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Radical 3-*exo-tet* cyclization of 1,3-dihalopropanes with SmI_2 to form cyclopropanes

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ABSTRACT

The preparation of 1,1-disubstituted and monosubstituted cyclopropanes from corresponding 2,2-disubstituted and 2-monosubstituted 1,3-dihalopropanes, respectively, with SmI_2 in THF was efficiently carried out. The reaction mechanism was proposed to proceed in a radical 3-*exo-tet* manner based on Baldwin's rule.

1. Introduction

The cyclopropane ring is highly strained; nevertheless, a wide variety of naturally occurring cyclopropane derivatives bearing potent biological activities are known.[1] Seaweed pheromones, hormosirene and dictyopterene, are examples of hydrocarbons containing cyclopropane and olefinic groups.[1b] Therefore, synthetic study of the cyclopropane ring is still very important. Formation of cyclopropanes with olefinic groups has been accomplished with free carbene derived from haloform under basic conditions,[2] diazo-olefins with Rh, Cu, or Co catalyst,[3] Ti(IV)-mediated cyclopropanation,[4] the Simmons–Smith reactions,[5] and others.[6] These cyclopropanation reactions proceed efficiently, particularly those that employ diazo-olefins with Rh or Cu catalyst and the Simmons–Smith reaction. However, in general, electron-rich olefins are required, because these reactions proceed in an electrophilic manner. On the other hand, the preparation of cyclopropanes via a radical pathway is interesting and challenging. Examples of the radical formation of cyclopropanes include radical 3-*exo-trig* cyclization (favored), radical 3-*exo-tet* cyclization (favored), and radical 3-*exo-dig* cyclization (disfavored), based on Baldwin's rule,[7] although studies are limited. Among them, a few reports on radical 3-*exo-trig* cyclization are available. In this cyclization, generally, cyclopropylmethyl radicals formed are thermodynamically disfavored because of ring strain[8] and carbon-centered radicals are generally nucleophilic and therefore require electron-deficient olefinic groups.[9] Thus, for the typical radical reaction system, methyl 5-bromo-4,4-dimethoxy-2-pentenoate was treated with Bu_3SnH and AIBN in refluxing benzene. However, the expected cyclopropane derivative was not formed[10] because 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 efficiently carried out to form corresponding cyclopropane.[11] Photolysis of 2-substituted butyrophenones gave corresponding cyclopropyl phenyl ketones through a Norrish II type pathway.[12] As examples of 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,[13] and treatment of δ-iodo- and δ-bromo-α,β-unsaturated esters with SmI_2 in the presence of *tert*-butyl alcohol in THF gave corresponding cyclopropanes.[14] 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 corresponding cyclopropanols via ketyl radicals.[15] Among these cyclopropanation methods, the SmI_2-mediated radical 3-*exo-trig* cyclization to cyclopropanes is the most effective and practical. To the best of our knowledge, studies of radical 3-*exo-tet* cyclization of 1,3-dihalopropanes are extremely limited. 1,3-Dihalopropanes, mainly 1,3-diiodopropane derivatives, can be reductively cyclized to cyclopropanes by metal reduction, such as Na,[16a–c] halogen–metal

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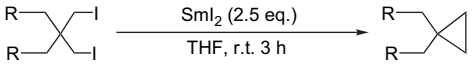
exchange, such as *t*-BuLi,[17] and metal hydride reduction, such as $LiAlH_4$,[16b,c] and it is proposed that some of these reactions proceed through a radical pathway. Treatment of 1,3-diiodopropane with benzoyl peroxide at 110 °C gave cyclopropane in quite good yield.[18] Treatment of 2,2-disubstituted 1,3-diiodopropane with Bu_3SnH in refluxing benzene gave corresponding cyclopropane in good yield.[16c] As a related reaction, the formation of substituted 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 homolytic cyclization of intermediate 3-iodopropyl radicals in a radical 3-*exo*-*tet* manner was reported, and radical cyclization proceeded in the range of 5×10^5 s^{-1}.[19]

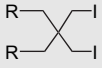
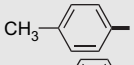
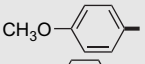
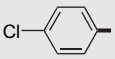
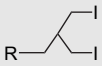
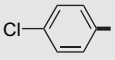
These results suggest that radical 3-*exo*-*tet* cyclization may proceed efficiently according to Baldwin's rule where 3-*exo*-*tet* cyclization is favored.[7] Recently, we reported the simple and efficient preparation of disubstituted and monosubstituted cyclopropanes from corresponding 1,3-dihalopropanes with zinc powder in refluxing ethanol.[20] However, the reactivity of 1,3-dichloropropanes was extremely poor and the reaction mechanism remains unknown. Here, as part of our study of environmentally benign organic synthesis using radical reactions,[21] we would like to report an efficient and simple SmI_2-mediated radical 3-*exo*-*tet* cyclization of 2,2-disubstituted and 2-monosubstituted 1,3-dihalopropanes to provide the corresponding cyclopropanes in THF, instead of typical, but toxic radical reagent Bu_3SnH.

2. Results and discussion

When 2,2-dibenzyl-1,3-diiodopropane was treated with SmI_2 (2.5 equiv), an excellent SET reagent,[22] in THF at room temperature, the deep blue color faded away after 2 h to provide 1,1-dibenzylcyclopropane in 99% yield, as shown in Table 1 (entry 1). Based on these results, 2,2-di(arylmethyl)-1,3-diiodopropanes bearing *p*-methyl, *p*-methoxy, and *p*-chloro groups were successfully cyclized to give corresponding 1,1-di(arylmethyl)cyclopropanes in good yields (entries 2–4). 2-Monoarylmethyl-1,3-diiodopropane could be also converted into corresponding cyclopropane in good yield under the same conditions (entry 7). However, the reactivity of 2,2-dialkyl substituted 1,3-diiodopropane was decreased (entry 5). Thus, the reaction was carried out under THF refluxing conditions (3 h) to give corresponding cyclopropane in good yield (entry 6).

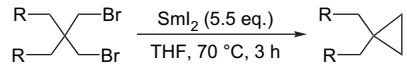
Table 1
Preparation of cyclopropanes from 1,3-diiodopropanes with SmI_2

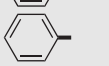
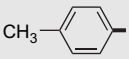
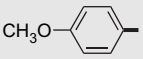
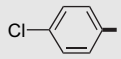
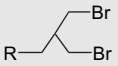
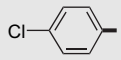


Entry	R=	Yield[a] (%)
1		99
2		93
3		98
4		98
5		57 (23)[b]
6[c]		84
7	 	70 (25)[b]

[a] Isolated yield.
[b] Yield of recovered starting material.
[c] Reaction was carried out at 70 °C for 3 h with SmI_2 (5.5 equiv).

Table 2
Preparation of cyclopropanes from 1,3-dibromopropanes with SmI_2



Entry	R=	Yield[a] (%)
1[b]		5 (90)[c]
2		87
3		80
4		82
5		80 (4)[c]
6		82
7	 	52 (4)[c]
8		90

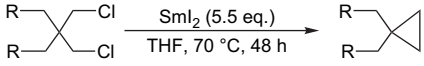
[a] Isolated yield.
[b] Reaction was carried out at rt.
[c] Yield of recovered starting material.

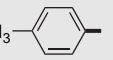
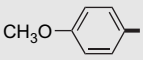
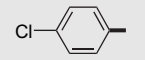
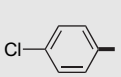
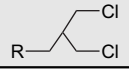
Then, 2,2-disubstituted and 2-monosubstituted 1,3-dibromopropanes were treated with SmI_2 (5.5 equiv) in THF at room temperature. However, the reaction did not proceed despite use of excess SmI_2, as shown in Table 2 (entry 1), and the starting material was recovered. Therefore, the reaction was carried out under THF refluxing conditions for 3 h to provide corresponding 1,1-disubstituted and monosubstituted cyclopropanes in good yields, as shown in Table 2 (entries 2–8).

The reactivity of 2,2-disubstituted and 2-monosubstituted 1,3-dichloropropanes was decreased. Thus, corresponding cyclopropanes were obtained in moderate yields (50–70%), together with the starting material, even if the reactions were carried out in THF under refluxing temperature for 48 h, as shown in Table 3.

From these results, the cyclization of 2,2-disubstituted and 2-monosubstituted 1,3-dihalopropanes to corresponding cyclopropanes with SmI_2 is useful and practical, especially for 2,2-

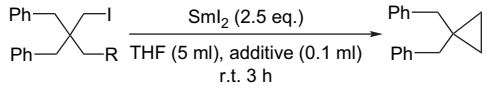
Table 3
Preparation of cyclopropanes from 1,3-dichrolopropanes with SmI_2

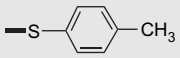
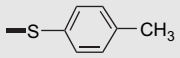
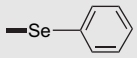
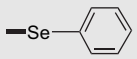


Entry	R=	Yield[a] (%)
1	 	69 (19)[b]
2		49 (34)[b]
3		23 (59)[b]
4		71
5		60 (15)[b]

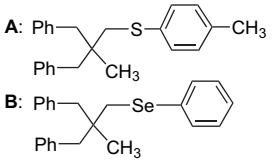
[a] Isolated yield.
[b] Yield of recovered starting material.

Table 4
Evidence of radical 3-*exo-tet* reaction mechanism with SmI_2



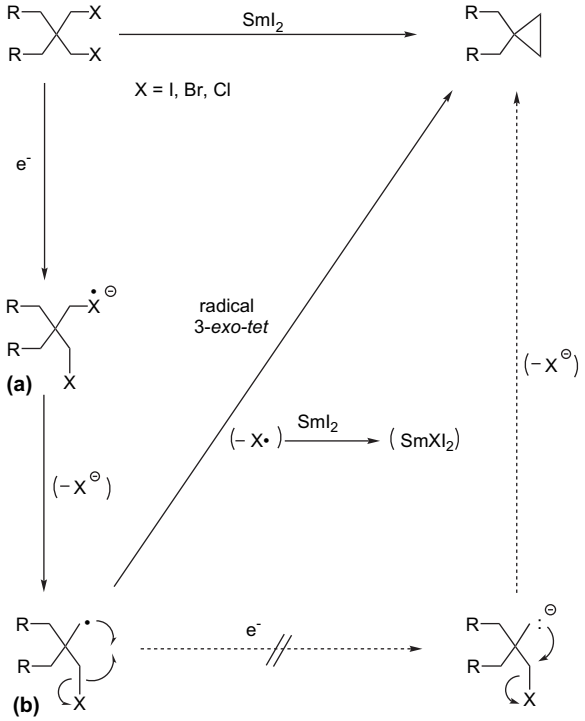
Entry	R	Additive	Yield[a] (%)
1		H_2O	27 (71)[b]
2		D_2O	19 (63)[b]
3		None	13 (73)[b] (14)[c]
4		D_2O	2 (52)[b] (23)[c]
5		None	7 (21)[b] (65)[d]
6[e]		None	28 (59)[d]

[a] Isolated yield.
[b] Yield of recovered starting material.
[c] Yield of reductive product **A**.
[d] Yield of reductive product **B**.
[e] Reaction was carried out at 70 °C.



disubstituted and 2-monosubstituted 1,3-diiodopropanes and 1,3-dibromopropanes.

To clarify the reaction mechanism, the following experiments were carried out. When 2,2-dibenzyl-1,3-diiodopropane was treated with SmI_2 (2.5 equiv) in THF containing H_2O (0.1 ml) at room temperature, 1,1-dibenzylcyclopropane was obtained in 27% yield, together with the staring material in 71% yield. Here, 2,2-dibenzyl-1-iodopropane and 2,2-dibenzylpropane, which could be formed by reacting of corresponding carbanions with H_2O, were not observed at all, as shown in Table 4 (entry 1), although the reactivity was markedly decreased. Similarly, when 2,2-dibenzyl-1,3-diiodopropane was treated with SmI_2 (2.5 equiv) in THF containing D_2O (0.1 ml) at room temperature, 1,1-dibenzylcyclopropane was obtained in 19% yield, together with the starting material in 63% yield. Here again, 2,2-dibenzyl-1-iodopropane-3d and 2,2-dibenzylpropane-1d,3d were not formed at all (entry2). These results suggest that the carbanion species, i.e., anion 3-*exo-tet* cyclization does not occur to form cyclopropanes. Today, it is well known that aryl chalcogenides (ArS and ArSe groups) are a good radical leaving group having high radicophilicity, similar to iodine and bromine atoms, especially for aryl selenide.[21c] Thus, 2,2-dibenzyl-3-(4′-methylphenylthio)-1-iodopropane and 2,2-dibenzyl-3-phenylseleno-1-iodopropane were treated with SmI_2 (2.5 equiv) in THF at room temperature and warming conditions, respectively, to give 1,1-dibenzylcyclopropane, the starting material, and 2,2-dibenzylpropyl 4′-methylphenyl sulfide and 2,2-dibenzylpropyl phenyl selenide, respectively, as shown in Table 4 (entries 3, 5, and 6), although the reactivity was lower than that of 2,2-dibenzyl-1,3-diiodopropane. However, 1,1-dibenzylcyclopropane was formed even at room temperature, and the yield was increased in THF under warming conditions (entry 6). It is well known that the radicophilicity of the phenylseleno group is higher than that of the phenylthio group.[21c] When the reaction of 2,2-dibenzyl-3-(4′-methylphenylthio)-1-iodopropane with SmI_2 (2.5 equiv) was carried out in THF containing D_2O (0.1 ml), again 2,2-dibenzyl-3d-propyl 4′-methylphenyl sulfide was not formed at all (entry 4). Based on these results, we propose that the present cyclization reaction of 2,2-disubstituted and 2-monosubstituted 1,3-dihalopropane with SmI_2 proceeds in a radical 3-*exo-tet* manner, as shown in Scheme 1. Thus, SET from SmI_2 to 1,3-dihalopropane occurs to form corresponding anion radical (**a**), followed by α-cleavage to provide 3-halopropyl radical (**b**). Then, radical 3-*exo-tet* cyclization of 3-halopropyl radical (**b**) occurs to form the corresponding cyclopropane.



Scheme 1.

As an another mechanism, formation of propan-1,3-biradical intermediate via simultaneous double-SET from 2 equiv of SmI_2, followed by its intramolecular radical coupling pathway can be also proposed. However, in view of high reactivity of carbon-centered radicals[9] and rapid radical 3-*exo-tet* cyclization rate,[19] we believe the present cyclization of 2,2-disubstituted and 2-monosubstituted 1,3-dihalopropanes to corresponding cyclopropanes proceeds via radical 3-*exo-tet* manner.

3. Conclusions

SmI_2-mediated cyclopropanation of 2,2-disubstituted and 2-monosubstituted 1,3-dihalopropanes in THF was successfully carried out in high yields, especially for 2,2-disubstituted and 2-monosubstituted 1,3-diiodopropanes and 1,3-dibromopropanes. The cyclization mechanism was proposed to proceed in a radical 3-*exo-tet* manner based on Baldwin's rule. The present cyclization with SmI_2 is another simple, practical, and environmentally benign method for the preparation of 1,1-disubstituted and monosubstituted cyclopropanes from corresponding 2,2-disubstituted and 2-monosubstituted 1,3-dihalopropanes.

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 parts per million 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-200 spectrometer. Melting points were determined

with 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. Sm powder was obtained from commercially available ingot (Aldrich).

4.2. General procedure for preparation of 2,2-disubstituted 1,3-dihalopropanes

NaH (60% purity, 3 mmol) was added to a solution of dimethyl malonate (1 mmol) in DMF (15 ml) at 0 °C. Then, benzylic bromide or alkyl bromide (3 mmol) was added and the obtained mixture was stirred at 70 °C for 1 h under argon atmosphere. The reaction mixture was quenched by the addition of water (5 ml) and was extracted with ether (20 ml×5). Ether extract was dried over Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by column chromatography on silica gel to provide α,α-disubstituted dimethyl malonate (85–90% yields).

$LiAlH_4$ (1.3 mmol) was added to a solution of α,α-disubstituted dimethyl malonate (1 mmol) in THF (10 ml) at 0 °C. After stirring for 1.5 h under THF refluxing conditions, the reaction mixture was quenched by the addition of water (5 ml) at 0 °C, and was extracted with ether (20 ml×3). Ether extract was dried over Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by column chromatography on silica gel to provide 2,2-disubstituted 1,3-propanediol (91–96% yields).

To a solution of 2,2-disubstituted 1,3-propanediol (1 mmol) in THF (15 ml) were added I_2 (3 mmol), triphenylphosphine (3 mmol), and imidazole (4 mmol) under argon atmosphere. The obtained mixture was stirred for 24 h under refluxing conditions. Then, the reaction mixture was quenched by the addition of satd aq Na_2SO_3 (3–5 ml) and was extracted with ether (20 ml×3). Ether extract was dried over Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by column chromatography on silica gel to give 2,2-disubstituted 1,3-diiodopropane (92–96% yields).

To a solution of 2,2-disubstituted 1,3-propanediol (1 mmol) in THF (15 ml) were added CBr_4 (2.5 mmol) and triphenylphosphine (3 mmol) under argon atmosphere. The obtained mixture was stirred for 24 h under refluxing conditions. Then, the reaction mixture was quenched by the addition of water (5 ml) and was extracted with ether (20 ml×3). Ether extract was dried over Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by column chromatography on silica gel to give 2,2-disubstituted 1,3-dibromopropane (86–95% yields).

To a solution of 2,2-disubstituted 1,3-propanediol (1 mmol) in CCl_4 (15 ml) was added triphenylphosphine (3 mmol) under argon atmosphere. The obtained mixture was stirred for 24 h under refluxing conditions. Then, the reaction mixture was quenched by the addition of water (5 ml) and was extracted with ether (20 ml×3). Ether extract was dried over Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by column chromatography on silica gel to give 2,2-disubstituted 1,3-dichloropropane (85–90% yields).

4.3. General procedure for SmI_2-mediated cyclopropanation of 1,3-diiodopropanes

All reactions were carried out under argon atmosphere. THF was dried and freshly distilled over sodium/benzophenone system. 1,3-Diiodopropane (1 mmol) was added to a solution of SmI_2 (2.5 mml) in THF (5 ml), which was prepared from the reaction of Sm (2.5 mmol) with 1,2-diiodoethane (2.5 mmol) in THF. After 3 h at room temperature, the reaction mixture was quenched by the additions of H_2O (0.1 ml), and was extracted with ether (20 ml×3). The ether extract was dried over Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by preparative TLC or column chromatography on silica gel to provide 1,1-dibenzylcyclopropane in 99% yield.

4.3.1. 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.

4.3.2. 1,1-Bis(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.

4.3.3. 1,1-Bis(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.

4.3.4. 1,1-Bis(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 (q), 131.8 (q), 130.6 (t), 128.2 (t), 40.8 (s), 20.6 (q), 10.8 (s); MS (FAB): *m*/*z* 290; HRMS (FAB) found: 290.0627 *m*/*z*, calcd for: M+H=290.0629.

4.3.5. 1,1-Didodecylcyclopropane

Oil; IR (neat) cm^{-1}; ^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: M^+=378.4226.

4.3.6. p-Chlorobenzylcyclopropane

Oil; IR (neat) 3080, 3000, 1490, 1070, 1010, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.24 (2H, d), 7.18 (2H, d), 2.51 (2H, d), 0.53 (1H, m), 0.19 (4H, d); ^{13}C NMR (100 MHz, $CDCl_3$) δ=140.5 (q), 132.6 (q), 129.6 (t), 128.3 (t), 39.6 (s), 11.7 (t), 4.6 (s); MS (FAB): *m*/*z* 210; HRMS (EI) found: 166.0551 *m*/*z*, calcd for $C_{10}H_{11}Cl$: M^+=166.0549.

4.3.7. Dodecylcyclopropane

Oil; IR (neat) 2920, 2850, 1460, 1020, 820, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=1.45–1.20 (20H, m), 1.19 (2H, dt, *J*=7.3, 7.0 Hz), 0.89 (3H, t, *J*=6.9 Hz), 0.72–0.60 (1H, m), 0.39 (2H, ddd, *J*=8.1, 5.5, 4.1 Hz), −0.01 (2H, dt, *J*=5.5, 4.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ=34.8 (s), 31.9 (s), 29.67 (s), 29.64 (s), 29.5 (s), 29.3 (s), 22.7 (s), 14.1 (p), 10.9 (t), 4.3 (s); MS (EI): *m*/*z* 210; HRMS (EI) found: 210.2361 *m*/*z*, calcd for $C_{15}H_{30}$: M^+=210.2348.

4.3.8. 2,2-Dibenzy-3-iodopropyl 4′-methylphenyl sulfide

Oil; IR (neat) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.52–7.40 (4H, m), 7.30–7.18 (8H, m), 7,09–7.05 (2H, m), 3.11 (2H, s), 2.94 (4H, s), 2.80 (2H, s), 2.31 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ=34.8 (s), 31.9 (s), 29.67 (s), 29.64 (s), 29.5 (s), 29.3 (s), 22.7 (s), 14.1 (p), 10.9 (t), 4.3 (s); MS (EI): *m*/*z* 472; HRMS (EI) found: 472.0730 *m*/*z*, calcd for: M^+=472.0722.

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References and notes

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