

Novel Behavior of Thiiranium Radical Cation Intermediates. Reactions of Dimethyl Disulfide with Alkenes in the Presence of Pd(OAc)₂

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Abstract: Reaction of dimethyl disulfide (**1**) with cyclohexene (**2a**) in AcOH in the presence of Pd(OAc)₂ yields *trans*-1-acetoxy-2-methylcyclohexane (**3a**). The equivalent reactions with hex-1-ene (**2b**) and 2-methylpent-1-ene (**2c**) or 1-methylcyclohex-1-ene (**2d**) preferentially give *anti*-Markovnikov and Markovnikov adducts **4** and **3**, respectively, by acetoxymethylthiolation of the alkene. The Markovnikov regioselectivity **3b/4b** for the reaction with **2b** is higher than that for the reaction using AgOAc instead of Pd(OAc)₂, which proceeds *via* a thiiranium ion. Addition of a polar solvent (MeCN or MeNO₂) to the reactions with **2b** or **2c** using Pd(OAc)₂ abnormally decreases the Markovnikov regioselectivity. The total yield of **3** and **4** increases with an increased concentration of AcOH. Compounds **3** and **4** are also formed and the reactions in MeCN or MeNO₂ not containing AcOH. A solution of Pd(OAc)₂ in **1** exhibits λ_{max} 380 nm (log ϵ 3.6) assigned to the absorption of a relatively stable sulfonium salt. These indicate that the reactions using Pd(OAc)₂ proceed by S_N2 ring-opening of a new type of thiiranium radical cations paired with [−]OAc *via* the sulfonium salts. The insensitivity of the **3/4** ratios to the reaction time at 25-60°C in the reactions with **2c-d** shows the ring-opening to be controlled kinetically, but the increased ratio with reaction time at 116°C in the reaction with **2b** suggests that the ring-opening is thermodynamically governed. The reaction product with **2d** also undergoes a skeletal rearrangement to a thietanium radical cation to give 1-acetoxymethyl-2-methylthiocyclohexane.

Keywords: Dimethyl disulfide, Palladium (II) acetate, Acetoxymethylthiolation, Thiiranium radical cation, Regioselectivity for S_N2 ring-opening, Solvent effects, Thietanium radical cation, Skeletal rearrangement.

Introduction

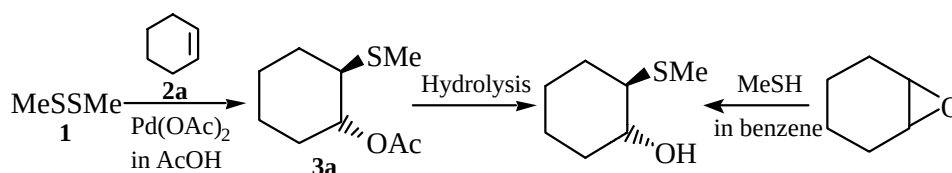
Thiiranium ion intermediates have been generated by reactions of disulfides with alkenes in the presence of oxidants such as $\text{Pb}(\text{OAc})_4$ [1-4], $\text{Mn}(\text{OAc})_3$ [2-4], $\text{Fe}(\text{OAc})_3$ [2-4] or $\text{Cu}(\text{OAc})_2$ [5], by reactions of β -thiohalides with AgY [6] and by reactions of thiiranes with RY [6]. The intermediates which have soft counterions such as BF_4^- , PF_6^- , SbF_6^- , SbCl_5^- , FSO_3^- and CF_3CO_2^- behave like carbenium ions [1] of a weakly bridged strong electrophile, undergoing a rapid ring-opening by the outer nucleophile at low temperature (-20 – 0°C) to give the observed predominant Markovnikov regioselectivity; in some cases, the skeletal rearrangement or stereoconversion of the thiiranium ions has been observed. We may infer that the reactions of RSCl with alkenes would generate not a σ -sulfurane but a strongly bridged thiiranium ion pairing tightly with hard Cl^- [1], and thus the ring-opening by the pairing Cl^- leads to the *anti*-Markovnikov regioselectivity without undergoing the stereoconversion and skeletal rearrangement.

In this work, reactions of dimethyl disulfide with 2-alkyl and 2,2-dialkylalkenes in AcOH in the presence of $\text{Pd}(\text{OAc})_2$ lead to the *anti*-Markovnikov and Markovnikov regioselectivity products, respectively, for the addition to the alkenes. Interestingly, the Markovnikov regioselectivity is lower than that observed for thiiranium ion intermediates, and is decreased by addition of polar solvents such as MeCN or MeNO_2 or the nonpolar solvent *n*-hexane. This novel behavior can be reasonably explained by considering a $\text{S}_\text{N}2$ ring-opening mechanism of a new type of thiiranium radical cation intermediates paired with ^-OAc . Furthermore, the reaction with 1-methylcyclohex-1-ene yields a product *via* an anionotropic rearrangement of the thiiranium radical cation intermediate to a thietanium radical cation intermediate.

Results and Discussion

Reactions with Cyclohexene (2a)

Reaction of dimethyl disulfide (**1**) with cyclohexene (**2a**) in AcOH in the presence of $\text{Pd}(\text{OAc})_2$ produced only *trans*-1-acetoxy-2-methylthiocyclohexane (**3a**) at 25 or 116°C (Table 1). The structure of **3a** was assigned to the *trans*-form on accord of the fact that the mass spectra of **3a** were identical with those of the product formed by the reaction of cyclohexene oxide with MeSH in benzene (Scheme 1). The *trans*-configuration shows that **3a** arises from an $\text{S}_\text{N}2$ ring-opening of a three-membered ring intermediate, and that the intermediate is still stable at 116°C without transforming to the corresponding carbocation at such a high temperature.



Scheme 1.

Table 1. Reactions in the presence of Pd(OAc)₂ (0.68 mmol) of dimethyl disulfide (**1**) (2.0 mmol) with 4.8 mmol of cyclohexene (**2a**) and hex-1-ene (**2b**) in AcOH (10.0 cm³) containing Ac₂O (1.0 cm³).

Alkene	T/°C	t/h	Yield ^a (%)		Ratio
			3	4	
2a	25	24	69 ^b	-	-
2a	116	24	68 ^b	-	-
2b	0	2.0	5.6	15	0.37
2b	0	4.0	8.8	24	0.37
2b	25	2.0	14	32	0.44
2b	25	24	16	37	0.43
2b	25	96	16	36	0.44
2b	60	1.0	13	29	0.45
2b	60	2.0	20	40	0.50
2b	116	1.0	17	23	0.74
2b	116	2.0	36	34	1.1
2b	116	24	76	17	4.5

^aThe yields are calculated to be 100% when two moles of product is formed from one mole of Pd(OAc)₂ used, and were obtained by GLC analysis; ¹H NMR analysis gave nearly the same results.

^bThe *trans*-stereochemistry is assigned by the fact that the compound given by hydrolysis of **3a** is identical with that formed by S_N2 reaction of cyclohexene oxide with MeSH in benzene.

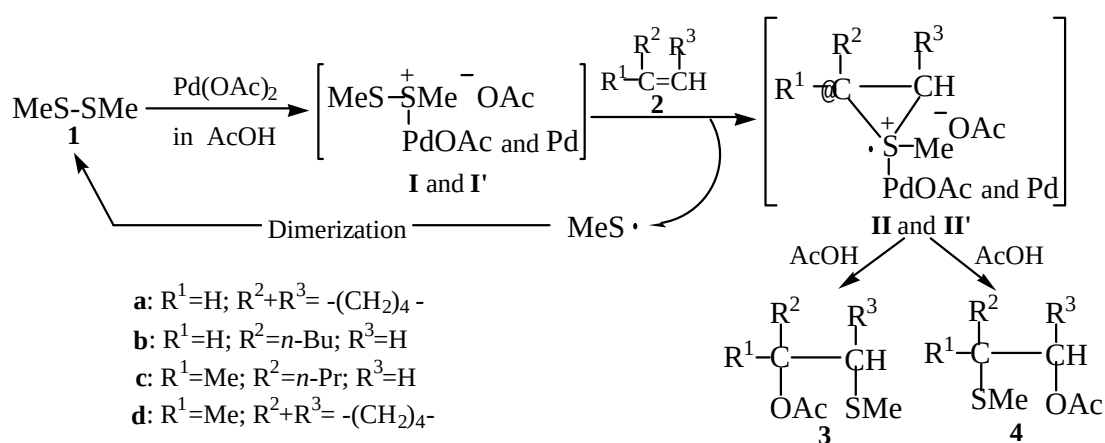
Reactions with Hex-1-ene (**2b**)

The reaction with hex-1-ene (**2b**) at 0–60°C gave preferentially the *anti*-Markovnikov adduct **4b**, and the **3b/4b** ratio was observed to increase with temperature (Table 1). The ratio at 0–60°C was almost insensitive to the reaction time whereas the ratio at 116°C was enhanced in the prolonged reaction (Table 1). The insensitivity of the ratio to the reaction time means that the reaction is controlled kinetically at 0–60°C, but thermodynamically governed at 116°C. In fact, when a mixture of **3b/4b** = 0.34 was treated in AcOH, the ratio **3b/4b** at 25°C did not change for 24 h, but the ratio at 116°C increased to 1.4 or 6.6 after 2 h or 24 h, respectively. The preferential formation of *anti*-Markovnikov adduct at 0–60°C suggests that the kinetic S_N2 ring-opening of the final three-membered ring intermediate is principally affected by steric factors (Scheme 2).

Formation of Thiiranium Radical Cations **II** and **II'** from Sulfonium Salts **I** and **I'**

From the above *trans*-addition, the final intermediate for the formation of the products should be logically three membered ring intermediates. As an oxidant Pd(OAc)₂ can act in two ways. The first action is electron transfer: One electron transfer from **1** to Pd(OAc)₂ forms a disulfide radical cation [7], and the radical cation and/or a sulfenium ion [8] arising from the radical cation should generate a thiiranium ion as the final intermediate by attack on the alkene. As seen in Tables 1 and 4, the reaction using Pd(OAc)₂ shows higher Markovnikov regioselectivity (**3b/4b** = 0.44) at 25°C than that observed at 25°C (0.27) in the reaction *via* a thiiranium ion [9] using AgOAc instead of Pd(OAc)₂. Furthermore,

the Markovnikov regioselectivity $3/4$ for the reaction using $\text{Pd}(\text{OAc})_2$ is unusually decreased on dilution with a polar solvent (MeCN or MeNO_2) while that using AgOAc is increased on dilution with MeNO_2 (Table 3). These data show that the reaction using $\text{Pd}(\text{OAc})_2$ does not proceed *via* a thiiranium ion, and thus this action for $\text{Pd}(\text{OAc})_2$ can be ruled out. Another action is coordination. $\text{Pd}(\text{OAc})_2$ coordinates to **1** to give sulfonium ions **I** and **I'** (Scheme 2). The sulfonium ions undergo a homolytic S-S scission by spontaneous or induced (by AcOH) decomposition to give $\text{MeS}\cdot$ and thiiranium radical cations **II** and **II'** which bond with the Pd atom (Scheme 2). If a heterolytic S-S scission of **I** and **I'** occurs, then thiiranium ion intermediates should be formed by reaction with sulfenium fragment. Thus, the heterolytic scission can be excluded. Therefore, the latter action predominates and **II** and **II'** as the final intermediates should be formed by the homolytic S-S scission of **I** and **I'** (Scheme 2). The following evidence supports the fact that the products are formed *via* thiiranium radical cations **II** and **II'** from sulfonium ions **I** and **I'**.



Scheme 2.

A solution containing $\text{Pd}(\text{OAc})_2$ in AcOH also containing Ac_2O (9.1% v/v) shows λ_{max} 397 nm ($\log \epsilon$ 2.3) at 25°C while a solution made by dissolving $\text{Pd}(\text{OAc})_2$ in **1** at 25°C has λ_{max} 380 nm ($\log \epsilon$ 3.6). The species with λ_{max} 380 nm shows the half life-time *ca.* 30 h in **1**, so that the species could not be the unstable disulfide radical cation [7] but rather a sulfonium salt **I** $[\text{MeS}-\text{S}^+(\text{Me})\text{PdOAc}]^+ \text{OAc}^-$. When different oxidants AgOAc and AlCl_3 are dissolved in **1**, we can observe the same λ_{max} 375 nm with a very short lifetime. Thus, the species with λ_{max} 375 nm might be the disulfide radical cation, which would be independent of oxidative metals [7]. Considering that the intermediate using AlCl_3 can bring about an aromatic methylthiolation [7] whereas that using AgOAc is not subject to the aromatic methylthiolation but can react with alkene to form a thiiranium ion [9], we can regard the following: a very small amount of the disulfide radical cation and a more large amount of a sulfonium ion $[\text{MeS}-\text{S}^+(\text{Me})\text{Ag}]^+ \text{OAc}^-$ (this has no visible absorption due to a σ S-Ag bond) are generated as the intermediates when AgOAc is dissolved in **1**. Dissolving AlCl_3 in **1**, the disulfide radical cation is only formed as the intermediate.

During the reaction of **1** with **2b** using $\text{Pd}(\text{OAc})_2$, we obtained a small amount of a dark reddish powdery precipitate having ν_{max} (KBr)/ cm^{-1} 2900 and 2980 (C-H), 1577 and 1410 ($-\text{CO}_2^-$), 1050, 1020, 950, 930 and 652 (C-S). This precipitate might be a sulfonium salt **I'** $[\text{MeS}-\text{S}^+(\text{Me})\text{Pd}]^+ \text{OAc}^-$; this salt does not have OAc attached to Pd since the carbonyl of $\text{Pd}(\text{OAc})_2$ appears at *ca.* 1610 cm^{-1} .

Considering that one mole of product is formed from one mole of $\text{Pd}(\text{OAc})_2$, then we observe that the total yield of **3** and **4** is more than 100%. Thus, the generation of the two species **I** and **I'** from one mole of $\text{Pd}(\text{OAc})_2$ is reasonable.

The novel behavior for the reaction using $\text{Pd}(\text{OAc})_2$ instead of AgOAc (*i.e.* the high **3b/4b** ratio using $\text{Pd}(\text{OAc})_2$ relative to AgOAc and the decreased **3b/4b** ratio upon addition of polar solvent) as described above is probably due to the higher positive charge on the C_2 -carbon of **II** than that of the corresponding thiiranium ion since **II** contains a positive Pd atom; the effect of polar solvent is explained below. The possibility that the final intermediate is a thiiranium dication formed by attack of thiiranium ion on $\text{Pd}(\text{OAc})_2$ can be excluded on account of charge-repulsion between the positive species on the attack.

Reactions with 2-Methylpent-1-ene (**2c**)

The reaction with 2-methylpent-1-ene **2c** gave the Markovnikov regioselectivity exhibiting **3c/4c** of *ca.* 1.8 at 0–60°C, and the ratio was almost insensitive to reaction time (Table 2). The time-insensitivity reflects the product stability, and means that the ring-opening of the intermediates **IIc** and **II'c** is controlled kinetically. The Markovnikov regioselectivity indicates that the ring-opening of **IIc** and **II'c** is mostly governed electronically. The reaction with **2c** at 116°C is described below.

Table 2. Reactions of dimethyl disulfide **1** (2.0 mmol) with 2-methylpent-1-ene **2c** and 1-methylcyclohex-1-ene **2d** of 4.8 mmol in the presence of $\text{Pd}(\text{OAc})_2$ (0.68 mmol) in AcOH (10 cm^3) containing Ac_2O (1.0 cm^3).

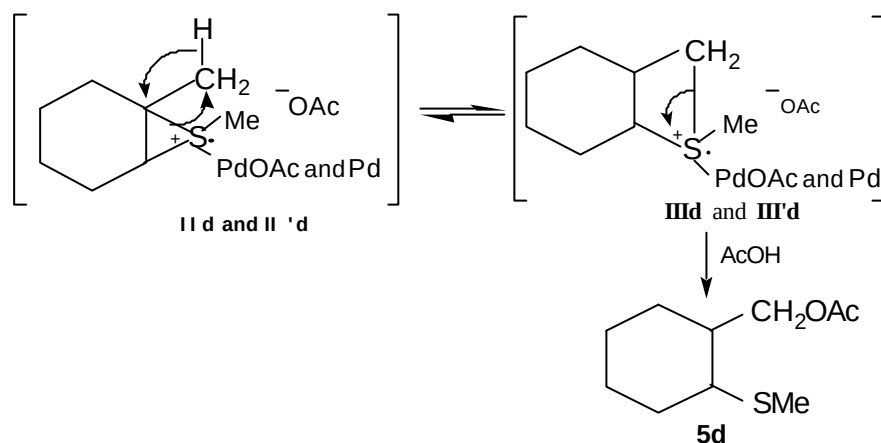
Alkene	T/°C	t/h	Yield ^a (%)			Ratio
			3	4	5	
2c	0	2.0	15	8.5	0	1.8
2c	0	4.0	20	11	0	1.8
2c	25	2.0	18	10	0	1.8
2c	25	24	34	17	0	2.0
2c	60	2.0	24	13	0	1.8
2c	60	4.0	47	26	0	1.8
2d	0	2.0	15	4.1	3.2	3.7
2d	0	4.0	26	7.4	2.8	3.5
2d	25	2.0	30	10	5.3	3.0
2d	25	24	39	14	3.5	2.8
2d	60	2.0	38	14	3.5	2.7
2d	60	4.0	44	20	4.1	2.2

^aThe yields are calculated as shown in Table 1. The products **3d** or **4d** correspond to *trans*-1-acetoxy-1- or -2-methyl-2-methylthiocyclohexane, respectively.

Reactions with 1-Methylcyclohex-1-ene (2d)

The reaction with 1-methylcyclohex-1-ene (**2d**) at 25–60°C gives predominantly Markovnikov *trans*-adduct (**3d/4d** = 3.7–2.2) (Table 2). This can be also interpreted by the idea that the S_N2 ring-opening of **II**d and **II'**d occurs under preferential electronic control. A slightly lower ratio in the prolonged reaction (Table 2) is presumably due to the thermodynamic instability of **3d** compared to **4d**.

We obtained 1-acetoxymethyl-2-methylthiocyclohexane (**5d**) in the reaction with **2d**, but did not obtain the corresponding **5c** in the reaction with **2c** (Table 2). According to the molecular model, the S-atom of **II**d and **II'**d is closer to the 2-methyl carbon than that of **II**c and **II'**c, so **II**d and **II'**d may rearrange to the thietanium radical cations **III**d and **III'**d by a concerted reaction involving C_2 -S bond breaking and hydride migration of the 2-methyl group, leading to **5d** (Scheme 3). A similar anionotropic rearrangement from thiiranium ion to thietanium ion has been proposed for the concerted reaction involving C_2 -S breaking and methyl migration at tertiary carbon [10–14].



Scheme 3.

The reaction with **2c** or **2d** at 116°C gave many unidentified products according to GLC analysis. A stable tertiary carbocation is probably formed by bridge-cleavage of **II**c and **II'**c or **II**d and **II'**d at a high temperature such as 116°C, hence this result. But **II**a and **II'**a or **II**b and **II'**b, which cannot generate a tertiary carbocation by the cleavage are still bridged at 116°C, thus yielding **3a** or **3b** and **4b** by the S_N2 ring-opening.

Effects of Solvent and Concentration of AcOH

The total yield of **3** and **4** in the reaction with **2b** or **2c** in AcOH–CH₂Cl₂ increases with an increase in the concentration of AcOH, and **3b** and **4b** are also produced in the reaction in MeCN or MeNO₂ not containing AcOH (Table 3). These indicate that **3** and **4** are formed by the S_N2 attack on **II** and **II'** of both AcOH and AcO[−] pairing with **II** and **II'** (Scheme 2).

In the reaction with **2b** or **2c**, the Markovnikov regioselectivity **3/4** was interestingly decreased upon dilution with CH₂Cl₂ or the polar solvents MeCN or MeNO₂, and it was also depressed on dilution with nonpolar *n*-hexane (Table 3). By contrast, in the reaction of **1** with **2b** using AgOAc instead of Pd (OAc)₂, the Markovnikov regioselectivity for the ring-opening of thiiranium ion was increased on dilution with MeNO₂ (Table 3).

Table 3. Effects of solvents on the reaction of dimethyl disulfide (**1**) (2.0 mmol) with hex-1-ene (**2b**) (4.8 mmol) or 2-methylpent-1-ene (**2c**) (4.8 mmol) in the presence of Pd(OAc)₂ (0.68 mmol) at 25°C for 24 h.

Alkene	Solvent (cm ³)					Yield ^a (%)		Ratio
	AcOH	CH ₂ Cl ₂	<i>n</i> -C ₆ H ₁₄	MeCN	MeNO ₂	3	4	
2b	10	0	0	0	0	16	37	0.43
2b	9.0	1.0	0	0	0	12	29	0.41
2b	5.0	5.0	0	0	0	10	26	0.38
2b	1.0	9.0	0	0	0	6.5	19	0.34
2b	5.0	0	5.0	0	0	5.3	14	0.38
2b	0	0	0	10	0	4.1	17	0.24
2b	0	0	0	0	10	3.2	17	0.19
2b	5.0	0	0	0	5.0	13	42	0.31
2b^b	10	0	0	0	0	5.2	19	0.27
2b^b	5.0	0	0	0	5.0	5.4	16	0.34
2c	10	0	0	0	0	34	17	2.0
2c	9.0	1.0	0	0	0	31	18	1.7
2c	5.0	5.0	0	0	0	24	18	1.3
2c	1.0	9.0	0	0	0	16	19	0.84
2c	9.0	0	1.0	0	0	32	20	1.6
2c	5.0	0	5.0	0	0	15	12	1.3
2c	1.0	0	9.0	0	0	17	13	1.3
2c	5.0	0	0	0	5.0	47	27	1.7

^aThe yields are calculated to be 100% when two moles of product is formed from one mole of Pd(OAc)₂ and from two moles of AgOAc, and were obtained by GLC analysis; Ac₂O (1.0 cm³) is added to these reactions, but Ac₂O is not used in the reactions with only MeCN or MeNO₂.

^bAgOAc (1.36 mmol) instead of Pd(OAc)₂ was used in this reaction.

The decreased Markovnikov regioselectivity observed on dilution with the polar solvents suggests that the solvation with the polar solvent occurs strongly at the highly charged C-2 of **II** and **II'** rather than at the low charged C-3, suppressing the S_N2 reactivity at C-2 relative to the C-3. The depressed **3b/4b** ratio upon dilution with nonpolar *n*-hexane allows us to infer that this dilution transforms the solvent separated ion-pair of **II** and **II'** into a tight ion-pair in which the counteranion interacts to a greater extent with the more positive C-2 of **II** and **II'** than the less positive C-3 to decrease the S_N2 reactivity more at the C-2 than the C-3, leading to the observed results.

Effects of Oxidants

As described above, the oxidative attack of Pd(OAc)₂ on **1** may form the sulfonium salts **I** and **I'**, giving thiiranium radical cations **II** and **II'** and MeS• (Scheme 2); MeS• dimerizes to give **1** because

of an unfavorable reaction with **2** [15]. An addition of $\text{Cu}(\text{OAc})_2$ to the reaction with **2b** using $\text{Pd}(\text{OAc})_2$ resulted in rather suppressed yields of **3b** and **4b** (Tables 1 and 4). The use of $\text{Cu}(\text{OAc})_2$, $\text{Mn}(\text{OAc})_3$ or $\text{Pb}(\text{OAc})_4$ instead of $\text{Pd}(\text{OAc})_2$ in the reaction with **2b** did not yield the products **3b** and **4b** (Table 4); $\text{Cu}(\text{OAc})_2$ forms a complex with the alkene, and thus it would not operate as oxidizing agent. $\text{Mn}(\text{OAc})_3$ is not effective since it oxidizes AcOH [16]. $\text{Pb}(\text{OAc})_4$ is too strong an oxidant to be effective, giving a lot of unidentified products. PdSO_4 is difficult to dissolve in AcOH , so that it could scarcely be effective. The use of H_2SO_4 gave many unidentified products due to the strong acidity, leading to only a trace of the target products. Since AgOAc is complexed with alkene, it would be not so effective for the reaction.

Table 4. Effects of oxidants in the reactions of dimethyl disulfide (**1**) (2.0 mmol) with hex-1-ene (**2b**) (4.8 mmol) in the presence of oxidant in AcOH (10 cm^3) containing Ac_2O (1.0 cm^3) at 25°C for 24 h.

Oxidant	Oxidant/mmol	Yield ^a (%)		Ratio 3b/4b
		3b	4b	
$\text{Pd}(\text{OAc})_2 + \text{Cu}(\text{OAc})_2$	<i>b</i>	7.7	17	0.45
$\text{Cu}(\text{OAc})_2$	0.68	0	0	-
H_2SO_4	0.68	trace	trace	-
PdSO_4	0.68	trace	trace	-
AgOAc	1.36	5.2	19	0.27
$\text{Mn}(\text{OAc})_3$	2.4	0	0	-
$\text{Pb}(\text{OAc})_4$	2.4	0	0	-

^aThe yields are calculated to be 100% when two moles of product are formed from one mole $\text{Pd}(\text{OAc})_2$ or $\text{Cu}(\text{OAc})_2$ and from two moles AgOAc .

^b $\text{Pd}(\text{OAc})_2$ (0.60 mmol) and $\text{Cu}(\text{OAc})_2$ (3.6 mmol) were used, and the yields are obtained on the basis of $\text{Pd}(\text{OAc})_2$.

Experimental

General

IR spectra were obtained on a JASCO Cooperation A-302 spectrometer. ^1H NMR spectra were taken with a Nippondenshi PMX-60SI instrument (*J* values are given in Hz). GLC-MS were recorded with a Shimadzu QP-5000 spectrometer linked to a Shimadzu GC-17A; the column (15 m $\times$ 0.25 mm, coated with a 0.25 μm film of DB-1) is made by J & W Scientific. GLC was performed with a Shimadzu GC-8A using a glass column (1m $\times$ 3 mm) packed with 10% SE-30 on 60-80 mesh Chromosorb W (AW-DMCS). Two runs agreed within 3% error for the yields of the products, which were determined by replicate GLC analyses. The isolation or separation (as a mixture) of the products was done by thin layer chromatography (using Merck Silicagel 60PF254). AcOH , CH_2Cl_2 , MeCN , MeNO_2 , *n*-hexane and ethyl acetate were purified by standard methods before use. The following compounds were reagent grade (Nacalai Tesque), and used without further purification: Ac_2O , H_2SO_4 , $\text{Pd}(\text{OAc})_2$, $\text{Cu}(\text{OAc})_2$, PdSO_4 , AgOAc , $\text{Mn}(\text{OAc})_3$, $\text{Pb}(\text{OAc})_4$, dimethyl disulfide (**1**), cyclohexene (**2a**), hex-1-ene (**2b**), 2-methylpent-1-ene (**2c**) and 1-methyl-cyclohex-1-ene (**2d**).

Experimental procedures

Reactions of dimethyl disulfide (1) with cyclohexene (2a), hex-1-ene (2b), 2-methylpent-1-ene (2c) and 1-methylcyclohex-1-ene (2d) in AcOH containing Ac₂O in the presence of Pd(OAc)₂

A mixture of **1** and alkene (**2a**, **2b**, **2c** or **2d**) was added to a mixture of AcOH and Ac₂O in the presence of Pd(OAc)₂ with stirring (using a magnetic stirrer) under the conditions described in Tables 1 and 2. After the reaction, any precipitate formed was filtered off, and aqueous Na₂CO₃ was added to the filtrate until the solution reached pH > 7. The organic layer was extracted with ethyl acetate. The yields of products **3a-d**, **4b-d** and **5d** were determined by GLC analysis, and the results are summarized in Tables 1 and 2. Product **3a** was isolated by thin layer chromatography, and the structure was confirmed as follows.

Trans-1-acetoxy-2-methylthiocyclohexane (3a)

Liquid, $\nu_{\max}$ (neat)/cm⁻¹ 2930, 2860, 1734, 1450, 1375, 1235 and 1048; δ_{H} (CDCl₃) 1.08-1.09 (8H, m, CH₂), 2.06 (3H, s, Me), 2.09 (3H, s, Me), 2.33-2.80 (1H, m, SCH) and 4.85-5.08 (1H, m, OCH); GLC-MS, m/z 188 (M⁺), 128, 113, 81, 80, 79, 77, 61 and 53. The GC-MS mass spectra for the compound which is formed by hydrolysis of **3a** in aq. NaOH were identical with those for the product [*i.e.* *trans*-1-hydroxy-2-methylthiocyclohexane; m/z 146 (M⁺), 98, 87, 81, 80, 79, 70, 61, 57, and 55] given by a reaction of cyclohexene oxide with MeSH in benzene. This indicates that product **3a** has a *trans*-configuration.

The products **3b** and **4b** were not isolated but rather obtained as a mixture by thin layer chromatography. This mixture showed the following spectral data: $\nu_{\max}$ (neat) /cm⁻¹ 2930, 2870, 1744, 1460, 1380, 1240, 1040 and 818; δ_{H} (CDCl₃) 0.85-1.88 (9H, m, MeCH₂CH₂CH₂), 2.08 (3H, s, SMe or OCOMe), 2.12 (3H, s, OCOMe or SMe), 2.48-2.78 (br, SCH₂ of **3b**), 2.78-2.3.08 (br, SCH of **4b**), 4.18 (ABq, $J=6$ Hz, OCH₂ of **4b**) and 4.88-5.23 (m, OCH of **3b**). The products **3b** and **4b** have the following mass spectra by GLC-MS: m/z for **3b** 130 (M⁺-AcOH), 115 [M⁺- (AcOH+Me)], 87 (*n*-BuCH⁺OH)), 82 (radical cation of *n*-BuC≡CH), 67, 61 (MeSCH₂⁺) and 55 (C₄H₇⁺); m/z for **4b** 130, 115, 88, 87, 82, 67, 61 and 55. The fact that the relative intensity of m/z 130 and 87 to m/z 55 is higher in **3b** than in **4b** also suggests these structures. The observation that the GLC peak for **3b** has a shorter retention time than that for **4b** supports the fact that the AcO group for **3b** is more shielded by non polar groups than the AcO group for **4b**. The yields of **3b** and **4b** were obtained using the assumption that these compounds have the same GLC response factors. A mixture (33 mg) containing **3b** and **4b** (**3b/4b** = 0.34) was treated in AcOH (10 cm³) containing Ac₂O (1.0 cm³) at 25°C for 24 h and at 116°C for 2 h or 24 h. Product **3c** was isolated by thin layer chromatography, and the structure was confirmed by the following spectra.

2-Acetoxy-2-methyl-1-methylthiopentane (3c)

Liquid, $\nu_{\max}$ (neat) /cm⁻¹ 2920, 2870, 1732, 1435, 1370, 1240, 1198, 1140, 1030 and 950; δ_{H} (CDCl₃) 0.77-1.88 (7H, m, MeCH₂CH₂), 1.47 (3H, s, Me), 1.96 (3H, s, OCOMe), 2.11 (3H, s, SMe) and 2.98 (2H, s, SCH₂); m/z 130 (M⁺-AcOH), 101 [M⁺-(AcOH+Et)], 87, 82, 67, 61, 59, 55 and 53.

Compound **4c** was obtained as a mixture with **3c**, and the proposed structure was supported by the

GLC-MS results; the GLC peak for **4c** has a longer retention time than that for **3c** because the AcO group of **4c** is less shielded by non polar groups than the AcO group of **3c**, and the mass spectra for **4c** showed the following peaks: m/z 130, 117 ($M^+ - CH_2OAc$), 101, 83, 82, 67, 61, 59, 55 and 53). The peak m/z 117 is not observed for **3c**, and the appearance of this peak is in good agreement with the proposed *anti*-Markovnikov structure of **4c**. The yield of **4c** was determined using the assumption that **4c** has the same GLC response factor as **3c**.

The products **3d**, **4d** and **5d** were also obtained as a mixture, and the mixture indicated the following spectra: ν_{max} (neat) / cm^{-1} 2920, 2860, 1728, 1440, 1368, 1242, 1173, 1147, 1112, 1040 and 1025; δ_H ($CDCl_3$) 4.75-4.05 (m, OCH of **4d**), 4.05 (s, CH_2OCOME of **5d**), 2.45-2.75 (m, SCH of **3d** and **5d**), 2.16 (3H, s, SMe), 2.00 (3H, s, OCOME), 1.56 (s, Me) and 1.05-1.65 (m, CH of **5d** and CH_2). The GLC-MS for these products exhibited the following separate mass spectra: m/z for **3d** 202 (M^+), 142 ($M^+ - AcOH$), 113, 95 [$M^+ - (AcOH + SMe)$], 94, 93, 79, 77, 67, 55 and 53; m/z for **4d** 202 (M^+), 142, 113, 95, 94, 93, 79, 77, 67, 55 and 53; m/z for **5d** 202 (M^+), 163, 142, 129 ($M^+ - CH_2OAc$), 95, 94, 81, 79, 77, 67, 61, 55 and 53. The comparatively strong peak for m/z 129 was observed for **5d** but for neither **3d** nor **4d**, and the 1H NMR spectra for the mixture of **3d**, **4d** and **5d** showed a peak at 4.05 ppm (singlet, CH_2OCOME). These results lend strong support to the structure of **5d**. Considering **2a** to be *trans*-compound, **3d** and **4d** should also have *trans*-configuration. The low retention time of **3d** compared to **4d** and the high relative-intensity for m/z 142 of **3d** relative to **4d** support the proposed structures for **3d** and **4d**. The configuration for **5d** is not unambiguous, but it seems reasonable to assume it to be in a *trans*-form in which the SMe and CH_2OAc groups are located at the stable equatorial positions. The yields of **3d**, **4d** and **5d** were also determined with the assumption that these compounds have identical GLC response factors.

Effects of solvents and concentration of AcOH on the reaction of dimethyl disulfide (1) with hex-1-ene (2b) or 2-methylpent-1-ene (2c)

The reaction of dimethyl disulfide (**1**) with hex-1-ene (**2b**) or 2-methylpent-1-ene (**2c**) was performed similarly using various solvents under the conditions indicated in Table 3. Analysis and characterization of the products were carried out as described above. The results are summarized in Table 3.

Effects of oxidants in the reaction of dimethyl disulfide (1) with hex-1-ene (2b)

The reaction of dimethyl disulfide (**1**) with hex-1-ene (**2b**) was also conducted with a variety of oxidants under the conditions shown in Table 4. The yields of **3b** and **4b** were determined by the same procedure as that described above, and the results are summarized in Table 4.

References and Notes

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Sample Availability: Available from the authors.