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Raney Ni–Al alloy-mediated reduction of benzils in water

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Raney Ni–Al alloy in a dilute aqueous alkaline solution has been shown to be a powerful reducing agent and is highly effective for the reduction of alkylbenzils and alkoxybenzils to afford the corresponding 1,2-diarylethers at 90 °C, in the absence of organic solvents. 4,4'-Dinitrobenzil was transformed selectively to 1,2-bis(4-aminophenyl)-ethane.

Keywords: benzils, Ni–Al alloy, reduction, 1,2-diarylethanes, aqueous reaction medium

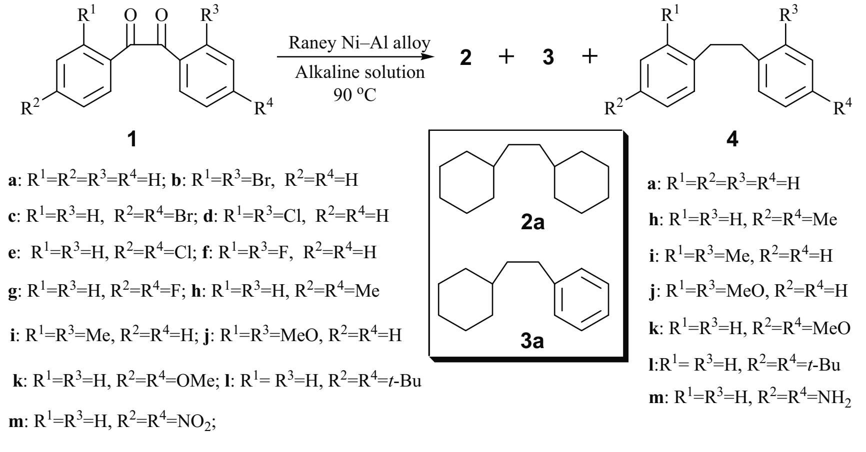
The reduction of functional groups to saturated systems is not always straightforward, especially where more stable functional groups such as the carbonyl function or the arene unit are involved. Nevertheless, the transformation of a carbonyl group to a methylene unit is of great importance in organic synthetic chemistry. Hither to the transformation has been accomplished mainly by such classical methods as metal–amalgam (Mg, Zn, Al or Sn/Hg) or metal-mediated reduction,[1] including the Clemmensen[2] and Wolf–Kishner–Huang–Minlon reductions.[3] In addition sodium dithionite-promoted reduction,[4] Pt and Pd catalysed hydrogenation,[5] Ru-mediated reduction in the presence of HCO_2H/Et_3N,[6] hydrogenation, catalysed by a sol-gel entrapped Pd–$[Rh(COD)Cl]_2$ (H_2, 400 psi),[7] electrochemical reduction,[8] and yeast-catalysed reduction[9] have been reported. Some of the literature methods have disadvantages and harsh reaction conditions or toxic reagents are used.

Raney Ni–Al alloy as a reducing agent in 10% NaOH aqueous solutions has been found to reduce ketones and aldehydes to alcohols and hydrocarbons sucessfully.[10] In the continuation of our work on the reduction of aromatic compounds with Raney Ni–Al alloy in aqueous media,[11] we turned our attention to the action of Raney Ni–Al alloy on benzils in the hope of developing a convenient and practical method for the conversion of benzils to 1,2-diarylethanes.

Results and discussion

We now report the reactivity of benzils towards Raney Ni–Al alloy. The reactions have been carried out in dilute basic solutions under mild conditions and in absence of any organic solvents. The results are summarised in Tables 1 and 2 and Schemes 1 and 2.

The reductions were carried out by adding an aqueous alkaline solution dropwise to a suspension of the benzil and Raney Ni–Al alloy in water, whilst the resulting mixture was heated at 90 °C. The reduction was monitored by GC. When a 1w% aq. KOH solution was added to a mixture of benzil (**1a**) and Raney–Ni alloy in water, **1a** was reduced to give a mixture of 1,2-dicyclohexylethane (**2a**), 1-cyclohexyl-2-phenylethane (**3a**), and 1,2-diphenylethane (**4a**) (Table 1, runs 1–9). There was a tendency for the amounts of **2a** and **3a** formed in the reaction to increase with the amount of Raney Ni–Al alloy employed (Table 1, run 1 *versus* runs 2–4). Similar experiments were carried out using 1w% solutions of other alkali and alkali earth hydroxides such as CsOH, NaOH, $Ca(OH)_2$, LiOH, or $Ba(OH)_2$. Again, mixtures of the reduction products of **2a**, **3a** and **4a** (Table 1, runs 5–9) were obtained. Also, the reduction of difluoro-, dibromo-, and dichlorobenzils (**1b–g**) provided a mixture of **2a, 3a** and **4a** under the conditions (Table 1, runs 10–15). As expected, the halo functions are not compatible with the reaction conditions. 2,2'-Dimethyl-, 4,4'-dimethyl-, 2,2'-dimethoxy-, 4,4'-dimethoxy- and 4,4'-di-*t*-butylbenzils (**1h–l**) were reduced to the corresponding 1,2-diarylethanes (**3h–l**) successfully with Raney Ni–Al alloy upon dropwise addition of a 1w% KOH solution (Table 1, runs 16–20). The reduction of 4,4'-dinitrobenzil (**1m)** afforded the corresponding 1,2-bis(4-aminophenyl)ethane (**4m**) selectively and in good yield (Table 1, run 21). Here, again no hydrogenation of the



a: R^1=R^2=R^3=R^4=H; **b**: R^1=R^3=Br, R^2=R^4=H

c: R^1=R^3=H, R^2=R^4=Br; **d**: R^1=R^3=Cl, R^2=R^4=H

e: R^1=R^3=H, R^2=R^4=Cl; **f**: R^1=R^3=F, R^2=R^4=H

g: R^1=R^3=H, R^2=R^4=F; **h**: R^1=R^3=H, R^2=R^4=Me

i: R^1=R^3=Me, R^2=R^4=H; **j**: R^1=R^3=MeO, R^2=R^4=H

k: R^1=R^3=H, R^2=R^4=OMe; **l**: R^1= R^3=H, R^2=R^4=*t*-Bu

m: R^1=R^3=H, R^2=R^4=NO_2;

a: R^1=R^2=R^3=R^4=H

h: R^1=R^3=H, R^2=R^4=Me

i: R^1=R^3=Me, R^2=R^4=H

j: R^1=R^3=MeO, R^2=R^4=H

k: R^1=R^3=H, R^2=R^4=MeO

l:R^1= R^3=H, R^2=R^4=*t*-Bu

m: R^1=R^3=H, R^2=R^4=NH_2

Scheme 1

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Table 1 Reduction of benzils (**1**)[a]

Run	Substrate	Ni–Al (g)	Alkaline solution[b]/mL	Time/h	Product	Ratio/%[c,d]		
						2	**3**	**4**
1	**1a**	2	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	26.4	49.5	24.1
2	**1a**	4	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	60.4 (55.7)[7]	26.3 (21.6)[12]	13.3 (8.8)[10]
3	**1a**	6	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	61.0	28.9	10.1
4	**1a**	8	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	62.2	28.3	9.5
5	**1a**	4	1%NaOH (40)/H_2O (40)	6	**2a, 3a, 4a**	58.9	27.2	13.9
6	**1a**	4	1%CsOH (40)/H_2O (40)	6	**2a, 3a, 4a**	62.3	25.1	12.6
7	**1a**	4	1%$Ca(OH)_2$ (40)/H_2O (40)	6	**2a, 3a, 4a**	45.2	26.9	27.9
8	**1a**	4	1%LiOH (40)/H_2O (40)	6	**2a, 3a, 4a**	24.5	25.5	50.0
9	**1a**	4	1%$Ba(OH)_2$ (40)/H_2O (40)	6	**2a, 3a, 4a**	18.8	16.8	64.4
10	**1b**	4	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	51.8 (45.7)	25.5 (20.2)	22.7 (17.8)
11	**1c**	4	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	50.0	24.1	25.9
12	**1d**	4	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	48.5	22.2	29.3
13	**1e**	4	1%KOH (40)/H_2O (40)	6	**2a, 3a, 4a**	50.4	21.2	28.4
14	**1f**	4	1%KOH (40)/H_2O (40)	7	**2a, 3a, 4a**	47.2	27.6	25.6
15	**1g**	4	1%KOH (40)/H_2O (40)	7	**2a, 3a, 4a**	45.1	27.0	27.9
16	**1h**	4	1%KOH (40)/H_2O (40)	8	**4h**	0	0	100 (84.7)[13]
17	**1i**	4	1%KOH (40)/H_2O (40)	8	**4i**	0	0	100 (87.4)[13]
18	**1j**	4	1%KOH (40)/H_2O (40)	8	**4j**	0	0	100 (86.7)[13]
19	**1k**	4	1%KOH (40)/H_2O (40)	8	**4k**	0	0	100 (85.5)[13]
20	**1l**	4	1%KOH (40)/H_2O (40)	8	**4l**	0	0	100 (84.4)[13b]
21	**1m**	4	1%KOH (40)/H_2O (40)	8	**4m**	0	0	100 (86.9)[14]

[a]**1** (10 mmol). [b]The alkaline solution was added dropwise within 1.0 h. [c]GC ratio. [d]Isolated yields in parentheses.

Table 2 Reduction of diones (**1n–r**)[a]

Run	Dione	Time/h	Yield/%[c,d]		
			2	**3**	**4**
1	**1n**	7	58.2 (51.2)[15]	25.1 (20.3)[18]	16.7 (13.2)[15]
2	**1o**	7	55.4 (50.2)[15]	23.5 (19.0)[19]	21.1 (18.0)[15]
3	**1p**	7	51.6 (46.0)[16]	24.5 (19.3)	24.0 (20.6)[16]
4	**1q**	7	52.7 (48.6)[17]	23.9 (19.5)	23.4 (19.9)[17]

[a]**1** (10 mmol), Raney Ni–Al alloy (4.0 g), water (40 mL), 90 °C. [b]1% KOH aqueous solution (40 mL) was added dropwise within 1.0 h. [c]Isolated yields.

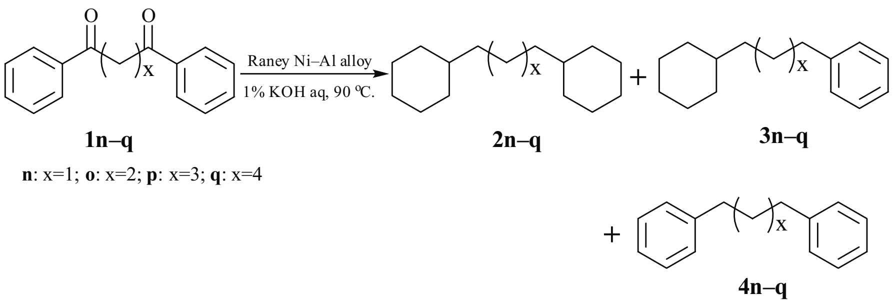
phenylene unit could be observed. Thus, treatment of halogenated benzils leads to ring-hydrogenated products, while alkylated and alkoxylated benzyls show a very selective transformation to the corresponding 1,2-diarylethanes.

The reduction of diones under the same reaction conditions was also investigated. The reduction of diones (**1n–q**) was carried out successfully by using Raney Ni–Al alloy with the dropwise addition of a 1wt% aqueous solution of KOH at 90 °C to produce alicyclic derivatives (**2n–q**) as main products, albeit with some amounts of phenylcyclohexyl alkanes (**3n–q**) and diphenylalkanes **(4n–q)** (Scheme 2, Table 2).

In conclusion, we have developed a new and efficient method for the reduction of alkylbenzils and alkoxybenzils using commercially available Raney Ni–Al alloy in a dilute alkaline solution. Alkyl- and alkoxybenzils were reduced easily to afford the corresponding 1,2-diphenylethanes (**4**) under mild reaction conditions. The advantages of the present approach for the reduction of these compounds lie in the ease of manipulation, speed of the reaction, and mildness of reaction conditions. Nevertheless, it must be noted that halo- and nitro functions are not compatible with the reaction conditions. 4,4'-Dinitrobenzil (**1m**) gives a clean transformation to 1,2-bis(4-aminophenyl)ethane (**4m**). Commercial Raney Ni–Al alloy is readily available and is, of course, cheaper than the Raney Ni catalyst made from it. Further work on the reduction of carbonyl compounds is currently underway in our laboratory and the results will be published in due course.

Experimental

IR spectra were measured with Nicolet FT-IR 360, JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer (^{1}H at 270 MHz and ^{13}C at 67.8 MHz) and a Bruker DMX-500. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer [electron impact mode (EI), 70 eV or fast atom bombardment (FAB)] and with a GC-MS 6890[GC]/HP MS5973 combination.



Scheme 2

The Raney Ni–Al alloy was acquired commercially from Jinzhou Catalyst Company (Jinzhou, P.R. China).

General procedure

An aq. 1w% KOH solution (40 mL) was added over 1.0 hour and at 90 °C, to a mixture of **1a** (2.1 g, 10.0 mmol), Raney Ni–Al alloy (4.0 g) and water (40 mL). After the mixture had been heated for an additional 6 h at 90 °C, it was cooled to rt and filtered over celite. The residue was washed with ethyl acetate. The filtrate was neutralised with hydrochloric acid and extracted with ethyl acetate (3 × 15 mL). The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed. A mixture of 1,2-dicyclohexylethane (**2a**), 1-cyclohexyl-2-phenylethane (**3a**), 1,2-diphenylethane (**4a**) was obtained in the ratio of 60.4: 26.3: 13.3, according to GC-analysis (Table 1, run 2). Compounds **2a**, **3a** and **4a** were separated by column chromatography on silica gel by using hexane as solvent.

1,2-Dicyclohexylethane (**2a**):[7] ^{1}H NMR: δ = 0.60–0.72 (4H, m), 1.02–1.14 (6H, m), 1.22–1.32 (2H, m), 1.42–1.62 (10H, m), 2.29 (4H, d, J = 6.4 Hz); GC/MS (m/z): 194 (M^{+}), 110, 96, 83, 67, 55 and 41.

1-Cyclohexyl-2-phenylethane (**3a**):[12] ^{1}H NMR: δ = 0.78–1.00 (2H, m), 1.20–1.35 (4H, m), 1.55–1.60 (2H, m), 1.70–1.86 (5H, m), 2.60 (2H, t, J = 6.0 Hz), 6.96–7.15 (2H, m), 7.20–7.26 (3H, m); GC/MS (m/z): 188 (M^{+}), 92, 83, 77, 67, 55 and 41.

1,3-Dicyclohexylpropane (**2n**):[15] ^{1}H NMR: δ = 0.60–0.72 (4H, m), 1.06–1.30 (12H, m), 1.40–1.60 (10H, m), 2.26 (2H, t, J = 6.8 Hz); δ_C (67.8 MHz, $CDCl_3$) = 26.2, 27.0, 28.2, 33.0, 36.1, 37.5; GC/MS (m/z): 208 (M^{+}), 124, 110, 67, 55 and 41.

1-Cyclohexyl-3-phenylpropane (**3n**):[18] ^{1}H NMR: δ = 0.66–0.78 (2H, m), 1.08–1.24 (6H, m), 1.52–1.72 (7H, m), 2.32 (2H, t, J = 6.9 Hz), 7.00–7.15 (2H, m), 7.22–7.30 (3H, m); δ_C (67.8 MHz, $CDCl_3$) = 26.4, 27.2, 28.8, 33.2, 36.3, 37.3, 37.8, 125.6, 128.0, 128.6, 143.1; GC/MS (m/z): 202 (M^{+}), 106, 97, 77, 67, 55 and 41.

1,4-Dicyclohexylbutane (**2o**):[15] ^{1}H NMR: δ = 0.60–0.72 (4H, m), 1.02–1.32 (12H, m), 1.42–1.62 (10H, m), 2.24 (4H, t, J = 6.6 Hz); δ_C (67.8 MHz, $CDCl_3$) = 26.4, 27.2, 28.6, 33.2, 36.0, 37.8; GC/MS (m/z): 222 (M^{+}), 138, 124, 112, 67, 55 and 41.

1-Cyclohexyl-4-phenylbutane (**3o**):[19] ^{1}H NMR: δ = 0.64–0.76 (2H, m), 1.06–1.22 (8H, m), 1.50–1.70 (7H, m), 2.30 (2H, t, J = 6.9 Hz), 7.04–7.18 (2H, m), 7.24–7.32 (3H, m); δ_C (67.8 MHz, $CDCl_3$) = 26.6, 26.9, 27.0, 32.2, 33.7, 36.3, 37.7, 38.3, 126.2, 128.4, 128.6, 143.2; GC/MS (m/z): 216 (M^{+}), 120, 106, 67, 55 and 41.

1,5-Dicyclohexylpentane (**2p**):[16] ^{1}H NMR: δ = 0.60–0.72 (4H, m), 1.00–1.30 (14H, m), 1.44–1.64 (12H, m), 2.23 (2H, t, J = 6.8 Hz); δ_C (67.8 MHz, $CDCl_3$) = 26.0, 27.4, 28.3, 33.0, 36.2, 37.4, 38.4; GC/MS (m/z): 236 (M^{+}), 150, 136, 124, 112, 67, 55 and 41.

1-Cyclohexyl-5-phenylpentane (**3p**): ^{1}H NMR: δ = 0.62–0.75 (2H, m), 1.04–1.20 (10H, m), 1.52–1.70 (7H, m), 2.27 (2H, t, J = 6.8 Hz), 7.02–7.16 (2H, m), 7.22–7.30 (3H, m); δ_C (67.8 MHz, $CDCl_3$) = 26.6, 26.9, 27.0, 32.2, 33.7, 36.3, 37.7, 38.3, 39.2, 126.0, 128.1, 128.3, 143.0; GC/MS (m/z): 230 (M^{+}), 134, 120, 106, 67, 55 and 41.

1,6-Dicyclohexylhexane (**2q**):[17] ^{1}H NMR: δ = 0.58–0.70 (4H, m), 1.00–1.30 (14H, m), 1.44–1.64 (12H, m), 2.23 (4H, t, J = 6.8 Hz); δ_C (67.8 MHz, $CDCl_3$) = 26.1, 27.3, 28.0, 33.2, 36.6, 37.1, 38.2; GC/MS (m/z): 250 (M^{+}), 164, 150, 138, 124, 112, 67, 55 and 41.

1-Cyclohexyl-6-phenylhexane (**3q**): ^{1}H NMR: δ = 0.62–0.75 (2H, m), 1.04–1.20 (12H, m), 1.50–1.71 (7H, m), 2.20 (2H, t, J = 6.6 Hz), 7.00–7.15 (2H, m), 7.22–7.28 (3H, m); δ_C (67.8 MHz, $CDCl_3$) = 26.4, 26.7, 27.2, 32.4, 33.4, 36.5, 37.6, 38.1, 39.0, 39.6, 126.2, 128.3, 128.1, 143.1; GC/MS (m/z): 244 (M^{+}), 148, 134, 120, 106, 67, 55 and 41.

1,2-Diphenylethane (**4a**):[10] ^{1}H NMR: δ = 2.92 (4H, s), 7.18–7.22 (6H, m), 7.22–7.32 (4H, m); δ_C (67.8 MHz, $CDCl_3$) = 38.3, 126.4, 128.6, 128.9 and 142.2; GC/MS (m/z): 182 (M^{+}), 91 and 77.

1,2-Bis(4-methylphenyl)ethane (**4h**):[13] ^{1}H NMR: δ = 2.36 (6H, s, 2CH_3), 2.90 (4H, s), 7.05 (4H, d, J = 8.2 Hz), 7.22 (4H, d, J = 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$) = 20.0, 34.1, 126.3, 130.1, 137.2, and 141.6; GC/MS (m/z): 210 (M^{+}), 178, 165, 115, 105 and 77.

1,2-Bis(2-methylphenyl)ethane (**4i**):[13] ^{1}H NMR: δ = 2.32 (6H, s), 2.86 (4H, s), 7.10–7.26 (8H, m); δ_C (67.8 MHz, $CDCl_3$) = 20.1, 34.6, 116.3, 126.6, 129.9, 130.2, 137.3 and 141.6; GC/MS (m/z): 210 (M^{+}), 178, 165, 115, 105 and 77.

1,2-Bis(2-methoxyphenyl)ethane (**4i**):[13] ^{1}H NMR: δ = 2.88 (4H, s), 3.84 (6H, s, 2OCH_3), 6.84–7.16 (8H, m); δ_C (67.8 MHz, $CDCl_3$) = 30.90, 55.62, 110.52, 120.68, 127.54, 130.22, 131.24 and 157.94; GC/MS (m/z): 242 (M^{+}), 211, 180, 121 and 77.

1,2-Bis(4-methoxyphenyl)ethane (**4k**):[13] ^{1}H NMR: δ = 2.86 (4H, s), 3.72 (6H, s, 2 OCH_3), 6.88 (2H, d, J = 8.4 Hz), 7.12 (2H, d, J = 8.4 Hz); δ_C (67.8 MHz, $CDCl_3$) = 30.9, 56.0, 126.5, 130.4, 132.2 and 154.4; GC/MS (m/z): 242 (M^{+}), 211, 180, 121 and 77.

1,2-Bis(4-tert-butylphenyl)ethane (**4l**):[13b] ^{1}H NMR: δ = 1.35 (18H, s, 2Bu^{t}), 2.96 (4H, s), 7.12 (2H, d, J = 8.2 Hz), 7.32 (2H, d, J = 8.2 Hz); δ_C (67.8 MHz, $CDCl_3$) = 22.2, 34.2, 40.2, 126.5, 130.4, 137.3 and 141.8; GC/MS (m/z): 294 (M^{+}), 237, 180, 147, 77 and 57.

1,2-Bis(4-aminophenyl)ethane (**4m**):[14] ^{1}H NMR: δ = 2.76 (4H, s), 3.60 (4H, bs, NH_2), 6.66 (2H, d, J = 8.4 Hz), 7.02 (2H, d, J = 8.4 Hz); δ_C (67.8 MHz, $CDCl_3$) = 20.0, 125.3, 131.1, 134.2, and 144.6; GC/MS (m/z): 242 (M^{+}), 106 and 77.

1,3-Diphenylpropane (**4n**):[15] ^{1}H NMR: δ = 1.72 (2H, t, J = 6.7 Hz), 2.66 (4H, t, J = 6.7 Hz), 7.16–7.26 (6H, m), 7.24–7.32 (4H, m); δ_C (67.8 MHz, $CDCl_3$) = 31.3, 35.9, 125.8, 128.4, 128.6 and 142.7; GC/MS (m/z): 196 (M^{+}), 119, 91 and 77.

1,4-Diphenylbutane (**4o**):[15] ^{1}H NMR: δ = 1.68 (4H, dt, J = 7.0 Hz), 2.62 (4H, t, J = 7.0 Hz), 7.12–7.22 (6H, m), 7.20–7.28 (4H, m); δ_C (67.8 MHz, $CDCl_3$) = 31.2, 35.9, 125.7, 128.3, 128.7 and 142.3; GC/MS (m/z): 210 (M^{+}), 105 and 77.

1,5-Diphenylpentane (**4p**):[16] ^{1}H NMR: δ = 1.22 (2H, t, J = 3.6 and 7.0 Hz), 1.66 (4H, m), 2.56 (4H, t, J = 7.0 Hz), 7.16–7.26 (6H, m), 7.24–7.32(4H, m); δ_C (67.8 MHz, $CDCl_3$) = 28.62, 31.30, 35.66, 125.15, 128.32, 128.55 and 142.10; GC/MS (m/z): 224 (M^{+}), 119, 105 and 77.

1,6-Diphenylhexane (**4q**):[17] ^{1}H NMR: δ = 1.22 (4H, dt, J = 3.6 and 7.0 Hz), 1.62 (4H, m), 2.52 (4H, t, J = 6.8 Hz), 7.10–7.20 (6H, m), 7.12–7.22 (4H, m); δ_C (67.8 MHz, $CDCl_3$) = 29.2, 31.3, 35.9, 125.7, 128.2, 128.7 and 141.9; GC/MS (m/z): 238 (M^{+}), 119, 105 and 77.

All of the compounds **2**, **3** and **4** were compared with authentic samples and their structures were assigned on the basis of IR, ^{1}H NMR and GC-MS spectroscopic data.

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