{25}$ +158°, while fraction c, which was dextrotatory, reached $[\alpha]_{365}^{25}$ +322°.[12] These could also be

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(8) Elemental analysis of PD2PyMA of DP = 27. Calcd for $C_{14}H_{15}N_2$-$(C_{22}H_{19}NO_2)_{26}$-H: C, 80.20; H, 5.85; N, 4.47. Found: C, 80.44; H, 6.02; N, 4.29. DP was determined by GPC measurement of the PMMA derived from PD2PyMA. The ^1H NMR spectra of the PMMA revealed that the PMMA was highly isotactic (>98%).

(9) The intensity ratio of CH_3/CH_2/aromatic was approximately 3:2:19, and several unknown minor peaks which may be due to the terminal groups of the polymer or helix-reversal points were also observed. Relatively higher intensity of aromatic protons may be due to the fact that the above CH_3 and CH_2 are assigned to only the units in the rather long helix but not to the units near chain ends and helix-reversal points.

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(11) The CD spectrum of PD2PyMA ($[\alpha]_{365}^{25}$ +1325°) in THF showed the peaks at 230 nm ($\Delta\epsilon$ +17.7) and 260 nm ($\Delta\epsilon$ +3.35) and that of the PD2PyMA ($[\alpha]_{365}^{25}$ +90°) after stereomutation at 230 nm ($\Delta\epsilon$ +0.66) and 252 nm ($\Delta\epsilon$ −0.12); PD2PyMA of $[\alpha]_{365}^{25}$ −532° showed the peaks at 230 nm ($\Delta\epsilon$ −5.85) and 260 nm ($\Delta\epsilon$ −1.18).

(12) The reason the rotation does not go to zero likely arises from the fact that the polymer of low DP, presumably the DP 27 and 30 studied here, is configurationally chiral because of different chain ends. It follows that the left- and right-handed helical conformations are related as diastereomers which could reasonably lead to a nonzero optical rotation at 365 nm at equilibrium. The discrepancy between two values (+158° and +322°) may arise from fractionation of the polymer according to molecular weight as well as helicity.

resolved into (+)- and (−)-fractions in the same manner as in Figure 2.

The results presented here clearly indicate that the loss of the optical rotation of PD2PyMA is not due to a helix-coil transition, since the chiral chromatography could not be expected to restore the helical conformation, but rather to a transition between helical states. Although experiments are underway to explore the precise conformational motions attending the helix reversal, the chiral chromatography experiment suggests that at equilibrium the sample is a mixture of diastereomeric helical chains.

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Ruthenium-Catalyzed Aldol and Michael Reactions of Activated Nitriles

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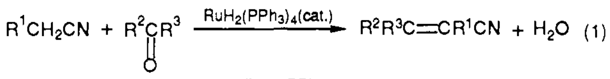
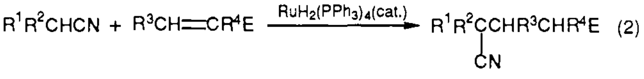
Transition-metal complex-catalyzed aldol and Michael reactions are one of the most attractive methods for selective carbon–carbon bond formation. However, the reported methods are limited to a few cases which involve rhodium-[1] and gold-[2] catalyzed aldol reactions. As part of programs aimed at the development of a method for activation of C–H bonds adjacent to hetero atoms with transition-metal complexes,[3] we have been investigating the activation of nitriles. We wish to report novel chemo- and stereoselective ruthenium-catalyzed aldol (eq 1) and Michael reactions (eq 2) of activated nitriles under mild and neutral conditions.



$$\mathrm{R^1CH_2CN + R^2C(=O)R^3 \xrightarrow{RuH_2(PPh_3)_4(cat.)} R^2R^3C{=}CR^1CN + H_2O} \quad (1)$$



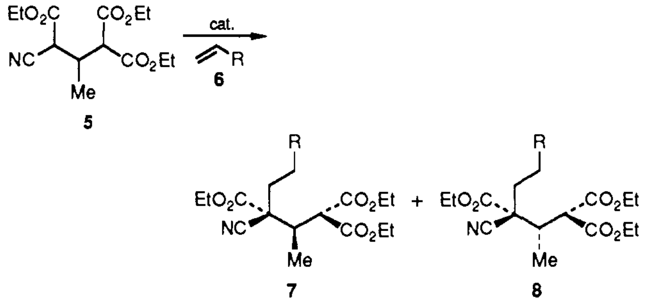
$$\mathrm{R^1R^2CHCN + R^3CH{=}CR^4E \xrightarrow{RuH_2(PPh_3)_4(cat.)} R^1R^2C(CN)CHR^3CHR^4E} \quad (2)$$

$\mathrm{RuH_2(PPh_3)_4}$ has proved to be the most effective catalyst for the carbon–carbon bond formations. Nitriles undergo condensation with various carbonyl compounds at room temperature to give α,β-unsaturated nitriles. Representative results of the condensation are shown in Table I. The stereochemistry of the product olefins was determined to be E (entries 1 and 2) by means of NMR spectral analyses.[4] The reactions of less reactive nitriles such as benzyl cyanide are enhanced remarkably by addition of a catalytic amount of bidentate phosphines such as 1,2-bis(diphenylphosphino)ethane (dppe) (entry 4), although addition of 1,3-bis(diphenylphosphino)propane (dppp) retards the reactions.[5]

Michael addition of nitriles to alkenes proceeds efficiently at room temperature under neutral conditions. Representative results are shown in Table I. The reaction of α,β-unsaturated carbonyl compounds gives Michael adducts without contamination by the corresponding aldol products (entries 5 and 6).

One important feature of the present reaction is the chemoselective reaction of nitriles with either carbonyl compounds or Michael acceptors in the presence of other active methylene compounds. Indeed, the $\mathrm{RuH_2(PPh_3)_4}$-catalyzed reaction of benzaldehyde with an equimolar mixture of ethyl cyanoacetate (**3**, $pK_a > 9$) and acetylacetone, which has a similar pK_a value ($pK_a = 9.0$),[6] gave ethyl (*E*)-2-cyano-3-phenylpropanoate (**4**, 80%) exclusively. In contrast, the reaction of benzaldehyde with the same mixture in the presence of a conventional base such as KOH and $\mathrm{AcONH_4}$ gave a mixture (3:1) of **4** and 3-benzylidene-2,4-pentanedione. Similarly, the treatment of crotononitrile with an equimolar mixture of **3** and nitroethane ($pK_a = 8.6$) gave ethyl 2,4-dicyano-3-methylbutanoate chemoselectively.

The utility of the present method has also been indicated by the high diastereoselectivity of the Michael additions. When cyano ester **5**, which can be readily obtained by the catalytic Michael addition of diethyl ethylidenemalonate to ethyl cyanoacetate (90% yield), was allowed to react with methyl vinyl ketone (**6a**) in the presence of $\mathrm{RuH_2(PPh_3)_4}$ catalyst, adduct **7a** was obtained with high diastereoselectivity (**7a**/**8a** = 97/3) in 72% yield. These are quite rare examples of catalytic diastereoselective Michael reactions.[7] Similar reaction of **5** with acrylonitrile (**6b**) gave **7b** selectively (**7b**/**8b** = 90/10, 40%). In contrast, the same reaction of **5** with **6a** or **6b** in the presence of a base catalyst such as Triton B (*N*-benzyltrimethylammonium hydroxide) gave **7** and **8** nonselectively (**7a**/**8a** = 75/25, 82%; **7b**/**8b** = 44/56, 37%). It is noteworthy that **7a** was obtained conveniently by one-pot, ruthenium-catalyzed reaction of diethyl ethylidenemalonate with ethyl cyanoacetate and subsequently with **6a** (**7a**/**8a** = 97/3, 78% yield). The present reaction can be also applied to the stereoselective construction of cyclohexanes by Michael-aldol ring closure. Typically, the ruthenium-catalyzed reaction of **5** with acrolein gave **9** selectively (**9**/**10** = 95/5) in 54% yield.[8] In



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[4] The stereochemistry of these alkenes was determined by ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR analysis. **1**: ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 7.66 (t, *J* = 7.8 Hz, 1 H, $\mathrm{CH{=}C(CN)CO_2Et}$); ^{13}C NMR ($\mathrm{CDCl_3}$, δ) 163.6 ($C^3$), 110.0 ($C^2$). **2**: ^{1}H NMR ($\mathrm{CDCl_3}$, δ) 8.20 (s, 1 H, $\mathrm{CH{=}C(CN)CO_2Et}$); ^{13}C NMR ($\mathrm{CDCl_3}$, δ) 155.9 ($C^3$), 98.9 ($C^2$). See: Hayashi, T. *J. Org. Chem.* **1966**, *31*, 3253.

[5] Ruthenium-catalyzed Michael addition of crotononitrile to ethyl cyanoacetate (at 20 °C) to give 2,4-dicyano-2-methylbutanoate (conversion 29%, yield 89%) was enhanced by addition of 1,4-bis(diphenylphosphino)butane (dppb) (52%, 99%) and retarded by addition of dppe (9%, 99%).

[6] Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

[7] Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Chem. Lett.* **1986**, 1017, 1817, **1987**, 743. For a review of noncatalytic diastereoselective reactions, see: Tomioka, K.; Koga, K. In *Asymmetric Synthesis*; Morrision, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, p 201.

[8] The stereochemistry of **9** and **10** was determined by NMR analysis: ^{1}H NMR signals were assigned through the use of ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and ^{1}H difference NOE experiments. The stereochemical assignments were determined based on ^{1}H difference NOE experiments and long-range deshielding by the cyano group (H^4(eq) signal of **9**; H^2(ax) and H^4(ax) signals of **10**). Typical spectral data are as follows. **9**: ^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) δ 1.93–2.00 (m, 2 H, H^4(ax), H^5(eq)), 2.16–2.30 (m, 1 H, H^5(ax)), 2.46 (ddd, *J* = 12.1, 5.5, 4.8 Hz, 1 H, H^4(eq)), 2.92 (br q, *J* = 7.1 Hz, 1 H, H^2(ax)), 4.11 (br, 1 H, H^6(ax)); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.9 MHz) δ 119.7 (CN), 73.0 ($\mathrm{C^6OH}$(eq)), 41.7 ($C^2\mathrm{CH_3}$(eq)). **10**: ^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz) δ 1.82–1.99 (m, 1 H, H^5(eq)), 2.10–2.22 (m, 2 H, H^4(eq), H^5(ax)), 2.23–2.36 (m, 1 H, H^4(ax)), 3.20 (q, *J* = 7.3 Hz, 1 H, H^2(ax)), 4.41 (br, 1 H, H^6(ax)); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.9 MHz) δ 119.6 (CN), 68.1 ($\mathrm{C^6OH}$(ax)), 37.0 ($C^2\mathrm{CH_3}$(eq)).

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