Electrochemically induced Favorskii rearrangement. α,β-Unsaturated amides and esters in the electrochemical reduction of polyhaloketones

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Electrochemically reduced polyhaloketones react with amines and phenols affording the corresponding α,β-unsaturated amides and esters in moderate yields. The formation of α-iminoketones and α-diimines (main products of the chemical reaction) is completely avoided. The stereochemistry of the α,β-unsaturated products is independent of the nature of the nucleophiles and haloketones.

In the last years it has been highlighted that α,α′-dihaloketones are valuable substrates for the synthesis of many organic compounds.[1] Particular attention has been devoted to the reactivity of polyhaloketones with amines.[2] This reactivity is strongly influenced by solvent and temperature; moreover, the type of ketone and the type of amine play an important role in determining the reaction products. Sterically hindered α,α′-dihaloketones and hindered amines did not react (except under drastic reaction conditions, *e.g.*, high temperature and very high excess of amine). Examining the reactivity of α,α′-dibromoketone with primary amines, De Kimpe and coworkers have brought out the possibility of selectively forming α-iminoketones and α-diimines. According to the proposed mechanisms,[2] Favorskii-derived products could be obtained only under the conditions that allow the formation of halocyclopropanone **A** as an intermediate (Scheme 1).

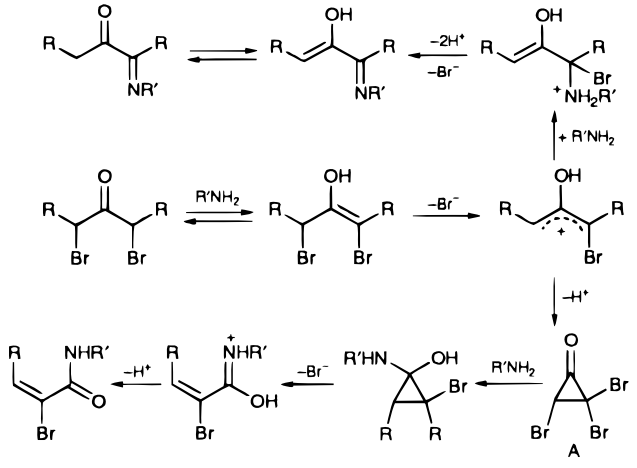
Recently many non-conventional synthetic processes, involving electrochemically generated intermediates, have been developed.[3] These reactions, carried out by the electrochemical reductions or oxidations of suitable substrates, often occur under mild conditions and with considerable improvement in selectivity with respect to the corresponding classical chemical way. In this context, the reduction of halo compounds has turned out to be particularly important, especially because of the subsequent transformations undergone by the corresponding intermediates, *i.e.* their reaction with the solvent, the parent molecule or with non-electroactive substrates purposely added to the solution, *etc.*[4]

Investigating the electrochemical behaviour of haloketones, we found that the electrochemical reduction of α,α′-dichloroketones **5**, carried out at their first voltammetric peak, involves the two-electron cleavage of a carbon–chlorine bond to yield the corresponding carbanion **6**. The chlorocyclopropanone **7** was also found to be one of the possible intermediates in the subsequent transformation of carbanion **8** (Scheme 2).[5]

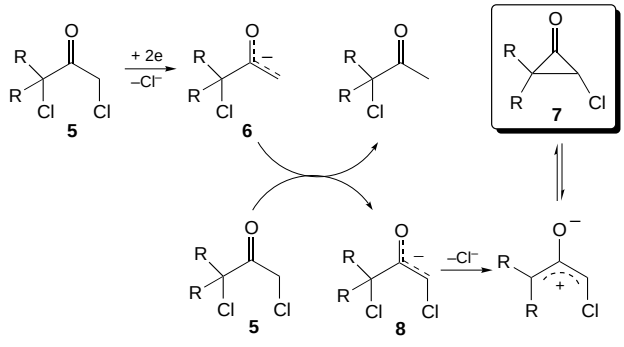
In this paper we investigate the possibility of an electrochemical activation of α,α′-polyhaloketones with respect to primary and secondary amines in order to obtain the selective formation of the Favorskii-rearrangement products. Consequently, we have used the polyhaloketones **1a**,**b** and **2a**,**b** and amines **3a**–**e**. Solutions containing polyhaloketone–amine systems were electrolysed at a potential negative enough to lead to the two-electron cleavage of the carbon–halogen bond so as to favour the formation of the halocyclopropanone intermediate. The investigation was also extended to the polyhaloketone–phenol **4a**–**c** systems. Thus we intend to determine the effect of the nucleophile nature on the reactivity of the polyhaloketones and on the stereochemistry of the products.

Results

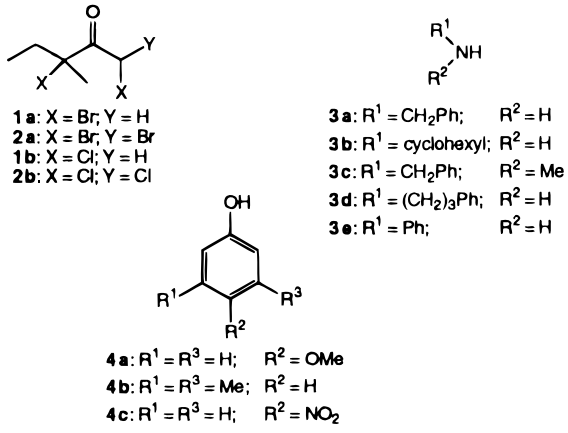
Solutions containing equimolar amounts of polyhaloketones **1a**,**b**, **2a**,**b** and amines **3a**–**e** (see Scheme 3) did not react at



Scheme 1



Scheme 2



Scheme 3

room temperature, even over a one-to-two day interval. α-Iminoketones and α-diimines were both absent when DMF, CH_3CN, THF and CH_2Cl_2 were used as solvents. The voltammetric curves of polyhaloketones **1a**,**b**, **2a**,**b** show two or more reduction peaks (Fig. 1); the first reduction peak can be related to the two-electron cleavage of a carbon–halogen bond ($E'_{p(1b)} = -1.53$ V; $E'_{p(2b)} = -0.99$ V; $E'_{p(1a)} = -1.08$ V; $E'_{p(2a)} = -0.6$ V *vs.* SCE; solvent DMF with 0.1 mol dm^{-3} TEAP; Hg cathode; $c = 1.0 \times 10^{-3}$ mol dm^{-3}; $v = 0.2$ V s^{-1}). The addition of amines **3a**–**e** did not cause significant variations in the voltammetric curves of **1a**,**b**, **2a**,**b**. On the contrary, the addition of phenols **4a**,**b** caused the appearance of a new peak characterised, independently of the ketone, by the same potential value ($E^* = -2.27$ V) (Fig. 1). Quite surprisingly, no new peak appeared when phenol **4c** was used.

Solutions of polyhaloketones **1a**,**b**, **2a**,**b** and amines **3a**–**e** or phenols **4a**–**c** in DMF with 0.1 mol dm^3 TEAP were electrolysed at a potential negative enough to allow the two-electron cleavage of a carbon–halogen bond so as to obtain the formation of the halocyclopropanone **11** intermediate as indicated in Scheme 4. The voltammetric curves, recorded from the cathodic solutions at the end of the electrolyses, have no

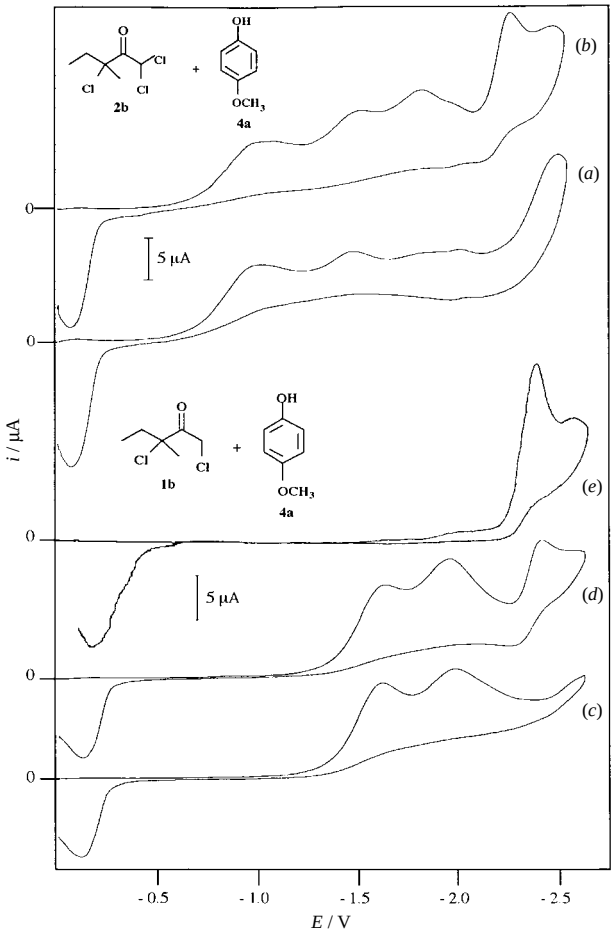
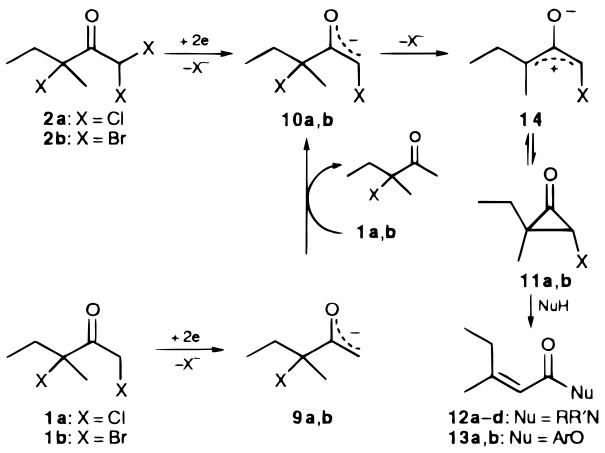


Fig. 1 Cyclic voltammetry curves at a Hg electrode of DMF with 0.1 mol dm^{-3} TEAP solutions of **2b** in the absence (*a*) and in the presence of **4a** (*b*) and of **1b** in the absence (*c*) and in the presence **4a** before the electrolysis (*d*) and at the end of the electrolysis (*e*) carried out at the potential $E = -1.0$ V, $v = 0.2$ V s^{-1}. Concentrations of **1b**, **2b** and **4a** are $c = 1.0 \times 10^{-3}$ mol dm^{-3} in all cases

Table 1 Coulometric data and yields of the Favorskii products of the electrochemical reduction of solutions (DMF with 0.1 mol dm^{-3} TEAP) of ketones **1a**,**b** and **2a**,**b** in the presence of substrates **3a**–**d** and **4a**,**b** at a mercury cathode

Entry	Ketone	Nucleophile[a]	$-E/V$	n_{app}[b]	Favorskii product Yields (%)[c]		$Z:E$ ratio
1	**1a**	**3a**	1.0	2.0	**12a**	29	67 : 33
2	**1a**	**3b**	1.0	2.0	**12b**	42	65 : 35
3	**1a**	**3c**	1.0	2.3	**12c**	41	66 : 34
4	**1a**	**3d**	1.0	1.8	**12d**	39	61 : 39
5	**1a**	**4a**	1.0	2.0	**13a**	33	58 : 42
6	**1a**	**4b**	1.0	2.1	**13b**	48	61 : 39
7	**2a**	**3a**	0.6	3.0	**12a**	47	65 : 35
8	**2a**	**3b**	0.6	3.0	**12b**	53	66 : 34
9	**2a**	**3c**	0.6	2.8	**12c**	59	59 : 41
10	**2a**	**3d**	0.6	1.7	**12d**	51	64 : 36
11	**2a**	**4a**	0.6	2.0	**13a**	44	63 : 37
12	**2a**	**4b**	0.6	2.8	**13b**	45	59 : 41
13	**1b**	**3a**	1.6	2.3	**12a**	68	54 : 46
14	**1b**	**3b**	1.6	1.9	**12b**	36	64 : 36
15	**1b**	**3c**	1.6	2.1	**12c**	44	66 : 34
16	**1b**	**3d**	1.6	2.0	**12d**	47	64 : 36
17	**1b**	**4a**	1.6	2.2	**13a**	64	77 : 23
18	**1b**	**4b**	1.6	2.7	**13b**	36	65 : 35
19	**2b**	**3a**	1.0	2.7	**12a**	74	73 : 27
20	**2b**	**3b**	1.0	2.8	**12b**	42	60 : 40
21	**2b**	**3c**	1.0	3.0	**12c**	58	62 : 38
22	**2b**	**3d**	1.0	1.6	**12d**	70	66 : 34
23	**2b**	**4a**	1.0	2.0	**13a**	42	64 : 36
24	**2b**	**4b**	1.0	2.9	**13b**	44	66 : 34

[a] The ratio between the concentrations of ketone and substrate is $\rho = 1$. [b] Number of Faraday mol^{-1} obtained by coulometry. [c] Yields with respect to the initial amount of ketone.



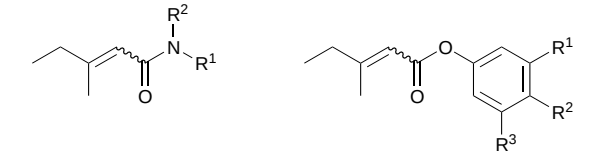
Scheme 4

peaks in the case of ketone–amine systems, whilst in the case of ketone-phenol (**4a**,**b**) systems there is still one peak at a potential $E^* = -2.27$ V (Fig. 1). In addition, the voltammetric analysis shows that α,β-unsaturated amides **12a**–**d** are not reducible at the potential preceding the discharge of the supporting electrolyte; on the other hand α,β-unsaturated esters **13a**,**b** are reducible at a potential of $E^* = -2.27$ V.

Accordingly, at the end of the electrolyses of polyhaloketone–amine **3a**–**d** systems (Table 1, entries 1–4, 7–10, 13–16, 19–22), we were able to isolate the α,β-unsaturated amides **12a**–**d** (see Scheme 5) from the cathodic solution, whereas polyhaloketone–phenol **4a**,**b** systems (entries 6–7, 11–12, 17–18, 23–24) yielded the α,β-unsaturated ester **13a**,**b**. Polyhaloketone–aniline **3e** and polyhaloketone-4-nitrophenol **4c** systems, on the contrary, did not provide the expected Favorskii-rearrangement products. In addition, in all the cathodic solutions both α-iminoketones and α-diimines were absent.

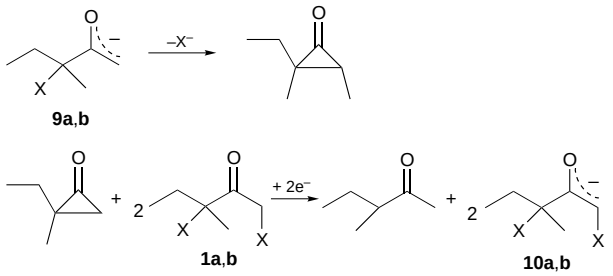
These results suggest that the electrochemical reduction was able to activate polyhaloketones towards amines **3a**–**d** and phenols **4a**,**b**, inducing the formation of the halocyclopropanone **11** as described in Scheme 4. This intermediate is able to react only with the substrates that are nucleophilic enough to add to its carbonyl group. In fact, amines **3a**–**d** and phenoxide anions of **4a**,**b** with $2 < pK_b < 5$[6,7] are nucleophiles that react with the haloketones yielding the corresponding Favorskii-rearrangement product; on the contrary aniline ($pK_b = 9.4$)[6] and 4-nitrophenoxide anion ($pK_b = 6.8$)[6] are unreactive.

The formation of cyclopropanone **11** ensues from different routes according to the starting haloketones (Scheme 4): α,α,-α′-trihaloketones **2a**,**b** undergo the electrochemical cleavage of a carbon–halogen bond yielding the carbanion **10**, which evolves to **11** *via* an intramolecular S_N reaction. In the case of α,α′-dihaloketones **1a**,**b**, the carbanion **10** is obtained both by the deprotonation of the parent molecule operated by the electrochemically generated carbanions **9a**,**b** and by means of a more complex mechanism (Scheme 6),[5] in which a single ion **9a**,**b** allows the deprotonation of two molecules of **1a**,**b** (in accordance with yields of **12** and **13** greater than 50%).

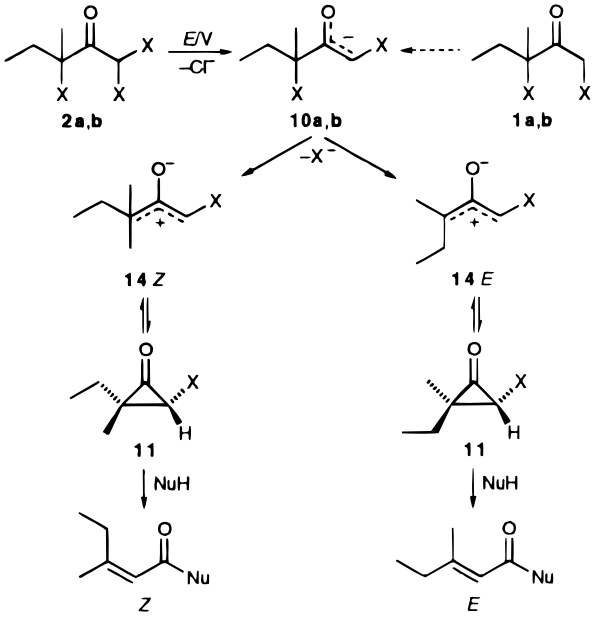


12a: $R^1 = CH_2Ph$; $R^2 = H$ **13a**: $R^1 = R^3 = H$;$R^2 = OCH_3$
12b: R^1 = Cyclohexyl; $R^2 = H$ **13b**: $R^1 = R^3 = CH_3$;$R^2 = H$
12c: $R^1 = CH_2Ph$; $R^2 = Me$
12d: $R^1 = (CH_2)_3Ph$; $R^2 = H$

Scheme 5



Scheme 6



Scheme 7

We also found that the Z/E ratio of the α,β-unsaturated amides **12a**–**d** and esters **13a**,**b** isolated from the cathodic solution was independent of the ketone–nucleophile system used (see Table 1). Moreover, it was pointed out[8] that the Z/E ratio in α,β-unsaturated esters is solely dependent on the ratio of the two pathways for halide elimination from **10** (Scheme 7). The formation of **11** and its opening are stereospecific (Scheme 4). In any case the electrochemical activation of **1a**,**b** and **2a**,**b** leads to the formation of halocyclopropanones **11** with the same Z/E ratio. In addition we found that the Z/E ratio in halide elimination from **10** is independent of the nature of the halogen atom.

Conclusion

The electrochemical reduction allows the activation of polyhalogenoketones that do not otherwise react with primary and secondary amines and phenols. α,β-Unsaturated amides and esters were isolated, after electrolyses, from solutions containing polyhaloketones **1a**,**b**, **2a**,**b** and amines **3a**–**d** or phenols **4a**,**b**. Their Z/E ratio was found to be independent of the polyhaloketone–nucleophile system used. The formation of α-ketoimines and α-diimines was completely avoided.

Experimental

Methods

Voltammetric measurements were carried out using an Amel 498 sessile mercury drop electrode with an AMEL 552 potentiostat equipped with an AMEL 566 function generator and an AMEL 563 multipurpose unit; the curves were displayed on an AMEL 863 recorder assisted by a Nicolet 3091 digital oscilloscope. Coulometry and controlled-potential electrolysis were carried out with an AMEL 552 potentiostat equipped

with an AMEL 721 integrator. The cells used for these techniques have already been described;[9] the cathode was a mercury pool, the counter electrode was a cylindrical platinum gauze and the reference electrode was the calomel type described by Fujinaga;[10] its potential is −0.020 V *vs.* SCE (saturated calomel electrode). All the potentials are given with respect to this electrode. *N*,*N*-Dimethylformamide (DMF, Carlo Erba) and tetraethylammonium perchlorate (TEAP, Fluka) were purified as previously described.[11] All the experiments were carried out at 20.0 ± 0.1 °C in DMF with 0.1 mol dm^{-3} TEAP solutions. The catholyte was degassed and pre-electrolysed at the working potential before the addition of the substrate. Column chromatography was performed on Merck Silica gel (70–230 mesh, 60 g per 1 g of crude mixture). GC analyses were carried out on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector, linear temperature programmer and a Hewlett Packard Model 3390A electronic integrator. The column used was a Supelco SP 2250 (30 mm × 0.32 mm). GC-MS measurements were carried out on a SE 54 capillary column using a Fisons 8000 gas chromatograph coupled with a Fisons MD 800 quadrupole mass selective detector. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AC 200 spectrometer with $CDCl_3$ as internal standard. All new compounds gave satisfactory elemental analyses (C ± 0.3%; H ± 0.2%; N ± 0.2%).

Materials

The amines **3a**–**e** and phenols **4a**–**c** were commercially available products of analytical grade. 1,3-Dibromo-3-methyl-2-pentanone (**1a**) and 1,1,3-tribromo-3-methyl-2-pentanone (**2a**) were prepared according to Rappe[12] from the bromination of 3-methyl-2-pentanone (Aldrich) with two or three moles of bromine, respectively. 1,3-Dichloro-3-methyl-2-pentanone (**1b**) was prepared as described in the literature;[8] 1,1,3-trichloro-3-methyl-2-pentanone (**2b**) was prepared using 3.0 equiv of sulfuryl chloride according to the procedure described by Sakai *et al.*[13]

1,3-Dibromo-3-methyl-2-pentanone (1a). ^{1}H NMR: δ($CDCl_3$) 4.43 (dd, AB, 2H, J_{AB} = 15.6 Hz, Δν = 10.8 Hz, CH_2BrCO), 2.18 (dq, 1H, *J* = 14.6, 7.3 Hz, CH_3CH_2), 2.03 (dq, 1H, *J* = 14.6, 7.3 Hz, CH_3CH_2), 1.85 (s, 3H, CH_3CBr), 1.01 (t, 3H, *J* = 7.3 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 197.6, 69.2, 34.7, 30.6, 26.6, 10.1; GC-MS *m*/*z*: $M^{+\cdot}$ absent, 165 (4%), 163 (4), 137 (53), 135 (49), 123 (16), 121 (14), 95 (14), 93 (16), 55 (100).

1,1,3-Tribromo-3-methyl-2-pentanone (2a). ^{1}H NMR: δ($CDCl_3$) 6.64 (s, 1H, CHBr$_2$CO), 2.27–1.99 (2H, m, CH_3CH_2), 1.89 (s, 3H, CH_3CBr), 1.05 (t, 3H, *J* = 7.3 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 192.6, 67.8, 36.3, 34.5, 26.6, 10.1; GC-MS *m*/*z*: $M^{+\cdot}$ absent, 203 (1%), 201 (2), 199 (1), 175 (4), 173 (8), 171 (4), 165 (9), 163 (10), 137 (53), 135 (56), 55 (100).

1,1,3-Trichloro-3-methyl-2-pentanone (2b). ^{1}H NMR: δ($CDCl_3$) 6.70 (s, 1H, CHCl$_2$CO), 2.10 (1H, dq, *J* = 7.3 Hz, CH_3CH_2), 1.97 (1H, dq, *J* = 7.3 Hz, CH_3CH_2), 1.72 (s, 3H, CH_3CCl), 1.04 (t, 3H, *J* = 7.3 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 199.4, 75.5, 46.3, 34.7, 26.9, 8.9; GC-MS *m*/*z*: $M^{+\cdot}$ absent, 121 (4%), 119 (12), 93 (38), 91 (96), 87 (3), 85 (10), 83 (18), 55 (100).

Reduction of haloketones in the presence of 3a–e or 4a–c

General procedure. The controlled-potential electrolyses were carried out at the potential corresponding to the first voltammetric peak of the haloketones by stepwise addition of haloketones (1.0 mmol) and nucleophiles (1.0 mmol) to DMF with 0.1 mol dm^{-3} TEAP (30 mL) in such a way that its concentration never exceeded 10^{-2} mol dm^{-3}. Each addition of ketone and nucleophiles was made when the current dropped from its initial value to that measured from the pre-electrolysis. At the end of the electrolysis, the catholyte was separated from the mercury, mixed with water (50 mL) and extracted with Et_2O (5 × 30 mL). The organic extracts were washed with water, dried (Na_2SO_4), analysed by TLC and the solvent evaporated under reduced pressure. The residue was chromatographed on silica gel to afford the two pure isomers of the corresponding α,β-unsaturated carbonyl compound. The double-bond geometry was assigned by means of ^{1}H NMR spectra. The yields are reported in Table 1. The *Z*/*E* ratio was determined by gas chromatography. The reduction of haloketones in the presence of **3e** and **4c** did not lead to the corresponding α,β-unsaturated carbonyl compounds.

***N*-Benzyl-3-methyl-2-pentenamide (12a).** *Z* isomer: ^{1}H NMR: δ($CDCl_3$) 7.73–7.27 (5H, m, ar), 5.68 (1H, br s, NH), 5.51 (1H, d, *J* = 1.3 Hz, CHC=C), 4.43 (2H, d, *J* = 5.7 Hz, CH_2Ph), 2.65 (2H, q, *J* = 7.5 Hz, CH_3CH_2), 1.81 (3H, d, *J* = 1.3 Hz, CH_3C=C), 1.06 (3H, t, *J* = 7.5 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 166.4, 156.8, 138.6, 128.6, 127.7, 127.3, 117.7, 43.2, 26.1, 24.2, 12.7; GC-MS *m*/*z*: 204 ($M^{+\cdot}$ + 1, 2%), 203 ($M^{+\cdot}$, 10), 188 (4), 97 (33), 91 (100), 41 (52).

E isomer: ^{1}H NMR: δ($CDCl_3$) 7.82–7.23 (5H, m, ar), 5.85 (1H, br s, NH), 5.53 (1H, d, *J* = 1.0 Hz, CHC=C), 4.42 (2H, d, *J* = 2.4 Hz, CH_2Ph), 2.64 (2H, q, *J* = 7.6 Hz, CH_3CH_2), 2.14 (3H, d, *J* = 1.0 Hz, CH_3C=C), 1.01 (3H, t, *J* = 7.6 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 167.0, 156.1, 138.7, 128.6, 127.7, 127.3, 116.7, 43.3, 29.3, 18.2, 12.0; GC-MS *m*/*z*: 204 ($M^{+\cdot}$ + 1, 2%), 203 ($M^{+\cdot}$, 9), 188 (4), 97 (43), 91 (100), 41 (58).

***N*-Cyclohexyl-3-methyl-2-pentenamide (12b).** *Z* isomer: ^{1}H NMR: δ($CDCl_3$) 5.45 (1H, s, CHC=C), 5.30 (1H, br s, NH), 3.74 (1H, m, NCH), 2.57 (2H, q, *J* = 7.5 Hz, CH_3CH_2), 1.76 (3H, s, CH_3C=C), 1.06 (3H, t, *J* = 7.5 Hz, CH_3CH_2), 1.91–0.98 (10H, m, −(CH_2)$_5$−); ^{13}C NMR: δ($CDCl_3$) 165.8, 155.1, 118.6, 47.8, 33.3, 29.3, 26.0, 24.9, 24.8, 12.7; GC-MS *m*/*z*: 196 (M^+ + 1, 3%), 195 ($M^{+\cdot}$, 8), 180 (4), 97 (92), 41 (100).

E isomer: ^{1}H NMR: δ($CDCl_3$) 5.47 (1H, d, *J* = 1.2 Hz, CHC=C), 5.35 (1H, br s, NH), 3.77 (1H, m, NCH), 2.57 (2H, q, *J* = 7.5 Hz, CH_3CH_2), 2.08 (3H, d, *J* = 1.2 Hz, CH_3C=C), 1.02 (3H, t, *J* = 7.5 Hz, CH_3CH_2), 1.86–0.96 (10H, m, −(CH_2)$_5$−); ^{13}C NMR: δ($CDCl_3$) 166.4, 154.6, 117.5, 47.8, 33.2, 26.1, 26.0, 24.9, 18.0, 12.0; GC-MS *m*/*z*: 196 (M^+ + 1, 3%), 195 ($M^{+\cdot}$, 9), 180 (5), 97 (100), 41 (97).

***N*-Methyl-*N*-benzyl-3-methyl-2-pentenamide (12c).** *Z* isomer: ^{1}H NMR: δ($CDCl_3$) 7.77–7.10 (5H, m, ar), 5.80 (1H, s, CHC=C), 4.53 (2H, s, CH_2Ph), 2.88 (3H, s, CH_3N), 2.35 (2H, q, *J* = 7.5 Hz, CH_3CH_2), 1.77 (3H, s, CH_3C=C), 1.05 (3H, t, *J* = 7.5 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 166.8, 152.1, 137.6, 128.8, 128.5, 126.9, 117.7, 54.0, 32.8, 29.6, 23.1, 12.5; GC-MS *m*/*z*: 217 ($M^{+\cdot}$, 4%), 202 (4), 97 (70), 91 (100), 41 (91).

E isomer: ^{1}H NMR: δ($CDCl_3$) 7.77–7.10 (5H, m, ar), 5.80 (1H, s, CHC=C), 4.60 (2H, s, CH_2Ph), 2.89 (3H, s, CH_3N), 2.35 (2H, q, *J* = 7.5 Hz, CH_3CH_2), 1.82 (3H, s, CH_3C=C), 1.05 (3H, t, *J* = 7.5 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 167.2, 151.5, 137.0, 128.7, 128.0, 126.6, 117.5, 54.4, 35.2, 26.8, 18.3, 12.0; GC-MS *m*/*z*: 217 ($M^{+\cdot}$, 5%), 202 (13), 97 (80), 91 (100), 41 (98).

***N*-(3-Phenylpropyl)-3-methyl-2-pentenamide (12d).** *Z* isomer: ^{1}H NMR: δ($CDCl_3$) 7.27–7.10 (5H, m, ar), 6.14 (1H, br s, NH), 5.50 (1H, s, CHC=C), 2.60 (2H, q, *J* = 7.7 Hz, CH_3CH_2), 2.59 (4H, m, CH_2N and CH_2Ph), 1.79 (3H, s, CH_3C=C), 1.76 (2H, m, $CH_2CH_2CH_2$), 1.03 (3H, t, *J* = 7.7 Hz, CH_3CH_2); ^{13}C NMR: δ($CDCl_3$) 166.6, 155.2, 141.4, 128.2,

128.1, 125.7, 118.1, 42.0, 38.6, 33.1, 30.1, 24.7, 12.6; GC-MS m/z: 232 ($M^{+\cdot}$ + 1, 3%), 231 ($M^{+\cdot}$, 19), 127 (55), 97 (100), 91 (43), 41 (83).

E isomer: ^{1}H NMR: $\delta(CDCl_3)$ 7.23–7.07 (5H, m, ar), 6.16 (1H, br s, N*H*), 5.53 (1H, s, C*H*C=C), 2.60 (2H, q, J = 7.7 Hz, CH_3CH_2), 2.59 (4H, m, CH_2N and CH_2Ph), 2.02 (3H, s, CH_3C=C), 1.76 (2H, m, $CH_2CH_2CH_2$), 0.99 (3H, t, J = 7.7 Hz, CH_3CH_2); ^{13}C NMR: $\delta(CDCl_3)$ 167.2, 154.6, 141.4, 128.1^3, 128.1^0, 125.7, 117.1, 41.4, 39.1, 33.2, 25.8, 17.9, 11.8; GC-MS m/z: 232 ($M^{+\cdot}$ + 1, 3%), 231 ($M^{+\cdot}$, 18), 127 (57), 97 (100), 91 (45), 41 (82).

4-Methoxyphenyl 3-methyl-2-pentenoate (13a). *Z* isomer: ^{1}H NMR: $\delta(CDCl_3)$ 7.02–6.84 (4H, m, ar), 5.83 (1H, s, C*H*C=C), 3.77 (3H, s, OCH_3), 2.66 (2H, q, J = 7.6 Hz, CH_3CH_2), 1.55 (3H, s, CH_3C=C), 1.10 (3H, t, J = 7.6 Hz, CH_3CH_2); ^{13}C NMR: $\delta(CDCl_3)$ 164.7, 164.3, 157.0, 144.3, 122.4, 114.6, 113.7, 55.5, 33.8, 24.7, 12.3; GC-MS m/z: 221 ($M^{+\cdot}$ + 1, 3%), 220 ($M^{+\cdot}$, 6), 124 (41), 97 (100), 41 (56).

E isomer: ^{1}H NMR: $\delta(CDCl_3)$ 7.02–6.87 (4H, m, ar), 5.86 (1H, d, J = 1.1 Hz, C*H*C=C), 3.77 (3H, s, OCH_3), 2.66 (2H, q, J = 7.6 Hz, CH_3CH_2), 1.94 (3H, d, J = 1.1 Hz, CH_3C=C), 1.07 (3H, t, J = 7.6 Hz, CH_3CH_2); ^{13}C NMR: $\delta(CDCl_3)$ 165.4, 164.8, 155.0, 144.3, 122.4, 114.6, 114.3, 55.5, 26.7, 18.9, 11.8; GC-MS m/z: 221 ($M^{+\cdot}$ + 1, 3%), 220 ($M^{+\cdot}$, 6), 124 (39), 97 (100), 41 (53).

3,5-Dimethylphenyl 3-methyl-2-pentenoate (13b). *Z* isomer: ^{1}H NMR: $\delta(CDCl_3)$ 7.13–6.81 (3H, m, ar), 5.86 (1H, s, C*H*C=C), 2.68 (2H, q, J = 7.5 Hz, CH_3CH_2), 2.25 (3H, s, CH_3Ph), 2.23 (3H, s, CH_3Ph), 1.96 (3H, s, CH_3C=C), 1.10 (3H, t, J = 7.5 Hz, CH_3CH_2); ^{13}C NMR: $\delta(CDCl_3)$ 164.9, 164.8, 148.6, 130.2, 122.7, 118.8, 114.7, 29.7, 24.9, 19.1, 12.4; GC-MS m/z: 218 ($M^{+\cdot}$, 3%), 122 (11), 97 (100), 41 (52).

E isomer: ^{1}H NMR: $\delta(CDCl_3)$ 7.14–6.81 (3H, m, ar), 5.89 (1H, d, J = 1.1 Hz, C*H*C=C), 2.68 (2H, q, J = 7.5 Hz, CH_3CH_2), 2.25 (3H, s, CH_3Ph), 2.23 (3H, s, CH_3Ph), 2.19 (3H, d, J = 1.1 Hz, CH_3C=C), 1.10 (3H, t, J = 7.5 Hz, CH_3CH_2); ^{13}C NMR: $\delta(CDCl_3)$ 165.4, 164.3, 148.6, 130.2, 122.7, 118.8, 113.7, 29.6, 24.8, 19.8, 11.8; GC-MS m/z: 218 ($M^{+\cdot}$, 4%), 122 (11), 97 (100), 41 (40).

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