

NAD(P)⁺-NAD(P)H Model. 62. The Mechanism of the Silica Gel-Catalyzed Reduction with an NAD(P)H Model

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The reduction of diethyl acetylenedicarboxylate, diethyl fumarate, and diethyl maleate as well as several α,β -unsaturated carbonyl compounds by a model of NAD(P)H on silica gel was examined. The order of the reactivity for the reduction was reverse to that of the degree of adsorption of the substrates onto the surface of silica gel. Semiquantitative analysis of the results suggests the possibility that silanol groups on the surface of silica gel act as general acid catalysts in the course of the reduction.

Recently, attentions have been focused on the utility of NAD(P)H models as reducing agents in organic synthesis.^{1–5)} The advantage of the reduction with an NAD(P)H model relies on its mildness in reducing ability. Thus, the model has a capacity to exert a novel selectivity in the reduction of a particular functional group with the aid of a certain catalyst. We reported previously that an NAD(P)H model selectively gives rise to reductive dehalogenation of an organic halide in the presence of a rhodium complex.¹⁾ Moreover, we found that silica gel is a selective catalyst for the 1,4-reduction of α,β -unsaturated carbonyl compounds by an NAD(P)H model, 3,5-bis(ethoxycarbonyl)-1,4-dihydro-2,6-dimethylpyridine (Hantzsch ester: HEH), in benzene.⁴⁾

Silica gel sometimes seems more useful catalyst in organic synthesis than an organometal complex such as a rhodium complex, since one can easily handle it and can remove it from the reaction mixture by filtration after completion of the reaction. Unfortunately, we have little informations in our hands

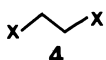
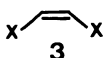
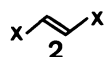
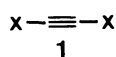
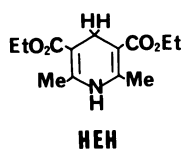
about the mechanism of catalysis by silica gel. In order to apply the silica gel-catalyzed reduction by an NAD(P)H model to other systems more widely, it may be important to reveal the details as to the role of silica gel.

We studied the mechanism of the reduction by using diethyl acetylenedicarboxylate (**1**), diethyl fumarate (**2**), and diethyl maleate (**3**) as model substrates. These substrates are expected to be adsorbed onto the surface of silica gel in a different manner due to their individual configurations. Through the product analyses for the reduction by HEH as well as the measurements of efficiency of substrate adsorption onto the surface of silica gel, we found several interesting facts. We report in this article the possibility that silanol groups on the surface of silica gel contribute to the reduction of the unsaturated carbon-carbon bonds in **1**, **2**, and **3** through general acid catalysis. We also mention briefly the results for the reduction of several α,β -unsaturated carbonyl compounds.

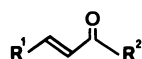
Results

NAD(P)H Model and Silica Gel. We have found that an NAD(P)H model, Hantzsch ester (HEH), has tolerance against self-decomposition in the presence of silica gel. Furthermore, in polar solvents such as acetonitrile, methanol, and chloroform, the reduction does not take place.⁴⁾ Based on these reasons, we employed HEH as an NAD(P)H model and benzene as the solvent in the present studies.

Use of silica gel with a fine mesh (e.g. 200 mesh) afforded scattered results for the yield, probably due to difficulty of complete removal of the materials from the surface of silica gel prior to the product analysis even when the catalyst was washed repeatedly with an appropriate solvent. Moreover, extremely slow rate of sedimentation of silica gel with a fine mesh after the stirring prevented accurate determination of the amount of adsorbed substrate. Then, we utilized silica gel 60 of 35–70 mesh (Nakarai Chem. CO.). The content of water in the silica gel 60 used in this study was measured to be 4.6 ± 0.2 mmol g⁻¹ on Kirl-Fisher



X = CO₂Et



5: R¹ = R² = Ph

6: R¹ = Ph, R² = p-Br-Ph

7: R¹ = Ph, R² = Me

8: R¹ = Me, R² = Ph

Chart

moisture content meter. Drying the silica gel over phosphorus pentoxide in vacuo at 100–120 °C for 7 h removed only ca. 20% of adsorbed water, then causing no appreciable alteration in the yield of the reduction. On the other hand, adsorption of the substrate and HEH as well as the reduction was dramatically suppressed when silica gel contains ca. 12 mmol g⁻¹ of water. Water content in the solvent was measured to be negligible relative to that in the silica gel.

Adsorption onto the Surface of Silica Gel. The efficiency of adsorption of diesters **1–3** and HEH as well as diethyl succinate (**4**) onto the surface of silica gel was examined initially. The amount of the substrate as well as HEH in the bulk phase (S_{Bulk}) was determined on vapor phase chromatography (VPC) for **1–4** or high performance liquid chromatography (HPLC) for HEH after stirring an appropriate amount of the substrate (or HEH) and 0.2 g of the silica gel in 1 ml of benzene at 70 °C under nitrogen atmosphere for 30 min.⁶ The adsorbed amount of the substrate (or HEH) (S_{Ad}) was given by subtracting S_{Bulk} from the stoichiometric amount of the substrate (or HEH).

In order to analyze the results, we assume a simple equilibrium with respect to the adsorption of substrate (or HEH) onto the surface of silica gel, as is expressed by Eq. 1.



$$Q_{\text{free}} = Q_0^{0.2} - S_{\text{Ad}} \quad (1b)$$

where S_{Bulk} and S_{Ad} are the amounts (mmol) of the substrate (or HEH) in bulk phase and adsorbed, respectively, and $Q_0^{0.2}$ is the maximum amount (mmol) of substrate being adsorbed onto the surface of 0.2 g of silica gel. Equilibrium constant K in Eq. 1 is given by Eq. 2

$$K = S_{\text{Ad}} / (S_{\text{Bulk}} \cdot Q_{\text{free}}) \quad (2)$$

Note that since these experiments were performed in 1 ml of the solvent, each term with dimension of mmol is equivalent to molarity, and, as a consequent, K has a dimension of M⁻¹ (=dm³/mol). We can readily lead Eq. 2 to Eq. 3.

$$\frac{1}{S_{\text{Ad}}} = \frac{1}{K \cdot Q_0^{0.2}} \cdot \frac{1}{S_{\text{Bulk}}} + \frac{1}{Q_0^{0.2}} \quad (3)$$

Equation 3 predicts that the plot of $1/S_{\text{Ad}}$ vs. $1/S_{\text{Bulk}}$ with the amount of the substrate being variable will give a straight line, and each line for different substrates will have a common intercept because the value of $Q_0^{0.2}$ could be reasonably considered to be identical for all substrates. This is indeed the case,

and the correlations for diesters **1–4** and HEH are exemplified in Fig. 1. The intercepts for five straight lines are identical within experimental error, affording $Q_0^{0.2} = (7.37 \pm 0.28) \times 10^{-2}$ mmol. Importantly, this value is compatible with the amounts of several types of modifying agents loaded onto the surface of silica gel.⁷ Thus, the value elucidated presently designates an “effective” amount of silanol groups on the surface. Dividing the intercept by the slope, we obtain equilibrium constants K for **1–4** and HEH. The values are summarized in Table 1.

Although the plots are scattered a little (correlation coefficient $r=0.98–0.998$), reinforcement for the validity of this treatment is given by similar examinations for chalcone (**5**), 4'-bromochalcone (**6**), benzylideneacetone (**7**), and crotonophenone (**8**). The relationships between $1/S_{\text{Ad}}$ and $1/S_{\text{Bulk}}$ for these substrates showed excellent linearity ($r>0.9999$ except for $r=0.9997$ for **7**) and from the intercepts of the lines (Fig. 2) the value of $Q_0^{0.2}$ was determined to be $(7.18 \pm 0.16) \times 10^{-2}$ mmol,⁸ which is consistent with that obtained from the set shown in Fig. 1. The K values for **5–8** are also summarized in Table 1. The results support our assumption that the ad-

Table 1. Equilibrium Constants K for Adsorption of Diesters, α,β -Unsaturated Carbonyl Compounds, and HEH onto the Surface of Silica Gel^{a)}

Substrate	K/M^{-1}	Substrate	K/M^{-1}
1	6.49	5	6.81
2	8.58	6	5.49
3	33.3	7	21.3
4	43.1	8	10.9
		HEH	51.1

a) At 70 °C.

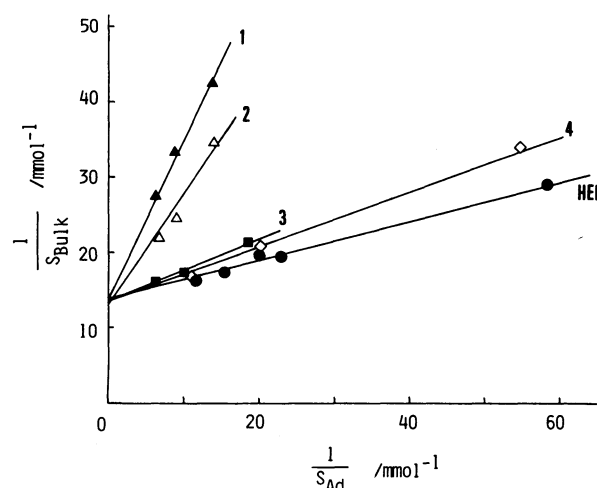


Fig. 1. $1/S_{\text{Ad}}$ vs. $1/S_{\text{Bulk}}$ plots for diesters and HEH with 0.2 g of the silica gel in 1 ml of benzene.

sorbed and free substrates (and HEH) are in equilibrium in the mixtures.

Silica Gel-Catalyzed Reduction by HEH. The reduction of diesters **1**–**3** were carried out in the presence of the silica gel in 1 ml of benzene at 70 °C under nitrogen atmosphere in the dark for 18 h. After removal of the silica gel by filtration followed by concentration of the filtrate, the residue was analyzed on VPC, GC/MS, and HPLC (see Experimental Section). It was confirmed that the unsaturated carbon-carbon bonds of the substrates are reduced, ester groups remaining intact. The yields of the reduction product(s) and the recovered starting material are listed in Table 2. Although the yields of the reduction product(s) for each run are not so high, the data listed in Table 2 are suggestive of the role of the silica gel when the *K* values listed in Table 1 are taken into consideration as well (vide infra).

The reduction of α,β -unsaturated carbonyl compounds **5**–**8** were also carried out under the same conditions mentioned above. Although these substrates were quantitatively reduced into the corresponding saturated carbonyl compounds, their relative reactivities can be roughly compared on the basis of the yield of reduction product after the reaction period of 4 h (Table 3).

We examined the catalytic abilities of heterogeneous acid catalysts, Amberlyst 15 and Nafion 511,

toward the reduction of **3** by HEH. Whereas 27 and 33% of 1.0×10^{-1} mmol of **3** was adsorbed on Amberlyst 15 and Nafion 511, respectively, in 1 ml of benzene at 70 °C, no reduction product was found from these systems. This is mainly due to rapid decomposition of HEH under the catalysis of the strong acids.

Table 2. Reduction of Diesters by HEH in the Presence of the Silica Gel^{a)}

Substrate	S.G. ^{c)} /g	Yield/% ^{b)}			
		1	2	3	4
1	0.01	49 ^{d)}	21	6	N.D. ^{e)}
	0.05	12 ^{d)}	38	11	Trace
	0.1	Trace ^{d)}	43	13	4
	0.2	N.D. ^{d,e)}	42	11	8
2	0.01	—	95 ^{d)}	—	N.D. ^{e)}
	0.05	—	74 ^{d)}	—	15
	0.2	—	53 ^{d)}	—	43
3	0.01	—	—	100 ^{d)}	N.D. ^{e)}
	0.05	—	—	86 ^{d)}	12
	0.2	—	—	57 ^{d)}	31

a) 1.0×10^{-1} mmol of a substrate and 1.5×10^{-1} mmol of HEH were used. The reaction was carried out in 1 ml of benzene at 70 °C in the dark under N₂ atmosphere for 18 h. b) The yield determined by VPC analysis based on the amount of the substrate used. c) The amount of silica gel 60. d) The yield of the recovered starting materials. e) Not detected.

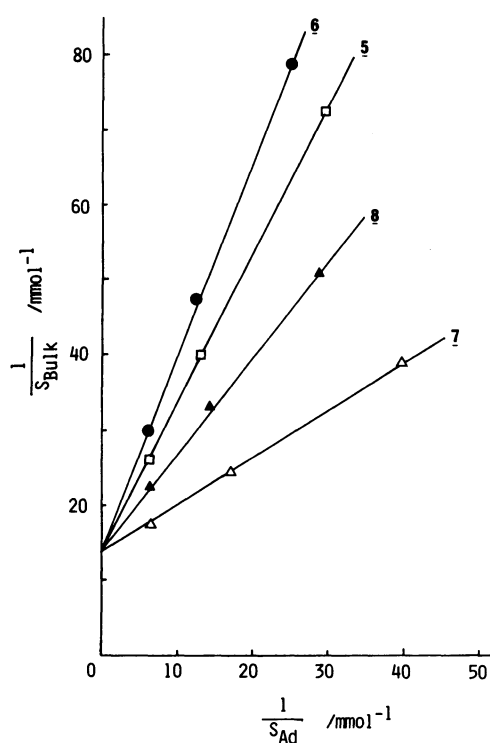


Fig. 2. $1/S_{Ad}$ vs. $1/S_{Bulk}$ plots for α,β -unsaturated carbonyl compounds with 0.2 g of the silica gel in 1 ml of benzene.

Table 3. Reduction of α,β -Unsaturated Carbonyl Compounds by HEH in the Presence of the Silica Gel^{a)}

Substrate	Reaction time/h	Yield/% ^{b)}	
		Recov. ^{c)}	Redn. ^{d)}
5	4	36	60
	18	N.D. ^{e)}	95 ^{f)}
6	4	19	76
	18	N.D. ^{e)}	88 ^{f)}
7	4	72	28
	18	<2	98
8	4	4	96

a) 1.0×10^{-1} mmol of a substrate, 1.5×10^{-1} mmol of HEH, and 0.2 g of silica gel 60 were used unless otherwise mentioned. The reaction was carried out in 1 ml of benzene at 70 °C in the dark under N₂ atmosphere. b) The yield determined by VPC analysis based on the amount of the substrate used. c) The yield of the recovered starting material. d) The yield of the reduction product, corresponding saturated carbonyl compound. e) Not detected. f) Isolated yield from the reaction of 5.0×10^{-1} mmol of a substrate with 7.5×10^{-1} mmol of HEH in the presence of 1.0 g of silica gel 60 in 5 ml of benzene.

Discussion

The order of K values for diesters is $1 < 2 \ll 3 < 4$ as shown in Table 1. The examination of CPK models reveals that four oxygen atoms of the two ester groups in **3** and **4** can approach closely, that is, **3**, and **4** are able to have both hydrophilic and hydrophobic faces within one molecule. On the other hand, **1** and **2** cannot assume such a conformation. Therefore, it is reasonably expected that the former substrates are adsorbed onto the surface of silica gel through hydrophilic interaction between the oxygens of the substrate and silanol group(s) on the surface of silica gel. HEH exhibits large K value, to which poor solubility of HEH in benzene may also contribute. The degree of adsorption of α, β -unsaturated carbonyl compounds **5–8** seems to depend on the electro-negativity of the carbonyl oxygen rather than on the steric factor.

Table 2 shows that the order of reactivity of diesters in the reduction by HEH is $1 > 2 > 3$; the reverse order of the equilibrium constant. The *trans*-alkene **2** is reported to have less negative reduction potential than the *cis*-alkene **3**.⁹ Moreover, it is well documented that a carbon-carbon triple bond is more susceptible to a nucleophile than a double bond.¹⁰ Reduction potential and electrophilicity are, of course, predominant factors in determining the reactivity of these reductions. Nevertheless, taking such limited factors alone into consideration, one obtains much less useful informations about the role of the silica gel. Here, it is worthwhile to emphasize that the larger the K value, the lower the reactivity toward the reduction. The reductions of α, β -unsaturated carbonyl compounds **5–8** gives similar results. Again, the tendency can be seen that the substrate with a larger K value is less reactive except for **8**. The compound **8** may belong to the category other than that for **5–7** because of difference in the structure, i.e., substitution of a methyl group in place of the β -phenyl group.

Now, we can simulate the amounts of the substrate and HEH on the surface of silica gel under the reaction conditions at the incipient stage of the reaction (S_{Ad}). Thus, S_{Ad} 's for two coexisting components are given by resolving Eqs. 4–6, which are derived from Eq. 2, simultaneously.

$$K_A = (S_{Ad})_A / ((S_0)_A - (S_{Bulk})_A) Q_{free} \quad (4)$$

$$K_B = (S_{Ad})_B / ((S_0)_B - (S_{Bulk})_B) Q_{free} \quad (5)$$

$$Q_{free} = Q_0^{0.2} - (S_{Ad})_A - (S_{Ad})_B \quad (6)$$

where subscripts A and B denote the parameters referred to components A and B, respectively, and S_0 is the stoichiometric amount of the substrate. Computation without any approximation afforded the S_{Ad} values as listed in Table 4 for each reduction. The validity of this treatment was supported by the

Table 4. Calculated S_{Ad} Values^{a)}

Component ($S_0 / \times 10^{-1}$ mmol) ^{b)}		S.G. ^{c)} /g	$S_{Ad}(\text{calcd}) / \times 10^{-2}$ mmol	
A	B		(S_{Ad}) _A	(S_{Ad}) _B
1 (1.00)	HEH (1.50)	0.01	0.0514	0.587
		0.05	0.134	1.45
		0.10	0.289	2.84
		0.20	0.668	5.41
2 (1.00)	HEH (1.50)	0.01	0.0663	0.574
		0.05	0.172	1.42
		0.10	0.368	2.78
		0.20	0.836	5.28
3 (1.00)	HEH (1.50)	0.01	0.200	0.456
		0.05	0.505	1.13
		0.10	1.02	2.23
		0.20	2.08	4.31
5 (1.00)	HEH (1.50)	0.20	0.695	5.39
6 (1.00)	HEH (1.50)	0.20	0.581	5.47
7 (1.00)	HEH (1.50)	0.20	1.60	4.69
8 (1.00)	HEH (1.50)	0.20	1.00	5.15
5 (0.504)	6 (0.508)	0.20	1.25 (1.28) ^{d)}	1.07 (1.08) ^{d)}
5 (1.47)	6 (0.988)	0.20	2.59 (2.73) ^{d)}	1.45 (1.48) ^{d)}

a) Based on $Q_0^{0.2} = 7.18 \times 10^{-2}$ mmol and the K values listed in Table 1. See text for details. b) The values in parentheses indicate the stoichiometric amount (S_0) of each component. c) The amount of the silica gel. d) The values in parentheses are observed ones.

excellent agreement between computed and observed S_{Ad} values for the solution containing **5** and **6**, where both values can be directly compared with each other because no reaction takes place in this mixture. The data are also listed in Table 4. Significantly, S_{Ad} values for the substrates to be reduced are not so large; in particular for the reduction of **1** with a small amount of the silica gel, S_{Ad} values for the substrate are nearly two orders less than the total amounts of the products generated. Note that the reduction product(s) is (are) adsorbed onto the surface of silica gel to the extent similar to or larger than that for the starting material as can be seen in Table 1.

One possible explanation for the role of silica gel is that it acts as a carrier of a substrate to its surface on which materials are concentrated to facilitate the reaction.¹¹ Such an effect would be essential in some heterogeneous catalyst-mediated reactions. In fact, the adsorbents other than silica gel, Celite 545 and cellulose, gave rise to no adsorption of **1–3** as well as HEH and then no reduction was observed in these systems. Yet, this effect does not appear to explain entirely the role of the silica gel at least in the present study. A perspective of S_{Ad} values in Table 4 suggests, instead, that the species in bulk phase is responsible for the reaction. There are several examples where an organic reagent adsorbed on heterogeneous catalyst

interacts with another organic reagent in bulk phase to afford a product.¹²⁾ Although the possibility cannot be excluded that HEH reduces the substrate only when both reagents are adsorbed in the vicinity of the surface of silica gel at the same time during the time course of dynamic equilibrium between the surface and bulk phase, it is safely speculated that the reaction takes place between HEH on the surface of silica gel and the substrate in bulk phase.¹³⁾

This concept is partly supported by the results from the experiments using acetonitrile as a solvent. In acetonitrile, neither the reduction of **3** by HEH nor adsorption of HEH onto the surface of silica gel was observed, while **3** was adsorbed onto the surface with the equilibrium constant of $4 \pm 1 \text{ M}^{-1}$.¹⁴⁾ This indicates the requirement of adsorption of HEH onto the surface of silica gel for the reaction, adsorption of the substrate being dispensable. Less adsorption in acetonitrile than that in benzene is attributable to higher solubility of the components in acetonitrile and/or stronger adsorption of the solvent molecule onto the surface. Interestingly, no reduction of **3** by HEH occur in the presence of active alumina (acidic and basic) in place of silica gel even though the adsorption of **3** onto the aluminas were 18–26% under the conditions where 1.0×10^{-1} mmol of **3** and 0.2 g of alumina were stirred in 1 ml of benzene at 70 °C for 30 min.

It is not probable that the trace amount of alumina in the silica gel plays an important role in the reactions, because no appreciable alteration in the reactivity of the reduction as well as the equilibrium constant K for the adsorption is recognized in the experiments using highly pure silica gel [special silica gel #923 (100–200 mesh) (Fuji Davison Chem. Co.); the content of alumina is 0.04%] in place of the silica gel 60 used in this study: the yield of the product in the reduction of **5** after the reaction period of 4 h is 55%; the K value for **5** is 8.2 M^{-1} ; and the value of $Q_0^{0.2}$ for the silica gel #923 is 8.5×10^{-2} mmol. These results are comparable to those obtained by using the silica gel 60.

Consider that in the present system the silica gel not only adsorbs reactants on the surface but also plays certainly a more crucial role for the reduction. Consequently, we propose the possibility that the silica gel facilitates the reduction with HEH through general acid catalysis of silanol group(s) on the surface.^{11b)} The possibility would persist provided that some quantity of silanol groups on the surface remains free.¹⁵⁾ It was also shown in this study that unnecessarily strong acid catalyst is unfavorable for the reduction due to the sensitivity of an NAD(P)H model toward the acid-catalyzed decomposition. Although the evidence obtained presently is not direct for supporting general acid catalysis by silica gel, the concept might be a useful working hypothesis

for the study on the role of silica gel.

Experimental

Apparatus. VPC, HPLC, and GC/MS analyses were performed on a Yanaco G-180 gas chromatograph, a Toyo Soda CCPD high-performance liquid chromatograph equipped with a UV-8000 UV-visible detector, and a Hewlett-Packard 5992B GC/MS spectrometer, respectively. ¹H NMR and IR spectra were recorded on a JASCO JNM-FX 100FT NMR spectrometer and a Hitachi 260-10 infrared spectrophotometer, respectively. Water content in the solvent and the silica gel was measured on a Kyoto Electronics MFG Karl-Fisher moisture content meter Model MK-AS. Computer-assisted simulations were run on an NEC PC-9801 personal computer VM2 with a N₈₈ BASIC program.

Materials. 3,5-Bis(ethoxycarbonyl)-1,4-dihydro-2,6-dimethylpyridine (HEH) was synthesized according to the procedure described in the literature.¹⁶⁾ Diesters **1–4** as well as α,β -unsaturated carbonyl compounds **5**, **7**, and **8** were commercially available. 4'-Bromochoalcone (**6**) was obtained by condensation of benzaldehyde with 4-bromoacetophenone followed by recrystallization from ethanol (mp 101–104 °C). Spectral data of these compounds were satisfactory. Heterogeneous catalysts, silica gel 60 (35–70 mesh) (Nakarai Chem. Co.), active aluminium oxide (acidic and basic) (Merck & Co. Inc.), Amberlyst 15 (Organo), and Nafion 511 (Toyo Soda),¹⁷⁾ were purchased and, if required, activated with ordinary method prior to the use. Benzene was distilled and deaerated with an inert gas, then the content of water was measured.

Measurement of Adsorption onto the Surface of Silica Gel. In 1 ml of benzene were vigorously stirred an appropriate amount of a substrate and 0.2 g of silica gel 60 (35–70 mesh) at 70 °C under nitrogen atmosphere for 30 min. A 25- μl aliquot from the supernatant was added to 100 μl of benzene containing an internal standard for VPC or HPLC analysis, then the solution was analyzed on VPC (for **1–8**; OV-330 column) or HPLC (for HEH; TSKgel ODS-80T_M column, methanol:water=7:3 (v/v) as eluent).

Product Analysis. In the presence of an appropriate amount of silica gel 60, 1.0×10^{-1} mmol of a substrate was allowed to react with 1.5×10^{-1} mmol of HEH at 70 °C in the dark under nitrogen atmosphere with vigorous stirring. After 18 h, the silica gel was filtered off through a glass filter, and washed repeatedly with several portions of 10 ml of benzene. Careful concentration of the filtrate below 40 °C in vacuo to dryness and subsequent addition of 1 ml of methanol to the residue afforded a transparent solution, which was analyzed on VPC, HPLC, and GC/MS. For the isolation of the product, the reaction was performed on the scale five times larger than that mentioned above. Then, the reduction product was isolated on column chromatography (silica gel No. III (200 mesh) (Nakarai Chem. Co.); benzene as eluent), and its ¹H NMR and IR spectra were recorded.

References

- 1) a) S. Yasui, K. Nakamura, and A. Ohno, *Chem. Lett.*, **1984**, 377; b) S. Yasui, K. Nakamura, M. Fujii, and A. Ohno, *J. Org. Chem.*, **50**, 3283 (1985).

- 2) K. Nakamura, A. Ohno, and S. Oka, *Tetrahedron Lett.*, **24**, 335 (1985).
 - 3) K. Nakamura, M. Fujii, A. Ohno, and S. Oka, *Chem. Lett.*, **1984**, 925.
 - 4) K. Nakamura, M. Fujii, A. Ohno, and S. Oka, *Tetrahedron Lett.*, **25**, 3983 (1984).
 - 5) S. H. Mashraqui and R. M. Kellogg, *J. Am. Chem. Soc.*, **105**, 7792 (1983).
 - 6) Equilibrium appears to be very rapidly established relative to the time scale in the experiments. Incubation for 30 min was required for thermostaticity of the mixture.
 - 7) a) D. M. Sindorf and G. E. Maciel, *J. Am. Chem. Soc.*, **105**, 1848 (1983); b) E. C. Kelusky and C. A. Fyfe, *ibid.*, **108**, 1746 (1986); c) J. F. W. Keana, M. Shimizu, and K. K. Jernstedt, *J. Org. Chem.*, **51**, 1641 (1986); d) T. Iwachido, H. Naito, F. Samukawa, K. Ishimaru, and K. Tôei, *Bull. Chem. Soc. Jpn.*, **59**, 1475 (1986); e) S. Shiraishi, M. Komiyama, and H. Hirai, *ibid.*, **59**, 507 (1986).
 - 8) In the later discussion we utilized this value for $Q_0^{0.2}$ because the value is more reliable than the former one which was obtained from the experiments with diesters **1**–**4** and HEH.
 - 9) C. Pac, M. Ihama, M. Yasuda, Y. Miyauchi, and H. Sakurai, *J. Am. Chem. Soc.*, **103**, 6495 (1981).
 - 10) Y. Amiel, "The Chemistry of Functional Groups, Supplement C: The Chemistry of Triple-bonded Functional Groups," ed by S. Patai and Z. Rappoport, John Wiley & Sons, New York (1983).
 - 11) a) S. Tamagaki, K. Suzuki, and W. Tagaki, *Chem. Lett.*, **1982**, 1237; b) K. Takahashi, T. Nishizuka, and H. Iida, *Tetrahedron Lett.*, **22**, 2389 (1981).
 - 12) a) T. Chihara, E. Waniguchi, T. Wakabayashi, and K. Taya, *Chem. Lett.*, **1983**, 1647; b) T. Chihara, E. Waniguchi, T. Wakabayashi, and K. Taya, *Bull. Chem. Soc. Jpn.*, **57**, 2479 (1984); b) H. Ogawa, T. Chihara, and K. Taya, *J. Am. Chem. Soc.*, **107**, 1365 (1985).
 - 13) The mechanism may be discussed in terms of Langmuir–Hinshelwood or Rideal mechanisms. Thus, our proposed mechanism could be related to the latter. However, it should be noted that the adsorptions in our system are not chemical but physical ones.
 - 14) It was confirmed that small amount of water in acetonitrile used does not affect both the reduction of **3** by HEH and adsorption of **3** and HEH onto the surface of silica gel.
 - 15) Table 4 shows, for example, that the amount of "free" silanol group on the surface of silica gel is 1.10×10^{-2} mmol in the reaction of 1.0×10^{-1} mmol of **1** with 1.5×10^{-1} mmol of HEH on 0.2 g of the silica gel at the incipient stage.
 - 16) A. Singer and S. M. McElvain, *Org. Synth. Coll. Vol.* **2**, 214 (1966).
 - 17) Nafion 511 was a gift from Toyo Soda Manufacturing Co.
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