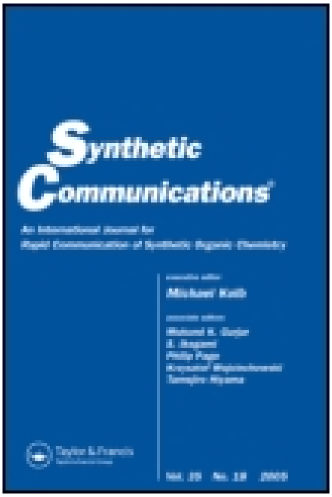

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Microwave-Assisted Epoxidation of Simple Alkenes in the Presence of Hydrogen Peroxide

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To cite this article: D. Bogdal , M. Lukasiewicz , J. Pielichowski & S. Bednarz (2005) Microwave-Assisted Epoxidation of Simple Alkenes in the Presence of Hydrogen Peroxide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:23, 2973-2983

To link to this article: http://dx.doi.org/10.1080/00397910500278479

Synthetic Communications®, 35: 2973–2983, 2005
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ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910500278479

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Abstract: A novel application of microwave irradiation for the epoxidation of some simple alkenes, in which hydrogen peroxide was used as an oxidant together with sodium tungsten and phosphorous acid under phase-transfer catalytic (PTC) conditions, is described as a new environmentally benign method. In comparison with conventional heating, the microwave process is a very useful alternative for introducing of the oxirane ring into some unsaturated hydrocarbons because of reduction of the reaction time and increase in yield.

Keywords: Alkenes, epoxidation, hydrogen peroxide, microwave

Received in Poland March 18, 2005

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INTRODUCTION

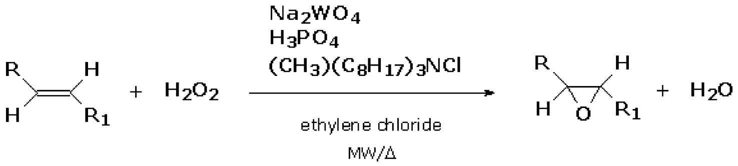
The epoxidation reactions of carbon–carbon double bonds are very useful transformations in organic synthesis because of the high reactivity of resulting oxirane rings, which are easy to open in a number of different chemical transformation to give hydroxy derivatives as main products.[1]

Use of aqueous hydrogen peroxide for the epoxidation of carbon–carbon double bonds under phase transfer catalytic (PTC) conditions was described by Venturello et al.,[2] who employed Na_2WO_4-H_3PO_4-quaternary ammonium salt as a combined catalyst and chlorinated hydrocarbons as solvents. However, Ishii et al.[3] improved PTC protocol by using tungsten-based heteropolyacid and N-cetylpyridinium chloride in a chloroform/water biphasic system; a more effective solvent- and halide-free version of this process was recently published by Sato et al.[4] They found that the substitution of ammonium chlorides with ammonium hydrogen sulfates under solventless organic/aqueous biphasic conditions in the presence of (aminomethyl)phosphonic acid led to the increase of the reaction yields as well as made the process clean, safe, and operationally simple.

Recently, it has been shown that application of microwave irradiation led to an acceleration of the reaction[5] including oxidation with hydrogen peroxide.[6] In particular, such a phenomenon is observed for many PTC-catalyzed reactions,[7] so we decided to explore such procedures for epoxidation of alkenes under microwave irradiation employing aqueous hydrogen peroxide. Because one of drawbacks of a number of procedures given in literature is the preparation of catalyst systems prior to reactions, we planned to elaborate a microwave procedure in which only commercially available reagents could be used.

RESULTS AND DISCUSSION

Under microwave irradiation, the epoxidation reactions of simple alkenes were carried out employing the modification of the classic Venturello's procedure given for PTC conditions.[2] In the course of the research, we obtained the best results when an 8% solution instead of a 30% solution of hydrogen peroxide was applied in the presence of Na_2WO_4, H_3PO_4, and Aliquat 336 as a PTC catalyst in a two-phase system water/ethylene chloride (Scheme 1).



Scheme 1. Epoxidation of alkenes in the presence of hydrogen peroxide.

The experimental procedure involves a simple mixing of $Na_2WO_4 \cdot 2H_2O$, a 40% solution of phosphoric acid, and an 8% solution of hydrogen peroxide followed by the addition of Aliquat 336 in ethylene chloride in a 1 : 5 : 140 : 1 molar ratio. Then, the mixture was stirred vigorously and an alkene was added to obtain the molar ratio of alkene to hydrogen peroxide of 4 : 5, while the pH of the solution was maintained at 1.6 by using a small amount of a 30% solution of sulfuric acid. The mixture was placed in an open vessel and irradiated in the microwave reactor at 70°C for the time needed for the consumption of hydrogen peroxide (ca. 15 min; monitored by the color reaction with $FeCl_3$ and $K_3Fe[CN]_6$); then in 15-min intervals, an 8% solution of hydrogen peroxide was added so that the final molar ratio of hydrogen peroxide to alkene was 5 : 1 and total reaction time 1 h. The same experiments were run under conventional conditions, and the results of all the experiments are summarized in Table 1.

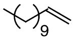
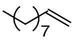
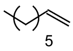
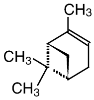
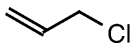
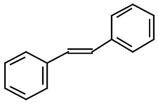
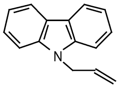
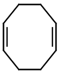
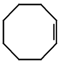
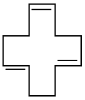
It is worth of pointing out that in the case of conventional reactions the final yields of the oxiranes was always lower than under microwave irradiation. Even though the reaction time under conventional conditions was longer, final products were separated in lower yield than in microwave experiments. For example, the yield of 1,2-epoxydodecane after 210 min reached only 85%.

In general, this protocol was most effective for simple unsubstituted linear or cyclic alkenes, whereas in the case of substituted olefins, yields of these reactions were lower. For example, after the epoxidation of α-pinene and *trans*-stillbene under microwave conditions, the desired products were afforded in 45 and 53% yields, respectively.

In the case of the epoxidation of N-allylcarbazole under conventional conditions, no traces of epoxy compound (i.e., N-[2,3-epoxypropyl]carbazole) were detected. The epoxidation under microwave irradiation allowed us to obtain N-(2,3-epoxypropyl)carbazole in 14% yield after 1.5 h. However, the yield was still low; according to our knowledge, it was first example of epoxidation of N-allylcarbazole. All epoxidation reaction attempts that followed protocols described by Rudolph et al.,[12] Yamaguchi et al.,[13] and Pillai et al.[14] in the presence of hydrogen peroxide failed; however, other alkenes were epoxidized, and we could only recover N-allylcarbazole from the reaction mixtures with <95% yield. Eventually, to obtain a reference sample of N-(2,3-epoxypropyl)carbazole, we managed to prepare it by the alkylation of carbazole with epichlohydrin under PTC conditions, applying microwave protocols as well.

To avoid compounds containing halogens such as ethylene chloride and PTC catalyst, ethylene chloride was replaced by toluene and halogen-free PTC catalyst was used (i.e., hexadecyl-trimethylammonium hydrogensulphate). The yield of these transformations was lower (for instance, 2,3-epoxyoctene was obtained in 68% yield in comparison with 90%), but it could be an interesting greener alternative for such epoxidation reactions. A solvent-free protocol under microwave conditions afforded epoxy

Table 1. Epoxidation of simple alkenes in the presence of hydrogen peroxide.

Product no.	Substrate	Yield (%)[a]		mp (°C)/bp (°C/mmHg)	
		Microwave	Conventional	Exp.	Lit.[8]
1		98 58[b] 89[c] 27[d]	62	123–124/15	124–125/15
2		91 62[b] 30[d]	65	92–93/15	94/15
3		90 68[b] 32[d]	76	61–63/15	60–62/15
4		45	38	100–101/50	102/50
5		35	10	114–117/760	115–117/760
6		53	44	63–67	67–69
7		14	0	109–111[g]	108–112[9]
8		98[f]	69	118–120/15	118/15[10]
9		97	68	47–50	49–51
10		95[f]	40	112/5	110/5[11]

[a] Isolated yield. The reaction time: 60 min.

[b] The reaction carried out in toluene using hexadecyltrimethylammonium hydrogensulphate.

[c] The reaction in the presence of 30% H_2O_2.

[d] The reaction in the solventless system.

[e] Yield of 5,10-dioxatricyclo[7.1.04,6]decane.

[f] Yield of 1,3-oxabicyclo[10.1.0.]trideca-4,8-diene.

[g] The compound was obtained by two other methods presented in the experimental section.

compounds in much lower yield. For example, 1,2-epoxyoctane, 1,2-epoxydecane, and 1,2-epoxydodecane were given in 32, 30, and 28% yields, respectively.

As far as the biphasic epoxidation with aqueous hydrogen peroxide is concerned, the use of lipophilic quartenary ammonium salts is crucial for the process.[2–4] We have shown that in the microwave-assisted reactions there is no need for the preparation of such ammonium salts prior to reactions, and they could be successfully substituted with commercially available ammonium salts.[6a] However, the study on the application of different PTC catalysts (Fig. 1) has shown that yield of the epoxidation reactions was strongly dependent on the types of salt cations. Cations that consist of long aliphatic chains were preferable as PTC catalysts, and the origin of an anion seems to have smaller influence. The lowest activity is observed for a non-salt-like catalyst such as polyethylene glycol (yield about 10%) or crown ethers (traces). The conversions of 1-dodecene to 1,2-epoxydodecane in the presence of different catalysts are shown in Fig. 1. Discussed effects are observed under both microwave and conventional conditions, which shows that they are independent of a heating method.

In conclusion, we have described an efficient microwave-assisted protocol for the epoxidation of carbon–carbon double bonds that is a modification of previous methods[2–4] of the synthesis of oxiranes by using hydrogen peroxide under PTC conditions. Because of the reduction of reaction times, the subsequent ring-opening reactions of the oxirane rings were limited, which influences both yield and selectivity of the processes. The advantages

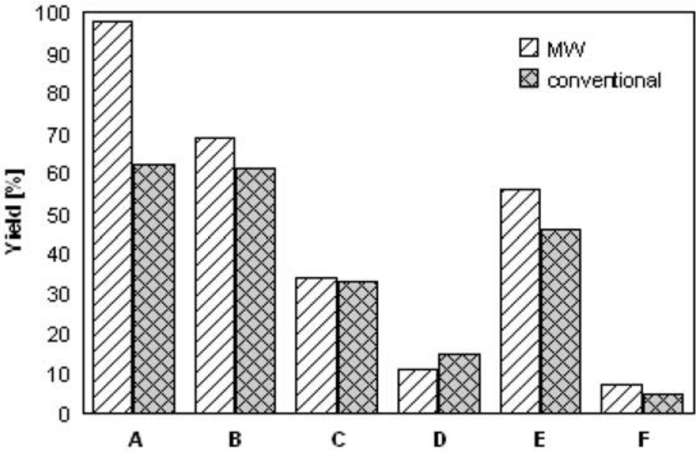


Figure 1. Conversion of 1-dodecene to 1,2-epoxydodecene in the presence of different PTC catalysts (1 h, 70°C): A, Aliquat 336; B, triethylbenzylammonium chloride; C, tetrabutylammonium bromide; D, PEG 2000; E, tetrabutylammonium hydrogensulphate; and F, triphenylphosphine hydrobromide.

of this microwave protocol include application of commercially available 8% or 30% aqueous solutions of hydrogen peroxide as well as PTC catalysts, shorter reaction times, and simple setup.

EXPERIMENTAL

All the chemicals were purchased from Aldrich and used as received. The reactions were carried out in a multimode microwave reactor with a continuous power regulation (PLAZMATRONIKA, Poland), which is equipped with magnetic stirrer and two inlets on the top and one side of the reactor. The inlets allowed applying an upright condenser and introducing a fiber-optical sensor (ReFlex, Nortech), which was used to control temperature during microwave experiments. IR spectra were recorded on FT-IR Biorad FTS-165 spectrophotometer as liquids on KBr disks or as pellets with KBr. ^{1}H NMR spectra were collected on Tesla 487C (80-MHz) spectrometer using TMS as an internal standard. GC/MS spectra were determined on GC/MS 5890 series II Hewlett-Packard gas chromatograph equipped with Ultra 2 (25 m × 0.25 mm × 0.25 μm) column with Hewlett-Packard 5971 series mass selective detector.

General Method for the Epoxidation of Alkenes

All the reactions were carried out according the epoxidation procedure given for 1-dodecene, which is representative of the general procedure employed for microwave and conventional conditions.

Microwave Procedure for the Epoxidation of 1-Dodecane

Sodium tungstate dihydrate (0.72 mmol, 0.24 g), 40% phosphoric acid (1.72 mmol, 0.17 g), 8% hydrogen peroxide (35 mmol, 4.50 g), Aliquat® 336 (trioctylmethylammonium chloride, 0.1 g), and ethylene chloride (2.1 mL) were mixed together. Then, the mixture was intensively stirred for 15 min at room temperature. After that, 1-dodecene (28 mmol, 4.7 g) was added, while the appropriate pH (ca.1.6) was estimated using 30% solution of sulfuric acid. The intensively stirred mixture was placed in a long-neck open vessel and irradiated in the microwave reactor at 70°C for time needed for the consumption of hydrogen peroxide (ca. 15 min; monitored by the color reaction with $FeCl_3$ and $K_3Fe[CN]_6$), and then in an 8% solution of hydrogen peroxide was added 15-min intervals so that the final molar ratio of hydrogen peroxide to alkene was 5 : 1 and total reaction time was 1 h. After completion of the reaction monitored by GC/MS, the phases were separated, the organic layer was evaporated, and the crude product was purified by Kugelrohr distillation at vacuum to afford 5.05 g (98% yield) of 1,2-epoxydodecane.

Conventional Procedure the Epoxidation of 1-Dodecane

Sodium tungstate dihydrate (0.72 mmol, 0.24 g), 40% phosphoric acid (1.72 mmol, 0.17 g), 8% hydrogen peroxide (35 mmol, 4.50 g), Aliquat® 336 (trioctylmethylammonium chloride, 0.1 g) and ethylene chloride (2.1 mL) were mixed together. Then, the mixture was intensively stirred for 15 min at room temperature. After that 1-dodecene (28 mmol, 4.7 g) was added, while the appropriate pH (ca.1.6) was estimated using a 30% solution of sulfuric acid. The intensively stirred mixture was placed in a long-neck open vessel and thermostated in a water bath at 70°C; then, in 15-min intervals, an 8% solution of hydrogen peroxide was added so that the final molar ratio of hydrogen peroxide to alkene was 5 : 1 and total reaction time was 1 h. After completion of the reaction monitored by GC/MS, the phases were separated, the organic layer was evaporated, and the crude product was purified by Kugelrohr distillation at vacuum to afford 3.2 g (62% yield) of 1,2-epoxydodecane.

1,2-Epoxydodecane (1): IR (KBr) v = 2956 (s), 2924 (s), 2866 (s), 1467 (m), 1129 (w), 917 (w), 834 (m), 772 (m) cm^{-1}. MS m/z = 183 [(M-1), 1%], 141 (1%), 127 (3%), 113 (5%), 98 (8%), 85 (23%), 71 (100%), 67 (49%), 57 (49%), 43 (69%), 29 (26%). ^{1}H NMR ($CDCl_3$) $\delta = 0.93$ (t, 3H, CH_3–), 1.18–1.55 (m, 18H, –CH_2–), 2.28 (dd, 1H, –CH), 2.56 (dd, 1H, –CH), 2.74 (m, 1H, –CH–) ppm.

1,2-Epoxydecane (2): IR (KBr) v = 2957 (m), 2926 (s), 2856 (s), 1467 (m), 1130 (w), 1079 (w), 916 (m), 845 (m), 723 (w) cm^{-1}. MS m/z = 155 [(M-1), 1%], 113 (8%), 98 (9%), 85 (16%), 71 (100%), 68 (45%), 57 (41%), 43 (64%), 41 (71%), 29 (32%). ^{1}H NMR ($CDCl_3$) $\delta = 0.90$ (t, 3H, CH_3–), 1.10–1.60 (m, 18H, –CH_2–), 2.29 (dd, 1H, –CH), 2.54 (dd, 1H, –CH), 2.71 (m, 1H, –CH–) ppm.

1,2-Epoxyoctane (3): IR (KBr) v = 2958 (s), 2930 (s), 2859 (s), 1467 (m), 1379 (m), 1130 (m), 1072 (w), 918 (m), 847 (m), 725 (m) cm^{-1}. MS m/z = 127 [(M-1), 1%], 99 (5%), 85 (14%), 71 (100%), 69 (25%), 58 (45%), 43 (32%), 41 (69%), 29 (36%). ^{1}H NMR ($CDCl_3$) $\delta = 0.91$ (t, 3H, CH_3–), 1.31–1.53 (m, 10H, –CH_2–), 2.47 (dd, 1H, –CH), 2.74 (dd, 1H, –CH), 2.91 (m, 1H, –CH–) ppm.

5,7,7-Trimethyl-3-oxa-tricyclo[4.1.1.02,4]octane (4): IR (KBr) v = 2978 (s), 2953 (s), 2917 (s), 1469 (m), 1460 (m), 1377 (m), 1196 (m), 1097 (m), 1045 (w), 934 (m), 867 (m), 840 (m), 767 (m) cm^{-1}. MS m/z = 152 [(M+), 1%], 137 (18%), 123 (2%), 119 (6%), 109 (38%), 95 (20%), 83 (40%), 67 (100%), 55 (38%), 53 (18%), 43 (58%), 41 (61%), 27 (3%). ^{1}H NMR ($CDCl_3$) $\delta = 0.94$ (s, 6H, CH_3–), 1.29 (m, 3H, –CH_3–), 1.62 (s, 2H, –CH_2–), 1.74–2.00 (m, 4H, –CH–, –CH_2–), 3.07 (t, 1H, –CH–) ppm.

2-(Chloromethyl)oxirane (5): IR (KBr) v = 3004 (m), 2963 (m), 2926 (m), 1438 (m), 1398 (m), 1267 (m), 1137 (m), 927 (s), 854 (s), 761 (s) cm^{-1}. MS m/z = 64 (5%), 62 (16%), 57 (100%), 49 (26%), 42 (8%), 31 (25%), 29 (26%), 27 (47%). ^1H NMR ($CDCl_3$) $\delta = 2.69$ (m, 1H, –CH–), 2.89 (m, 1H, –CH–), 3.26 (m, 1H, –CH–), 3.57 (m, 1H, –CH–) ppm.

2,3-Diphenyloxirane (7): IR (KBr) v = 3036 (m), 2990 (m), 1604 (m), 1501 (m), 1463 (m), 1348 (m), 1095 (m), 836 (m), 749 (s), 697 (s) cm^{-1}. MS m/z = 196 [(M+), 100%], 195 (42%), 178 (14%), 167 (84%), 152 (9%), 132 (1%), 118 (4%), 105 (11%), 90 (69%), 89 (60%), 77 (20%), 63 (16%), 51 (13%). ^1H NMR ($CDCl_3$) $\delta = 7.06–7.22$ (m, 10H, ArH–), 7.44 (s, 2H, –CH–) ppm.

5,10-Dioxa-tricyclo[7.1.0.4,6]decane (8): IR (KBr) v = 2939 (s), 2916 (m), 2848 (s), 1463 (m), 1437 (m), 1090 (w), 1050 (w), 1020 (m), 941 (m), 913 (w), 868 (m), 780 (m) cm^{-1}. MS m/z = 121 (0.5%), 111 (0.5%), 95 (1%), 83 (13%), 79 (14%), 69 (11%), 67 (43%), 55 (39%), 43 (23%), 41 (100%), 39 (43%), 29 (22%), 27 (19%). ^1H NMR ($CDCl_3$) $\delta = 2.13$ (m, 8H, –CH_2–), 2.89 (m, 4H, –CH–) ppm.

cis-9-Oxabicyclo[6.1.0.]nonane (9): IR (KBr) v = 2971 (m), 2928 (s), 2855 (m), 1471 (m), 1464 (m), 1289 (w), 1185 (w), 1016 (m), 923 (m), 846 (s), 767 (s), 741 (m) cm^{-1}. MS m/z = 126 [(M+), 2%], 111 (6%), 99 (1%), 97 (20%), 83 (29%), 69 (19%), 67 (53%), 55 (100%), 41 (64%), 39 (43%), 29 (24%), 27 (25%). ^1H NMR (CCl4) ^1H NMR ($CDCl_3$) $\delta = 0.95–1.88$ (m, 2H, –CH–), 2.13 (m, 2H, –CH_2–), 2.89 (m, 10H, –CH_2–) ppm.

13-Oxabicyclo[10.1.0.]tridecadiene (10): IR (KBr) v = 2931 (s), 2918 (s), 2866 (s), 1658 (w), 1438 (s), 1405 (w), 1312 (m), 1284 (w), 1190 (m), 1108 (m), 978 (s), 958 (s), 874 (s), 766 (m), 703 (s), 609 (m) cm^{-1}. MS m/z = 178 [(M+), 1%], 163 (2%), 149 (6%), 134 (3%), 123 (21%), 109 (20%), 97 (16%), 93 (22%), 81 (42%), 79 (71%), 67 (90%), 54 (80%), 41 (100%), 27 (33%). ^1H NMR ($CDCl_3$) $\delta = 2.37$ (m, 4H, –CH_2–, –CH=), 2.78 (m, 4H, –CH_2–), 3.18 (m, 4H, –CH_2–), 4.38 (m, 2H, –CH–), 5.45 (m, 4H, –CH_2–, –CH=) ppm.

Microwave Procedure for the Synthesis of N-(2,3-Epoxypropyl)carbazole[15]

Carbazole (30 mmol, 5.0 g), potassium carbonate (120 mmol, 16.5 g), powdered potassium hydroxide (30 mmol, 1.7 g), epichlorohydrin (195 mmol, 18 g), and tetrabutylammonium bromide (15 mmol, 0.50 g) were placed in a toluene solution (90 mL) in a one-necked 250-mL round-bottom flask equipped with an upright condenser. The reaction mixture was stirred quickly with a magnetic stirrer and irradiated with the full power in the microwave reactor Plazmatronika for 5 min; then, the power of microwave irradiation was reduced to 50%, and the reaction was continued for another 5 min. The mixture boiled intensively during the reaction, and its temperature (measured by means of a pyrometer) was maintained at 105–106°C. The reaction mixture was passed through a funnel to remove salts, and the salt was rinsed with toluene and acetone. The solvent was removed from the filtered solution to give a yellowish mass that was dissolved and recrystallized from ethanol to afford 6.0 g (90% yield; mp 109–111°C) of N-(2,3-epoxypropyl)carbazole.

Conventional Procedure for the Synthesis of N-(2,3-Epoxypropyl)carbazole[15]

Carbazole (26 mmol, 4.3 g), potassium carbonate (174 mmol, 24.1 g), powdered potassium hydroxide (19 mmol, 1.05 g), epichlorohydrin (175 mmol, 16.2 g), and tetrabutylammonium bromide (2.6 mmol, 0.83 g) were placed in an acetone solution (100 mL) in a one-necked 250-mL round-bottom flask equipped with an upright condenser. The reaction mixture was stirred quickly with a mechanical stirrer and heated at a water bath at 52°C for 1 h. Then, potassium carbonate (87 mmol, 12.0 g) and powdered potassium hydroxide (19 mmol, 1.05 g) were added to the mixture, and the reaction was continued for another 3 h. Then, inorganic substances were separated by filtration, and the solid was rinse with acetone. The solvent was removed from the filtered solution to give a yellowish mass that was dissolved and recrystallized from ethanol to afford 5.3 g (88% yield; mp 109–111°C) of N-(2,3-epoxypropyl)carbazole.

N-(2,3-Epoxypropyl)carbazole (6): IR (KBr) v = 3048 (w), 1625 (m), 1595 (m), 1485 (m), 1455 (s), 1417 (m), 1350 (m), 1328 (m), 1224 (m), 1152 (m), 901 (m), 839 (w), 747 (s), 720 (s), 631 (w), 563 (w), 458 (w) cm^{-1}. MS m/z = 224 [(M + 1), 10%], 223 [(M +), 57%], 204 (1%), 192 (2%), 180 (100%), 166 (4%), 152 (14%), 140 (4%), 127 (2%), 112 (2%), 90 (2%), 76 (2%), 63 (3%), 39 (2%). ^{1}H NMR ($CDCl_3$) $\delta = 2.602–2.626$ (m, 1H, $-CH_2$), 2.831–2.86 (m, 1H, $-CH_2$); 3.367–3.416 (m, 1H, –CH–); 4.409–4.704 (m, 2H, $-CH_2-$); 7.27–7.343 (m, 2H, Ar-H); 7.485–7.552 (m, 4H, Ar-H); 8.123–8.156 (d, 2H, Ar-H) ppm.

ACKNOWLEDGMENTS

This work was undertaken as part of the EU-sponsored D32 COST Program (Chemistry in High-Energy Microenvironments).

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