Palladium-Catalyzed [2,3] Rearrangement of Alkyl Allyl Sulfites to Alkyl Allylsulfonates

Yoshinao Tamaru* and Kazuki Nagao

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

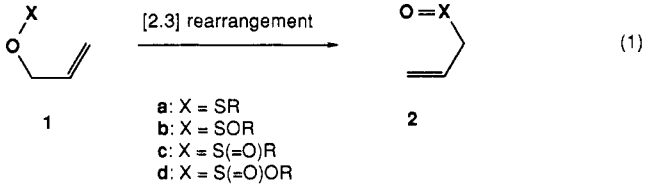
Takashi Bando and Zen-ichi Yoshida

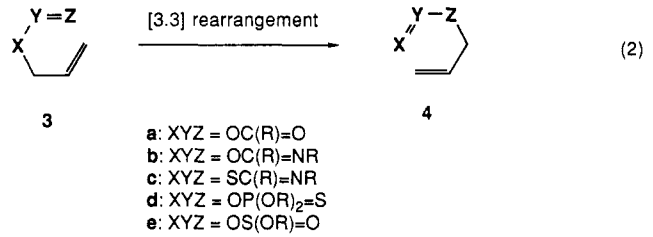
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Received September 20, 1988 (Revised Manuscript Received September 26, 1989)

Acyclic and cyclic allyl sulfites undergo a [2,3] rearrangement to furnish allylsulfonates and 1-vinyl-substituted sultones, respectively, by the catalysis of $(dba)_3Pd_2C_6H_6$–triethyl phosphite. Unsymmetrically substituted allylic groups of acyclic allyl sulfites rearrange to provide allylsulfonates with more substituents on the allylic positions. The rearrangement of cis and trans mixtures of cyclic allyl sulfites accompanies the stereochemical isomerization of the substituents and selectively provides trans-1,2-disubstituted sultones.

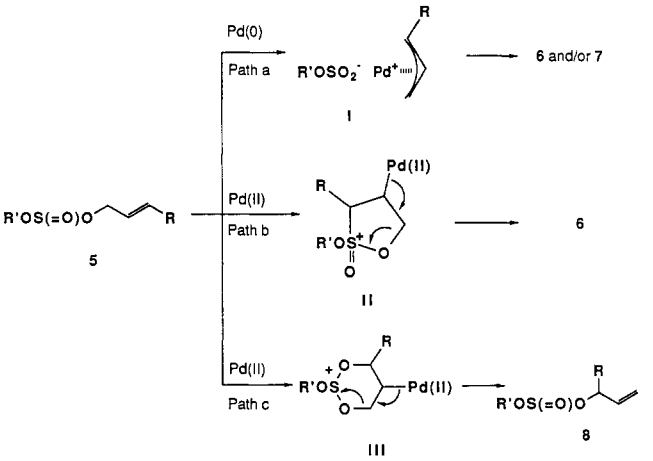
Sigmatropic rearrangement is a quickly expanding field owing to its synthetic and theoretical interest. On thermal activation, [2,3] sigmatropic rearrangements (eq 1) readily occur with allylic sulfenate (**1a**, X = SR),[1] sulfoxilates (**1b**, X = SOR),[2] and sulfinates (**1c**, X = S(=O)R).[3] Interestingly, however, no reports have appeared for the rearrangement with allylic sulfites (**1d**, X = S(=O)OR).[4] This may be owing to its reluctance, since the lone-pair electrons on the sulfur atom of sulfites **1d** are accommodated in an orbital relatively lower in energy than those of the other sulfur esters in the lower oxidation states (**1a–c**).





Mechanistic considerations based on the recently developed palladium(II)-catalyzed [3,3] rearrangement of allylic acetates **3a**,[5] imidates **3b**,[6] thioimidates **3c**,[7] and thionophosphates **3d**,[8] etc.[9] (eq 2), suggest that alkyl allyl sulfites **5** possess an inherent potential to undergo [2,3] and/or [3,3] rearrangements (Scheme I, paths b and c, respectively). In the former case, the sulfur atom and, in the latter case, the S=O oxygen atom serve as nucleophiles toward the double bond activated by the coordination of palladium(II), forming intermediates II and III, respectively.

Scheme I



This paper discloses that acyclic **5** and cyclic allylic sulfites **11**, that are thermally stable and even distillable without accompanying either a [2,3] or a [3,3] sigmatropic rearrangement, readily undergo a formal [2,3] sigmatropic rearrangement to give allylsulfonates **6** and/or **7** and 1-vinyl sultones **12**, respectively, in good yields by treatment with a catalytic amount of palladium(0) species (eqs 3 and 5, path a, Scheme I). Palladium(II) species did not promote either [2,3] (path b, Scheme I) or [3,3] rearrangement (path c, Scheme I). The rearrangement shows unique regio- and stereoselectivities: (1) unsymmetrical allylic groups of acyclic alkyl allyl sulfites rearrange to give alkyl allylsulfonates with more substituents on the allylic position (**6** predominating over **7**), and (2) cis and trans mixtures of cyclic allylic sulfites rearrange to give trans-

(1) (a) Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869. (b) Tang, R.; Mislow, K. *Ibid.* **1970**, *92*, 2100. (c) Barton, D. H. R.; Prabhakar, S. *J. Chem. Soc., Perkin Trans. 1* **1974**, 781.

(2) (a) Braverman, S.; Segev, D. *J. Am. Chem. Soc.* **1974**, *96*, 1245. (b) Büchi, G.; Freidinger, R. M. *Ibid.* **1974**, *96*, 3332.

(3) (a) Braverman, S.; Globerman, T. *Tetrahedron* **1974**, *30*, 3873. (b) Braverman, S.; Mechoulam, H. *Ibid.* **1974**, *30*, 3883.

(4) A mechanism involving [2,3] sigmatropic rearrangement was proposed for thermal isomerization of dipropargylic sulfite: (a) Beetz, T.; Kellog, R. M.; Kiers, C. T.; Piepenbroek, A. *J. Org. Chem.* **1975**, *40*, 3308. For the rearrangement of propargyl dichlorophosphites, see: (b) Macomber, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 3072.

(5) (a) Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321. (b) Grieco, P. A.; Tanigawa, T.; Bongers, S. L.; Tanaka, H. *J. Am. Chem. Soc.* **1980**, *102*, 7587. (c) Tamaru, Y.; Yamada, Y.; Ochiai, H.; Nakajo, E.; Yoshida, Z. *Tetrahedron* **1984**, *40*, 1791.

(6) Ikariya, T.; Ishikawa, Y.; Hirai, K.; Yoshikawa, S. *Chem. Lett.* **1982**, 1815.

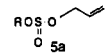
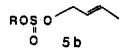
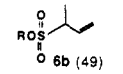
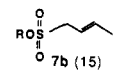
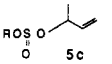
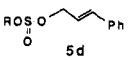
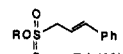
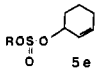
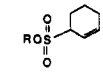
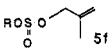
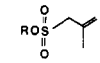
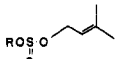
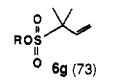
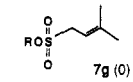
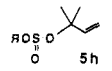
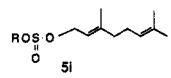
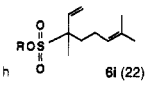
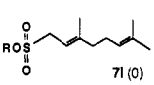
(7) Mizutani, M.; Sanemitsu, Y.; Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* **1985**, *50*, 764.

(8) (a) Tamaru, Y.; Yoshida, Z.; Yamada, Y.; Mukai, K.; Yoshioka, H. *J. Org. Chem.* **1983**, *48*, 1293. (b) Yamada, Y.; Suzukano, G.; Yoshioka, H.; Tamura, Y.; Yoshida, Z. *Tetrahedron Lett.* **1984**, *25*, 3599.

(9) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: London, 1985.

0022-3263/90/1955-1823$02.50/0

Table I. Palladium-Catalyzed Allyl Sulfite–Allylsulfonate Rearrangement

run	allyl sulfite 5[a]	conditns[b]	allylsulfonate 6 and/or 7 (% isolated)
1	 5a	r.t., 18 h	 6a (72)
2	5a[c]	r.t., 23 h	6a (89)
3	5a[d]	r.t., 15 h	6a (59)[e]
4	 5b	r.t., 18 h	 6b (49)  7b (15)
5	 5c	r.t., 17 h	6b (69) 7b (21)
6	 5d	r.t., 20 h	 6d (0)  7d (69)
7	 5e	r.t., 26 h	 6e (63)
8	 5f	r.t., 45 h	 6f (77)
9	 5g	r.t., 13 h	 6g (73)  7g (0)
10	 5h	r.t., 42 h	6g (72) 7g (0)
11	 5i	r.t., 48 h	 6i (22)  7i (0)

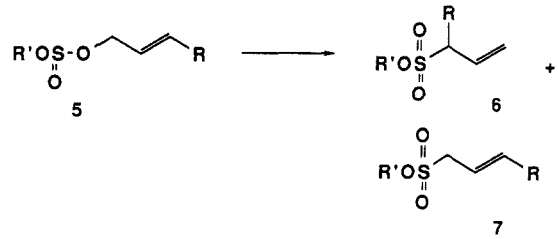
[a] R is meant to refer to the 2-phenylethyl group. [b] Usual conditions: 5 (1.0 mmol), $(dba)_3Pd_2C_6H_6$ (0.03 mmol), $(EtO)_3P$ (0.24 mmol) in dry dioxane (5 mL). [c] **5a** (10.0 mmol), $(dba)_3Pd_2C_6H_6$ (0.1 mmol), $(EtO)_3P$ (0.8 mmol) in dry dioxane (25 mL). [d] **5** (1.0 mmol), $PdCl_2$ (0.03 mmol), PPh_3 (0.12 mmol) in dry dioxane (5 mL). [e] In addition to **6a**, 2-phenylethyl alcohol (23%) was isolated.

1,2-disubstituted sultones selectively. This reaction comprises a rare example of [2,3] rearrangement catalyzed by palladium.

Results and Discussion

2-Phenylethyl allylic sulfites **5** were prepared by the reaction of 2-phenylethyl chlorosulfite[10] and the corresponding allylic alcohols. These sulfites **5a–i** (Table I) are stable at room temperature for a few weeks, but slightly decompose during standing at room temperature for longer periods of time, the extent being dependent on the structure of the allylic moiety. Sulfites **5a–c** and **5g** are distillable under reduced pressure without noticeable decomposition. No thermal rearrangements were observed during the distillation at about 150 °C. Some sulfites (e.g., **5d** and **5f**) do not withstand heating at 150 °C and provide intractable mixtures of decomposition products.

After having confirmed that allylic sulfites do not undergo any rearrangements by thermal activation, we examined the palladium(2+)-catalyzed rearrangements (paths b and c, Scheme I). Most attempts examined with Pd(II) salts as catalysts, however, resulted either in the recovery of the starting material or in providing decomposition products. For example, starting material **5a** was recovered by the use of the following Pd(II) salts in dry dioxane under argon: $PdCl_2$ (3 mol %, reflux for 6 h), $PdCl_2(PPh_3)_2$ (3 mol %, reflux for 6 h), $PdCl_2$[1,2-bis(diphenylphosphino)ethane] (3 mol %, reflux for 11 h), $PdCl_2(n\text{-}Bu_3P)_2$ (3 mol %, reflux for 6 h), $PdCl_2(PhCN)_2$ (3 mol %, reflux for 7 h). Sulfite **5a** decomposed to give 2-phenylethyl alcohol as the main product when exposed to the follwing catalytic systems in dry dioxane under argon: $PdCl_2$ and triethyl phosphite (3 mol %–12 mol %, reflux for 7 h), $Pd(OAc)_2$ and triethyl phosphite (3 mol %–12 mol %, at 60 °C for 28 h).



(3)

After many trials, eventually we have found that a rather unique catalytic system, $(dba)_3Pd_2C_6H_6$ (3 mol %)[11]–triethyl phosphite (24 mol %), nicely catalyzes the [2,3] rearrangement (eq 3). Results are summarized in Table I. Reaction 3 proceeds at room temperature (20–25 °C) irrespectively of the substitution pattern of the allylic moiety. Generally, the reaction was performed on a 1-mmol scale with respect to **5** in the presence of 3 mol % of the palladium catalyst. The reaction may be applied to a larger scale with a smaller amount of the catalyst (entry 2).

For a successful reaction, the use of 8 equiv of triethyl phosphite with respect to $(dba)_3Pd_2C_6H_6$ is essential. By the use of relatively smaller amounts of phosphite to Pd, both the yield and the reactivity gradually go down: 55% of **6a** for [triethyl phosphite]/$[(dba)_3Pd_2C_6H_6]$ = 6 (room temperature, 1 day); 8% of **6a** for [triethyl phosphite]/$[(dba)_3Pd_2C_6H_6]$ = 4 (room temperature, 5 days). Finally, when $(dba)_3Pd_2C_6H_6$ alone is used, the reaction essentially stops. At elevated temperatures, sulfite **5a** decomposes to give 2-phenylethyl alcohol as the main product (50–60% yield, at room temperature for 13 h, at 60 °C for 11 h, and then at reflux for 7 h). Triphenylphosphine also serves as a cocatalyst. However, generally the yields of the rearranged product **6** are poorer than those of the corresponding reactions using triethyl phosphite, e.g., 59% of **6a** for $[PPh_3]/[(dba)_3Pd_2C_6H_6]$ = 8 (room temperature, 1 day); 40% of **6a** for $[PPh_3]/[(dba)_3Pd_2C_6H_6]$ = 6 (room temperature, 3 days); 20% of **6a** for $[PPh_3]/[(dba)_3Pd_2C_6H_6]$ = 4 (room temperature, 3 days). Tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, the most commonly used palladium(0) catalyst, was ineffective and gave 2-phenylethyl alcohol as the major product together with a small amount of the rearranged product **6a** (5–25%).

Interestingly, $PdCl_2$ and PPh_3 (3 mol %–12 mol %) showed considerable catalytic activity (run 3), which is in contrast to the results observed for the related catalysts, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$, etc. (vide supra). All these results indicate that the rearrangement of **5** only proceeds under very specific conditions with respect to the kinds of palladium species and the amounts and kinds of cocatalysts. The specificity may stem from either poisoning of catalyst by some sulfur-containing decomposition products or strong coordination of the starting sulfite **5**[12] to palladium species through the lone-pair electrons on the sulfur atom, which might prohibit an approach of palladium species to the allylic moiety of **5** and seriously retard the rearrangement.

The most characteristic feature of the present rearrangement is the regioselectivity (**6** vs **7**, eq 3), exclusively

(10) Newman, M. S.; Fones, W. S. *J. Am. Chem. Soc.* **1947**, *69*, 1046.

(11) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253.

(12) Schenk, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 98.

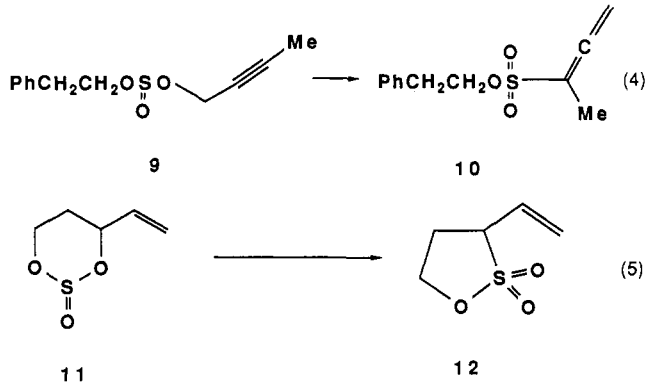
or highly selectively providing the allylsulfonates **6** with the higher numbers of substitutents on the allylic positions. For example, both **5g** and **5h** rearrange to specifically provide **6g**. Both **5b** and **5c** furnish mixtures of products **6b** and **7b**, favoring the secondary sulfonate **6b** over the primary one **7b** in the same ratios of 77:23. The primary allylic sulfite **5i**, similarly to **5g**, rearranges to specifically provide the tertiary allylsulfonate **6i**. The reaction of **5d** is the only exception examined (entry 6), which provides the primary sulfonate **7d** as the single product.

These regioselectivities apparently eliminate the mechanism involving an intermediate II (path b, Scheme I). Through this intermediate only the allylsulfonates with complete geometric allylic inversion may be produced. Two pairs of results, runs 4 and 5 and runs 9 and 10, suggest that the reaction proceeds via a common intermediate, most likely via (π-allyl)palladium species I, which might be formed by an oxidative addition of Pd(0) to **5** (path a, Scheme I). However, the regioselectivities, favoring the more substituted allylic termini in the carbon–sulfur bond formation, follow the reverse of a general trend reported for the reactions of unsymmetrically substituted (π-allyl)palladium complexes with nucleophiles.[9,13]

It is well established that allylic sulfones undergo an allylic transposition in the presence of a Pd(0) catalyst and the thermodynamically more stable allylic sulfones (e.g., primary sulfones) are preferentially produced over the secondary or tertiary ones.[14] The allylic sulfonates **6** and **7**, on the other hand, were found to be immune to allylic transposition under the reaction conditions applied for the rearrangement of **5** or even under forcing conditions. For example, the ratio of the mixture of **6b** and **7b** (77:23) did not change after heating at 60 °C for 18 h in the presence of $(dba)_3PdC_6H_6$ (3 mol %) and $(EtO)_3P$ (24 mol %). Accordingly, the regioselectivity in Table I seems to owe its uniqueness to the stability of the products against the palladium-catalyzed allylic transposition. Although we could not detect any traces of **6d** during the course of the reaction, in this particular case, the firstly formed **6d** most likely rearranges to **7d**, judging from the structural arrangement of **6d** highly suitable to the palladium(0)-catalyzed rearrangement and also the large difference of thermodynamic stabilities between **6d** and **7d**.

In relation to the above-mentioned regioselectivities, the reaction behavior of **5** over silica gel should be noted. Although the sulfites **5a** and **5d** are stable over silica gel and can be purified by means of column chromatography over silica gel without noticeable decomposition, the sulfites **5e** and **5g** are unstable and totally decompose during purification over silica gel. Among many decomposition products, a small amount of allylsulfonate was isolated (**6e** in 5% yield from **5e**; **7g** in 9% yield from **5g**). The interesting fact is that **5g** provides only the primary sulfonate **7g**, and its regioisomer **6g**, obtained specifically by the Pd(0)-catalyzed reaction, is not detected.

The present reaction is applicable to the propargyl sulfite–allenesulfonate rearrangement (eq 4), though only in a marginal success.[4] 2-Phenylethyl 2-butynyl sulfite (**9**) undergoes rearrangement to furnish 2′-phenylethyl 1-methylallenesulfonate (**10**) in 33% yield (60% conversion, $(dba)_3Pd_2C_6H_6$–$(EtO)_3P$ (3 mol %–24 mol %) in dioxane at reflux for 11 h). A slightly better result was obtained by exposing **9** to $PdCl_2(n\text{-}Bu_3P)_2$ (3 mol %) in dioxane at reflux for 12 h (46% yield based on 79% conversion). However, dipropargyl sulfite and 2-phenylethyl propargyl sulfite only provided intractable mixtures of products under the conditions mentioned above.



In relation to the unique regioselectivity observed for the rearrangement of acyclic sulfites **5**, we next examined cyclic sulfites **11** in order to get further insight into the reaction mechanism the stereochemical course of the reaction.

Cyclic sulfites **11** are readily prepared in high yields by esterification of 1-vinylpropane-1,3-diols with thionyl chloride.[15] Generally, these cyclic sulfites are much more stable than acyclic sulfites **5** and withstand distillation at around 150 °C under reduced pressures. They are also stable enough to be purified by means of column chromatography over silica gel, and each of the diastereomers, which originate from asymmetries of carbon skeleton and sulfinate moieties, may be separated cleanly (see Experimental Section).

These sulfites **11** undergo a clean rearrangement to give cyclic sulfonates **12** (sultones) in high yields under the catalytic conditions established for acyclic sulfites **5** (eq 5). The results are summarized in Table II. Interestingly, making sharp contrast to the reaction for acyclic sulfite **5**, triphenylphosphine was totally ineffective as a cocatalyst for the rearrangement of cyclic sulfite **11** and only caused decomposition of **11** without yielding any trace amounts of rearranged product **12** for any ratios of $[PPh_3]$–$[(dba)_3Pd_2C_6H_6]$ = 8, 6, and 4.

From a diastereomeric mixture **11a** (1:1) was obtained sultone **12a** as a single isomer. This rearrangement accompanies an isomerization of a 1,2-disubstituted propane-1,3-diol moiety, and trans-1,2-disubstituted sultones **12b** and **12d** were specifically obtained from **11b** and **11d**, respectively.

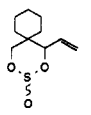
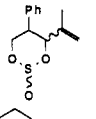
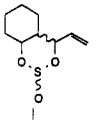
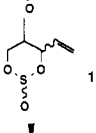
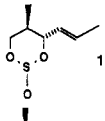
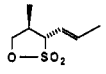
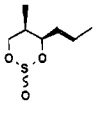
Much information on the mechanistic aspects can be obtained from the stereochemical outcomes of the rearrangements of **11e**, **11e′**, and **11f** (entries 5 and 6, Scheme II). From **11e** and **11e′** was produced the identical sultone **12e** as a single isomer, which indicates that the diastereoisomerism stemming from the asymmetry of the S=O bonds does not influence the stereochemical course of the reaction. From **11f**, a mixture of **12f** and **12f′** was furnished almost in equal amounts. The isomers **12e** and **12f** are the products formed with retention of configuration at C_3 and olefin. On the other hand, **12f′** is a double-inversion product with respect to the stereochemistry of C_3 and olefin. The formation of **12e** and **12f** may be similarly rationalized by a double-inversion (net retention) mecha-

(13) The regioselectivity markedly depends both on the ligands of (π-allyl)palladium and on the steric requirement of the nucleophiles: (a) Åkermark, B.; Vitagliano, A. *Organometallics* **1985**, *4*, 1275. (b) Åkermark, B.; Zetterberg, K.; Hansson, S.; Krakenberger, B. *J. Organomet. Chem.* **1987**, *335*, 133.

(14) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979. (b) Inomata, K.; Yamamoto, T.; Kotake, H. *Chem. Lett.* **1981**, 1357.

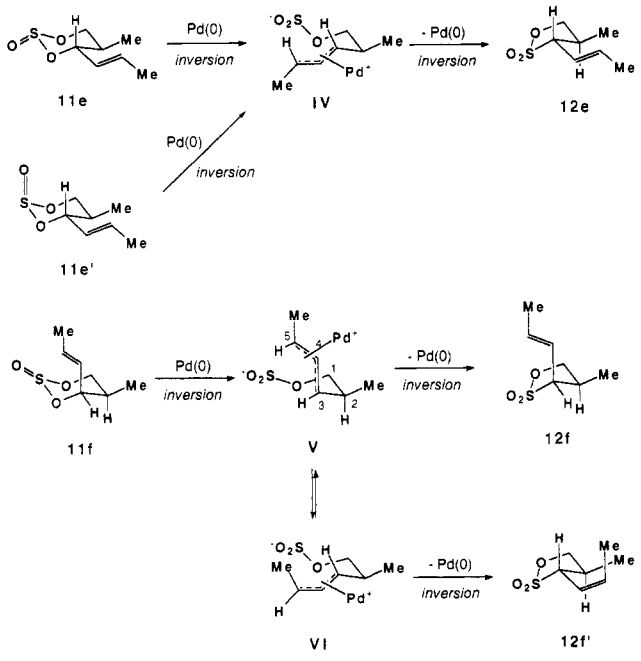
(15) Lauterbur, P. C.; Pritchard, J. G.; Vollmer, R. L. *J. Chem. Soc.* **1963**, 5307.

Table II. Palladium-Catalyzed Rearrangement of Cyclic 1-Vinylpropane-1,3-diol Sulfites 11

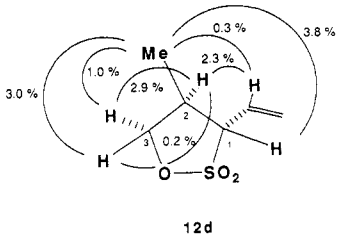
run	substrate 11[a]	conditns[b]	product (% isolated yield)[c]
1	 **11a** (1:1)	60 °C, 24 h	 **12a** (90)
2	 **11b** (8:9:5)	60 °C, 8 h	 **12b** (96)
3	 **11c**[d]	60 °C, 11 h	 **12c** (77)[e]
4	 **11d** (1:1:1:1)	60 °C, 5 h	 **12d** (61)
5	 **11e**	60 °C, 5 h	 **12e** (63)
6	 **11f**	60 °C, 5 h	 **12f** (34)  **12f'** (49)

[a] Figures in parentheses are meant to refer to the diastereomeric ratio of cyclic sulfites 11, used for rearrangements. [b] Reaction conditions are as follows: $(dba)_3Pd_2C_6H_6$ (0.03 mmol), $(EtO)_3P$ (0.24 mmol) in dioxane (5 mL) for 11 (1 mmol). [c] Yields refer to the isolated ones. In all cases, the conversions are complete. [d] 11e consists of at least six diastereomers, and their ratio is not determined. [e] A diastereomeric mixture (3:2:1) of sultones **12c** is obtained.

Scheme II

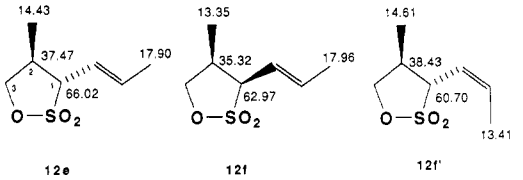


nism: an inversion of the C_3 configuration on an oxidative addition of Pd(0) to the C_3–O bond of **11e** and **11f**, followed by an inversion at C_3 during an intramolecular nucleophilic attack of ROS(=O)$^-$ anion over the (π-allyl)-palladium species, IV and V, respectively (Scheme II). In a transition state from V to **12f**, a severe gauche interaction between C_1 and π-allyl moieties may emerge, and hence



12d

Figure 1. ^1H NOE effect.



12e 12f 12f'

Figure 2. Selected ^{13}C NMR data ($CDCl_3$, δ in parts per million).

V may have an occasion to isomerize to VI through a rotation around the C_4–C_5 bond of C_5–Pd (σ-allyl)palladium intermediate. The intermediate VI is, in turn, plagued with steric repulsion caused by the cis double bond. As a consequence, a mixture of **12f** and **12f'** may be formed from **11f**.

The structure of **12d** was determined on the basis of ^1H NOE experiments (Figure 1). The large NOEs between C_1H and CH_3 and C_2H and the internal olefinic proton correspond to the trans structure. The selected data of the ^{13}C NMR chemical shifts for the stereoisomers **12e**, **12f**, and **12f'** are given in Figure 2. The higher field resonances of the C_1, C_2, and C_2*Me* carbons of **12f**, as compared with those of **12e**, and the higher field resonances of the C_1 and olefinic Me of **12f'**, as compared with those of the other two isomers, are good criteria for the structure determination of these isomers, together with the vicinal coupling constants of olefinic protons in their ^1H NMR spectra [J = 15.1 Hz (**12e**), 15.1 Hz (**12f**), 10.6 Hz (**12f'**)].

In summary, in this paper is described a novel Pd(0) catalyzed [2,3] rearrangement of allyl sulfites to allylsulfonates. As the palladium species, $(dba)_3Pd_2C_6H_6$ complex in combination with triethyl phosphite is most effective. The reaction shows rather unique regio- and stereoselectivities. Unsymmetrically substituted acyclic allyl sulfites **5** selectively isomerize to allylsulfonates **6** and/or **7** with more substituents on the allylic positions. The rearrangement of cyclic allylic sulfites **11** to sultones **12** accompanies the stereochemical isomerization of the substituents on the carbon skeleton and shows a strong tendency to selectively furnish the thermodynamically more stable trans isomers.

Experimental Section

Melting points were determined in capillary tubes with a Büchi apparatus and were not corrected. Unless otherwise specified, short-path (bulb-to-bulb) distillations were carried out in a Kugelrohr apparatus. Microanalyses were performed by the Microanalysis Center of Kyoto University. Infrared spectra were measured with a Hitachi Model EPI-G3 grating spectrophotometer. Proton magnetic resonance spectra were determined either at 90 MHz on a JEOL-FX90Q instrument or at 400 MHz on a JEOL-GX400 instrument with tetramethylsilane as an internal standard. Carbon-13 NMR spectra were determined at 22.4 MHz on a JEOL-FX90Q instrument. Mass spectra were measured on a JEOL D-300 instrument (high-resolution mass spectrophotometer). R_f values were measured over Merck precoated TLC plates, silica gel 60F-254.

Solvents and Reagents. Tetrahydrofuran and ether were dried and distilled from benzophenone–Na, dioxane was distilled from Na, and dichloromethane was distilled from calcium hydride

and kept under an argon atmosphere. $(dba)_3Pd_2(C_6H_6)$,[11] 2-phenylethyl chlorosulfite,[10] and 1-vinylpropane-1,3-diols[16] were prepared according to the reported methods.

General Procedure for Preparation of Alkyl Allyl Sulfites 5. Sulfites **5a**, **5b**, **5d**, and **5g** were prepared according to method A described below. Sulfites **5c**, **5e**, **5f**, **5h**, and **5i** could not be prepared by method A, and these sulfites were prepared according to method B described below.

Method A. To a solution of an appropriate allylic alcohol (5 mmol) and pyridine (5 mmol) in dry ether (5 mL) was added 2-phenylethyl chlorosulfite (5 mmol) via a syringe with water-bath cooling, and the solution was stirred at room temperature for 1 h. Then 2 N HCl (1 mL) was added, and the mixture was extracted with ethyl acetate (10 mL × 4). After the extracts were dried over magnesium sulfate, the solvents were evaporated to give an oil, which was purified either by means of distillation (in the cases of **5a**, **5b**, **5g**) or by means of column chromatography over silica gel (in the case of **5d**).

Method B. To a solution of an appropriate allylic alcohol (3 mmol) in dry THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 1.88 mL, 3 mmol) via a syringe at −78 °C. After stirring for 10 min, 2-phenylethyl chlorosulfite (3 mmol) was added and the mixture was stirred at the same temperature for 1 h. Then H_2O was added, and the mixture was extracted with ethyl acetate (15 mL × 3). The extracts were dried over magnesium sulfate and then concentrated, to give a crude product. The sulfite **5c** was purified by distillation. The sufites **5e**, **5f**, **5h**, and **5i** were directly used for the rearrangement without further purification. One typical example for each method is shown below.

2-Phenylethyl Allyl Sulfite (5a) (Method A). To a solution of allyl alcohol (1.02 mL, 15 mmol) and pyridine (1.21 mL, 15 mmol) in ether (20 mL) was added 2-phenylethyl chlorosulfite (1.65 mL, 15 mmol) via a syringe with water-bath cooling. After stirring at room temperature for 5 h, 2 N HCl (5 mL) was added and the mixture was extracted with ethyl acetate (20 mL × 4). The extracts were dried over magnesium sulfate and concentrated, to give a crude product (2.47 g). Kugelrohr distillation afforded pure sulfite **5a**, 1.99 g (8.8 mmol, 88% yield). **5a**: oil; bp 140 °C (6 mmHg); IR (neat film) 3050 (w), 1630 (w), 1230 (s), 960 (s), 720 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.99 (t, J = 6.8 Hz, 2 H), 4.08–4.32 (m, 2 H), 4.35 (d, J = 5.6 Hz, 2 H), 5.15–5.43 (m, 2 H), 5.86 (ddt, J = 17.1, 10.0, 5.6 Hz, 2 H), 7.14–7.34 (m, 5 H).

2-Phenylethyl 1-Methylallyl Sulfite (5c) (Method B). To a solution of 3-buten-2-ol (181 mg, 2.51 mmol) in dry THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 1.57 mL, 2.51 mmol) via a syringe at −78 °C. After stirring for 20 min, 2-phenylethyl chlorosulfite (0.414 mL, 2.51 mmol) was added and the mixture was stirred for 2 h at −20 °C. Then H_2O was added, and the mixture was extracted with ethyl acetate (20 mL × 3). The extracts were dried over magnesium sulfate and concentrated, to give a crude product (542 mg). Distillation under reduced pressure afforded sulfite **5c**, 486 mg (2.02 mmol, 81% yield). **5c** (a mixture of diastereomers with the ratio of 1:1): oil; bp 130 °C (2 mmHg); IR (neat film) 2980 (m), 1640 (w), 1375 (m), 1210 (s), 1045 (m), 750 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, J = 7.3 Hz, 3 H of one diastereomer), 1.37 (d, J = 6.6 Hz, 3 H of the other diastereomer), 2.97 (t, J = 7.1 Hz, 2 H), 3.94–4.46 (m, 2 H), 4.78–4.98 (m, 1 H), 4.50–5.35 (m, 2 H), 5.62–6.04 (m, 1 H), 7.17–7.33 (m, 5 H).

2-Phenylethyl *trans*-2-butenyl sulfite (5b): oil; bp 150 °C (5 mmHg); IR (neat film) 2960 (m), 1680 (m), 1385 (m), 1220 (s), 975 (m), 705 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (d, J = 5.9 Hz, 3 H), 2.98 (t, J = 6.8 Hz, 2 H), 4.03–4.37 (m, 24 H), 5.29–5.99 (m, 2 H), 7.18–7.39 (m, 5 H).

2-Phenylethyl cinnamyl sulfite (5d): oil; IR (neat film) 3040 (w), 1500 (m), 1455 (m), 1205 (s), 970 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.99 (t, J = 6.9 Hz, 2 H), 3.96–4.39 (m, 2 H), 4.50 (d, J = 6.0 Hz, 2 H), 6.17 (dt, J = 15.9, 6.0 Hz, 1 H), 6.61 (d, J = 15.6 Hz, 1 H), 7.13–7.46 (m, 10 H).

2-Phenylethyl 2-cyclohexenyl sulfite (5e): oil; IR (neat film) 2950 (m), 1740 (w), 1455 (m), 1205 (s), 600 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42–2.17 (m, 6 H), 2.99 (t, J = 7.1 Hz, 2 H), 3.97–4.44 (m, 2 H), 4.83–5.05 (m, 1 H), 5.44–5.70 (m, 1 H), 5.83–6.08 (m, 1 H), 7.14–7.34 (m, 5 H).

2-Phenylethyl 2-methylallyl sulfite (5f): oil; IR (neat film) 2960 (m), 1660 (w), 1455 (m), 1210 (s), 905 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (s, 3 H), 2.98 (t, J = 7.1 Hz, 2 H), 4.04–4.34 (m, 4 H), 4.90–5.04 (m, 2 H), 7.18–7.33 (m, 5 H).

2-Phenylethyl 3,3-dimethylallyl sulfite (5g): oil; bp 150 °C (3 mmHg); IR (neat film) 2960 (m), 1675 (w), 1470 (m), 1210 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (d, J = 1.0 Hz, 3 H), 1.75 (s, 3 H), 2.98 (t, J = 7.1 Hz, 2 H), 4.04–4.32 (m, 2 H), 4.38 (d, J = 7.6 Hz, 2 H), 5.29 (t, J = 7.6 Hz, 1 H), 7.13–7.36 (m, 5 H).

2-Phenylethyl 1,1-dimethylallyl sulfite (5h): oil; IR (neat film) 2980 (m), 1640 (w), 1455 (m), 1190 (s), 1130 (m), 940 (s), 850 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (s, 3 H), 1.48 (s, 3 H), 2.98 (t, J = 7.1 Hz, 3 H), 3.99–4.53 (m, 2 H), 5.05–5.36 (m, 2 H), 5.96 (dd, J = 10.5, 17.3 Hz, 1 H), 7.25 (s, 5 H).

2-Phenylethyl geranyl sulfite (5i): oil; IR (neat film) 2930 (m), 1670 (m), 1455 (m), 1210 (s), 910 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.67 (s, 6 H), 2.01–2.16 (m, 2 H), 2.98 (t, J = 6.8 Hz, 2 H), 4.02–4.33 (m, 2 H), 4.40 (d, J = 7.3 Hz, 2 H), 5.07 (br, 1 H), 5.30 (t, J = 7.3 Hz, 1 H), 7.13–7.46 (m, 5 H).

2-Phenylethyl 2-butynyl sulfite (9): oil; bp 210 °C (3 mmHg); IR (neat film) 2970 (m), 2245 (m), 1460 (m), 1210 (s), 960 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84 (t, J = 2.4 Hz, 3 H), 2.99 (t, J = 7.1 Hz, 2 H), 4.07–4.39 (m, 2 H), 4.46 (q, J = 2.4 Hz, 2 H), 7.12–7.34 (m, 5 H).

General Procedure for Preparation of 1-Vinylpropane-1,3-diol Sulfites 11. To a solution of 1-vinylpropane-1,3-diol (5 mmol) and triethylamine (20 mmol) in dry dichloromethane (20 mL) was added thionyl chloride (6 mmol) at −78 °C via a syringe. Then the solution was allowed to warm slowly to room temperature and stirred for several h. After addition of 2 N HCl (7.5 mL), the mixture was extracted with ethyl acetate (20 mL × 4). The combined extracts were washed with brine, dried over magnesium sulfate, and concentrated, to give an oil, which was purified either by means of distillation under reduced pressure or by means of column chromatography over silica gel. One typical example is as follows.

2,2-Pentamethylene-1-vinylpropane-1,3-diol Sulfite (11a). To a solution of 2,2-pentamethylene-1-vinylpropane-1,3-diol (1.60 g, 9.40 mmol) and triethylamine (6.56 mL, 47.2 mmol) in dry dichloromethane (50 mL) was added thionyl chloride (1.03 mL, 14.1 mmol) at −78 °C via a syringe. Then the solution was allowed to warm slowly to room temperature (over about a 1-h period) and stirred overnight at room temperature. After addition of 2 N HCl (19 mL), the mixture was extracted with ethyl acetate (30 mL × 4). The combined extracts were washed with brine and dried over magnesium sulfate. Evaporation of the solvent afforded a crude product (2.61 g). Two diastereomers were separated by means of column chromatography over silica gel (hexane–Et_2O gradient), to give 0.97 g each (8.92 mmol, 95%). **One diastereomer**: oil; bp 150 °C (1 mmHg); R_f = 0.47 in hexane–Et_2O, 3:1; IR (neat film) 2950 (m), 1645 (w), 1455 (m), 1195 (s), 960 (s), 795 (s), 715 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07–1.84 (m, 10 H), 4.10 (d, J = 11.7 Hz, 1 H), 4.58 (d, J = 11.7 Hz, 1 H), 5.16 (d, J = 6.8 Hz, 1 H), 5.22–5.45 (m, 2 H), 5.87 (ddd, J = 7.1, 9.0, 17.8 Hz, 1 H).

The other diastereomer: oil; bp 150 °C (1 mmHg); R_f = 0.40 in hexane–Et_2O, 3:1; IR (neat film) 2910 (s), 1640 (w), 1450 (m), 1190 (s), 970 (s), 800 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11–1.87 (m, 10 H), 3.83 (dd, J = 0.7, 12.2 Hz, 1 H), 4.43 (d, J = 8.5 Hz, 1 H), 4.66 (d, J = 12.1 Hz, 1 H), 5.21–5.48 (m, 2 H), 6.28 (ddd, J = 8.5, 9.8, 18.3 Hz, 1 H).

1-(1′-Methylvinyl)-2-phenylpropane-1,3-diol Sulfite (11b). Three diastereomers (8:9:5 in the order of elution) were separated by means of column chromatography over silica gel. **The sulfite with R_f = 0.69 in benzene**: oil; bp 160 °C (2 mmHg); IR (neat film) 3030 (m), 1475 (m), 1210 (s), 990 (s), 895 (s), 810 (s), 730 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (t, J = 1.2 Hz, 3 H), 3.48 (ddd, J = 4.6, 11.0, 12.0 Hz, 1 H), 3.89 (dd, J = 4.6, 11.5 Hz, 1 H), 4.79–5.10 (m, 3 H), 5.58 (d, J = 11.0 Hz, 1 H), 7.12–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.2, 45.1, 60.8, 74.9, 117.4, 127.7, 127.9, 128.6, 136.2, 139.0.

The sulfite with R_f = 0.53 in benzene: solid; bp 160 °C (2 mmHg); mp 77–78 °C; IR (neat film) 2930 (m), 1660 (w), 1455

(16) Tamaru, Y.; Hojo, M.; Kawamura, S.; Sawada, S.; Yoshida, Z. *J. Org. Chem.* **1987**, *52*, 4062.

(m), 1190 (s), 1020 (s), 960 (s), 845 (s), 675 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (d, J = 0.7 Hz, 3 H), 3.01 (dt, J = 1.5, 3.4 Hz, 1 H), 3.99 (dd, J = 1.5, 11.5 Hz, 1 H, coalescing to d, J = 11.5 Hz, by irradiation at 3.01), 4.72–4.93 (m, 2 H), 5.40 (dd, J = 3.4, 11.5 Hz, 1 H, coalescing to d, J = 11.5 Hz, by irradiation at 3.01), 5.67–5.80 (m, 1 H), 7.14–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 18.4, 43.6, 62.6, 69.2, 112.6, 127.1, 128.0, 129.0, 137.4, 139.4.

The sulfite with R_f = 0.39 in benzene: oil; bp 160 °C (2 mmHg); IR (neat film) 2930 (m), 1650 (w), 1455 (m), 1235 (s), 965 (s), 785 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (dd, J = 1.9, 1.5 Hz, 3 H), 3.51 (ddd, J = 6.1, 8.8, 10.0 Hz, 1 H), 4.26–4.73 (m, 2 H), 4.73–5.07 (m, 3 H), 7.07–7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.2, 43.9, 67.8, 84.3, 113.0, 117.1, 127.8, 128.7, 129.4, 139.2.

1-Vinyl-2,3-tetramethylenepropane-1,3-diol sulfite (11c): a mixture of at least six diastereomers; oil; bp 150 °C (3 mmHg); IR (neat film) 2950 (s), 1455 (m), 1230 (s), 1190 (m), 994 (m), 940 (s), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87–2.59 (m, 9 H), 4.27–6.86 (m, 5 H).

1-Vinyl-2-methylpropane-1,3-diol sulfite (11d): a mixture of four diastereomers (1:1:1:1); oil; bp 150 °C (10 mmHg); IR (neat film) 2980 (m), 1645 (w), 1235 (m), 1190 (s), 970 (s), 940 (s), 795 (m), 710 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (d, J = 6.8 Hz, Me), 0.92 (d, J = 6.8 Hz, Me), 1.00 (d, J = 6.8 Hz, Me), 1.23 (d, J = 6.8 Hz, Me), 1.65–2.02 (m, 1 H of one isomer), 2.02–2.47 (m, 1 H of the other three isomers), 3.59–4.60 (m, 1 H), 4.60–6.41 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 11.6, 12.6 (Me's), 32.3, 33.2, 33.5, 34.5, 61.4, 63.6, 64.8, 67.6, 69.4, 74.1, 81.1, 83.0, 116.9, 118.8, 119.4, 120.1, 133.1, 133.3, 133.6, 133.9.

***trans*-1-(*trans*-1′-Propenyl)-2-methylpropane-1,3-diol sulfite 11e**: oil; bp 150 °C (9 mmHg); IR (neat film) 2950 (m), 1465 (m), 1190 (s), 1090 (m), 975 (s), 815 (m), 710 (m), 660 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (d, J = 6.8 Hz, 3 H), 1.74 (dd, J = 1.5, 6.3 Hz, 3 H), 1.95–2.53 (m, 1 H), 3.77 (dd, J = 4.4, 11.2 Hz, 1 H), 4.53 (dd, J = 11.2, 11.5 Hz, 1 H), 4.95 (dd, J = 8.3, 10.3 Hz, 1 H), 5.41 (ddq, J = 8.3, 15.1, 1.5 Hz, 1 H), 5.89 (dq, J = 15.1, 6.3 Hz, 1 H).

***trans*-1-(*trans*-1′-Propenyl)-2-methylpropane-1,3-diol sulfite 11e′**: oil; bp 150 °C (9 mmHg); IR (neat film) 2970 (m), 1465 (m), 1380 (m), 1230 (s), 970 (m), 810 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (d, J = 6.8 Hz, 3 H), 1.75 (d, J = 5.8 Hz, 3 H), 1.88–2.43 (m, 1 H), 3.93 (dd, J = 9.5, 12.0 Hz, 1 H), 4.24–4.54 (m, 2 H), 5.54 (dd, J = 7.3, 15.1 Hz, 1 H), 5.87 (dq, J = 15.1, 5.8 Hz, 1 H).

***cis*-1-(*trans*-1′-Propenyl)-2-methylpropane-1,3-diol sulfite (11f)**: oil; bp 150 °C (9 mmHg); IR (neat film) 2980 (m), 1460 (m), 1190 (s), 1055 (m), 970 (m), 935 (s), 810 (m), 720 (m), 675 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (d, J = 7.1 Hz, 3 H), 1.73 (d, J = 5.9 Hz, 3 H), 1.48–1.98 (m, 1 H), 3.67 (dd, J = 2.0, 11.2 Hz, 1 H), 5.14 (dd, J = 2.4, 11.2 Hz, 1 H), 5.34–6.10 (m, 3 H).

General Procedure for Palladium-Catalyzed Rearrangement. Into a flask containing $(dba)_3Pd_2C_6H_6$ (0.03 mmol), equipped with a rubber balloon filled with argon, were added a solution of sulite (1 mmol) in dry dioxane (5 mL) and triethyl phosphite (0.24 mmol) via a syringe. The mixture was stirred for the periods of time and at the temperatures indicated in Tables I and II. Then, the solvent was evaporated and the residue was directly subjected to column chromatography over silica gel (hexane–ether gradient). Two typical examples are given below.

2′-Phenylethyl 2-Propenesulfonate (6a). Run 1, Table I: Into a flask containing $(dba)_3Pd_2C_6H_6$ (29.8 mg, 0.03 mmol), equipped with a rubber balloon filled with argon, were added a solution of **5a** (226 mg, 1.0 mmol) in dry dioxane (5 mL) and triethyl phosphite (0.041 mL, 0.24 mmol) via a syringe. The mixture was stirred at room temperature for 18 h. The reaction was followed by means of TLC (**5a**, R_f = 0.44; **6a**, R_f = 0.21; hexane–ether, 1:1). The solvent was removed, and the residue was directly subjected to column chromatography over silica gel (hexane–ether gradient): yield 162.7 mg (0.72 mmol, 72%); oil; bp 150 °C (2 mmHg); IR (neat film) 3130 (m), 1630 (w), 1380 (s), 1190 (s), 990 (s), 780 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.04 (t, J = 7.1 Hz, 2 H), 3.70 (d, J = 6.8 Hz, 2 H), 4.42 (t, J = 7.1 Hz, 2 H), 5.20–5.48 (m, 2 H), 5.79 (ddt, J = 10.5, 16.4, 6.8 Hz, 1 H), 7.10–7.42 (m, 5 H). Anal. Calcd for $C_{11}H_{14}SO_3$: C, 58.39; H, 6.24; S, 14.17. Found: C, 58.38; H, 6.22; S, 14.18.

***trans*-1-Vinyl-2-methyl-1,3-propanesultone (12d).** Run 4, Table II: Into a flask containing $(dba)_3Pd_2C_6H_6$ (42.2 mg, 0.0424 mmol), equipped with a rubber balloon filled with argon, were added a solution of **11d** (1:1:1:1 diastereomeric mixture, 230 mg, 1.42 mmol) in dry dioxane (5 mL) and triethyl phosphite (0.0577 mL, 0.340 mmol) via a syringe. The mixture was stirred at 60 °C for 5 h. The reaction was followed by means of TLC (**11d**, R_f = 0.66; **12d**, R_f = 0.38; hexane–ether, 1:1). The solvent was evaporated, and the residue was directly subjected to column chromatography over silica gel (hexane–ether gradient): yield 139 mg (0.857 mmol, 61%); oil; bp 150 °C (6 mmHg); IR (neat film) 2980 (m), 1640 (m), 1460 (m), 1345 (s), 1170 (s), 1090 (m), 990 (s), 950 (s), 910 (s), 820 (s), 760 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, J = 6.7 Hz, 3 H), 2.71–2.83 (m, 1 H, C_2H), 3.42 (dd, J = 8.9, 11.2 Hz, 1 H, C_1H), 3.96 (dd, J = 8.8, 10.3 Hz, 1 H, C_3H), 4.54 (dd, J = 7.3, 8.8 Hz, 1 H, C_3H), 5.53 (d, J = 17.0 Hz, 1 H), 5.57 (d, J = 10.0 Hz, 1 H), 5.75 (ddd, J = 8.9, 10.1, 17.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 37.4, 66.4, 73.1, 124.2, 126.8. Anal. Calcd for $C_6H_{10}SO_3$: C, 44.43; H, 6.21; S, 19.77. Found: C, 44.48; H, 6.30; S, 19.73.

2′-Phenylethyl 1-methyl-2-propenesulfonate (6b) and 2′-phenylethyl *trans*-2-butenesulfonate (7b): **6b**:**7b** = 77:23; oil; bp 150 °C (2 mmHg); IR (neat film) 3040 (w), 2950 (w), 1460 (m), 1355 (s), 1170 (s), 970 (s), 705 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (d, J = 6.8 Hz, 3 H of **6b**), 1.72 (d, J = 6.1 Hz, 3 H of **7b**), 3.03 (t, J = 7.1 Hz, 2 H), 3.55–3.92 (m, 1 H of **6b** and 2 H of **7b**), 4.41 (t, J = 6.8 Hz, 2 H), 5.17–5.43 (m, 2 H of **6b**), 5.43–6.05 (m, 2 H of **7b**), 5.85 (ddd, J = 7.3, 8.5, 18.3 Hz, 1 H of **6b**), 7.13–7.33 (m, 5 H). Anal. Calcd for $C_{12}H_{16}SO_3$: C, 59.98; H, 6.71; S, 13.34. Found: C, 60.22; H, 6.75; S, 13.48.

2′-Phenylethyl 3-phenyl-2-propenesulfonate (7d): mp 77–79 °C (hexane–ether); IR (KBr disk) 2980 (m), 1455 (m), 1340 (s), 1150 (s), 970 (s), 925 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.03 (t, J = 7.1 Hz, 2 H), 3.86 (dd, J = 1.0, 7.3 Hz, 2 H), 4.44 (t, J = 7.1 Hz, 2 H), 6.06 (dt, J = 15.9, 7.3 Hz, 1 H), 6.60 (dd, J = 15.9, 1.0 Hz, 1 H), 7.11–7.42 (m, 10 H). Anal. Calcd for $C_{17}H_{18}SO_3$: C, 67.52; H, 6.00; S, 10.60. Found: C, 67.47; H, 6.09; S, 10.69.

2′-Phenylethyl 2-cyclohexenesulfonate (6e): oil; bp 180 °C (3 mmHg); IR (neat film) 2950 (m), 1650 (w), 1345 (s), 1170 (s), 960 (m), 700 (m), cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.19 (m, 6 H), 3.04 (t, J = 6.8 Hz, 2 H), 3.58–3.87 (m, 1 H), 5.54 (t, J = 6.8 Hz, 2 H), 5.58–5.81 (m, 1 H), 5.95–6.22 (m, 1 H), 7.13–7.49 (m, 5 H). Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.13; H, 6.81; S, 12.04. Found: C, 63.37; H, 6.94; S, 11.95.

2′-Phenylethyl 2-methyl-2-propenesulfonate (6f): oil; bp 170 °C (4 mmHg); IR (neat film) 2930 (m), 1645 (m), 1360 (s), 1170 (s), 960 (s), 920 (m), 730 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89 (dd, J = 0.7, 1.5 Hz, 3 H), 3.04 (t, J = 7.1 Hz, 2 H), 3.68 (d, J = 0.7 Hz, 1 H), 4.42 (t, J = 7.1 Hz, 2 H), 4.98–5.18 (m, 2 H), 7.22–7.33 (m, 5 H). Anal. Calcd for $C_{12}H_{16}SO_3$: C, 59.98; H, 6.71; S, 13.34. Found: C, 60.04; H, 6.76; S, 13.52.

2′-Phenylethyl 1,1-dimethyl-2-propenesulfonate (6g): oil; bp 170 °C (2 mmHg); IR (neat film) 3000 (m), 1640 (w), 1350 (s), 1190 (s), 1035 (s), 970 (s), 900 (s), 770 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (s, 3 H), 3.02 (t, J = 6.8 Hz, 2 H), 4.39 (t, J = 6.8 Hz, 1 H), 5.16–5.40 (m, 2 H), 5.98 (dd, J = 9.8, 18.1 Hz, 1 H), 7.09–7.39 (m, 5 H). Anal. Calcd for $C_{13}H_{18}SO_3$: C, 61.39; H, 7.13; S, 12.60. Found: C, 61.64; H, 7.28; S, 12.84.

2′-Phenylethyl 3-methyl-2-butenesulfonate (7g): oil; bp 170 °C (2 mmHg); IR (neat film) 2930 (m), 1670 (m), 1455 (m), 1360 (s), 1175 (s), 965 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (s, 3 H), 1.77 (s, 3 H), 3.03 (t, J = 6.8 Hz, 2 H), 3.71 (d, J = 7.5 Hz, 2 H), 4.39 (t, J = 6.8 Hz, 2 H), 5.16 (t, J = 7.5 Hz, 1 H), 7.10–7.42 (m, 5 H). Anal. Calcd for $C_{13}H_{18}SO_3$: C, 61.39; H, 7.13; S, 12.60. Found: C, 61.53; H, 7.20; S, 12.43.

2′-Phenylethyl 3,7-dimethyl-1,6-octadiene-3-sulfonate (6i): oil; bp 200 °C (3 mmHg); IR (neat film) 2970 (m), 1345 (s), 1175 (s), 960 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (s, 3 H), 1.56 (s, 3 H), 1.68 (s, 3 H), 1.80–2.05 (m, 4 H), 3.01 (t, J = 7.1 H, 2 H), 4.39 (t, J = 7.1 Hz, 2 H), 5.03 (br s, 1 H), 5.14–5.48 (m, 2 H), 5.88 (dd, J = 10.5, 17.1 Hz, 1 H), 7.01–7.46 (m, 5 H). Anal. Calcd for $C_{18}H_{26}SO_3$: C, 67.05; H, 8.13; S, 9.94. Found: C, 67.35; H, 7.96; S, 10.03.

2′-Phenylethyl 1-methylallenesulfonate (10): oil; bp 200 °C (3 mmHg); IR (neat film) 2970 (m), 1975 (m), 1460 (m), 1360 (s), 965 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.87 (t, J = 3.2 Hz, 3 H), 3.05 (t, J = 6.8 Hz, 2 H), 4.33 (t, J = 6.8 Hz, 3 H), 5.31 (q, J = 3.2 Hz, 2 H), 7.19–7.37 (m, 5 H). Anal. Calcd for $C_{12}H_{14}SO_3$:

C, 60.48; H, 5.92; S, 13.45. Found: C, 60.42; H, 6.04; S, 13.69.

1-Vinyl-2,2-pentamethylene-1,3-propanesultone (12a): oil; bp 150 °C (1 mmHg); IR (neat film) 2930 (s), 1650 (w), 1350 (s), 1185 (s), 960 (s), 820 (s), 775 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–1.99 (m, 10 H), 3.50 (d, J = 9.4 Hz, 1 H), 4.42 (d, J = 9.4 Hz, 1 H), 5.31–5.65 (m, 2 H), 5.90 (ddd, J = 9.0, 10.0, 16.4 Hz, 1 H); mass spectrum, m/z (relative intensity) 216 (M, 0.1), 152 (M – SO_2, 0.5), 135 (2), 122 (19), 107 (7), 94 (100). Anal. Calcd for $C_{10}H_{16}SO_3$: C, 55.53; H, 7.46; S, 14.82. Found: C, 55.51; H, 7.54; S, 14.94.

***trans*-1-(1′-Methylvinyl)-2-phenyl-1,3-propanesultone (12b)**: mp 88–89 °C (hexane–ether); IR (neat film) 2940 (m), 1640 (m), 1330 (s), 1160 (s), 940 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (dd, J = 1.0, 1.5 Hz, 3 H), 3.98–3.41 (m, 3 H), 4.55–4.77 (m, 1 H), 5.15–5.28 (m, 2 H), 7.16–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.9, 45.4, 68.2, 72.3, 120.3, 127.2, 128.4, 129.2, 133.1, 135.0. Anal. Calcd for $C_{12}H_{14}SO_3$: C, 60.48; H, 5.92; S, 13.45. Found: C, 60.37; H, 5.83; S, 13.62.

1-Vinyl-2,3-tetramethylene-1,3-propanesultone (12c): a mixture of diastereomers (3:2:1); oil; bp 160 °C (2 mmHg); IR (neat film) 2950 (m), 1640 (w), 1350 (s), 1165 (s), 990 (m), 815 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96–2.89 (m, 9 H), 3.50–4.28 and 4.61–4.86 (m, 2 H), 5.25–6.13 (m, 3 H). Anal. Calcd for $C_9H_{14}SO_3$: C, 53.44; H, 6.98; S, 15.85. Found: C, 54.12; H, 7.15; S, 15.76.

***trans*-1-(*trans*-1′-Propenyl)-2-methyl-1,3-propanesultone (12e)**: bp 180 °C (2 mmHg); IR (neat film) 1665 (m), 1450 (m), 1345 (s), 1175 (s), 950 (m), 835 (m), 675 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (d, J = 6.6 Hz, 3 H), 1.81 (dd, J = 1.5, 6.5 Hz, 3 H), 2.36–3.01 (m, 1 H), 3.37 (dd, J = 8.8, 11.5 Hz, 1 H), 3.91 (dd, J = 8.8, 10.0 Hz, 1 H), 4.50 (dd, J = 7.3, 8.8 Hz, 1 H), 5.35 (ddq, J = 8.8, 15.1, 1.5 Hz, 1 H), 5.95 (dq, J = 15.1, 6.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.4, 17.9, 37.5, 66.0, 73.0, 119.4, 136.1. Anal. Calcd for $C_7H_{12}SO_3$: C, 47.71; H, 6.86; S, 18.19. Found: C, 47.94; H, 6.92; S, 18.29.

***cis*-1-(*trans*-1′-Propenyl)-2-methyl-1,3-propanesultone (12f)**: bp 180 °C (2 mmHg); IR (neat film) 1665 (m), 1450 (m), 1340 (s), 1165 (s), 970 (m), 870 (m), 815 (m), 770 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (d, J = 7.1 Hz, 3 H), 1.82 (dd, J = 1.5, 6.3 Hz, 3 H), 3.04 (pseudosept, J = 7.2 Hz, 1 H), 3.88 (dd, J = 7.6, 9.8 Hz, 1 H), 4.00 (dd, J = 7.3, 8.9 Hz, 1 H), 4.50 (dd, J = 7.1, 8.9 Hz, 1 H, 5.41 (ddq, J = 9.8, 15.1, 1.5 Hz, 1 H), 5.92 (dq, J = 15.1, 6.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.4, 18.0, 35.3, 63.0, 73.2, 118.0, 136.2.

***trans*-1-(*cis*-1′-Propenyl)-2-methyl-1,3-propanesultone (12f′)**: bp 180 °C (2 mmHg); IR (neat film) 1655 (w), 1460 (m), 1340 (s), 1160 (s), 950 (m), 830 (m), 770 (m), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (d, J = 6.6 Hz, 3 H), 1.81 (dd, J = 2.0, 7.1 Hz, 3 H), 2.48–3.01 (m, 1 H), 3.80 (dd, J = 9.8, 10.5 Hz, 1 H), 3.98 (dd, J = 8.8, 10.0 Hz, 1 H), 4.53 (dd, J = 7.3, 8.8 Hz, 1 H), 5.17–5.53 (m, 1 H, coalescing to dd, J = 9.8, 10.6 Hz, by irradiation at 1.81), 6.11 (dq, J = 10.6, 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.4, 14.6, 38.4, 60.7, 73.3, 119.1, 134.7. Anal. Calcd for $C_7H_{12}SO_3$: C, 47.71; H, 6.86; S, 18.19. Found: C, 47.91; H, 6.79; S, 18.34.

Acknowledgment. We acknowledge partial financial support from the Ministry of Education, Science and Culture, the Japanese Government (Grant-in-Aid for Special Project No. 61125002 and Scientific Research B No. 61470094).

Aromatic Nucleophilic Substitution Reactions of 1-(Alkylamino)-2,4-dinitronaphthalenes with Various Primary Amines in Dimethyl Sulfoxide[1]

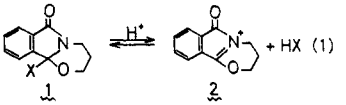
Shizen Sekiguchi,* Tohru Suzuki, Yukitoshi Hirosawa, and Hiromi Ishikura

Department of Synthetic Chemistry, Gunma University, Ten-jin cho, Kiryu, Gunma 376, Japan

Received July 7, 1989

The alkylamino group (e.g., methyl-, ethyl-, butyl, isopropyl, and *tert*-butylamino) of 1-(alkylamino)-2,4-dinitronaphthalenes is found to be quickly and easily replaced by primary alkylamines at room temperature in dimethyl sulfoxide in comparatively high yields. The arylamino group of 1-(arylamino)-2,4-dinitronaphthalenes is also replaced by alkylamines in the same solvent, although detachment for arylamino groups is much slower than that for alkylamino groups in the case of 1-(alkylamino)-2,4-dinitronaphthalenes. The reaction mechanism is discussed.

In the aromatic nucleophilic substitution reaction (S_NAr) nucleofuges that have been used thus far include alkoxyl, aryloxy, halogeno, phosphoryl, dialkylsulfonio, trialkylammonio, azido, dimethylamino, alkyl- or arylsulfinyl, alkyl- or arylsulfonyl groups, and others.[2] Since the time that Berliner and Monack measured the rate of reaction of *N,N*-dimethyl-4-bromo-2-nitroaniline with excess piperidine at 25 °C and found it to be very slow,[3] dialkylamino groups have been regarded as poor leaving groups.[4,5] On the other hand, Gravitz and Jencks[6,7] reported the mechanism for the acid-catalyzed hydrolysis of the breakdown and formation of the tetrahedral addition compounds **1** formed from *N,O*-trimethylenephthalimidium ion (**2**) and alcohols or amines and concluded that



for a given basicity secondary amines are expelled from protonated **1** much more rapidly than are alkoxide ions (uncatalyzed) [eq 1, see references for details]. Furthermore, Bernasconi et al.[8] showed that the rate of departure

(1) Aromatic Nucleophilic Substitution. 27. For part 26, see: Sekiguchi, S.; Suzuki, T.; Hosokawa, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1783.

(2) (a) Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: New York, 1968; Chapter 5. (b) Bernasconi, C. F. *MTP Inter. Rev. Sci. Arom. Compounds Org. Chem. Ser. Ones* **1973**, *3*, 33. (c) Terrier, F. *Chem. Rev.* **1982**, *82*, 77.

(3) Berliner, E.; Monack, L. C. *J. Am. Chem. Soc.* **1952**, *74*, 1574.

(4) Bunnett, J. F.; Zahler, R. E. *Chem Rev.* **1951**, *49*, 273.

(5) Ross, S. D. *Progr. Phys. Org. Chem.* **1963**, *1*, 31.

(6) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705.

(7) (a) Gravitz, N.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 499; (b) 507.

0022-3263/90/1955-1829$02.50/0