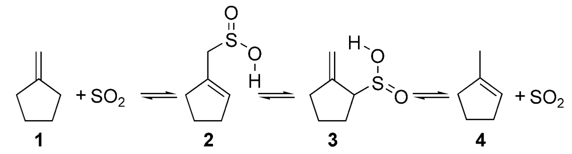
Alkene Isomerization

Polysulfones: Catalysts for Alkene Isomerization**

Dean Marković and Pierre Vogel*

It has long been known that alkenes can be isomerized by sulfur dioxide. The process is generally explained by invoking an ene reaction between an SO_2 molecule and the alkene to give a β,γ-unsaturated sulfinic acid intermediate (e.g. **1**+ SO_2→**2**; Scheme 1), which then undergoes a [1,3] sigmatropic shift to form an isomeric β,γ-unsaturated sulfinic acid (**2**→**3**), followed by a retro-ene reaction that eliminates SO_2 (**3**→**4** + SO_2).[1]



Scheme 1. General mechanism for SO_2-catalyzed isomerization of methylidenecyclopentane (**1**).

When we treated methylidenecyclopentane (**1**) with various amounts of SO_2 in CD_2Cl_2 at 0 °C, isomerization into 1-methylcyclopentene (**4**) occurred within a few hours. However, in the presence of a small amount of CH_2I_2, the reaction was totally inhibited. As 1,1-diodoalkanes in the presence of SO_2 are suspected to generate iodine radicals,[2] this striking observation suggests that the SO_2-promoted isomerization **1**→**4** does not follow the generally accepted mechanism **1**→**2**→**3**→**4**, but rather another mechanism that involves radical intermediates. This hypothesis was confirmed by the observation that TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) and Bu_3SnH both efficiently inhibit the SO_2-promoted isomerization **1**→**4**. In the absence of radical-scavenging agents, the kinetics of the SO_2-promoted isomerization **1**→**4** showed an induction period, the duration of which increased upon decreasing the SO_2 concentration. This period was followed by a zeroth-order reaction until about 70 % conversion. During the induction period a white precipitate formed, the amount of which increased upon

---

[*] D. Marković, Prof. Dr. P. Vogel
Institute of Chemical Sciences and Engineering,
Swiss Federal Institute of Technology (EPFL),
BCH, 1015 Lausanne (Switzerland)
Fax: (+41) 21-693-9355
E-mail: pierre.vogel@epfl.ch

[**] This work was supported by the Swiss National Science Foundation (Grant No. 2000-20100002/1) and the Office Fédéral de L'Education et de la Science (OFES) (Grant No. COI.0071, COST D13/010/01). We also thank Mr. Martial Rey for technical help and Professor L. Forro (EPFL) for access to ESR instruments.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

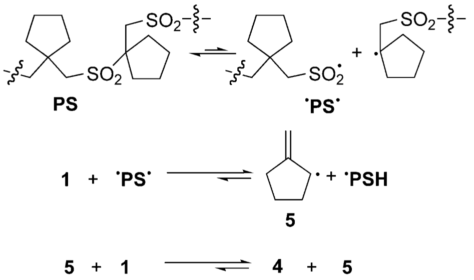
DOI: 10.1002/ange.200453897

increasing the proportion of SO_2. Elemental analysis and IR spectra confirmed that the precipitate is a 1:1 copolymer of **1** and SO_2, a polysulfone (**PS**). Titration of this polymer with aqueous NaOH (0.1 M) neutralized the free sulfinic acid moieties and allowed us to evaluate an average molecular mass of 230000.

The ESR spectrum of the polymer **PS** taken during its formation showed typical signals for carbon-centered (tertiary) and sulfonyl radicals.[3] At 298 K, their estimated concentrations amount to approximately 10^{-6} M.

When freshly prepared **PS** or neutralized **PS** (with aqueous NaOH) was added to a solution of **1** in CD_2Cl_2 an immediate zeroth-order isomerization **1**→**4** occurred at 0 °C. The reaction was inhibited efficiently with TEMPO and Bu_3SnH. Polysulfones are known to equilibrate with radicals upon heating (ceiling temperature of polysulfone formation).[4,5] These radicals can abstract a hydrogen atom from **1** to give the allyl radical intermediate **5** (initiation step, Scheme 2.). Intermediate **5** then reacts with **1** to produce **4** during which allyl radical **5** is regenerated (propagation step).

Isomerization of **1**→**4** was also induced upon irradiation or heating (120 °C) of **1** in the presence of a catalytic quantity of $(PhSO_2)_2$ (diphenyldisulfone);[6] however, polymeric material was also formed. Therefore the $PhSO_2^{\bullet}$ radical generated under these conditions is not as selective a catalyst as **PS** for the alkene isomerization, perhaps because of its ability to add to the alkene concurrently with hydrogen abstraction. All the experiments reported above are consistent with the radical chain mechanism shown in Scheme 2. Further proof was obtained in the following way.



Scheme 2. Radical mechanism for the polysulfone-catalyzed isomerization of alkenes.

Upon treatment with nondeuterated **PS** at 0 °C, a 1:1.06 mixture of hexadeuterated methylidenecyclopentane (**6**)[7] and **1** in CD_2Cl_2 (toluene, $[D_8]$toluene as internal reference) was isomerized into a mixture of nondeuterated and partially deuterated 1-methylcyclopentenes. The $^2H\{^1H\}$-NMR spectrum of the mixture displayed three signals for the methyl group corresponding to CH_2D, CHD_2, and CD_3 with relative integrations of 1.31:1.93:1 (Figure 1).[8] This observation proves the intermolecular nature of hydrogen migration between the allylic methylene group in **1** (**6**) and the terminal carbon atom of the allyl radicals. Thus the signal for CHD_2 is due to a hydrogen atom transfer from **1** to the allyl radical $[D_5]$**5** (which arises from **6**), whereas the signal for CH_2D is a result of a deuterium atom transfer from **6** to the nondeuterated allyl radical **5**. At the end of the isomerization (20 more half-lives), the ^1H- and $^2H\{^1H\}$-NMR spectra did not change, showing that the exchange between positions C3,4 and the methyl groups in 1-methylcyclopentenes is much slower than the isomerization **1**→**4**.

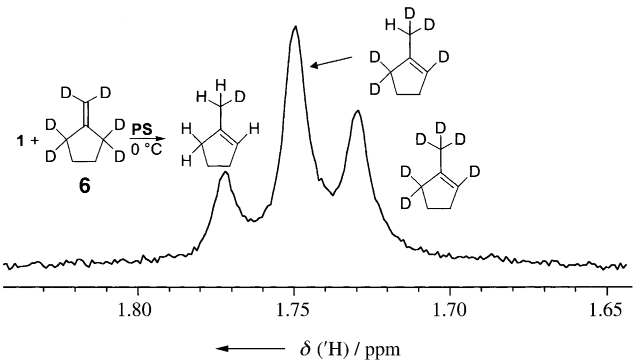


Figure 1. Partial $^2H\{^1H\}$-NMR spectrum of 1-methylcyclopentene (methyl region) arising from the reaction **1**+**6**→**4** (CD_2Cl_2, 0 °C).

The polysulfone **PS** catalyzed the isomerization of the methylidenecyclohexane into 1-methylcyclohexene, 2-methylbut-1-ene into 2-methylbut-2-ene, 2-ethylbut-1-ene into 2-ethylbut-2-ene, and 2-methylhept-1-ene into 2-methylhept-2-ene in CD_2Cl_2 at room temperature. All reactions were high-yielding, with no formation of polymeric material (^1H NMR spectroscopic analysis). This was not the case with the SO_2-induced isomerizations, which were all accompanied by the formation of polymers.

In summary, we have uncovered a new mechanism for alkene isomerization induced by sulfur dioxide: The polysulfone polymers resulting from their co-condensation are organic catalysts for the alkene isomerization.

Received: January 30, 2004 [Z53897]

Keywords: alkenes · isomerization · organocatalysts · polysulfones · radicals

---

[1] a) D. Masilamani, M. M. Rogic, *J. Am. Chem. Soc.* **1977**, *99*, 5219–5220; b) D. Masilamani, M. M. Rogic, *J. Am. Chem. Soc.* **1978**, *100*, 4634–4635; c) M. S. Raasch, B. E. Smart, *J. Am. Chem. Soc.* **1979**, *101*, 7733; d) D. Masilamani, M. E. Reuman, M. M. Rogic, *J. Org. Chem.* **1980**, *45*, 4602–4605; activation parameters, stereoselectivity, as well as the kinetic isotope effect support a concerted, one-step mechanism for the retro-ene desulfitation of β,γ-unsaturated sulfinic acids: e) S. D. Hiscock, N. S. Isaacs, M. D. King, R. E. Sue, R. H. White, D. J. Young, *J. Org. Chem.* **1995**, *60*, 7166–7169; f) S. Braveman in *The Chemistry of Sulfinic Acids, Esters, and Their Derivatives* (Ed.: S. Patai), Wiley, New York, **1990**, pp. 298–300; g) J.-B. Baudin, S. Julia, *Bull. Soc. Chim. Fr.* **1995**, *132*, 196–214.

[2] For examples, see: a) E. Block, M. Aslam, V. Eswarakrishnan, K. Gebreyes, J. Hutchinson, R. Iyer, J. A. Laffitte, A. Wall, *J. Am. Chem. Soc.* **1986**, *108*, 4568–4580; b) A. Commeyras, H. Blancou, A. Lantz (Produits Chimiques Ugine Kuhlmann, Fr.), Ger. Offen., DE 2756169, **1978** [*Chem. Abstr.* **1978**, *89*, 108161e]; c) A. T. Hallowell, G. T. Vaala. (E.I. du Pont de Nemours & Co.), US 2393247, **1946** [*Chem. Abstr.* **1945**, *40*, 1980 7].

[3] a) N. L. Zutty, C. W. Wilson III, *Tetrahedron Lett.* **1963**, 2181–2188; b) N. L. Zutty, C. W. Wilson III, G. H. Potter, D. C. Priest, C. J. Whitworth, *J. Polym. Sci. Part A* **1965**, *3*, 2781–2799.

[4] a) W. K. Busfield, *Aspects Degrad. Stab. Polym.* **1978**, 39–78; b) T. N. Bowmer, J. H. O'Donnell, *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *19*, 45–50.

[5] At any temperature, including that of its formation, the polysulfone equilibrates with diradicals (tertiary alkyl radicals and sulfonyl radicals), a phenomenon arising from the entropy of fragmentation (mostly translational entropy) which increases with the molecular mass of the polymer.

[6] a) M. Kobayashi, K. Tanaka, H. Minato, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2906–2909; b) T. Ho Huu, O. Ito, M. Iino, M. Matsuda, *J. Phys. Chem.* **1978**, *82*, 314–319.

[7] Compound **6** was made according to: T. B. Malloy, Jr., R. M. Hedges, F. Fisher, *J. Org. Chem.* **1970**, *35*, 4256–4257.

[8] For an example of intrinsic isotope effects on the deuterium chemical shifts of CD_3-, CD_2H-, and CH_2D- containing compounds, see: N. H. Werstiuk, G. Timmins, B. Sayer, *Can. J. Chem.* **1986**, *64*, 1465–1466.