

Silcaphosphine (Silphos): a filterable reagent for the conversion of alcohols and thiols to alkyl bromides and iodides

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Received 24 August 2004; revised 13 January 2005; accepted 27 January 2005

Available online 27 April 2005

Abstract—Silcaphosphine (Silphos), $[P(Cl)_{3-n}(SiO_2)_n]$, as a new heterogeneous reagent is introduced. This reagent converts alcohols and thiols to their corresponding bromides and iodides in the presence of X_2 ($X = Br, I$) in refluxing CH_3CN in high to quantitative yields. Use of Silphos provides a highly practical method for the easy separation of the Silphos oxide byproduct by a simple filtration.
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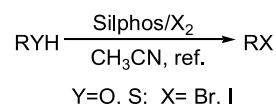
1. Introduction

The conversion of alcohols to alkyl halides with tertiary phosphines and different sources of halogens has widely been studied.^{1–9} A common drawback of all these systems is the formation of a stoichiometric amount of phosphine-oxide as a byproduct, of which its separation from the reaction mixture is usually a difficult task and requires time consuming column or more frequently plate chromatography techniques. As a solution to this problem, the use of expensive and not easily available reagents such as polymer-supported triphenylphosphine,^{5a,10–12} or tris[4-(1*H*,1*H*-perfluorooctyloxyphenyl)] phosphine¹³ is reported. The use of diphos-1,2-bis (diphenylphosphino-ethane),¹⁴ as another source of phosphine for this purpose still has the technical problem that only 75% of diphos oxide can be removed under the most suitable conditions.

2. Results and discussion

Recently, we reported on the application of Ph_3P in the presence of *N*-halosuccinimides¹⁵ or DDQ¹⁶ for the conversion of alcohols and thiols into alkyl halides. In continuation of this work on the use of phosphines in organic synthesis, and in order to advance the problems encountered with the isolation process of the byproduct phosphine oxide, we now introduce silcaphosphine

(Silphos), $[P(Cl)_{3-n}(SiO_2)_n]$, as a cheap, easily prepared, and stable reagent which can be used as a new source of filterable phosphine. This reagent was successfully applied for the efficient conversion of alcohols and thiols to their corresponding bromides and iodides with molecular bromine and iodine in refluxing CH_3CN as the most suitable solvent (Scheme 1).



Scheme 1. Conversion of alcohols and thiols to their corresponding bromides and iodides.

In order to select the best supporting bed and conditions for the preparation of a suitable phosphine reagent, we first reacted different types of silica and alumina with excess of $P(OEt)_3$ under argon atmosphere. The obtained results are shown in Table 1. From all these reactions, the reagent which was obtained after filtration, washing with dry CH_2Cl_2 and drying, showed a considerable weight increase. As demonstrated in Table 1, the weight increase in the cases of using plate silica gel is considerably higher. The use of these supported phosphine reagents (Table 1, entries 1–4), in conjunction with molecular bromine for the conversion of benzyl alcohol to benzyl bromide was found to be unsuitable, since the formation of some undesired products also occurred as side reactions. We then chose plate silica gel and reacted it with $P(OEt)_3$ with stoichiometry of 3:1. The maximum replacement of $-OEt$ groups with hydroxyl groups of silica was obtained after 6 days heating in an oil bath at 100–110 °C. The reagent which was obtained under

Keywords: Silphos; Silcaphosphine; Alcohol; Thiol; Alkyl bromide; Alkyl iodide.

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Table 1. Preparation of different supported reagents using P(OEt)₃ and their uses for transformation of benzyl alcohol to benzyl bromide

Entry	Supporting bed ^a	Molar ratio of supporting bed/ P(OEt) ₃ ^b	Reaction time (day)	% of weight increase	Reaction time and conversion yield for transformation of benzyl alcohol to benzyl bromide
1	Aluminum oxide 150, basic	Excess of P(OEt) ₃	7	22–25	3 h, mixture of benzyl bromide (45%) + side products ^d (30%)
2	Column SiO ₂ -gel	Excess of P(OEt) ₃	7	16–18	3 h, mixture of benzyl bromide (40%) + side products ^d (35%)
3	Activated plate SiO ₂ -gel ^c	Excess of P(OEt) ₃	7	28–31	3 h, mixture of benzyl bromide (45%) + side products ^d (25%)
4	Plate SiO ₂ -gel	Excess of P(OEt) ₃	7	38–42	1 h, mixture of benzyl bromide (70%) + side products ^d (30%)
5	Dried plate SiO ₂ -gel	3:1[P(OEt) ₃]	4	28–32	45 min, mixture of benzyl bromide (70%) + side products ^d (30%)
6	Dried plate SiO ₂ -gel	3:1[P(OEt) ₃]	5	24–26	0.5 h, mixture of benzyl bromide (90%) + side products ^d (10%)
7	Dried plate SiO ₂ -gel	3:1[P(OEt) ₃]	6	20–22	20 min (100%)
8	Dried plate SiO ₂ -gel	3:1[P(OEt) ₃]	7	20–22	20 min (100%)

^a Plate SiO₂-gel (type 60, 15–40 μm) and column SiO₂ gel (type 60, 63–200 μm) were used.

^b The mixture was heated at 100–110 °C in an oil bath under argon atmosphere. The filtered cake was then washed with CH₂Cl₂, and dried under vacuum.

^c Silica-gel was activated by refluxing in concentrated HCl for 4 h. It was filtered, washed with CH₂Cl₂ and dried at 200 °C under vacuum.

^d A mixture of benzaldehyde and dibenzyl ether was produced.

these conditions (Table 1, entry 7) converted benzyl alcohol to benzyl bromide quantitatively in the presence of molecular bromine after 20 min in refluxing acetonitrile. Increase of the reaction time for the preparation of Silphos did not show any change in the efficiency of the reagent (Table 1, entry 8).

Activation and drying of plate silica gel did not lead to a considerable difference in the capacity and reactivity of the obtained reagent.

To reduce the reaction time for the preparation of the reagent, we turned our attention to the use of more reactive

PCl₃ instead of P(OEt)₃. The optimized conditions for the reaction of plate silica gel and PCl₃ with a stoichiometry of 3:1 are shown in Table 2. The results of this study show that the reaction time for the preparation of Silphos using PCl₃ compared to P(OEt)₃ is considerably shorter (30 min and 6 days, respectively). A quantitative conversion of benzyl alcohol to benzyl bromide was observed with this reagent and bromine after 5 min in refluxing acetonitrile.

The structure of Silphos obtained from the reaction of plate silica gel and PCl₃ is not very clear to us. The presence of a Cl atom in the structure of Silphos was determined by titration of the produced HCl by aqueous NaOH. This

Table 2. Preparation of Silphos from silica-gel (type 60, 15–40 μm) and PCl₃ with stoichiometry of 3:1 under different conditions and its use for transformation of benzyl alcohol to benzyl bromide

Entry	Different conditions for preparation of Silphos ^a			% Conversion of benzyl alcohol to benzyl bromide after 5 min ^b
	Temperature	Time (h)	% of weight increase	
1	rt	0.5	23–25	100
2	rt	1	23–25	100
3	rt	2	23–25	100
4	50–55 °C	0.5	20–23	100
5	50–55 °C	1	20–23	100
6	50–55 °C	2	22–24	100

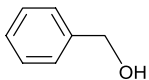
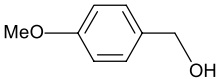
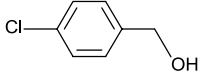
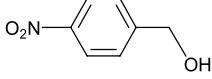
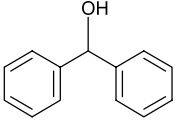
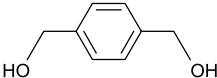
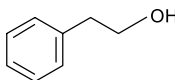
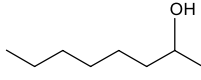
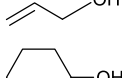
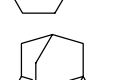
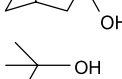
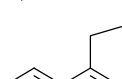
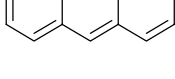
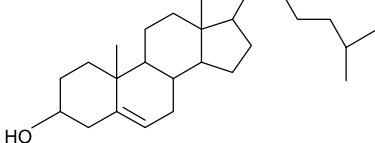
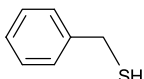
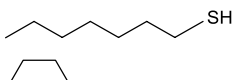
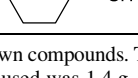
^a Reactions were performed under argon atmosphere.

^b Molar ratio of benzyl alcohol to bromine is 1:1.4 and 1.0 g of Silphos is used in CH₃CN under reflux condition.

Table 3. Different conditions for the reaction of benzyl alcohol (1.0 mmol) with different quantities of Br₂ and Silphos in refluxing acetonitrile

Entry	Br ₂ (mmol) + Silphos (g)	Temperature	Time	Conversion (%) to benzyl bromide
1	1 + 0.2	rt	10 h	20
2	1 + 0.4	rt	10 h	30
3	1 + 0.6	rt	10 h	55
4	1.0 + 1.0	rt	10 h	80
5	1.2 + 1.0	rt	10 h	100
6	1.2 + 1.0	Reflux	45 min	100
7	1.4 + 1.0	Reflux	5 min	100

Table 4. Conversion of alcohols to their corresponding bromides and iodides using 1 g of Silphos in refluxing acetonitrile

Entry	Substrate	Molar ratio of ROH/ Br ₂ ROH/I ₂	Time	Isolated yield (%) ^a
1		1:1.4	5 min	97
		1:1.4	2 min	94
2		1:1.4	1 min	99
		1:1.4	< 1 min	98
3		1:1.4	3 h	89
		1:1.4	2.5 h	90
4		1:2.2 ^b	40 min	92
		1:2.2 ^b	35 min	89
5		1:1.4	30 min	98
		1:1.4	1 h	95
6		1:2 ^c	10 min	97
		1:2 ^c	5 min	95
7		1:1.4	25 min	96
		1:1.4	40 min	94
8		1:2 ^c	2 h	91
		1:2 ^c	2 h	87
9		1:1.4	10 min	84
		1:1.4	8 min	78
10		1:1.4	25 min	93
		1:1.4	20 min	91
11		1:1.4	30 min	95
		1:1.4	45 min	95
12		1:1.4	35 min	90
		1:1.4	40 min	91
13		1:2 ^c	45 min	97
		1:2 ^c	50 min	96
14		1:1.4	40 min	99
		1:1.4	40 min	94
15		1:1.4	10 min	92
		1:1.4	5 min	95
16		1:1.4	45 min	90
		1:1.4	30 min	93
17		1:1.4	40 min	92
		1:1.4	30 min	90

^a All the products are known compounds. The spectral data of the products were compared with those of known samples prepared according to the literature.^{16–20}

^b The amount of Silphos used was 1.4 g.

^c The amount of Silphos used was 1.2 g.

analysis showed that not all the Cl atoms of PCl_3 are replaced with silica and the general structure of Silphos could be represented as $\text{P}(\text{Cl})_{3-n}(\text{SiO}_2)_n$. The amount of active phosphorus content of the reagent was determined by reacting Silphos with an excess of molecular bromine in refluxing acetonitrile until the consumption of Br_2 was stopped. On the basis of titration of unreacted bromine by sodium thiosulfate, the phosphorus content of Silphos was determined to be 1 mmol per 0.6 g of the reagent. The IR spectrum ($400\text{--}4000\text{ cm}^{-1}$) of the Silphos and plate silica gel are similar and both show a very strong and broad band centered about 1100 cm^{-1} and a strong band centered at 1000 cm^{-1} . However, Silphos oxide which was obtained from the transformation of benzyl alcohol to benzyl halides is similar to the one which was obtained from oxidation of Silphos by aqueous hydrogen peroxide and showed the additional characteristic $\text{P}=\text{O}$ band as a shoulder about 1300 cm^{-1} .

Since the introduced filterable Silphos $[\text{P}(\text{Cl})_{3-n}(\text{SiO}_2)_n]$ as an inorganic silica based polymeric phosphine showed excellent reactivity for the conversion of benzyl alcohol to its bromide and provided very simple and practical isolation of the product, we decided to study its applicability as a general reagent for the conversion of different classes of alcohols into their bromides and iodides. We optimized the conditions for the conversion of benzyl alcohol to its corresponding bromide using different ratios of bromine and Silphos (Table 3).

We then applied the optimized conditions for the reaction of structurally different alcohols. By this method, primary, secondary, and tertiary alcohols were converted into their bromides and iodides with excellent yield (Table 4). The presence of electron-withdrawing groups such as $-\text{Cl}$ or $-\text{NO}_2$ in the substrates increases the reaction time but the yields are still excellent. We also used Silphos for the successful conversion of thiols to their corresponding bromides and iodides in excellent yields under the same reaction conditions as applied for alcohols (Table 4, entries 15–17).

In order to have more insight into the applicability of this method, some competitive reactions were performed between structurally different alcohols in binary mixtures. The results which are tabulated in Table 5 show high selectivity between 1° aliphatic and 1° benzylic alcohols, benzyl alcohol and 4-nitrobenzyl alcohol, and also between 1° and 2° alcohols.

3. Conclusion

The use of Silphos as a cheap, stable and very easily prepared supported reagent provides an attractive and practical method for the clean conversion of alcohols and thiols to their corresponding alkyl bromides and iodides. The work-up is by simple filtration to isolate the product without interference from the Silphos oxide byproduct. The filterable nature of produced Silphos oxide provides a potential application for Silphos as a heterogeneous oxophilic reagent in organic synthesis.

4. Experimental

4.1. General comments

Chemicals were obtained from Merck and Fluka chemical companies. Infrared spectra were recorded on a Perkin–Elmer 781 spectrometer. Nuclear magnetic resonance spectra were recorded on a Bruker Advanced DPX-250 MHz spectrometer using tetramethylsilane as internal standard. The plate silica-gel used for the preparation of Silphos was type 60 ($15\text{--}40\text{ }\mu\text{m}$) which was dried in a vacuum oven at $200\text{ }^\circ\text{C}$ for 24 h before use.

4.2. General procedure for the preparation of Silphos

Under an argon atmosphere, to a flask containing dried silica-gel (type 60, $15\text{--}40\text{ }\mu\text{m}$) (18.0 g, 0.3 mol) was added PCl_3 (13.8 g, 0.1 mol) at rt and stirred slowly with a mechanical stirrer for 30 min. The mixture was then heated to $60\text{ }^\circ\text{C}$ while it was stirring (400 cycle/min) under pressure of argon for 3 h to remove all HCl. The reaction mixture was washed with 50 mL of dry CH_2Cl_2 and dried under vacuum. Silphos was obtained as a white solid (21.6–22.3 g), which was stored in a capped bottle. The reagent can be kept without any change for months. The presence of chloride in the reagent was determined by titration of the produced HCl from the above reaction with 0.1 M aq NaOH. The results obtained from several runs showed the formation of 0.156–0.165 mol of HCl. This shows that not all the chlorine atoms of PCl_3 are replaced and each mole of Silphos could contain 1.35–1.44 mol of chloride atom in its structure. In order to determine the amount of active phosphorus content of the reagent, Silphos was reacted with excess of bromine in acetonitrile and stirred for 1 h under reflux conditions. On the basis of titration of unreacted bromine with an aqueous solution of sodium thiosulfate, the amount of active phosphorus content was determined to be 1 mmol per

Table 5. Competitive reactions of different binary mixtures with Silphos (1 g) and molecular bromine or iodine (1.4 mmol) in refluxing acetonitrile

Entry	Binary mixture of alcohols	Halogen	Time (min)	Conversion % to alkyl halide ^a
1	$\text{PhCH}_2\text{OH} + \text{PhCH}_2\text{CH}_2\text{OH}$	Br_2	5	90:10
2	$\text{PhCH}_2\text{OH} + \text{PhCH}_2\text{CH}_2\text{OH}$	I_2	3	85:15
3	$\text{PhCH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$	Br_2	5	90:10
4	$\text{PhCH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$	I_2	3	88:12
5	$\text{PhCH}_2\text{OH} + 4\text{-NO}_2\text{-C}_6\text{H}_4\text{CH}_2\text{OH}$	Br_2 or I_2	5	100:0
6	$\text{PhCH}_2\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$	Br_2	5	80:20
7	$\text{PhCH}_2\text{CH}_2\text{OH} + \text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$	I_2	3	75:25

^a GC yield using *n*-octane or *n*-nonane as an internal standard.

0.6 g of Silphos; IR (KBr disk) ν (cm⁻¹): 3200, 1100, 1000, 800, 680, and 500.

4.3. A typical procedure for the conversion of benzyl alcohol to benzyl bromide

To a flask containing a stirring mixture of Silphos (3.0 g) and Br₂ (0.67 g, 4.2 mmol) in refluxing dry acetonitrile (20 mL), was added benzyl alcohol (0.324 g, 3 mmol). The orange color of the reaction mixture became yellow after 5 min and GC analysis showed the completion of the reaction. Then, enough powdered sodium thiosulfate was added in portions to the reaction mixture and stirred vigorously to decolorize the unreacted bromine. The mixture was then filtered and the solvent was evaporated under vacuum in a rotary evaporator. Benzyl bromide was obtained as a colorless liquid (0.265 g, 97%, bp 195 °C, lit.¹⁹ bp 196–198 °C). The product was found to be highly pure by GC and NMR analysis. Spectral data for benzyl bromide [100-39-0]; IR (neat) ν (cm⁻¹): 3070, 3060, 3025, 1500, 1440, 1220, 1200, 1050, 1000, 750, 690, 600, ¹H NMR (CDCl₃) δ (ppm) 7.19–7.36 (5H, m), 4.52 (2H, s); ¹³C NMR (CDCl₃) δ (ppm) 137.4, 129.0, 128.6, 128.3, 33.5.

4.4. A typical procedure for the conversion of allyl alcohol to 3-iodo-1-propene

To a flask containing a stirring mixture of 1 g of Silphos and I₂ (0.36 g, 1.4 mmol) in refluxing dry acetonitrile, was added allyl alcohol (0.06 g, 1 mmol). The progress of the reaction was monitored by GC. After the completion of the reaction (10 min), enough powdered sodium thiosulfate was added with vigorous stirring to react with the unreacted iodine. The mixture was then filtered and the solvent was removed under vacuum. Pure 3-iodo-1-propene was obtained (0.13 g, 78%), bp 100 °C, lit.¹⁹ bp 102 °C. The product was found to be highly pure by GC and NMR analysis. Spectral data for 3-iodo-1-propene [556-56-9], IR (neat) ν (cm⁻¹): 3050, 2970, 2960, 1640, 1430, 1400, 1145, 990, 910, 840, 670. ¹H NMR (CDCl₃) δ (ppm) 6.0–6.1 (1H, m), 5.27–5.33 (1H, m), 5.09–5.12 (1H, m), 3.89 (2H, d, *J* = 7.5 Hz); ¹³C NMR (CDCl₃) δ (ppm) 135.2, 117.1, 5.3.

Acknowledgements

We gratefully acknowledge the support of this study by Shiraz University Research Council and Management and Programming Organization of Iran.

References and notes

- Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964–965.
- Schaefer, J. P.; Higgins, J. G.; Shenoy, P. K. *Org. Synth.* **1969**, *49*, 6–9.
- Bose, A. K.; Lal, B. *Tetrahedron Lett.* **1973**, *40*, 3937–3940.
- Wiess, R. G.; Synder, E. I. *Chem. Commun.* **1968**, 1358–1359.
- (a) Harrison, C. R.; Hodge, P.; Hunt, B. J.; Khoshdel, E.; Richardson, G. *J. Org. Chem.* **1983**, *48*, 3721–3728. (b) Clive, D. L. J.; Denyer, C. V. *J. Chem. Soc., Chem. Commun.* **1972**, 773–774. (c) Still, I. W. J.; Kutney, G. W.; Mc Lean, D. *J. Org. Chem.* **1982**, *47*, 560–561.
- Lee, J. B.; Nolan, T. J. *Can. J. Chem.* **1966**, *44*, 1331–1334.
- Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86–87.
- Trippet, S. *J. Chem. Soc.* **1962**, 2337–2340.
- (a) Burns, A. J.; Cadogan, J. I. G. *J. Chem. Soc.* **1963**, 5788–5796. (b) Sugimoto, O.; Mori, M.; Tanji, K. *Tetrahedron Lett.* **1999**, *40*, 7477–7478.
- Anilkumar, G.; Nambu, H.; Kita, Y. *Org. Proc. Res. Dev.* **2002**, *6*, 190–191.
- Arsted, E.; Barrett, A. G. M.; Hopkins, B. T.; Kobberling, J. *Org. Lett.* **2002**, *4*, 1975–1977.
- Caldarelli, M.; Habermann, J.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1999**, 107–110.
- Desmaris, L.; Percina, N.; Cottier, L.; Sinou, D. *Tetrahedron Lett.* **2003**, *44*, 7589–7591.
- Pollastri, M. P.; Sagal, J. F.; Chang, G. *Tetrahedron Lett.* **2001**, *42*, 2459–2460.
- Iranpoor, N.; Firouzabadi, H.; Aghapour, G. *Synlett* **2001**, *7*, 1176–1178.
- Iranpoor, N.; Firouzabadi, H.; Aghapour, G.; Vaez Zadeh, A. R. *Tetrahedron* **2002**, *58*, 8689–8693.
- Bandgar, B. P.; Sadavarte, V. S.; Uppalla, L. S. *Tetrahedron Lett.* **2001**, 951–953.
- Firouzabadi, H.; Iranpoor, N.; Jafarpour, M. *Tetrahedron Lett.* **2004**, *45*, 7451–7454.
- Fluka Chemie *Chemica—Biochemica* 1993–1994.
- Registry number and H NMR (CDCl₃, 250 MHz) of the products: **benzyl iodide** [620-05-3], δ (ppm) 7.23–7.39 (5H, m), 4.43 (2H, s); **4-methoxy-benzyl bromide** [2746-25-0], δ (ppm) 6.83–7.27 (4H, m), 4.38–4.50 (2H, s), 3.79 (3H, s); **4-methoxy benzyl iodide** [70887-29-5], δ (ppm) 6.79–7.32 (4H, m), 4.46 (2H, s), 3.78 (3H, s); **4-chloro benzyl bromide** [622-95-7], δ (ppm) 7.22–7.28 (4H, m), 4.42 (2H, s); **4-chloro-benzyl iodide** [35424-56-7], δ (ppm) 7.23–7.32 (4H, m), 4.49 (2H, s); **4-nitro benzyl bromide** [100-1108], δ (ppm) 7.50–8.12 (4H, m), 4.45 (2H, s); **4-nitro benzyl iodide** [3145-86-6], δ (ppm) 7.50–8.23 (4H, m), 4.48 (2H, s); **1,1-diphenyl methyl bromide** [776-74-9], δ (ppm) 7.44–7.50 (10H, m), 6.04 (1H, s); **1,1-diphenyl methyl iodide** [Ref. No. 17,18] δ (ppm) 7.20–7.32 (10H, m), 6.17 (1H, s); **α,α' -dibromo-p-xylene** [623-24-5], δ (ppm) 7.20–7.28 (4H, m), 4.43 (4H, s); **α,α' -diiodo-p-xylene**, δ (ppm) 7.15–7.18 (4H, m), 4.39 (4H, s); **1-bromo-2-phenyl ethane** [103-63-9], δ (ppm) 7.08–7.17 (5H, m), 3.36–3.42 (2H, m), 2.99–3.15 (2H, m); **1-iodo-2-phenyl-ethane** [17376-04-4], δ (ppm) 7.00–7.12 (5H, m), 3.30–3.35 (2H, m), 2.91–2.95 (2H, d, m); **2-bromo octane** [557-35-7], δ (ppm) 3.82–3.91 (1H, m), 1.66–1.68 (3H, m), 1.43–1.63 (2H, m), 1.07 (2H, m), 1.28–1.30 (6H, m), 0.85–0.87 (3H, m); **2-iodo octane** [557-36-8], δ (ppm) 3.85–3.92 (1H, m), 1.66–1.69 (3H, m), 1.45–1.65 (2H, m), 1.09 (2H, m), 1.28–1.31 (6H, m), 0.87–0.89 (3H, m); **3-bromo-1-propene** [106-95-6], δ (ppm) 5.96–6.02 (1H, m), 5.26–5.31 (1H, m), 5.09–5.12 (1H, m), 3.87 (2H, d, *J* = 7.2); **bromo-cyclohexane** [108-85-0], δ (ppm) 3.32 (1H, m), 1.38–1.72 (6H, m), 0.81–0.96 (4H, m); **iodo cyclohexane** [626-62-0], δ (ppm) 3.89 (1H, m), 1.40–1.75 (6H, m), 0.85–0.99 (4H, m); **adamantyl bromide** δ (ppm) 2.31 (6H, s), 2.08 (3H, s), 1.73 (6H, s); **adamantyl iodide** [768-90-1], δ (ppm) 2.40 (6H, s), 2.20 (3H, s), 1.85 (6H, s); **2-bromo-2-methyl propane** [507-19-7], δ (ppm) 1.76 (9H, s); **2-iodo-2-methyl propane** [558-17-8], δ (ppm) 1.81 (9H, s); **9-bromomethyl anthracene** [2417-77-8], δ (ppm) 8.43 (1H, s), 7.72–7.76 (4H,

m), 7.58–7.61 (2H, m), 7.23–7.27 (2H, m), 4.98 (2H, s); **9-iodomethyl-anthracene** [260365-89-7], δ (ppm) 8.44 (1H, s), 7.72–7.77 (4H, m), 7.58–7.62 (2H, m), 7.25–7.30 (2H, m), 5.05 (2H, s); **3-bromocholest-5-ene** [516-91-6], δ (ppm) 5.42 (1H, s), 4.01 (1H, s), 2.50–2.70 (2H, m), 0.70–2.20 (41H, complex); **3-iodocholest-5-ene** [2930-80-5], δ (ppm) 5.45

(1H, s), 4.03 (1H, s), 2.60–2.85 (2H, m), 0.78–2.31 (41H, complex); **1-bromo octane** [111-83-1], δ (ppm) 3.36–3.38 (2H, m), 1.21–1.32 (12H, m), 0.90–0.94 (3H, m); **1-iodo octane** [629-27-6], δ (ppm) 3.29–3.32 (2H, m), 1.27–1.35 (12H, m), 0.91–0.94 (3H, m).