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3-*exo-tet* Cyclization of 2,2-disubstituted 1,3-dihalopropanes with indium in aqueous and ionic liquid solvent system

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ABSTRACT

The 3-*exo-tet* cyclization of 2,2-disubstituted 1,3-dihalopropanes with In powder in THF solution of 20% H_2O, dioxane solution of 20% H_2O, and ionic liquids, such as [bmim]Br, [bmim]Cl, and [bmin]BF_4, respectively, was efficiently carried out to form the corresponding 1,1-disubstituted cyclopropanes in good yields. The cyclopropanation of 2,2-disubstituted 1,3-dihalopropanes with In powder in ionic liquids, such as [bmim]Br, [bmim]Cl, and [bmin]BF_4, was markedly accelerated compared with that in a THF solution of 20% H_2O and a dioxane solution of 20% H_2O. The mechanism was proposed to involve the radical 3-*exo-tet* cyclization of the formed 3-halopropyl radical.

1. Introduction

Highly strained cyclopropane structures are known to exist in a wide variety of naturally occurring products which are in some cases, potent biological activity.[1] For example, hormosirene and dictyopterene, which are seaweed pheromones, are hydrocarbons containing cyclopropane and olefinic groups.[1b] Therefore, the synthetic study of the cyclopropane ring is very important. The most useful and practical methods for the formation of cyclopropanes with olefinic groups have been well carried out with free carbene derived from haloform under basic conditions,[2] diazo-olefins with the Rh catalyst,[3] the Simmons–Smith reactions,[4] and others.[5] These cyclopropanation reactions proceed effectively, especially in the case of diazo-olefins with the Rh catalyst and the Simmons–Smith reaction. However, generally, electron-rich olefins are required as these reactions proceed via an electrophilic manner. On the other hand, the preparation of cyclopropanes via radical pathway is very attractive and challenging. There are three types for the radical formation of cyclopropanes, i.e., radical 3-*exo-trig* cyclization, radical 3-*exo-tet* cyclization, and radical 3-*exo-dig* cyclization, based on Baldwin's rule,[6] although the study is rather limited. A few reports of cyclopropanation in the radical 3-*exo-trig* manner are known. However, for radical 3-*exo-trig* cyclization, the formed cyclopropylmethyl radicals are thermodynamically unstable because of ring strain[7] and the carbon-centered radicals are generally nucleophilic; therefore, electron-deficient olefinic groups are required.[8] Initially, when methyl 5-bromo-4,4-dimethoxy-2-pentenoate was treated with Bu_3SnH and AIBN in refluxing benzene, the expected cyclopropane derivative was not formed[9] because the ring-opening reaction of the formed cyclopropylmethyl radical occurred rapidly. On the other hand, electrochemical reductive cyclization of ethyl 5-methanesulfonyloxy-4,4-dimethyl-2-pentenoate was effectively carried out to form the corresponding cyclopropane.[10] Photolysis of 2-substituted butyrophenones gave the corresponding cyclopropyl phenyl ketones through a Norrish II type pathway.[11] As regards metal-induced radical 3-*exo-trig* cyclization, the formation of 11β-hydroxy-5,9-cyclopregnane-3,20-dione by single electron transfer (SET) reduction of 9α-bromo-11β-hydroxyprogesterone bearing a δ-bromo-α,β-unsaturated ketone group, with chromous acetate was reported.[12] Treatment of δ-iodo- and δ-bromo-α,β-unsaturated esters with SmI_2 in the presence of *tert*-butyl alcohol in THF gave the corresponding cyclopropanes.[13] The same treatment of γ,γ-disubstituted δ-oxo-α,β-unsaturated esters with SmI_2 in the presence of *tert*-butyl alcohol in THF provided the corresponding cyclopropanols via ketyl radicals.[14] To the best of our knowledge, studies of the radical 3-*exo-tet* cyclization of 1,3-dihalopropanes are extremely limited. Thus, 1,3-dihalides, mainly 1,3-diiodopropane derivatives, could be reductively cyclized to cyclopropanes by metal reduction with Na,[15a–c] halogen–metal exchange using *t*-BuLi,[16] and use of a metal hydride, such as $LiAlH_4$.[15b,c] It is proposed that some of these reactions proceed through a radical pathway. Treatment of 1,3-diiodopropane with benzoyl peroxide at 110 °C gave cyclopropane in

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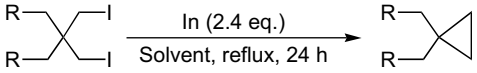
quite good yield.[17] Treatment of 2,2-disubstituted 1,3-diiodopropane with Bu_3SnH in refluxing benzene gave the corresponding cyclopropane in good yield.[15c] As a related reaction, the formation of cyclopropanes from the reaction of 2-substituted 1,3-diiodopropanes with $(C_6F_{13}CH_2CH_2)_3SnH$ or Ph_3SnH and AIBN under highly diluted conditions through the homolytic cyclization of the intermediate 3-iodoalkyl radicals, radical 3-*exo*-*tet* manner, was reported, and the radical cyclization proceeds in the range of 5×10^5 s^{-1}.[18] These results suggest that radical 3-*exo*-*tet* cyclization may proceed effectively according to Baldwin's rule where 3-*exo*-*tet* cyclization is favored.[6] Recently, we reported a simple and efficient method for the preparation of disubstituted and monosubstituted cyclopropanes from corresponding 1,3-dihalopropanes. The first one involved the reaction of 1,3-dihalopropanes with Zn powder in refluxing ethanol.[19] However, the yields of cyclopropanes when 1,3-dibromopropanes were used, were low, while 1,3-dichloropropanes did not react at all under the same conditions. The second one involved the reaction of 1,3-dihalopropanes with SmI_2 in refluxing THF.[20] However, SmI_2 is extremely air-sensitive and is therefore not easy to handle.

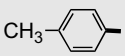
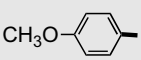
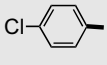
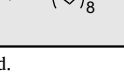
Here, as part of our study toward environmentally benign organic syntheses using radical reactions,[21] we would like to report a simple yet efficient In-mediated 3-*exo*-*tet* cyclization of 2,2-disubstituted 1,3-dihalopropanes to provide the corresponding cyclopropanes in good yields in a THF solution of 20% H_2O, a dioxane solution of 20% H_2O, and ionic liquids, such as [bmim]Br, [bmim]Cl, and [bmin]BF_4.

2. Results and discussion

When 2,2-dibenzyl-1,3-diiodopropane was treated with In powder (2.4 equiv), which is known as one of the SET reagents,[22] for 24 h in THF, dioxane, THF solution of 20% H_2O, dioxane solution of 20% H_2O, 1,1-dibenzylcyclopropane was obtained in 9%, 93%, 100%, and 97% yields, respectively, as shown in Table 1 (entries 1–4).

Table 1
Preparation of cyclopropanes from 1,3-diiodopropanes with In powder



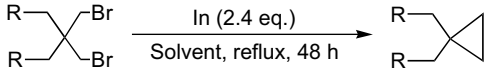
Entry	R–	Solvent	Yield[a] (%)
1		THF	9 (80)[b]
2		Dioxane	93
3		THF of 20% H_2O	100
4		dioxane of 20% H_2O	97
5		THF	50 (36)[b]
6		Dioxane	82 (17)[b]
7		THF of 20% H_2O	88
8		Dioxane of 20% H2O	88
9		THF	12 (70)[b]
10		Dioxane	9 (83)[b]
11		THF of 20% H_2O	81
12		Dioxane of 20% H_2O	87
13		THF	0 (80)[b]
14		Dioxane	83
15		THF of 20% H_2O	89
16		Dioxane of 20% H_2O	98
17		THF	10 (85)[b]
18		Dioxane	100
19		THF of 20% H_2O	95
20		Dioxane of 20% H_2O	91
21		THF	17 (76)[b]
22		Dioxane	39 (61)[b]
23		THF of 20% H_2O	99
24		Dioxane of 20% H_2O	98

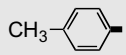
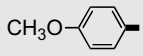
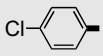
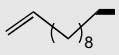
[a] Isolated yield.
[b] Yield of recovered starting material.

Dioxane, a mixture of THF and water, and a mixture of dioxane and water worked as good reaction solvents. However, THF alone did not work efficiently (entry 1). Based on these results, 2,2-di(arylmethyl)-1,3-diiodopropanes bearing *p*-methylphenyl, *p*-methoxyphenyl, and *p*-chlorophenyl groups were treated with In powder to give the corresponding 1,1-di(arylmethyl)cyclopropanes in good yields (entries 5–16), especially in THF solution of 20% H_2O and dioxane solution of 20% H_2O. The reactivity of 2,2-dialkyl and 2,2-dialkenyl substituted 1,3-diiodopropanes was also sufficient in refluxing THF solution of 20% H_2O and dioxane solution of 20% H_2O, although THF alone did not work well again (entries 17–24).

Then, 2,2-di(arylmethyl)-1,3-dibromopropanes were treated with In powder (2.4 equiv) for 24 h in the same solvents under refluxing conditions. However, the reaction did not proceed efficiently in spite of use of an excess amount of In powder, and the starting material was recovered. Therefore, the reaction was carried out for 48 h under refluxing conditions in THF, dioxane, THF solution of 20% H_2O, and dioxane solution of 20% H_2O to provide the corresponding 1,1-di(arylmethyl)cyclopropanes, as shown in Table 2. Again, dioxane solution of 20% H_2O and THF solution of 20% H_2O under refluxing conditions showed good reactivity to provide the corresponding cyclopropanes in good yields (entries 1–16). The same treatment of 2,2-dialkyl and 2,2-alkenyl 1,3-dibromopropanes with In powder in THF solution of 20% H_2O and dioxane solution of 20% H_2O gave the corresponding cyclopropanes in good yields.

Table 2
Preparation of cyclopropanes from 1,3-dibromopropanes with In powder



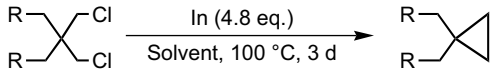
Entry	R–	Solvent	Yield[a] (%)
1		THF	10 (79)[b]
2		Dioxane	33 (60)[b]
3		THF of 20% H_2O	76
4		Dioxane of 20% H_2O	81
5		THF	10 (74)[b]
6		Dioxane	10 (71)[b]
7		THF of 20% H_2O	87
8		Dioxane of 20% H_2O	92
9		THF	10 (85)[b]
10		Dioxane	89
11		THF of 20% H_2O	16 (74)[b]
12		Dioxane of 20% H_2O	89
13		THF	30 (55)[b]
14		Dioxane	85
15		THF of 20% H_2O	86
16		Dioxane of 20% H_2O	94
17		THF	65 (28)[b]
18		Dioxane	87
19		THF of 20% H_2O	78 (10)[b]
20		Dioxane of 20% H_2O	88
21		THF	13 (67)[b]
22		Dioxane	67 (20)[b]
23		THF of 20% H_2O	78
24		Dioxane of 20% H_2O	88

[a] Isolated yield.
[b] Yeild of recovered starting material.

On the other hand, the reactivity of 2,2-dibenzyl 1,3-dichloropropanes was very low, and the corresponding cyclopropanes were obtained in low yields (0–42%), together with the starting material, depending on the solvents used. The best conditions were the reaction in DMF solution of 20% H_2O at 100 °C for 7 days, as shown in Table 3 (entry 6).

Today, environmentally friendly organic synthesis has become extremely popular, aiming toward green chemistry. Especially, room temperature ionic liquids are attracting great interest as

Table 3
Preparation of cyclopropanes from 1,3-dichlorpropanes with In powder



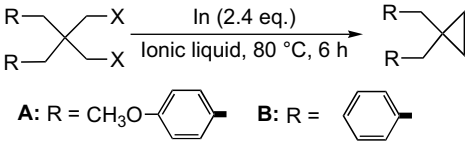
Entry	R–	Solvent	Yield[a] (%)
1		Dioxane	0 (100)[b]
2[c]		Dioxane of 20% DMF	7 (72)[b]
3		DMF	2 (88)[b]
4[c]		DMF	24 (49)[b]
5[c,d]		DMF	31 (21)[b]
6[d]		DMF of 20% H_2O	42 (42)[b]

[a] Isolated yield.
[b] Yield of recovered starting material.
[c] NaI (2.0 equiv) was added.
[d] Reaction time was 7 d.

environmentally friendly reaction media and reaction promotion media for organic synthesis.[23] These solvents possess interesting and useful advantages, such as negligible vapor pressure, non-flammability, high thermal stability at a wide range of temperatures, and easy reusability.

Thus, we expected that ionic liquids would accelerate SET from In powder to the substrate.[24] First, we treated 2,2-di(*p*-methoxybenzyl)-1,3-diiodopropane with In powder (2.4 equiv) at 80 °C in many kinds of ionic liquids, such as [bmim]Br, [bmim]Cl, [bmim]BF_4, [emim]OTs, [bmpy]NTf_2, and [bmim]PF_6, and found that [bmim]Br, [bmim]Cl, and [bmim]BF_4 promoted the cyclopropanation efficiently to give 1,1-di(*p*-methoxybenzyl)cyclopropane in high yields (entries 1–6). Based on these results, 2,2-di(*p*-methoxybenzyl)-1,3-dibromopropane was successfully cyclized to give the corresponding 1,1-di(*p*-methoxybenzyl)cyclopropane in good yields in these ionic liquids, respectively (entries 7–9). However, the same treatment of 2,2-di(*p*-methoxybenzyl)-1,3-dichloropropane with In powder gave the corresponding cyclopropane in moderate yields, especially in [bmim]Br (entries 10–12). Here, ionic liquid [bmim]BF_4 could be reused without any loss of chemical yield of the cyclopropane. Thus, 2,2-di(*p*-methoxybenzyl)-1,3-dibromopropane was treated with In powder (2.4 equiv) in [bmim]BF_4 at 80 °C. After extraction of the cyclopropane from the reaction mixture with ether, the ionic liquid reaction media could be reused for the same reaction, consistently providing good yields untill the 5th time as shown in

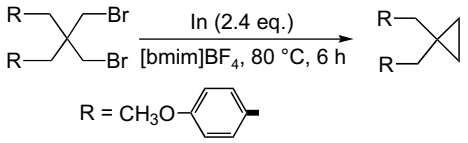
Table 4
Preparation of cyclopropanes from 1,3-dihalopropanes with In powder in ionic liquids



Entry		X	Ionic liquid	Yield[a] (%)
1	**A**	I	[bmim]Br	84
2		I	[bmim]Cl	84
3		I	[bmim]BF_4	92
4		I	[emim]OTs	71 (7)[b]
5		I	[bmpy]NTf_2	6 (94)[b]
6		I	[bmim]PF_5	46 (32)[b]
7		Br	[bmim]Br	98
8		Br	[bmim]Cl	87
9		Br	[bmim]BF_4	72 (14)[b]
10[c]		Cl	[bmim]Br	48 (50)[b]
11[c]		Cl	[bmim]Cl	30 (42)[b]
12[c]		Cl	[bmim]BF_4	31 (53)[b]
13	**B**	I	[bmim]Br	95
14		I	[bmim]Cl	98
15		I	[bmim]BF_4	97
16		I	[emim]OTs	92
17		I	[bmpy]NTf_2	7 (84)[b]
18		I	[bmim]PF_5	26 (64)[b]
19		Br	[bmim]Br	72
20		Br	[bmim]Cl	81 (13)[b]
21		Br	[bmim]BF_4	91

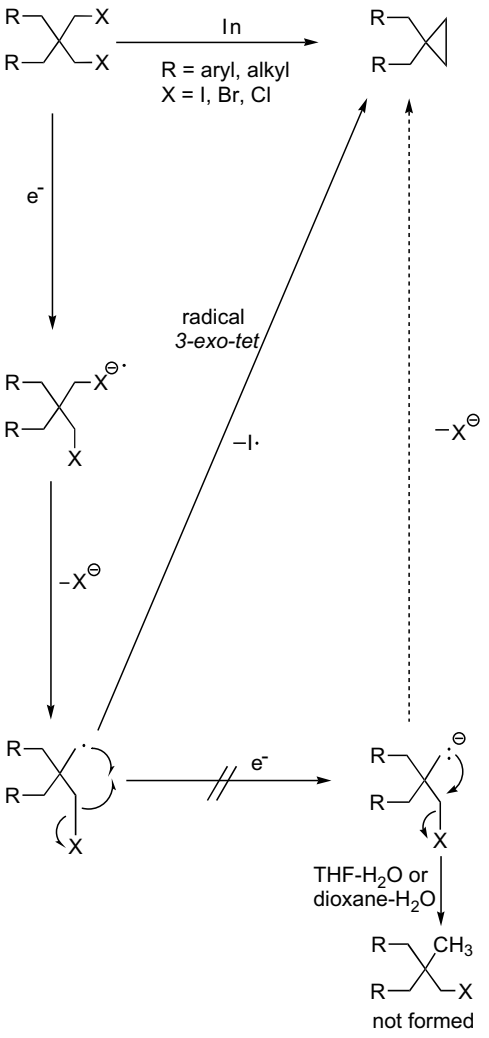
[a] Isolated yield.
[b] Yield of recovered starting material.
[c] Reaction time was 48 h, and In (4.8 equiv) used.

Table 5
Reuse of ionic liquid for the cyclopropanation of 2,2-di(*p*-methoxybenzyl)-1,3-dibromopropane



Reuse	Yield[a] (%)
0	88
1	85
2	85
3	87
4	83
5	91

[a] Isolated yield.



Scheme 1. Plausible Reaction Mechanism.

Table 5. The same treatment of 2,2-dibenzyl-1,3-diiodopropane and 2,2-dibenzyl-1,3-dibromopropane with In powder in [bmim]Br, [bmim]Cl, and [bmim]BF_4 provided 1,1-dibenzylcyclopropane in good yields, respectively (entries 13–15 and 19–21, Table 4).

As regards the reaction mechanism, when 2,2-disubstituted-1,3-diiodopropanes were treated with In powder (2.4 equiv) in THF solution of 20% H_2O and dioxane solution of 20% H_2O, only 1,1-disubstituted cyclopropanes were obtained in high yields without the formation of 2,2-disubstituted 1-iodopropanes and 2,2-disubstituted propanes, which could be formed through the reactions of the corresponding carbanions with H_2O. This result suggests that the present cyclization reaction of 2,2-disubstituted 1,3-dihalopropane with In powder may proceed in the radical 3-*exo*-*tet* manner, as shown in Scheme 1.

3. Conclusion

The In-mediated cyclopropanation of 2,2-disubstituted 1,3-diiodopropanes and 1,3-dibromopropanes in dioxane solution of 20% H_2O and THF solution of 20% H_2O was successfully achieved in moderately high yields. Extraction of the reaction mixture provided the products in high purity (purity ≥95%). However, the cyclopropanation of 2,2-disubstituted-1,3-dichloropropanes did not proceed efficiently. On the other hand, the cyclopropanation of 2,2-disubstituted-1,3-diiodopropanes and 2,2-disubstituted 1,3-dibromopropanes with In powder in ionic liquids, such as [bmim]Br, [bmim]Cl, and [bmim]BF_4, at 80 °C for 6 h proceeded smoothly to provide the corresponding cyclopropanes in good yields with high purity (purity ≥95%) without purification, although the reactivity of 2,2-disubstituted 1,3-dichloropropane was not sufficient to provide the corresponding cyclopropane in moderate yield. The mechanism was proposed to involve the radical 3-*exo*-*tet* cyclization based on Baldwin's rule.

4. Experimental section

4.1. General

^1H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-GSX-400, JEOL-JNM-LA-400, and JEOL-JNM-LA-500 spectrometers. Chemical shifts are expressed in ppm downfield from TMS in δ units. Mass spectra were recorded on JEOL-HX-110 and JEOL-JMS-ATII15 spectrometers. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Melting points were determined on a Yamato Melting Point Apparatus Model MP-21. Silica Gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative TLC. In powder (Aldrich) was commercially available.

4.2. General procedure for cyclopropanation of 1,3-diiodopropanes with In powder in Aq solvents

All reactions were carried out under an argon atmosphere. 1,3-Diiodopropane (0.4 mmol) and In powder (0.96 mmol) were added to a THF solution of 20% H_2O (3 mL) in a reaction flask. The mixture was refluxed for 24 h. Then, the reaction mixture was extracted with ether (10 mL×3). The ether extract was dried over Na_2SO_4 and filtered. Then, the solvent was removed to give crude cyclopropane (purity ≥95%). If necessary, the residue was purified by preparative TLC or column chromatography on silica gel to provide pure corresponding cyclopropane.

4.3. General procedure for cyclopropanation of 1,3-diiodopropanes with In powder in ionic liquid

All reactions were carried out under an argon atmosphere. Before the reaction, the ionic liquid, [bmim]BF_4 (1 mL) was dried with a vacuum pump for 1 h at 80 °C. 1,3-Diiodopropane (0.4 mmol) and In powder (0.96 mmol) were added to [bmim]BF_4 (1 mL), and the mixture was heated for 6 h at 80 °C. Then, the reaction mixture was extracted with ether (10 mL×3). The solvent was removed to give crude cyclopropane (purity ≥95%). If necessary, the residue was purified by preparative TLC or column chromatography on silica gel to provide pure corresponding cyclopropane.

4.4. General procedure for recyclic use of ionic liquids with In powder

All reactions were carried out under an argon atmosphere. Before the reaction, the ionic liquid, [bmim]BF_4 (1 mL) was dried with a vaccum pump for 1 h at 80 °C. 1,3-Dibromopropane (0.4 mmol) and In powder (0.96 mmol) were added to [bmim]BF_4 (1 mL), and the mixture was heated for 6 h at 80 °C. Then, the reaction mixture was extracted with ether (10 mL×3). Ether solvent was removed to give crude cyclopropane (purity ≥95%). After removal of the solvent, the residue was purified by preparative TLC or column chromatography on silica gel to provide pure corresponding cyclopropane. [Bmim]BF_4 reaction media was reused as above, after drying by vacuum pump for one hour at 80 °C.

4.4.1. 1,1-Dibenzylcyclopropane

Oil; IR (neat) 3030, 2920, 1500, 1460, 1020, 760, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.31–7.25 (4H, m), 7.24–7.16 (6H, m), 2.56 (4H, s), 0.52 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ=140.1 (q), 129.5 (t), 128.0 (t), 126.0 (t), 41.5 (s), 20.8 (q), 10.7 (s); MS (FAB): *m*/*z* 222; HRMS (EI) found: 222.1422 *m*/*z*, calcd for $C_{17}H_{18}$: M^+=222.1409.

4.4.2. 1,1-Di(p-methylbenzyl)cyclopropane

Oil; IR (neat) 3000, 2920, 1520, 1020, 810 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.08 (8H, d, *J*=1.7 Hz), 2.51 (4H, s), 2.33 (6H, s), 0.48 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ=137.0 (q), 135.3 (q), 129.4 (t), 128.7 (t), 41.1 (s), 21.0 (p), 20.9 (q), 10.6 (s); MS (FAB): *m*/*z* 250; HRMS (EI) found: 250.1734 *m*/*z*, calcd for $C_{19}H_{22}$: M^+=250.1722.

4.4.3. 1,1-Di(p-methoxybenzyl)cyclopropane

Oil; IR (neat) 2910, 2840, 1610, 1510, 1250, 1180, 1040, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.09 (4H, d, *J*=8.7 Hz), 6.83 (4H, d, *J*=8.7 Hz), 3.80 (6H, s), 2.49 (4H, s), 0.47 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ=157.8 (q), 132.2 (q), 130.3 (t), 113.5 (t), 55.2 (p), 40.6 (s), 21.1 (q), 10.5 (s); MS (FAB): *m*/*z* 283; HRMS (FAB) found: 282.1620 *m*/*z*, calcd for $C_{19}H_{22}O_2$: M+H=282.1620.

4.4.4. 1,1-Di(p-chlorobenzyl)cyclopropane

Oil; IR (neat) 2920, 1490, 1400, 1070, 1010, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.24 (4H, d, *J*=8.4 Hz), 7.07 (4H, d, *J*=8.4 Hz), 2.48 (4H, s), 0.53 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ=138.2 (s), 130.0 (s), 128.0 (s), 41.0 (s), 21.0 (s), 11.0 (s); MS (FAB): *m*/*z* 290; HRMS (FAB) found: *m*/*z*, calcd for $C_{17}H_{16}Cl_2$: M+H=290.0629.

4.4.5. 1,1-Di(dodecyl)cyclopropane

Oil; ^1H NMR (400 MHz, $CDCl_3$) δ=3.19 (4H, s), 1.43–1.10 (44H, m), 0.88 (6H, t, *J*=6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=36.0 (s), 31.9 (s), 29.9 (s), 29.6 (s), 29.4 (s), 26.6 (s), 22.7 (s), 19.2 (q), 14.1 (p), 11.9 (s); MS (FAB): *m*/*z* 378; HRMS (EI) found: 378.4230 *m*/*z*, calcd for $C_{27}H_{54}$: M^+=378.4226.

4.4.6. 1,1-Di-(10-undecenyl)cyclopropane

Oil; ^1H NMR (400 MHz, $CDCl_3$) δ=5.82 (2H, ddt, *J*=17.2, 10.2, 6.8 Hz), 5.04–4.97 (2H, ddt, *J*=17.2, 2.1, 1.7 Hz), 4.96–4.91 (2H, ddt, *J*=10.2, 2.1, 1.2 Hz), 2.05 (4H, m), 1.45–1.22 (28H, m), 1.18 (4H, dt, *J*=7.5, 7.0 Hz), 0.15 (4H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ=139.2 (t), 114.0 (s), 43.1 (s), 34.7 (s), 31.8 (s), 29.67 (s), 29.61 (s), 29.59 (s), 25.6

(s), 17.8 (t), 9.9 (s); MS (FAB): *m*/*z* 346; HRMS (FAB) found: 346.3617 *m*/*z*, calcd for $C_{25}H_{46}$: M=346.3600.

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