

# Novel dehydration of stilbene oxides to diphenylacetylene using flash vacuum thermolysis with solid acid catalysts

Adri C.L.M. van der Waals<sup>a</sup>, Antonius J.H. Klunder<sup>a</sup>, Frederik R. van Buren<sup>b</sup>,  
Binne Zwanenburg<sup>a,\*</sup>

<sup>a</sup> Department of Organic Chemistry, NSR Center for Molecular Structure, Design and Synthesis, University of Nijmegen, Toernooiveld,  
6525 ED Nijmegen, Netherlands

<sup>b</sup> Dow Benelux, Postbus 48, 4530 AA Terneuzen, Netherlands

Received 14 October 1997; accepted 26 November 1997

## Abstract

Isomerization of *cis*- and *trans*-stilbene oxide was achieved under catalytic flash vacuum thermolysis (FVT), using silica–alumina and clay as catalysts. Depending on the amount of catalyst and reaction temperature, rearrangement to diphenylacetaldehyde or deoxybenzoin, a new dehydration reaction to produce diphenylacetylene was observed. It was shown that diphenylacetylene is formed from deoxybenzoin as the actual precursor. A mechanistic explanation is presented. For comparison, two other arylketones were subjected to catalytic FVT. However, these ketones produced substituted indenones as the major product via a different mechanism. No alkynes were observed. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Catalytic flash vacuum thermolysis; Epoxide rearrangement; Clay; Amorphous silica–aluminas; Indenones; Gas phase reactions

## 1. Introduction

The isomerization of epoxides to carbonyl compounds is an important transformation in organic synthesis [1–5]. Epoxides can be rearranged thermolytically [6,7] or with the aid of protic or Lewis acids [8]. Besides conventional catalysts such as BF<sub>3</sub>, environmentally benign catalysts such as silica gel [9–11], alumina [12–14], silica–alumina [15], (mixed) metal oxides [14,16] clays [15] and zeolites [9,17] have been applied to effect this reaction under mild condi-

tions. All these studies have been carried out in the liquid phase.

As part of our study regarding the application of solid acid catalysts, such as amorphous (silica-) aluminas and clays, and its effect on acid-catalyzed reactions under dynamic gas phase conditions, we now report on the isomerization of *cis*- (**1a**) and *trans*-stilbene oxide (**1b**) in a catalytic FVT set-up. It was our aim to achieve thermolysis at lower temperatures and obtain higher product selectivities than under non-catalyzed FVT conditions.

The catalytic FVT set-up used is schematically displayed in Fig. 1. It essentially consists of an evaporation section, the thermolysis sec-

\* Corresponding author.

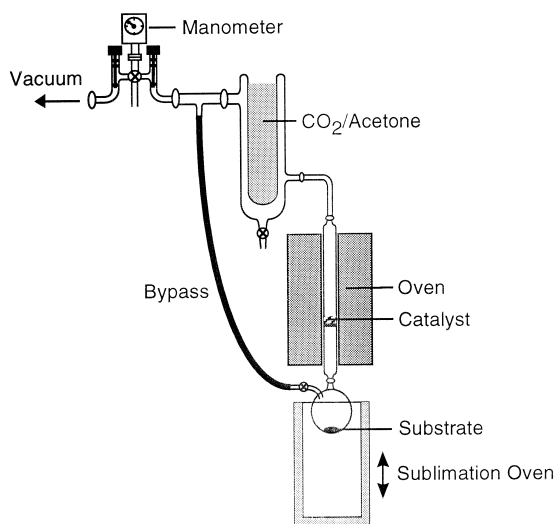


Fig. 1. Overview of the catalytic Flash Vacuum Thermolysis apparatus.

tion being a vertically mounted quartz tube with a porous quartz filter in the middle, wherein a catalyst and a cooling device to collect the products are placed. The bypass, which is closed during the actual thermolysis, is needed to prevent the catalyst to be blown from the quartz filter into the apparatus during evacuation.

## 2. Experimental

### 2.1. General remarks

Reported percentages are molar percentages (% *m/m*). Gas chromatographic (GC) analyses were carried out with a Hewlett-Packard HP-5890 gas chromatograph (flame ionization detector, FID) equipped with an HP-3396 integrator and an apolar HP-1 capillary column (25 m × 0.32 mm × 0.17 μm). Infrared spectra were recorded on a Perkin Elmer 298 or a Bio-Rad FTS-25 (FT) infrared spectrophotometer. For mass spectrometric (MS) analysis, a double focusing VG Analytical 7070E mass spectrometer or a Varian Saturn II GC–MS set-up equipped with an HP-1 capillary column and Varian 8100 Autosampler was used. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker

AC-100 (<sup>1</sup>H at 100 MHz, <sup>13</sup>C at 25 MHz) or on a Bruker AM-400 (<sup>1</sup>H at 400 MHz, <sup>13</sup>C at 100 MHz) spectrometer using the solvent or SiMe<sub>4</sub> as an internal standard, respectively. Spectra recorded on the AC-100 spectrometer were analyzed using WIN-NMR (version 3.0). 2-D correlation experiments (NOESY [18]) were performed on a Bruker AM-400 spectrometer. Preparative chromatography was carried out under ambient pressure using Merck kieselgel 60, or as ‘flash’ chromatography at ca. 1.5 bar with Merck kieselgel 60H. Commercially available starting materials (Aldrich) were used as received. All solvents used were dried and distilled according to standard procedures.

### 2.2. Catalytic materials

All catalysts were used as received without any pretreatment. Removal of physisorbed water was partly affected in situ by equilibration of the catalysts at the measurement temperature prior to the experiment. All catalysts were pressed (3 t/cm<sup>2</sup>), fractured, sieved to the desired particle size fraction of 150–425 μm and stored under ambient atmosphere.

Two comparable amorphous silica–aluminas (HA-SHPV and B698D-25) and two acid-activated natural clays (F-1 and F-25) were used. Nitrogen physisorption measurements showed that the HA-SHPV and B698D-25 catalysts have an open mesoporous texture with a total pore volume of about 0.75 ml/g. The F-1 and F-25 clays have an average pore diameter of 4.5 nm and a total pore volume of 0.29 ml/g and 0.41 ml/g, respectively. The amorphous materials, and to a lesser extent also the F-1 clay were shown by DRIFT analyses to be predominantly Lewis-acidic, whereas the F-25 clay possesses primarily Brønsted acidic sites.

### 2.3. Catalytic flash vacuum thermolysis apparatus

The catalytic FVT set-up used is schematically displayed in Fig. 1. The apparatus consisted of a Büchi TO-50 hot air evaporation

oven, a vertically placed Heraeus Br-1.6/18 oven which was controlled by an Heraeus RK 42 power supply, and a receiving cooler. A quartz tube with a length of 180 mm and an internal diameter of 16 mm was used as the reactor. Directly behind the cooler an Edwards PRE 10K/Pirani combination, connected by a 9 mm three-way valve (Louwers–Hapert) was used to record the pressure. The vacuum was generated using an Edwards 8 two-stage pump via a ‘speedivalve’ shutter. Two cold-traps immersed in liquid nitrogen guarded the pump from any volatile contamination. The various glass parts were joined by Rotulex fittings fitted with silicon rubber rings.

#### 2.4. General procedure for catalytic FVT experiments

In a typical procedure, 0.15 ml (i.e., 60 mg; a plug of  $10 \times 14 \text{ mm}^2$ ) or 0.75 ml (i.e., 290 mg; a plug of  $50 \times 14 \text{ mm}^2$ ) of a fractured catalyst (150–425  $\mu\text{m}$ ) was placed on a porous filter in the center of the quartz tube. The thermolysis oven was brought to the reaction temperature and the catalyst was equilibrated for 15 min during which physisorbed water was released. The vacuum gauge was carefully opened ( $P > 0.1 \text{ mbar}$ ) and an optimal vacuum (0.05 mbar) was achieved after 5–10 min. Then the collecting cooler was charged with  $\text{CO}_2/\text{acetone}$  ( $-78^\circ\text{C}$ ) or liquid nitrogen ( $-196^\circ\text{C}$ ). An amount of 50 or 200 mg of substrate was vaporized at room temperature or with the aid of an evaporation oven at such a rate that evaporation was complete after about 50 min. After another 10 min, the system was purged with nitrogen. Products were rinsed from the cooler and analyzed using gas chromatography. Mass balances were determined from the weight difference of the receiving cooler and were better than 80%, unless stated otherwise. A series of runs were performed using the same catalyst while the temperature was increased by  $50^\circ$  each run. Reference experiments were carried out without a catalyst.

#### 2.5. Catalytic FVT of *cis*-1 and *trans*-stilbene oxide (**1b**), diphenylacetaldehyde (**2**) and deoxybenzoin (**3**)

The substrate (50 mg) was vaporized at  $100^\circ\text{C}$  and thermolyzed using 0.15 or 0.75 ml catalyst. The cooler ( $-78^\circ\text{C}$ ) was rinsed with a small volume (about 5 ml) of  $\text{CDCl}_3$ . Since several compounds showed identical GC-retention times, product analysis was carried out from the integrals of diagnostic  $^1\text{H-NMR}$  signals combined with the results of GC and GC–MS analyses. Selected characteristic analytical data are given below. Analytically pure diphenylacetylene (**4**) was characterized as a white solid (mp  $58\text{--}59^\circ\text{C}$ ) after chromatographic purification (*n*-hexane:ethyl acetate = 5:1) of the crude pyrolysate.

##### 2.5.1. Diphenylacetaldehyde (**2**)

$^1\text{H-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.96 (d,  $J = 2.5 \text{ Hz}$ , 1H,  $\text{Ph}_2\text{CHCHO}$ ), 7.56–7.16 (10H, arom. H), 4.90 (d,  $J = 2.5 \text{ Hz}$ , 1H,  $\text{Ph}_2\text{CHCHO}$ ). EI/GC–MS:  $m/e$  (%) 196 (3,  $\text{M}^+$ ), 167 (100,  $-\text{CHO}^+$ ), 152 (8,  $-\text{C}_2\text{H}_4\text{O}^+$ ).

##### 2.5.2. Deoxybenzoin (**3**)

$^1\text{H-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.07–7.97 (m, 2H,  $\text{PhH}_2\text{CCOPh}$  (H-ortho)), 7.64–7.08 (m, 8H, arom. H), 4.27 (s, 2H,  $\text{PhH}_2\text{CCOPh}$ ). EI/GC–MS:  $m/e$  (%) 196 (1,  $\text{M}^+$ ), 105 (100,  $-\text{PhCH}_2^+$ ), 91 (8,  $-\text{PhCO}^+$ ), 77 (18,  $\text{C}_6\text{H}_5^+$ ), 65 (5,  $\text{C}_5\text{H}_5^+$ ), 51 (11,  $\text{C}_4\text{H}_3^+$ ).

##### 2.5.3. Diphenylacetylene (**4**)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56–7.53 (m, 4H, ( $\text{PhC}$ )<sub>2</sub> (H-ortho)), 7.37–7.34 (m, 6H, ( $\text{PhC}$ )<sub>2</sub>, H-meta, -para).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  131.6 (d), 128.3 (d), 128.2 (d), 123.2 (s), 89.3 (s). IR ( $\text{CHCl}_3$ ):  $\nu$  3083, 3065, 3009, 1601, 1499, 1443, 1070, 1027, 915, 690  $\text{cm}^{-1}$ . EI/GC–MS:  $m/e$  (%) 178 (100,  $\text{M}^+$ ), 151 (6,  $-\text{C}_2\text{H}_3^+$ ). EI/HRMS:  $m/e$  178.0782 (calc. for  $\text{C}_{14}\text{H}_{10}$  ( $\text{M}^+$ ): 178.0782).

### 2.5.4. Benzophenone (5)

$^1\text{H-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86–7.78 (m, 4H,  $\text{Ph}_2\text{CO}$ , H-ortho), 7.59–7.16 (m, 6H, H-meta, -para). EI/GC-MS:  $m/e$  (%) 182 (71,  $\text{M}^+$ ), 105 (100,  $-\text{C}_6\text{H}_5^+$ ), 77 (50,  $-\text{PhCO}^+$ ), 51 (45,  $\text{C}_4\text{H}_3^+$ ).

### 2.5.5. Diphenylmethane (6)

$^1\text{H-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58–7.12 (m, 10H, arom. H), 3.98 (s, 2H,  $\text{PhCH}_2$ ). EI/GC-MS:  $m/e$  (%) 168 (64,  $\text{M}^+$ ), 167 (100,  $-\text{H}^+$ ), 152 (20,  $-\text{CH}_4^+$ ), 91 (12,  $-\text{C}_6\text{H}_5^+$ ), 65 (5,  $\text{C}_5\text{H}_5^+$ ), 51 (11,  $\text{C}_4\text{H}_3^+$ ), 39 (18,  $\text{C}_3\text{H}_3^+$ ).

## 2.6. Catalytic FVT of dibenzoylmethane (7)

The substrate (50 mg) was vaporized at  $150^\circ\text{C}$  and thermolyzed over 0.75 ml of catalyst. The cooler ( $-78^\circ\text{C}$ ) was rinsed with acetone. By a series of runs using 200 mg substrate each, a preparatively useful amount of the product mixture was obtained for chromatographic purification (*n*-hexane:ethyl acetate = 9:1). Then, the crude dark-yellow thermolysate was hydrogenated over Pd/C (10%) in methanol in about 15 min. The dark-yellow solution decolorized upon hydrogenation. After filtration and concentration in vacuo the resulting mixture was chromatographically purified (*n*-hexane:ethyl acetate = 9:1) to give analytically pure 3-phenyl-1-indanone as a yellowish oil. 3-Phenyl-1-indenone (8) was identified as the indenone derivative after hydrogenation.<sup>1</sup>

### 2.6.1. 3-Phenyl-1-indanone

$^1\text{H-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86–7.07 (m, 9H, arom. H), 4.58 (dd,  $J_{3,\text{H}2\alpha} = 8.0$  Hz,  $J_{3,\text{H}2\beta} = 3.9$  Hz, 1H,  $\text{H}_3$ ), 3.25 A of AB (dd,  $J_{\text{H}2\alpha,\text{H}2\beta} = 19.2$  Hz,  $J_{\text{H}2\alpha,3} = 8.0$  Hz, 1H,  $\text{H}_{2\alpha}$ ), 2.68 B of AB (dd,  $J_{\text{H}2\alpha,\text{H}2\beta} = 19.2$  Hz,  $J_{\text{H}2\beta,3} = 3.9$  Hz, 1H,  $\text{H}_{2\beta}$ ).  $^{13}\text{C-NMR}$  (25 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.0 (C-1), 157.9 (C-4), 143.6

(C-1'), 136.7 (C-9), 135.0 (C-6), 128.8 (C-3' and C-5'), 127.8 (C-7), 127.6 (C-2' and C-6'), 126.9 (C-4'), 126.8 (C-5), 123.3 (C-8), 46.8 (C-2), 44.4 (C-3). IR ( $\text{CCl}_4$ ):  $\nu$  1720 (C=O)  $\text{cm}^{-1}$ . EI/GC-MS:  $m/e$  (%) 208 (100,  $\text{M}^+$ ), 193 (22,  $-\text{CH}_3^+$ ), 178 (44,  $-\text{CH}_2\text{O}^+$ ), 165 (35,  $-\text{CO}^+$ ,  $-\text{CH}_2^+$ ), 152 (12,  $-\text{CO}^+$ ,  $-\text{C}_2\text{H}_4^+$ ), 130 (16,  $-\text{C}_6\text{H}_6^+$ ), 103 (20,  $-\text{C}_2\text{H}_3^+$ ,  $-\text{C}_6\text{H}_6^+$ ), 77 (33,  $\text{C}_6\text{H}_5^+$ ), 51 (29,  $\text{C}_4\text{H}_3^+$ ). EI/HRMS:  $m/e$  208.0889 (calc. for  $\text{C}_{15}\text{H}_{12}\text{O}$  ( $\text{M}^+$ ): 208.0888).

## 2.7. Catalytic FVT of benzoylacetone (11)

The substrate (50 mg) was vaporized at  $150^\circ\text{C}$  and thermolyzed over 0.75 ml of catalyst. The cooler ( $-78^\circ\text{C}$ ) was rinsed with acetone. By a series of runs using 200 mg substrate each, a preparatively useful amount of the product mixture was obtained for separation by 'flash' chromatography (*n*-hexane:ethyl acetate = 9:1). Assignment of the various proton signals was achieved by 2-D NOESY [18] experiments. Atom numbering is analogous to 3-phenyl-1-indanone.

### 2.7.1. 3-Methyl-1-indenone (12)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (d,  $J_{5,6}$  or  $J_{7,8} = 7.1$  Hz, 1H,  $\text{H}_5$  or  $\text{H}_8$ ), 7.37 (t,  $J_{5,6} = J_{6,7}$  or  $J_{6,7} = J_{7,8} = 7.3$  Hz, 1H,  $\text{H}_6$  or  $\text{H}_7$ ), 7.25 (t,  $J_{5,6} = J_{6,7}$  or  $J_{6,7} = J_{7,8} = 7.3$  Hz, 1H,  $\text{H}_6$  or  $\text{H}_7$ ), 7.09 (d,  $J_{5,6}$  or  $J_{7,8} = 7.1$  Hz, 1H,  $\text{H}_5$  or  $\text{H}_8$ ), 5.69 (d,  $J_{2,\text{CH}_3} = 1.5$  Hz, 1H,  $\text{H}_2$ ), 2.23 (d,  $J_{2,\text{CH}_3} = 1.5$  Hz, 1H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.8 (s), 162.3 (s), 145.6 (s), 133.1 (d), 131.4 (s), 129.1 (d), 123.7 (d), 121.6 (d), 119.3 (d), 14.1 (q). IR:  $\nu$  1710 (C=O;  $\text{CHCl}_3$ ), 1719 (C=O;  $\text{CCl}_4$ )  $\text{cm}^{-1}$ . EI/GC-MS:  $m/e$  (%) 144 (71,  $\text{M}^+$ ), 129 (3,  $-\text{CH}_3^+$ ), 115 (100,  $-\text{CHO}^+$ ), 101 (3,  $-\text{CH}_3^+$ ,  $-\text{CO}^+$ ), 88 (5,  $-\text{C}_2\text{H}_4^+$ ,  $-\text{CO}^+$ ), 74 (9,  $-\text{C}_3\text{H}_6^+$ ,  $-\text{CO}^+$ ), 63 (9,  $-\text{C}_4\text{H}_5^+$ ,  $-\text{CO}$ ), 50 (11,  $-\text{C}_5\text{H}_6^+$ ,  $-\text{CO}^+$ ), 43 (12,  $\text{CH}_3^+$ ,  $\text{CO}^+$ ), 39 (17,  $\text{C}_3\text{H}_3^+$ ). EI/HRMS:  $m/e$  144.0575 (calc. for  $\text{C}_{10}\text{H}_8\text{O}$  ( $\text{M}^+$ ): 144.0575).

<sup>1</sup> Structural assignment of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR signals was performed according to Refs. [19,20], respectively.

### 2.7.2. 3-methylene-1-indanone (**13**)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (d,  $J_{7,8} = 7.7$  Hz, 1H,  $\text{H}_8$ ), 7.79 (d,  $J_{5,6} = 7.3$  Hz, 1H,  $\text{H}_5$ ), 7.64 (t,  $J_{6,7} = 7.5$  Hz, 1H,  $\text{H}_7$ ), 7.44 (t,  $J_{6,7} = 7.5$  Hz, 1H,  $\text{H}_6$ ), 5.85 (t,  $J_{9s,\text{CH}_2} = 2.0$  Hz, 1H,  $\text{H}_{9s}$ ), 5.33 (s, 1H,  $\text{H}_{9a}$ ), 3.30 (t,  $J_{9s,\text{CH}_2} = 1.7$  Hz, 2H,  $\text{H}_{2\alpha,2\beta}$ ).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.9 (s), 149.8 (s), 139.7 (s), 137.3 (s), 134.8 (d), 129.1 (d), 123.4 (d), 121.2 (d), 107.9 (t), 42.1 (t). IR ( $\text{CHCl}_3$ ):  $\nu$  1715 ( $\text{C=O}$ )  $\text{cm}^{-1}$ . EI/GC-MS:  $m/e$  (%) 144 (60,  $\text{M}^+$ ), 129 (1,  $-\text{CH}_3^+$ ), 115 (100,  $-\text{CHO}^+$ ), 101 (1,  $-\text{CH}_3^+$ ,  $-\text{CO}^+$ ), 89 (7,  $-\text{C}_2\text{H}_3^+$ ,  $-\text{CO}^+$ ), 74 (8,  $-\text{C}_3\text{H}_6^+$ ,  $-\text{CO}^+$ ), 63 (10,  $-\text{C}_4\text{H}_5^+$ ,  $-\text{CO}$ ), 50 (10,  $-\text{C}_5\text{H}_6^+$ ,  $-\text{CO}^+$ ), 43 (15,  $\text{CH}_3^+$ ,  $\text{CO}^+$ ), 39 (16,  $\text{C}_3\text{H}_3^+$ ). EI/HRMS:  $m/e$  144.0575 (calc. for  $\text{C}_{10}\text{H}_8\text{O}$  ( $\text{M}^+$ ): 144.0575).

## 3. Results and discussion

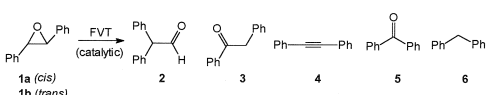
### 3.1. Catalytic FVT of *cis*- and *trans*-stilbene oxide

The thermal reactivity of the stilbene oxides was determined by runs without applying a catalyst (Table 1, entries 1–5). In contrast to Oyewale and Aitken [7], who reported no significant reaction below  $600^\circ\text{C}$ , almost complete conversion (92%) of *trans*-stilbene oxide (**1b**) to diphenylacetaldehyde (**2**) (85%) resulting from a 1,2-phenyl shift, was observed already at  $300^\circ\text{C}$ . Other products were deoxybenzoin (**3**) (14%) formed by a formal 1,2-H shift and a trace (1%) of benzophenone (**5**). Increasing the temperature to  $600^\circ\text{C}$  alters the reaction selectivity in favor of deoxybenzoin (**3**), whereas at  $700^\circ\text{C}$  fragmentation pathways become dominant as illustrated by the formation of diphenylmethane (**6**) (11%).

Epoxide opening was effectively catalyzed when 0.15 ml (i.e., a turnover of 1 g subst./h.g cat.) of the HA-SHPV amorphous silica–alumina was used (Table 1, entries 6–14). Complete conversion was reached already at  $100^\circ\text{C}$  whereby the isomeric diphenylaldehyde (**2**) was

Table 1

FVT of *trans*-stilbene oxide **1b** using amorphous silica–alumina catalysts



Entry	Catalyst <sup>a</sup>	$T^b$ (conv.) <sup>c</sup>	Selectivity <sup>c</sup>					
			2	3	4	5	6	Others <sup>d</sup>
1	none	300 (92)	85	14	0	1	0	0
2		400 (98)	81	16	0	3	0	0
3		500	76	19	0	5	0	0
4		600	61	29	0	7	1	2
5		700	15	45	0	6	11	23
6	HA-SHPV	100	88	11	0	1	0	0
7	(0.15 ml)	150	82	14	0	3	0	1
8		200	83	14	0	2	0	1
9		250	81	15	0	2	0	2
10		300	69	27	0	3	0	1
11		350	46	50	0	3	0	1
12		400	18	69	10	1	0	2
13		450	8	75	16	1	0	0
14		500	8	66	26	0	0	0
15	HA-SHPV	300	0	56	5	0	27	12
16		350	0	65	27	0	3	5
17		400	0	42	54	0	0	4
18		450	0	14	84	0	0	2
19		500	0	4	96	0	0	0
20		550	0	1	98	0	0	1
21		500	0	1	97	0	0	2
22		450	0	14	85	0	0	1
23		400	0	42	57	0	0	1
24		350	0	76	23	0	0	1
25		300	0	94	5	0	0	1
26	HA-SHPV	300	0	55	7	0	21	16
27		300	0	61	2	1	4	32
28		300	4	85	6	1	2	2
29		300	7	83	8	0	1	1
30		300	12	77	6	2	0	3
31	HA-SHPV	550	0	0	96	0	0	4
32		550	0	0	97	0	0	3
33		550	0	0	98	0	0	2
34		550	0	0	98	0	0	2
35		550	0	0	98	0	0	2
36	B698D-25	300	0	65	17	0	5	3
37		350	0	65	29	1	1	4
38		400	0	32	64	1	1	2
39		450	0	12	85	0	1	2
40		500	0	4	93	0	1	2
41		550	0	1	95	1	1	2

<sup>a</sup>A total of 0.75 ml of catalyst was used unless mentioned otherwise.

<sup>b</sup>Temperatures in  $^\circ\text{C}$ ; evaporation temperature is  $100^\circ\text{C}$ .

<sup>c</sup>Conversion and selectivity in mol%; conversion  $> 99\%$  unless stated otherwise between brackets.

<sup>d</sup>'Others' refers to various unidentified compounds.

produced with 88% selectivity together with the ketone deoxybenzoin (**3**) (11%). Increasing the reaction temperature to 350°C shifted the product distribution toward deoxybenzoin (**3**), analogously to the uncatalyzed case. Further temperature increase to 400°C gave a new product which was identified<sup>2</sup> as diphenylacetylene (**4**). This remarkable dehydration reaction became more pronounced at 500°C when the pyrolysate contained 26% of this acetylene. Diphenylacetylene (**4**) could be obtained as the exclusive product when the reaction was performed at about 550°C using 0.75 ml of catalyst (i.e., a turnover of 0.21 g subst./h.g cat.; Table 1, entry 20).

Although dehydration of alcohols [22,23] and hydration of acetylene [24] over solid acid catalysts are well-known processes, gas phase dehydration of  $\alpha$ -hydrogen containing carbonyl compounds to substituted acetylenes has only one precedent [25]. Applying a solid, polyphosphoric acid (UOP no. 1) gas phase dehydration of acetophenone to phenylacetylene has been accomplished, however, in moderate yields.

The deactivation of the catalyst was also investigated by studying hysteresis effects (Table 1, entries 15–25). The remarkably high selectivity (27%) to diphenylmethane (**6**) observed in the first run at 300°C (entry 15) was no longer present in the return part of the hysteresis loop (entry 25). This product is therefore believed to be generated by a strongly acidic active site present only on the surface of the fresh and in situ dehydrated catalyst. Related to its specific activity this site is rapidly deactivated.

To gain further insight in the deactivation of the catalyst two series of experiments were performed at temperatures of 300°C and 550°C, respectively. In the first run at 300°C (Table 1, entry 26) besides deoxybenzoin (**3**), again relatively large amounts of diphenylmethane (**6**)

were produced together with some unidentified products. From the 3rd to the 5th run (Table 1, entries 28–30), a gradual increase of diphenylacetaldehyde (**2**) with simultaneous decrease of deoxybenzoin (**3**) was observable. Surprisingly, **6** was completely absent at 550°C whereas diphenylacetylene (**4**) was produced in high yield and without any detectable deactivation of the catalyst.

The B698D-25 silica–alumina catalyst yielded results similar to HA-SHPV although less **6** was obtained in the first run.

Interesting information was obtained when *cis*-stilbene oxide (**1a**), diphenylacetaldehyde (**2**)

Table 2

Catalytic FVT of *cis*-(**1a**) and *trans*-stilbene oxide (**1b**), diphenylacetaldehyde (**2**) and deoxybenzoin (**3**) using amorphous silica–alumina (HA-SHPV) and natural clay (F-1 and F-25) catalysts

Entry	Substrate	Catalyst <sup>a</sup>	<i>T</i> <sup>b</sup> (conv.) <sup>c</sup>	Selectivity <sup>c</sup>					
				<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	Others <sup>d</sup>
1	<b>1a</b>	HA-SHPV	300	0	67	8	3	13	9
2			350	0	73	18	3	2	4
3			400	0	48	47	2	1	2
4			450	0	22	74	2	1	1
5			500	0	11	85	2	1	1
6			550	0	3	92	1	2	2
7	<b>2</b>	HA-SHPV	300	–	60	0	6	16	18
8			350	–	75	13	5	2	5
9			550	–	2	89	4	2	3
10	<b>3</b>	HA-SHPV	300 (15)	0	–	47	0	13	40
11			350 (44)	0	–	86	0	2	12
12			400 (72)	0	–	97	0	0	3
13			450 (90)	0	–	99	0	0	1
14			500 (97)	0	–	98	0	0	2
15			550 (98)	0	–	99	0	0	1
16	<b>1b</b>	F-1	300	0	88	8	1	1	2
17			350	0	86	12	0	0	2
18			400	0	84	14	0	0	2
19			450	0	65	30	0	0	5
20			500	0	49	45	1	1	4
21			550	0	34	60	1	1	4
22	<b>1b</b>	F-25	300	0	82	9	0	1	8
23			350	0	82	17	0	0	1
24			400	0	70	28	0	0	2
25			450	0	63	35	0	0	2
26			500	0	48	49	0	1	2
27			550	0	36	62	0	1	1

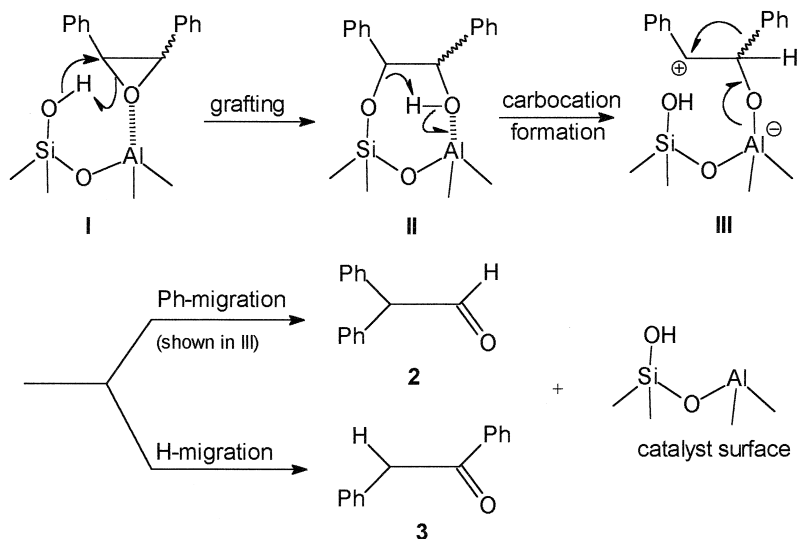
<sup>a</sup>A total of 0.75 ml of catalyst was used.

<sup>b</sup>Temperatures in °C; evaporation temperature is 100°C.

<sup>c</sup>Conversion and selectivity in mol%; conversion > 99% unless stated otherwise (in parentheses).

<sup>d</sup>'Others' refers to various unidentified compounds.

<sup>2</sup>All spectroscopic data matched an authentic sample (cf. Ref. [21]). See Section 2 for analytical data.

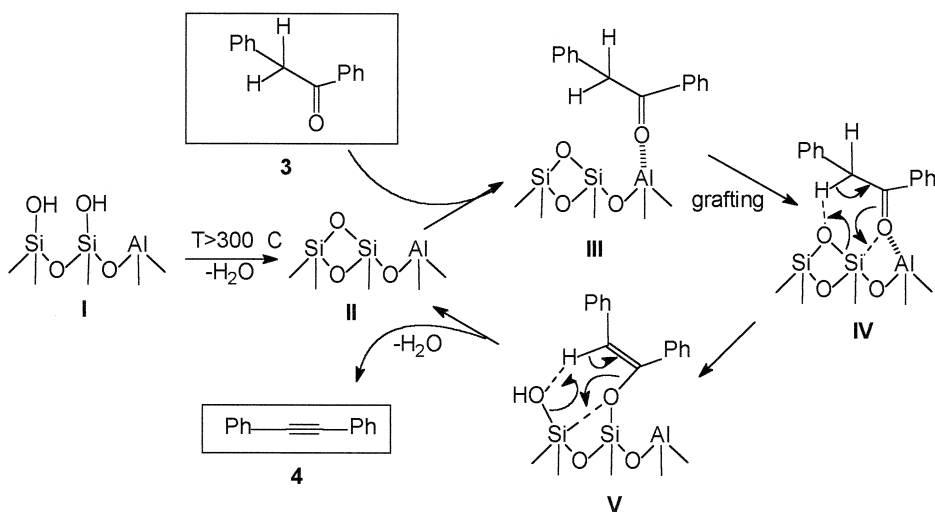


Scheme 1. Mechanism of the acid-catalyzed rearrangement of stilbene oxide (1).

or deoxybenzoin (3) were reacted under catalytic FVT conditions (Table 2). No significant stereoisomeric effect was observed since *cis*- and *trans*-stilbene oxide displayed a similar isomerization pattern, although a somewhat higher diphenylacetylene (4)/deoxybenzoin (3) ratio was observed for the *trans*-stilbene oxide. More interestingly, aldehyde 2 predominantly rearranged to ketone 3 at lower temperatures but yielded acetylene 4 at 550°C, whereas ketone 3

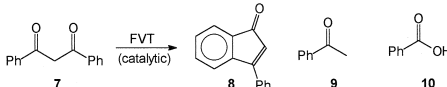
did not produce any aldehyde but rather exclusively dehydrated to diphenylacetylene (4) in the entire temperature range (entries 10–15). It can be concluded that the isomerization pathways are temperature dependent and that at higher temperature dehydration becomes dominant.

The formation of diphenylacetaldehyde and deoxybenzoin from stilbene oxides (1) can be rationalized by adopting a mechanism analo-



Scheme 2. Mechanism of dehydration of deoxybenzoin (3) to diphenylacetylene (4).

Table 3  
(Catalytic) Flash vacuum thermolysis of dibenzoylmethane (7)



Entry	Catalyst <sup>a</sup>	T <sup>b</sup>	Conv. <sup>c</sup>	Selectivity <sup>c</sup>			
				8	9	10	Others <sup>d</sup>
1	none	300	0	0	0	0	0
2		400	0	0	0	0	0
3		500	0	0	0	0	0
4		600	4	0	0	0	100
5	HA-SHPV	300	75	19	73	0	8
6		350	63	33	48	14	5
7		400	85	44	36	20	0
8		450	92	55	30	14	1
9		500	98	50	35	7	8
10		550	99	44	35	4	17

<sup>a</sup>A total of 0.75 ml of catalyst was used.

<sup>b</sup>Temperature in °C; evaporation temperature is 150°C.

<sup>c</sup>Conversion and selectivity in mol%.

<sup>d</sup>'Others' refers to various unidentified products.

gous to that proposed by Ruiz-Hitzky and Casal [6] for the rearrangement of styrene oxide into phenylacetaldehyde induced by an amorphous silica–alumina or mineral catalyst under liquid-phase conditions. Initial coordination of the epoxide to the electron-deficient aluminum center (**I**) results in grafting of the epoxide onto the surface (**II**) of the catalyst (Scheme 1). Carbocation formation (**III**) and subsequent rearrangement involving either migration of a phenyl or a hydride results in the products **2** and **3**. Rearrangement of **1** to **2**, using solid catalysts, has been reported previously (immobilized organometal catalysts [26,27] organoboron compounds [28], silica gel [29–31], aluminosilicates [15], metal oxides [15] and transition metal complexes [32,33]). Under homogeneous liquid-phase conditions rearrangement of **1** to **2** and **3** has also been observed using among others MgBr<sub>2</sub> as the catalyst [34,35].

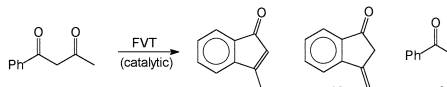
The results presented above clearly demonstrate that deoxybenzoin is the actual precursor for the formation of diphenylacetylene (**4**). This reaction can be explained in analogy with previously postulated [36,37] working models for silica–alumina surfaces. It is well established

[38,39] that pure silica is gradually dehydroxylated upon heating, thereby generating reactive siloxane sites like (**II**) in the temperature range between 200–400°C (Scheme 2). When an epoxide or carbonyl compound coordinates to a Lewis-acidic alumina site (**III**) a grafting reaction produces an enol-type surface species (**IV**). The free silanol group generated can act as a base forming the acetylenic bond with concomitant regeneration of the active site (**V**). More extensive surface dehydroxylation at higher temperatures accounts for the increased yield of diphenylacetylene (**4**) at 500–550°C compared with 300°C.

### 3.2. Catalytic FVT of dibenzoylmethane and benzoylacetone

It is of interest to investigate whether the conversion of deoxybenzoin into diphenylacetylene can be extended to other enolizable ketones. For this purpose, dibenzoylmethane (**7**) and benzoylacetone (**11**) were subjected to catalytic FVT conditions using the same catalysts as for deoxybenzoin.

Table 4  
(Catalytic) Flash vacuum thermolysis of benzoylacetone (**11**)



Entry	Catalyst <sup>a</sup>	T <sup>b</sup>	Conv. <sup>c</sup>	Selectivity <sup>c</sup>			
				12	13	9	Others <sup>d</sup>
1	none	300	0	0	0	0	0
2		400	0	0	0	0	0
3		500	0	0	0	0	0
4		600	4	0	0	0	100
5	HA-SHPV	300	60	5	3	80	12
6		350	72	11	7	76	6
7		400	88	15	10	67	8
8		450	100	23	16	51	10
9		500	100	28	20	34	18
10		550	100	32	22	22	24

<sup>a</sup>A total of 0.75 ml of catalyst was used.

<sup>b</sup>Temperature in °C; evaporation temperature is 70°C.

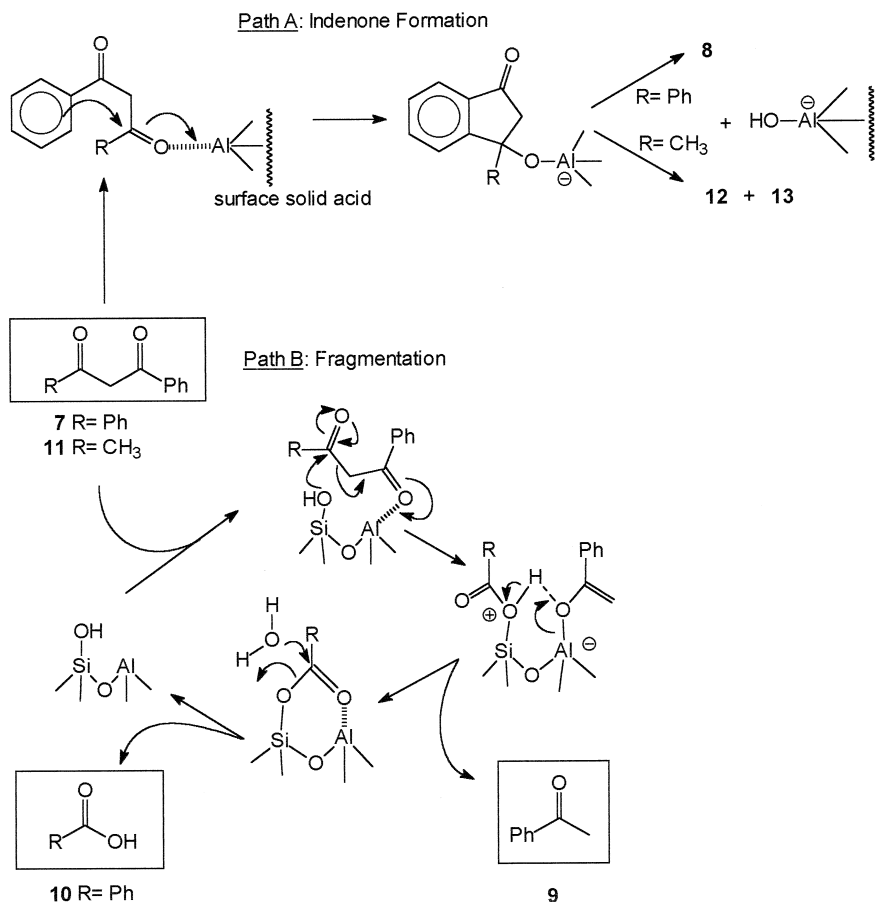
<sup>c</sup>Conversion and selectivity in mol%.

<sup>d</sup>'Others' refers to various unidentified products.



A number of runs without a catalyst prior to the catalytic experiments showed that dibenzoylmethane (**7**) was quite inert since at 600°C a mere 4% conversion was observed (Table 3). With 0.75 ml of the HA-SHPV amorphous silica–alumina, however, 75% conversion was achieved already at 300°C yielding mainly acetophenone (**9**) with 73% selectivity together with a dehydration product (19%) that was identified as 3-phenyl-1-indenone (**8**). At higher temperature also some benzoic acid (**10**) was concurrently formed with the aforementioned products **8** and **9** (Table 3). It should be noted that no trace of 1,3-diphenylpropynone, the acetylene that in principle could arise by dehydration of **7**, was detected.

Dehydration of benzoylacetone (**11**) under catalytic FVT conditions revealed an analogous behavior. This substrate was also rather inert under thermal conditions, since only traces of products were formed at temperatures as high as 600°C (Table 4). In the presence of the HA-SHPV catalyst a complete conversion was already achieved at 450°C. Two dehydration products viz. 3-methyl-1-indenone (**12**) and isomeric 3-methylene-1-indanone (**13**) were obtained in about equal selectivities (28% and 20%, respectively) at 500°C. A slight preference for **12** over its *exo*-methylene isomer **13** was observed in the entire temperature range. It is of importance to note that again no trace of an acetylenic compound, the conceivable dehydra-



Scheme 3. Mechanisms for formation of indenones **8**, **12** and **13** (path A), and acetophenone (**9**) and benzoic acid (**10**) (path B) from dibenzoylmethane (**7**) and benzoylacetone (**11**).

tion product (vide infra) was detected. In analogy with dibenzoylmethane (**7**), acetophenone (**9**) was found to be the major fragmentation product at lower temperature.

The formation of indenones **8**, **12** and **13** from **7** and **11** can be rationalized by invoking an intramolecular electrophilic aromatic substitution as pictured in Scheme 3 (path A). The observation that **11** leads to a mixture of indenones **12** and **13** is in line with the observation that alkyl- $\alpha,\beta$ -unsaturated indenones rearrange to *exo*-methylene isomers due to the anti-aromatic character of the former [40]. The formation of the fragmentation products obtained from both substrates can be envisaged as depicted in Scheme 3 (path B). After initial coordination to the surface, grafting takes place, which is followed by an  $\alpha$ -bond cleavage. From **11** also acetone and acetic acid are expected as cleavage products, which are probably too volatile to be detected. In addition, the absence of major amounts of benzoic acid and acetic acid in the thermolysis of **7** and **11**, respectively, can be explained by the requirement of the presence of sufficient quantities of water to release the acids from the catalytic surface by hydrolysis of the initially formed silanyl esters. However, under the conditions of the reaction, water is only present in low concentrations leaving most of the silanyl ester on the surface of the alumina–silica. This could eventually lead to complete deactivation of the solid acid.

#### 4. Conclusions

In conclusion, conversion of *cis*-(**1a**) and *trans*-stilbene oxide (**1b**) was successfully achieved under catalytic FVT conditions using amorphous silica–aluminas and acid-activated natural clays. In all cases, conversion was about 100%. With a small amount of catalyst isomerization, either of the stilbene oxides produced diphenylacetaldehyde (**2**) with a selectivity of about 88 mol% in the 100–250°C range, whereas at higher temperatures (250–500°C), deoxyben-

zoin (**3**) was mainly (selectivity of about 75 mol%) produced. With a larger amount of catalyst per unit substrate, a selectivity of 65% of deoxybenzoin (**3**) was obtained at 350°C. Further temperature increase to 550°C produced almost exclusively diphenylacetylene (**4**) (98%) at 550°C via a novel dehydration reaction of deoxybenzoin.

The formation of diphenylacetaldehyde and deoxybenzoin from stilbene oxide mechanistically proceeds via a grafting process followed by either phenyl or hydride migration, whereas the formation of the diphenylacetylene is the result of efficient dehydration of the silanylenol ether derived from deoxybenzoin via elimination of siloxanes sites on the surface.

Dibenzoylmethane (**7**) and benzoylacetone (**11**) show a behavior quite different from that of deoxybenzoin (**3**). No acetylenic products were obtained but instead substituted indenones were produced along with some fragmentation products. These indenones are probably formed via an intramolecular electrophilic aromatic substitution on the catalytic surface.

#### Acknowledgements

The authors wish to thank Dr. C.R. Bayense (Engelhard De Meern), and Dr. F.R. Mas Cabré (AKZO Chemicals) for generous gifts of catalytic materials and helpful discussions. The Innovation Oriented Research Program on Catalysis (IOP-Katalyse) of the Netherlands Ministry of Economic Affairs is gratefully acknowledged for the financial support (grant no. 90043).

#### References

- [1] R.E. Parker, N.S. Isaacs, Chem. Rev. 59 (1959) 737.
- [2] Gorzynski Smith, J. Synth. (1984) 629.
- [3] M. Bartók, K.L. Láng, in: A. Hassner (Ed.), Small Ring Heterocycles; The Chemistry of Heterocyclic Compounds, Vol. 42, Part 3, Interscience, New York, 1985, 65 pp.
- [4] A. Rosowsky, in: A. Weisberger (Ed.), Heterocyclic Compounds with 3- and 4-Membered Rings; The Chemistry of

- Heterocyclic Compounds, Part 1, Interscience, New York, 1964, 231 pp.
- [5] A.S. Rao, S.K. Paknikar, J.G. Kirtane, *Tetrahedron* 39 (1983) 2323.
- [6] R.F.C. Brown, in *Pyrolytic Methods in Organic Chemistry, Organic Chemistry Monographs, Vol. 41*, New York, 1980.
- [7] A.O. Oyewale, R.A. Aitken, *Russ. Chem. Bull.* 44 (1995) 919.
- [8] B. Rickborn, in: G. Pattenden (Ed.), *Comprehensive Organic Synthesis: Carbon–Carbon  $\sigma$ -Bond Formation*, Chap. 3.3, Vol. 3, Pergamon Press, 1991.
- [9] G. Paparatto, G. Gregorio, *Tetrahedron Lett.* 29 (1988) 1471.
- [10] T. Bharati Rao, R. Madhusudana, *J. Synth. Commun.* 23 (1993) 1527.
- [11] C. Lemini, M. Ordoñez, J. Pérez-Flores, R. Cruz-Almanza, *Synth. Commun.* 25 (1995) 2695.
- [12] S. Dev, V.S. Joshi, *Tetrahedron* 33 (1977) 2955.
- [13] G. Posner, *Angew. Chem.* 90 (1978) 527.
- [14] Á. Molnár, I. Bucsi, M. Bartók, *Stud. Surf. Sci. Catal.* 59 (1991) 549.
- [15] E. Ruiz-Hitzky, B. Casal, *J. Catal.* 92 (1985) 291.
- [16] K. Arata, H. Nakamura, Y. Nakamura, *Bull. Chem. Soc. Jpn.* 67 (1994) 2351.
- [17] M. Nomura, Y. Fujihara, *Chem. Express* 7 (1992) 121.
- [18] M. Hesse, H. Meier, B. Zeeh, in *Spektroskopische Methoden in der Organischen Chemie*, 3rd edn., Thieme Verlag, Stuttgart, 1987, 127 pp.
- [19] A. Patra, S.K. Misra, *Indian J. Chem. Sect. B* 29 (1990) 66.
- [20] A. Patra, S.K. Misra, *Magn. Res. Chem.* 29 (1991) 749.
- [21] C.J. Pouchert, J. Behnke, in *The Aldrich Library of  $^{13}\text{C}$  and  $^1\text{H}$  FT NMR Spectra*, 1st edn., Vol. 3, Aldrich Chemical, 1993, 533 pp.
- [22] M.L. Kantam, P.L. Santhi, M.F. Siddiqui, *Tetrahedron Lett.* 34 (1993) 1185.
- [23] S. Srinivasan, C.R. Narayanan, A. Biaglow, R. Gorte, A.K. Datye, *Appl. Catal. A* 132 (1995) 271.
- [24] G. Onyestyák, D. Kalló, *J. Mol. Catal. A* 106 (1996) 103.
- [25] J.J. Harrison, *J. Org. Chem.* 44 (1979) 3578.
- [26] K. Maruoka, S. Nagahara, T. Ooi, H. Yamamoto, *Tetrahedron Lett.* 30 (1989) 5607.
- [27] S. Nagahara, K. Maruoka, H. Yamamoto, *Chem. Lett.* (1992) 1193.
- [28] K. Ishihara, N. Hanaki, H. Yamamoto, *Synlett.* (1995) 721.
- [29] G. Paparatto, G. Gregorio, *Tetrahedron Lett.* 29 (1988) 1471.
- [30] T. Bharati Rao, R. Madhusudana, *J. Synth. Commun.* 23 (1993) 1527.
- [31] C. Lemini, M. Ordoñez, J. Pérez-Flores, R. Cruz-Almanza, *Synth. Commun.* 25 (1995) 2695.
- [32] A. Miyashita, T. Shimada, A. Sugawara, H. Nohira, *Chem. Lett.* (1986) 1323.
- [33] A. Cabrera, F. Mathé, Y. Castanet, A. Mortreux, F. Petit, *J. Mol. Catal.* 64 (1991) L11.
- [34] H.O. House, *J. Am. Chem. Soc.* 77 (1955) 3070.
- [35] D.J. Reif, H.O. House, *Org. Synth. Coll. IV* (1963) 375.
- [36] G. Posner, *Angew. Chem.* 90 (1978) 527.
- [37] Á. Molnár, I. Bucsi, M. Bartók, *Stud. Surf. Sci. Catal.* 59 (1991) 549.
- [38] B. Elvers, S. Hawkins, W. Russey, G. Schulz (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edn., Vol. A23, VCH, Weinheim, 1993, 616 pp.
- [39] E.F. VanSant, P. Van der Voort, K.C. Vrancken, *Stud. Surf. Sci. Catal.* 93 (1995) 62.
- [40] R.C. Larock, M.J. Doty, S.J. Cacchi, *J. Org. Chem.* 58 (1993) 4579.