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Dehydration-Hydration of α-Alkynols over Zeolite Catalyst. Selective Synthesis of Conjugated Enynes and α,β-Unsaturated Ketones.

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Abstract: α-Alkynols **1** are converted in high yield and selectivity into conjugated enynes **2** or α,β-unsaturated ketones **3** by treatment with acid zeolites. The exclusive production of compounds **2** or **3** depends on the nature of the starting material **1** and experimental conditions.

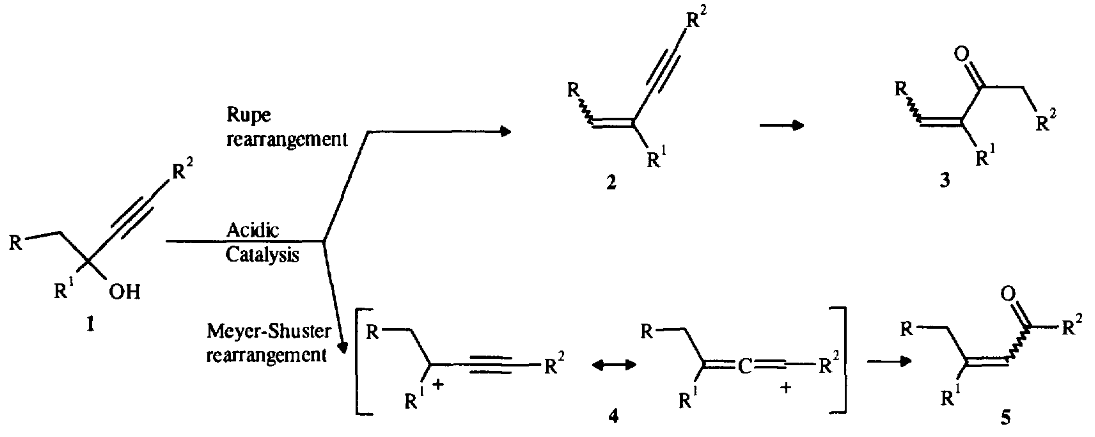
Introduction

The manufacture of fine chemicals and chemical intermediates is a process normally performed in liquid phase and in which heterogeneous catalysis has traditionally been little used. Nevertheless, the new industrial legislation requires more stringent environmental protection and promotes a growing interest in the use of "Environmentally Friendly Catalysts" in all sections of preparative organic chemistry.[1] Zeolite and zeolite-related materials play a very important role in heterogeneous and clean catalysis. The ability to control the zeolite properties through the preparation of new materials and modification of commercially available ones continues to be of great importance in order to achieve highly-selective reactions.[2]

Our own research interests have recently focused on the use of heterogeneous catalysts to promote selective Friedel-Crafts reactions and we have, in particular, reinvestigated the alkenylation of arenes with acetylene derivatives over zeolite HSZ-360.[3] Attempting to synthesise heterocyclic compounds[4] from phenols or aromatic amines and α-alkynols in the presence of solid acids, we have found the production of mixtures of enynes and α,β-unsaturated ketones to be in agreement with the Rupe or Meyer-Shuster rearrangements.[5] Thus, we have undertaken an investigation into the use of zeolites as promoters of the above reactions and after considerable experimentation we have developed a practical and extremely selective route toward α,β-unsaturated ketones and conjugated enynes.

The Rupe and Meyer-Shuster rearrangements of α-alkynols with the production of α,β-unsaturated carbonyl compounds have been known for sometime.[6] The Rupe rearrangement proceeds through a dehydration-hydration sequence with enynes **2** as intermediates, whereas in the Meyer-Shuster rearrangement the intermediate alkynyl cation **4** furnishes the carbonyl compound **5** on work-up.

A wide variety of acidic materials catalyses the reactions. The more utilised of these are mixtures of formic and sulfuric acids, phosphoric acid diluted with acetic acid or, alternatively, a cation-exchanger like DOWEX-50 in acetic acid. Under these conditions the process is frequently contaminated by production of isomeric Rupe or Meyer-Shuster ketones (Scheme 1), esterification and loss of acetylene.



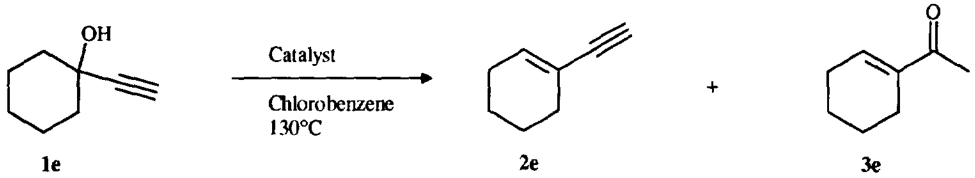
Scheme 1

Results and Discussion

In order to initiate our investigation, the isomerization of the model substrate **1e** to **3e** over zeolites HSZ-360 and HSZ-320 supplied by TOSOH Corporation was analysed (Table 1). HSZ-360 is a HY-zeolite having a pore size of 8 Å and SiO_2/Al_2O_3 molar ratio = 14.5 and was heated at 120°C or at 550°C for 5 hours or treated with NH_4NO_3 solution followed by heating at 550°C for 5 hours before use; HSZ-320 is a NaY-zeolite with the same pore size, with Na_2O/Al_2O_3 molar ratio = 1.0 and SiO_2/Al_2O_3 molar ratio = 5.6.[7] The catalyst was converted into the H-form by standard treatment with NH_4NO_3 solution followed by heating at 550°C for 5 hours.[8] The surface acidity of the catalysts was measured by butylamine titration using *p*-dimethylaminoazobenzene as indicator following the early reported procedure.[9] All reactions were carried out as follows: 500 mg of the catalyst were added to a solution of 1-ethynyl-1-cyclohexanol (**1e**) (1.2 g, 10 mmol) in chlorobenzene (8 ml); the mixture was heated at 130°C for the required time under magnetic stirring; after cooling to room temperature and filtration, the conversion and yield were determined by gas chromatographic analysis.[10]

As reported in Table 1 a trend toward higher yields of **3e** was observed by increasing the catalyst acidity. For example, the use of HSZ-360 (heated at 550°C for 6 hours) [acidity 0.29 meq H^+/g] for 1 hour produced 47% conversion of **1e** to a mixture of **3e** and **2e** (molar ratio 63/37) [entry **b**]. The reaction only progressed to 61% conversion after an additional 2 hours giving a larger amount of compound **3e** (molar ratio 73/27).

Table 1. Dehydration-hydration process of 1-ethynyl-1-cyclohexanol **1e** over zeolitic catalysts.



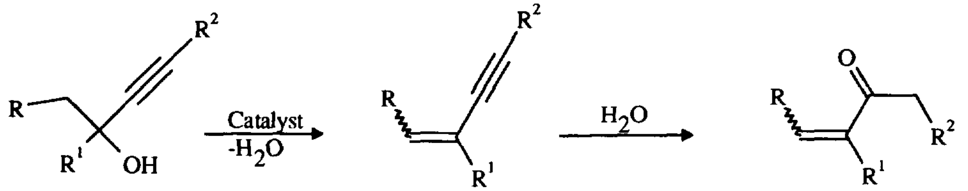
Entry	Catalyst	Catalyst acidity	Reaction time: 1h		Reaction time: 3h	
		(meq H^+/g)	Recovered **1e** (%)	**3e** / **2e**	Recovered **1e** (%)	**3e** / **2e**
a	HSZ-360 (120°C, 6h)	0.27	53	60/40	49	73/27
b	HSZ-360 (550°C, 6h)	0.29	70	63/37	67	73/27
c	HSZ-360/NH_4NO_3 (550°C, 6h)	0.30	48	92/8	37	100/0
d	HSZ-320/NH_4NO_3 (550°C, 6h)	0.89	29	100/0	0	100/0

Better results were obtained by using the same catalyst treated with NH_4NO_3 and heated at 550°C for 6 hours [acidity 0.30 meq H^+/g], yielding compound **3e** as the sole product in 63% yield after 3 hours (entry **c**). As expected, the best result was achieved by using the more acidic HSZ-320 converted into the H-form [acidity 0.89 meq H^+/g]. Complete conversion of **1e** was attained with this catalyst after 3 hours at 130°C and **3e** was recovered in 100% yield (entry **d**).

We next sought to define the generality of this reaction by subjecting a variety of α-alkynols **1a-n** to the optimised conditions (Table 1, entry d). As illustrated in Table 2, the course of the reaction was strongly dependent upon the substituents R, R^1 and R^2 of the starting reagent **1**.

In fact α,β-unsaturated ketones **3a-g**[11] were obtained in 45-100% yield in the reaction of α-alkynols **1** bearing alkyl groups in 1 and 3 positions, probably *via* a dehydration-hydration process (Rupe rearrangement). On the contrary, substrates **1** with one or two aryl substituents in the 1 or 3 position reacted under the same conditions to give complex mixtures from which enynes **2h-n** were detected in low yields (5-20%). Therefore, attempts to rehydrate some of these enynes (**2h**, **2j** and **2m**) by adding stoichiometric amount of water either at the beginning or at the end of the reactions failed to produce the corresponding α,β-unsaturated ketones.

Table 2. Synthesis of enynes **2** and α,β-unsaturated ketones **3** from α-alkynols **1** over zeolite catalysts.



1a-n **2h-n** **3a-g**

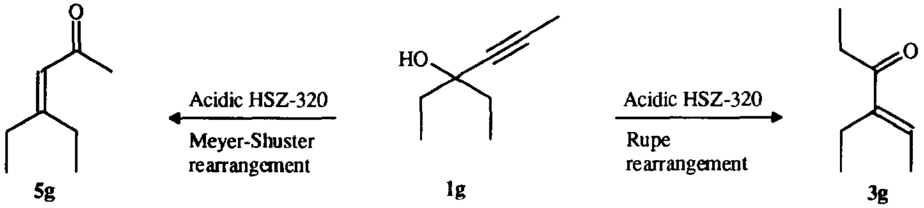
Entry	Comp. 1	R	R^1	R^2	Catalyst	Temp. (°C)	Rec. 1 (%)	2	Yield (%)	3	Yield (%)
a	**1a**	CH_2-$(CH_2)_2$-CH_2		C_4H_9	HSZ-320	130	-		-	**3a**	95
b	**1b**	C_5H_{11}	CH_3	H	"	"	12		-	**3b**	(E)85
c	**1c**	H	"	"	"	"	50		-	**3c**	45
d	**1d**	CH_3	"	"	"	"	-		-	**3d**	(E)100
e	**1e**	CH_2-$(CH_2)_2$-CH_2		"	"	"	-		-	**3e**	100
f	**1f**	C_3H_7	C_2H_5	"	"	"	-		-	**3f**	(E)65[*]
g	**1g**	CH_3	"	CH_3	"	"	-		-	**3g**	(E)80[§]
h	**1h**	"	C_6H_5	H	HSZ-360	65	-	**2h**	(E)100	-	
i	**1i**	H	"	CH_3	"	"	-	**2i**	100	-	
j	**1j**	CH_3	"	C_6H_5	"	"	-	**2j**	(Z)100	-	
k	**1k**	CH_2-$(CH_2)_2$-CH_2		"	"	"	-	**2k**	93	-	
l	**1l**	H	C_6H_5	H	"	"	5	**2l**	85	-	
m	**1m**	"	3-NO_2-C_6H_4	CH_3	"	"	-	**2m**	95	-	
n	**1n**	C_2H_5	H	C_6H_5	"	"	-	**2n**	(E+Z)100[#]	-	

[*] The isomer 3-ethyliden-heptan-2-one (E) (**3fbis**) was also isolated in 35% yield.
[§] Gas-mass analysis showed the presence of traces (~7%) of the isomer **4g**.
[#] A 1:1 ratio of the two isomers was detected.

On focusing these results we decided to perform the synthesis of conjugated enynes *via* dehydration of α-alkynols promoted by less acidic zeolite under milder conditions.[12] Thus, compounds **2h-n** were obtained in 85-100% yield by heating α-alkynols **1h-n** with HSZ-360 at 65°C for 2 hours in chlorobenzene (entries h-n). It is noteworthy that the enynes **2h(E)** and **2j(Z)** were obtained, having the substituents R and R^1 in opposition, probably due to the less steric hindrance of the linear carbon-carbon triple bond with respect to the aromatic ring.

The configuration of these compounds was assigned by a ^{1}H NMR NOESY experiments. In fact the cross-peak correlations in the 2D spectra showed a strong space interaction between the vinyl proton and the aromatic protons in 2 and 6 position of the substituent $R^1 = C_6H_5$.

In order to support the mechanism involving the Rupe rearrangement we studied the reaction of a mixture of acidic HSZ-320 (0.5 g) and the alkynol **1g** (1.3 g, 10 mmol) which could produce both the Rupe and Meyer-Shuster ketones **3g** and **5g** (Scheme 2). We verified that at 130°C compound **1g** was converted into the Rupe ketone **3g** in 80% yield accompanied by traces (~7%) of the isomeric Meyer-Shuster ketone **5g**.



Scheme 2

In conclusion these results suggest that in all cases alkynols **1** are firstly converted into enynes **2** which undergo further hydration to α,β-unsaturated ketones **3** only when the substituents R, R^1 and R^2 are alkyl groups. Moreover, when R, R^1 or R^2 are aryl groups, the hydration process is inhibited and the corresponding enynes are recovered as the sole reaction products.

Experimental

Melting and boiling points were obtained on an Electrothermal melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet PC5 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AMX400 spectrometer at 400 MHz and on a Bruker AC300 at 300 MHz. Chemical shifts are expressed in ppm relative to TMS as internal standard. Mass spectra were obtained on a Hewlett-Packard HP-5971 A instrument. Gas chromatographic analyses were performed on a Dani 8221-a instrument [SPB-1 Supelco column, 30 m, 40°C (4), 10°C/min, 200°C] connected with a Hewlett-Packard HP 3396A integrator with . Microanalyses were carried out by Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica dell'Università di Parma. TLC analyses were performed on Stratocrom SIF silica gel plates (Carlo Erba) developed with hexane-ethyl acetate mixtures. All reagents were of commercial quality from freshly opened containers. The zeolites were supplied by Tosoh Corporation. The NH_4NO_3-exchanged zeolite HSZ-320 was prepared by ion-exchanging three times at 100°C with 0.3 M aqueous ammonium nitrate (3 x 300 ml) the zeolite HSZ-320 (15 g); the catalyst recovered by filtration was washed with distilled water, dried (100°C for 5 h) and heated (550°C, 5 h).[8]

Synthesis of alkynols 1a-n. General Procedure A. The alkynols were synthesised as reported in the literature.[13]

1-Hexinylcyclohexanol (1a). Colourless oil, bp 66-68°C/11mmHg (Found: C, 80.11; H, 11.30. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 0.91 (t, 3H, CH_3, J=7.1 Hz), 1.1-2.0 (m, 10H, 5 CH_2), 2.21 (t, 4H, 2 CH_2, J=6.8 Hz), 2.34 (t, 2H, CH_2, J=6.7 Hz); IR (NaCl) 3407 (OH), 2235 (C≡C); MS (EI) m/e 180 (M^+, 4%), 165 (9), 151 (14), 137 (100).

3-Methyl-1-nonyn-3-ol (1b). Colourless oil, bp 103-105°C/30mmHg (lit[14] bp 88°C/15mmHg).

3-Ethyl-1-heptyn-3-ol (1f). Colourless oil, bp 46-49°C/3mmHg (lit[15] bp 87-94°C/30mmHg).

4-Ethyl-2-hexyn-4-ol (1g). Colourless oil, bp 44-46°C/26mmHg[16]; ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 1.01 (t, 6H, 2 CH_3, J=7.4 Hz), 1.63 (q, 4H, 2 CH_2, J=7.4 Hz), 1.84 (s, 3H, CH_3), 3.7 (br s, 1H, OH); IR (NaCl) 3423 (OH), 2237 (C≡C); MS (EI) m/e 126 (M^+, 1%), 97 (100).

3-Phenyl-1-pentyn-3-ol (1h). Colourless oil, bp 84-86°C/2mmHg (lit[17] bp 86-87°C/2mmHg).

4-Phenyl-2-pentyn-4-ol (1i). White solid, mp 41-42.5 °C (Found: C, 82.46; H, 7.55. Calc. for $C_{11}H_{12}O$: C, 82.30; H, 7.70%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 1.75 (s, 3H, CH_3-≡), 1.92 (s, 3H, CH_3-C-OH), 2.31 (s, 1H, OH), 7.28 (tt, 1H, H-4', J=7.0 and 1.4 Hz), 7.36 (t, 2H, H-3' and H-5', J=7.0 Hz), 7.66 (dd, 2H, H-2' and H-6', J=7.0 and 1.4 Hz); IR (KBr) 3308 (OH), 2250 (C≡C); MS (EI) m/e 160 (M^+, 3%), 159 (13), 145 (100), 115 (14).

1,3-Diphenyl-1-pentyn-3-ol (1j). Pale yellow oil, bp 197-199°C/21mmHg (Found: C, 86.41; H, 6.82. Calc. for $C_{17}H_{16}O$: C, 86.31; H, 6.73%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 1.04 (t, 3H, CH_3, J=7.4 Hz), 2.01 (dq, 1H, ½CH_2, J=14.3 and 7.4 Hz), 2.10 (dq, 1H, ½CH_2, J=14.3 and 7.4 Hz), 2.6 (br s, 1H, OH), 7.2-7.6 (m, 8H, H-arom), 7.70 (dd, 2H, H-2' and H-6' or H-2" and H-6", J=7.2 and 1.6 Hz); IR (NaCl) 3583 (OH), 2300 (C≡C); MS (EI) m/e 236 (M^+, 1%), 207 (100), 129 (45).

1-(Phenylethynyl)cyclohexanol (1k). White solid, mp 60-62°C (lit[18] mp 61-62°C).

4-(3'-Nitrophenyl)-2-pentyn-4-ol (1m). White solid, mp 44-46°C (Found: C, 64.38; H, 5.40; N, 6.83. Calc. for $C_{11}H_{11}NO_3$: C, 64.50; H, 5.53; N, 6.70%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 1.75 (s, 3H, CH_3-≡), 1.91 (s, 3H, CH_3-C-OH), 3.5 (br s, 1H, OH), 7.52 (t, 1H, H-5', J=8.0 Hz), 7.99 (ddd, 1H, H-4' or H-6', J=8.1, 2.3 and 1.0 Hz), 8.10 (ddd, 1H, H-6' or H-4', J=7.7, 1.7 and 1.0 Hz), 8.48 (t, 1H, H-2', J=2.0 Hz); IR (KBr) 3409 (OH), 2260 (C≡C); MS (EI) m/e 205 (M^+, 1%), 204 (7), 190 (100), 115 (20).

1-Phenyl-1-esyn-3-ol (1n). Colourless oil, bp 117-118°C/3mmHg (lit[19] bp 112°C/2mmHg).

Synthesis of enynes 2h-n. General Procedure B. The zeolite HSZ-360 (0.5 g) is added to a solution of the selected alkynol (10 mmol) in dry chlorobenzene (8 ml). The mixture is heated at 65°C for 2 h with magnetic stirring. After cooling to rt, the catalyst is removed by filtration, the solvent distilled off and the crude is chromatographed on silica gel plates with hexane to give the products.

1-Ethynyl-1-cyclohexene (2e). Pale yellow oil, bp 58-59°C/30mmHg (lit[10] bp 42-43°C/13mmHg).

3-Phenyl-4-yn-pent-2-ene (E) (2h). Pale yellow oil, bp 76-77°C/1mmHg (lit[20] bp 69-71°C/0.5mmHg).

2-Phenyl-3-yn-pent-1-ene (2i). Colourless oil, dec. at 1mmHg before boiling (Found: C, 92.91; H, 7.09. Calc. for $C_{11}H_{10}$: C, 92.80; H, 7.20%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.00 (s, 3H, CH_3), 5.56 (s, 1H, ½CH_2=), 5.81 (s, 1H, ½CH_2=), 7.2-7.7 (m, 5H, H-arom); IR (NaCl) 2300 (C≡C); MS (EI) m/e 142 (M^+, 100%), 127 (15), 115 (40).

3,5-Diphenyl-4-yn-pent-5-ene (Z) (2j). Pale yellow oil, dec. at 1mmHg before boiling (Found: C, 93.54; H, 6.46. Calc. for $C_{17}H_{14}$: C, 93.30; H, 6.70%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.19 (d, 3H, CH_3, J=7.0 Hz), 6.56 (q, 1H, CH, J=7.0 Hz), 7.2-7.8 (m, 10H, H-arom); IR (NaCl) 2300 (C≡C); MS (EI) m/e 218 (M^+, 100%), 217 (71), 202 (78), 189 (38).

Phenylethynylcyclohexene (2k). Colourless oil, bp 133-134°C/1mmHg (lit[21] bp 122-123°C/0.5mmHg).

2-Phenyl-3-yn-but-1-ene (2l). Colourless oil, dec. at 1mmHg before boiling (Found: C, 93.71; H, 6.29. Calc. for $C_{10}H_8$: C, 93.55; H, 6.45%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 3.12 (s, 1H, CH≡), 5.77 (s, 1H, ½CH_2=), 5.99 (s, 1H, ½CH_2=), 7.3-7.7 (m, 5H, H-arom); IR (NaCl) 2306 (C≡C); MS (EI) m/e 128 (M^+, 100%), 102 (26).

2-(3'-Nitrophenyl)-3-yn-pent-1-ene (2m). Pale brown oil, dec. at 1mmHg before boiling (Found: C, 70.58; H, 4.85; N, 7.48. Calc. for $C_{11}H_9NO_2$: C, 70.40; H, 4.71; N, 7.61%); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 2.08 (s, 3H, CH_3), 5.72 (s, 1H, ½CH_2=), 5.96 (s, 1H, ½CH_2=), 7.52 (t, 1H, H-5', J=8.1 Hz), 7.97 (dt, 1H, H-4' or H-6', J=8.1 and 2.0 Hz), 8.14 (dt, 1H, H-6' or H-4', J=8.1 and 2.0 Hz), 8.48 (t, 1H, H-2', J=2.0 Hz); IR (NaCl) 2306 (C≡C); MS (EI) m/e 187 (M^+, 100%), 139 (30), 115 (72).

1-Phenyl-1-yn-hex-3-ene (E) (2nE). Colourless oil, bp 70-71°C/1mmHg (lit[22] bp 71-72°C/1mmHg); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 1.04 (t, 3H, CH_3, J=7.4 Hz), 2.17 (m, 2H, CH_2, J=7.4 and 1.6 Hz), 5.68 (dt, 1H, CH-≡, J=15.8 and 1.6 Hz), 6.28 (dt, 1H, CH, J=15.8 and 6.6 Hz), 7.2-7.5 (m, 5H, H-arom); IR (NaCl) 2212 (C≡C); MS (EI) m/e 156 (M^+, 100%), 141 (92), 115 (86).

1-Phenyl-1-yn-hex-3-ene (Z) (2nZ). Colourless oil, bp 71-72°C/1mmHg (lit[22] bp 71-72°C/1mmHg); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) 1.07 (t, 3H, CH_3, J=7.6 Hz), 2.41 (m, 2H, CH_2, J=7.6 and 1.4 Hz), 5.65 (dt, 1H, CH-≡, J=10.7 and 1.4 Hz), 5.97 (dt, 1H, CH, J=10.7 and 7.3 Hz), 7.2-7.5 (m, 5H, H-arom); IR (NaCl) 2200 (C≡C); MS (EI) m/e 156 (M^+, 100%), 141 (90), 115 (80).

Synthesis of ketones 3a-g. General Procedure C. The NH_4NO_3-exchanged zeolite HSZ-320 (0.5 g) is added to a solution of the selected alkynol (10 mmol) in dry chlorobenzene (8 ml). The mixture is heated at 130°C for 4 h with magnetic stirring. After cooling to rt, the catalyst is removed by filtration, the solvent distilled off and the crude is chromatographed on silica gel plates with hexane/ethyl acetate : 90/10 to give the products.

1-Cyclohexenylhexan-1-one (3a). Yellow oil, bp 132-134°C/30mmHg (lit[23] bp 121-123°C/18mmHg).

3-Methyl-3-en-nonan-2-one (E) (3b). Yellow oil, bp 92-94°C/11mmHg (lit[24] bp 98-100°C/16mmHg).

3-Methyl-3-en-butan-2-one (3c). Yellow liquid, bp 103-105°C (lit[25] bp 37-38°C/75mmHg).

3-Methyl-3-en-pentan-2-one (E) (3d). Yellow liquid, bp 137-139°C (lit[26] bp: 138-139°C).

1-(1-Cyclohexen-1-yl)-ethanone (3e). Yellow solid, bp 98-100°C/30mmHg (lit[10] mp 111-114°C/50mmHg).

3-Ethyl-3-en-heptan-2-one (E) (3f). Yellow liquid, bp 191-193°C (lit[27] bp 189-190°C/746mmHg).

3-Ethyliden-heptan-2-one (E) (3fbis). Yellow liquid, bp 93-95°C/30mmHg (lit[28] bp 58-60°C/5mmHg).

3-Ethyl-2-hexen-4-one (E) (3g). Yellow liquid, bp 165-166°C (lit[29] bp 167°C).

4-Ethyl-3-hexen-2-one (5g). Yellow liquid, bp 47-48°C/11mmHg (lit[30] bp 48°C/11mmHg).

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