J = 2.3, 18.1 Hz, 1 H), 5.22 (dd, J = 2.3, 10.5 Hz, 1 H), 2.37 (m, 2 H), 2.12 (s, 3 H), 1.91–0.80 (m, 11 H), 0.93 (s, 9 H), and 0.14 and 0.12 (2 s, combined 6 H); ^{13}C NMR ($CDCl_3$) δ 209.3, 136.8, 116.6, 86.1, 42.6, 41.0, 32.7, 29.5, 28.1, 26.3, 24.4, 23.9, 23.0, 18.3, and −5.5. Anal. Calcd for $C_{18}H_{34}O_3Si$: C, 66.2; H, 10.4. Found: C, 65.87; H, 10.25.

1-Hydroperoxy-2-(2-oxobut-4-yl)cyclohexanecarboxaldehyde *tert*-Butyldimethylsilyl Ether (7). The olefin **6** (289.5 mg, 0.916 mmol) was dissolved in methanol (10 mL) and cooled to −78 °C, and ozone was passed into the resulting solution until it turned blue. Dimethyl sulfide (1.0 mL) was added, and the resulting solution was warmed to room temperature, stirred for 7 h, and then concentrated under reduced pressure. The residue was chromatographed on silica gel (15 g) with 15:5:80 ethyl acetate–methylene chloride–hexane. The fractions containing the desired material were combined and concentrated under reduced pressure to yield 226.6 mg (75%) of an unstable, clear, colorless oil: IR (neat) 3550 (w), 2940 (s), 2870 (s), and 1720 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.68 (s, 1 H) and minor isomer 9.93 (s), 2.07 (s, 3 H), 2.1–0.9 (m, 13 H), 0.88 (s, 9 H), and 0.12 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 207.7, 203.9, 89.4, 41.9, 39.5, 29.6, 27.3, 26.3, 26.1, 25.6, 22.6, 21.3, 18.2, and −5.8. Integration of the aldehyde peaks showed at most 10% of the minor isomer.

Cyclization of 1-Hydroperoxy-2-(2-oxobut-4-yl)cyclohexanecarboxaldehyde *tert*-Butyldimethylsilyl Ether. Preparation of 8. The aldehyde **7** (35.3 mg, 0.107 mmol) was dissolved in anhydrous THF (5 mL), and tetra-*n*-butylammonium fluoride (0.2 mL of a 1 M solution in THF, 0.2 mmol) was added. After 3 h at room temperature, the resulting solution was concentrated under reduced pressure and chromatographed on silica gel (10 g) with 30:70 ethyl acetate–hexane. The fractions containing the major product were combined to yield 12.3 mg (57%) of a white, crystalline solid: ^{1}H NMR (pyridine-d_5) δ 5.16 (br s, 2 H, OH), (4.24 (d, J = 5.4 Hz, 1 H) and minor isomers 4.62 (d, J = 5.6 Hz) and 4.08 (d, J = 5.4 Hz),[9] 2.51–0.50 (m, 15 H including 1.42 (s)); ^{13}C NMR (pyridine-d_5) δ 104.4 (s), 85.9 (s), 70.9 (d), 43.6 (d), 37.7 (d), 34.8 (t), 31.9 (t), 27.2 (t), 25.2 (t), 24.6 (q), and 22.0 (t). Crystal data: needles suitable for X-ray diffraction studies were obtained by recrystallization from acetone. Single crystals are monoclinic; space group $P2_1/n$ (no. 14); a = 11.444 (3) Å, b = 5.813 (4) Å, c = 16.351 (3) Å, β = 107.49 (3)°, Z = 4. Three dimensional X-ray diffraction data were collected for 2022 reflections of which 595 were independent, having $4° < 2\theta > 45°$ on a computer-controlled Enraf-Nonius CAD4 X-ray diffractometer with graphite monochromated Mo Kα radiation (λ 0.7107 Å) and $\theta - 2\theta$ scanning technique. The nonhydrogen atoms were located by using the direct methods program MULTAN. Hydrogen atoms were located from a difference Fourier map, and the resulting structure converged at R = 0.035. Tables of the final atomic positional parameters, the atomic thermal parameters, and the bond distances and angles may be found in the supplementary material.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The 300-MHz NMR was partially supported by Grant PCM8115599 from the National Science Foundation.

Registry No. **3**, 96165-23-0; **4**, 96165-24-1; **5**, 96165-25-2; **6**, 96165-26-3; **7**, 96165-27-4; **8**, 96165-28-5; methyl 3-(2-ethylidenecyclohex-1-yl)propionate, 96165-21-8; 3-(2-ethylidenecyclohex-1-yl)propionic acid, 96165-22-9; methyl 3-(2-oxocyclohex-2-yl)propionate, 10407-33-7.

Supplementary Material Available: Proton NMR spectra of **8** at 90 and 300 MHz, carbon spectrum of **8** at 22.5 MHz, tables of positional parameters, temperature factors, bond angles, and distances for **8** as determined by single-crystal X-ray diffraction (9 pages). Ordering information is given on any current masthead page.

Novel Smiles-Type Rearrangement in a Thienamycin Derivative

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Since the discovery of thienamycin,[1] chemical modifications[2] of its C-2 side chain have been investigated extensively to improve its chemical stability[2a] and decrease its metabolism by renal dehydropeptidase I.[3] We have studied the reactivity of the vinyl sulfide system,[4] a moiety of thienamycin, using the thienamycin model compound **1**,[4] and applied the results thus obtained for modification at the 2-position of thienamycin. This report describes the synthesis of the C-2 aza-substituted 1-carbapenem derivative **9** by novel Smiles-type rearrangement.

In the course of studies on the vinyl sulfide system,[4] we became interested in the chemistry of the vinyl sulfonium salt[5] **2**. The sulfide **1** was treated with 1.5 equiv of methyl iodide (MeI) in the presence of 1.2 equiv of silver tetrafluoroborate[6] in nitromethane to afford the sulfonium salt **2**, which was further treated without purification with 1.0 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dimethyl sulfoxide (Me_2SO) to give the rearranged product **4** in 50% yield from compound **1** (see Scheme I). The structure of compound **4** was supported by NMR, IR, and mass spectra. The NMR spectrum of **4** exhibited a singlet at δ 2.12 (3 H) assignable to the SMe group and a multiplet due to the methylene protons (NCH_2) at δ 3.66–3.83, which was shifted to lower field, in contrast to that of the starting material **1** at δ 3.39. The similar shift to lower field proved to be a common characteristic of all the rearranged products reported here. Compound **4** was assumed to be produced via the intermediate **3** formed by the intramolecular Michael addition,[7] followed by β-elimination[8] as shown in

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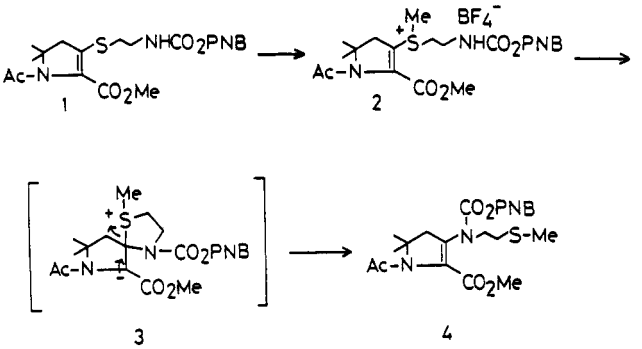
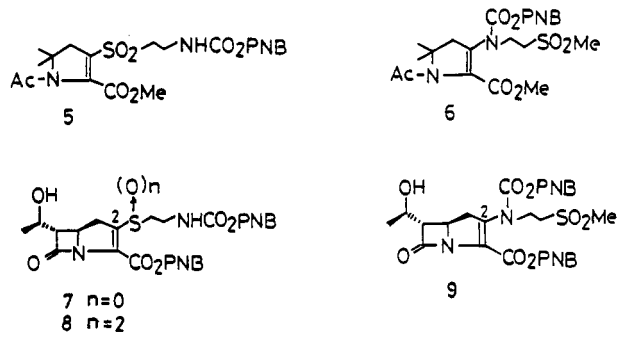
Scheme I[a]



[a] PNB = *p*-nitrobenzyl.

Chart I



Scheme I. This reaction is a new example of the Smiles-type rearrangement[9] in which the intramolecular nucleophilic attack occurs on a vinylic carbon other than an aromatic carbon.

This reaction was then extended to the sulfone **5** (Chart I). Oxidation of **1** with 2.2 equiv of *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 gave the sulfone **5** in 66% yield. In the reaction of the sulfone **5** with DBU in Me_2SO or *N*,*N*-dimethylformamide (DMF), the Smiles-type rearrangement was not observed and the starting material **5** was recovered. However, when the sulfone **5** was treated with a stronger base such as sodium hydride (NaH) in DMF, the rearranged compound **6** was obtained in 52% yield after methylation of the resulting sulfinic acid with MeI.[8b,c]

The success of the Smiles-type rearrangement of the thienamycin model compounds **2** and **5** prompted us to apply this methodology to the thienamycin derivatives **7** and **8**. First, the bis-protected thienamycin **7**[10] was treated with MeI and $AgBF_4$ in nitromethane to result in the decomposition of the β-lactam ring. Then, the thienamycin sulfone **8**[11] was prepared for the trial of the Smiles-type rearrangement. When the sulfone **8** was treated with 1.0 equiv of DBU[12] in the presence of 4.0 equiv of MeI in DMF at room temperature for 15 min, the rearranged product **9**[13] was obtained in 14% yield as an amorphous powder after purification by reverse-phase HPLC.

In summary, a new type of the C-2 aza-substituted 1-carbapenem derivative **9** was synthesized by novel Smiles-type rearrangement of the thienamycin sulfone **8**. To our knowledge, the compound **9** is the first C-2 aza-substituted 1-carbapenem derivative in the literature.

Experimental Section

General Methods. Melting points were taken on a Yanagimoto melting point apparatus and uncorrected. Infrared spectra (IR) were recorded on a Hitachi 260-30 infrared spectrophotometer. Proton NMR spectra were obtained on a Hitachi R-40 (90 MHz) or a Varian XL-200 (200 MHz) spectrometer. Chemical shifts are reported in parts per million relative to tetramethylsilane (δ units). Mass spectra were recorded on a JEOL JMS-01SG-2 or a JMS-D300 mass spectrometer. HPLC purifications were performed on a Waters ALC/GPC Model 201.

1-Acetyl-5,5-dimethyl-2-(methoxycarbonyl)-3-[methyl-(2-[([(*p*-nitrobenzyl)oxy]carbonyl)amino]ethyl)sulfonio]-2-pyrroline Tetrafluoroborate (2). To a stirred solution of **1** (90 mg, 0.2 mmol) in nitromethane (3 mL) were added MeI (43 mg, 0.3 mmol) and $AgBF_4$ (50 mg, 0.25 mmol) at room temperature. After being stirred for 1.5 h, the reaction mixture was filtered. The filtrate was concentrated and the residue was washed with benzene to give **2** as a syrup, which was used for the next reaction without further purification: ^1H NMR (Me_2SO-d_6, 90 MHz) δ 1.59 (6 H, s, 2 × CH_3), 2.18 (3 H, s, CH_3CO), 3.04 (2 H, s, C_4H_2), 3.14 (3 H, s, SCH_3), 3.43–3.75 (4 H, m, SCH_2CH_2N), 3.83 (3 H, s, CO_2CH_3), 5.23 (2 H, s, NCO_2CH_2 Ar), 7.64 (2 H, d, J = 9 Hz, Ar H), 8.25 (2 H, d, J = 9 Hz, Ar H).

1-Acetyl-5,5-dimethyl-2-(methoxycarbonyl)-3-[*N*-[2-(methylthio)ethyl]([(*p*-nitrobenzyl)oxy]carbonyl)-amino]-2-pyrroline (4). DBU (30 mg, 0.2 mmol) was added to a solution of **2** (prepared from 90 mg of the compound **1**) in Me_2SO at room temperature. After stirring for 0.5 h, the reaction mixture was diluted with ethyl acetate and washed with 1 M KH_2PO_4 solution. The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by preparative TLC on Merck silica gel 60 F254 plate using benzene–ethyl acetate (1:1) to afford 50 mg (50%) of **4** as an oil: IR ($CHCl_3$) 1710, 1635 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.55 (6 H, s, 2 × CH_3), 2.07 (3 H, s, CH_3CO), 2.12 (3 H, s, SCH_3), 2.69 (2 H, t, J = 6 Hz, SCH_2), 2.70 (2 H, s, C_4H_2), 3.66–3.83 (2 H, m, NCH_2), 3.78 (3 H, s, CO_2CH_3), 5.25 (2 H, s, NCO_2CH_2 Ar), 7.45 (2 H, d, J = 9 Hz, Ar H), 8.25 (2 H, d, J = 9 Hz, Ar H); Anal. Calcd for $C_{21}H_{27}N_3O_7S$: C, 54.18; H, 5.85; N, 9.03. Found: C, 53.73; H, 5.65; N, 8.90; exact mass calcd for $C_{21}H_{27}N_3O_7S$ 465.1567, found 465.1535.

1-Acetyl-5,5-dimethyl-2-(methoxycarbonyl)-3-[(2-[([(*p*-nitrobenzyl)oxy]carbonyl)amino]ethyl)sulfonyl]-2-pyrroline (5). A solution of **1** (451 mg, 1 mmol) and *m*-CPBA (450 mg, 2.2 mmol) in CH_2Cl_2 (15 mL) was stirred at 0 °C for 2 h. The reaction mixture was diluted with CH_2Cl_2, washed with 5% $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (15 g) using benzene–ethyl acetate (1:1) to give 320 mg (66%) of **5** as a colorless oil, which crystallized on standing at room temperature: mp 126–128 °C; IR (KBr) 1740, 1720, 1670 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.61 (6 H, s, 2 × CH_3), 2.21 (3 H, s, CH_3CO), 2.89 (2 H, s, C_4H_2), 3.2–3.4 (2 H, m, SO_2CH_2), 3.6–3.8 (2 H, m, NCH_2), 3.92 (3 H, s, CO_2CH_3), 5.23 (2 H, s, NCO_2CH_2 Ar), 5.9 (1 H, m, NH), 7.54 (2 H, d, J = 9 Hz, Ar H), 8.24 (2 H, d, J = 9 Hz, Ar H); Anal. Calcd for $C_{20}H_{25}N_3O_9S$: C, 49.68; H, 5.21; N, 8.69. Found: C, 49.39; H, 5.12; N, 8.45.

1-Acetyl-5,5-dimethyl-2-(methoxycarbonyl)-3-[[2-(methylsulfonyl)ethyl]([(*p*-nitrobenzyl)oxy]carbonyl)-amino]-2-pyrroline (6). To a stirred solution of **5** (48 mg, 0.1 mmol) in DMF (1 mL) was added NaH (5 mg, 0.1 mol) at −30 °C under argon, and then the reaction mixture was allowed to warm to −15 °C. After stirring for 1.5 h at the same temperature, MeI (3 drops) was added to the mixture and stirring was continued for an additional 0.5 h. The reaction mixture was diluted with ethyl acetate, washed with 0.5 N HCl and water, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (3 g) using ethyl acetate to give 26 mg (52%) of **6** as a pale yellow foam: IR ($CHCl_3$) 1715, 1640, 1520, 1350, 1310, 1135 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.55 (6 H, s, 2 × CH_3), 2.08 (3 H,

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(11) The sulfone **8** was prepared according to the method described in Merck's patent: *Jpn. Kokai Tokkyo Koho* JP79-52092; *Chem. Abstr.* **1980**, *92*, 41785c.

(12) Attempted rearrangement of **8** using NaH as a base resulted in the decomposition of the β-lactam ring.

(13) We confirmed that the rearranged product **9** was different from the corresponding *N*-methyl analogue of the starting material **8**, which was synthesized by another method.

s, CH_3CO), 2.69 (2 H, s, C_4H_2), 2.97 (3 H, s, SO_2CH_3), 3.38 (2 H, t, J = 6 Hz, SO_2CH_2), 3.73 (3 H, s, CO_2CH_3), 3.96 (2 H, t, J = 6 Hz, NCH_2), 5.23 (2 H, s, NCO_2CH_2 Ar), 7.52 (2 H, d, J = 9 Hz, Ar H), 8.23 (2 H, d, J = 9 Hz, Ar H); Anal. Calcd for $C_{21}H_{27}N_3O_9S$: C, 50.69; H, 5.47; N, 8.45. Found: C, 50.38; H, 5.42; N, 8.21. Mass spectrum (FD), m/e 497 (M^+).

***p*-Nitrobenzyl (5*R*,6*S*)-6-[(*R*)-1-Hydroxyethyl]-2-([2-(([(*p*-nitrobenzyl)oxy]carbonyl)amino)ethyl]sulfonyl)carbapen-2-em-3-carboxylate (8).** To a stirred solution of 7 (400 mg, 0.68 mmol) in THF (20 mL) was added *m*-CPBA (298 mg, 1.50 mmol) at 0 °C under argon. After stirring for 15 min at the same temperature, Na_2HPO_4 (237 mg, 1.69 mmol) was added to the mixture. The reaction mixture was allowed to warm to room temperature and stirring was continued for 5 h at room temperature. The reaction mixture was diluted with ethyl acetate, washed with 5% $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The residue was purified by HPLC [Nucleosil $5C_{18}$ column 20 mm × 30 cm, acetonitrile–water (2:1)] to afford 130 mg (31%) of 8 as a colorless powder: mp 79–92 °C dec; IR (KBr) 1785, 1720, 1700 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.32 (3 H, d, J = 6 Hz, CH_3), 3.1–3.4 (2 H, m, C_1H_2), 3.4–3.6 (3 H, m, SO_2CH_2 and C_6H), 3.6–3.8 (2 H, m, NCH_2), 4.28 (1 H, m, C_8H), 4.42 (1 H, m, C_5H), 5.20 and 5.29 (2 H, ABq, J = 14 Hz, CO_2CH_2 Ar), 5.43 and 5.52 (2 H, ABq, J = 14 Hz, CO_2CH_2 Ar), 5.66 (1 H, m, NH), 7.56 (2 H, d, J = 9 Hz, Ar H), 7.66 (2 H, d, J = 9 Hz, Ar H), 8.28 (2 H, d, J = 9 Hz, Ar H), 8.30 (2 H, d, J = 9 Hz, Ar H). Anal. Calcd for $C_{26}H_{26}N_4O_{12}S \cdot {}^1/_2H_2O$: C, 49.76; H, 4.34; N, 8.93. Found: C, 49.45; H, 4.23; N, 8.66.

***p*-Nitrobenzyl (5*R*,6*S*)-6-[(*R*)-1-Hydroxyethyl]-2-[[2-(methylsulfonyl)ethyl]([(*p*-nitrobenzyl)oxy]carbonyl)-amino]carbapen-2-em-3-carboxylate (9).** To a stirred solution of 8 (31 mg, 0.05 mmol) in DMF (0.5 mL) was added DBU (8 mg, 0.05 mmol) at room temperature under argon. After being stirred for 15 min, the reaction mixture was diluted with ethyl acetate, washed with 0.5 N HCl and water, dried ($MgSO_4$), and concentrated. The residue was purified by HPLC [Nucleosil $5C_{18}$ column 20 mm × 30 cm, acetonitrile–water (3:1)] to give 4 mg (14%) of 9 as a colorless powder: mp 70–78 °C dec; IR (KBr) 1780, 1720, 1520, 1350, 1300, 1130 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.38 (3 H, d, J = 6 Hz, CH_3), 2.96 (3 H, s, SO_2CH_3), 3.16 (1 H, dd, J = 10, 20 Hz, $C_{1a}H$), 3.26 (1 H, dd, J = 8, 20 Hz, $C_{1b}H$), 3.35 (1 H, dd, J = 2.4, 6.4 Hz, C_6H), 3.40 (2 H, m, CH_2SO_2), 4.02 (2 H, m, NCH_2), 4.2–4.4 (2 H, m, C_5H and C_8H), 5.22 (2 H, s, NCO_2CH_2Ar), 5.18 and 5.36 (2 H, ABq, J = 14 Hz, CO_2CH_2 Ar), 7.42 (2 H, d, J = 9 Hz, Ar H), 7.63 (2 H, d, J = 9 Hz, Ar H), 8.22 (4 H, d, J = 9 Hz, Ar H). Anal. Calcd for $C_{27}H_{28}N_4O_{12}S$: C, 51.26; H, 4.46; N, 8.86. Found: C, 50.82; H, 4.34; N, 9.34. Mass spectrum (FD), m/e 632 (M^+), 630, 586, 546.

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A Convenient Preparation of Cyclopentadiene from Its Dimer

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Cyclopentadiene has been prepared on a laboratory scale by thermolysis of dicyclopentadiene (1), either by reflux (170 °C) of neat 1[1] or by addition of 1 to some high-boiling oil, at 250–260 °C.[2] It is recommended that the vapors are fractionated to remove refluxing, uncracked dimer and entrained liquid. In commercial procedures, the dimer is cracked at 350–360 °C with a short contact time,[2] which avoids the otherwise necessary fractionation to remove the dimer.

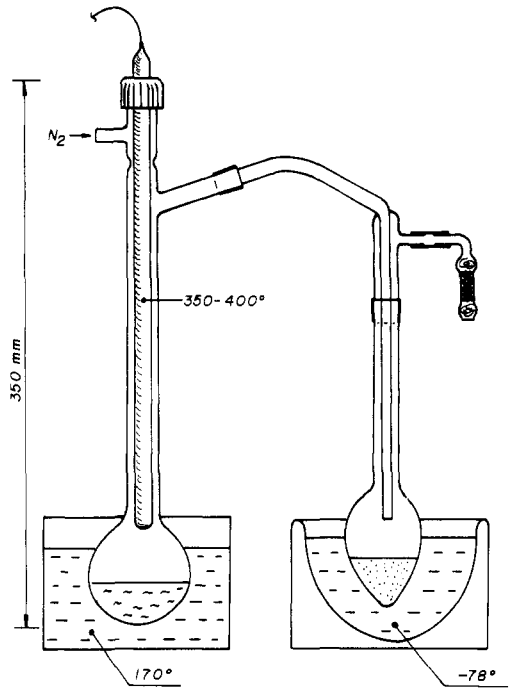

Figure 1. Apparatus for the preparation of cyclopentadiene.

We now report a simplified laboratory procedure which mimics commercial vapor-phase cracking procedures. The hot (350–400 °C) surface is provided by an electrically heated Red-Rod, mounted vertically above the surface of hot (170 °C) dicyclopentadiene. This arrangement permits a rapid and efficient preparation of cyclopentadiene from commercial dicyclopentadiene. In a typical experiment, 5.2 g of dimer gave 4.7 g (91%) of cyclopentadiene within 20 min.

The present apparatus can also be used for the preparation of dimethylketene from its dimer.[3]

Experimental Section

The glassware was dried before use to avoid ice formation in the product. The Red-Rod was purchased from Electrothermal Engineering Ltd.[4]

Dicyclopentadiene (analytical grade; 5.2 g) was charged in the round-bottomed flask (Figure 1). A slow (ca. 30 mL/min) stream of nitrogen was maintained throughout the operation. The Red-Rod was allowed to reach operating temperature (350–400 °C), approximately 25 V to the Red-Rod, and the dicyclopentadiene was heated (oil bath 170 °C). After ca. 20 min, the reaction was completed and cyclopentadiene (4.7 g, 91%) had condensed in the receiver. The product had n_D 1.4435 (lit. n_D 1.433;[1] 1.4429;[2] 1.4440[5]).

Acknowledgment. This work was supported by the Swedish Natural Science Research Council and the Swedish Board for Technical Development.

Registry No. 1, 77-73-6; cyclopentadiene, 542-92-7.

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