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Tetraaryldisilanes as a Novel Strategic Radical Reagent

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Abstract: Reactivity of 1,1,2,2-tetraaryldisilanes as a radical reagent in ethanol was studied in reduction of alkyl bromides, addition to olefins and alkylation onto heteroaromatic bases with alkyl bromides. The present organodisilanes showed moderate to good reactivities for these three types of radical reactions. Among some disilanes prepared, 1,1,2,2-tetraphenyldisilane is the most useful in view of its reactivity and ease of preparation. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

Free radical reactions have become increasingly important in organic synthesis in the last two decades.[1] In synthetic organic chemistry, both tributyltin hydride in reduction and reductive addition reactions, and hexabutylditin in non-reductive reactions have been frequently used as radical mediators as shown in Fig. 1. However, unfortunately, it is well known that organotin compounds are highly toxic, and the complete removal of the tin species from the reaction products is difficult. This is one major reason why the excellent radical reactions with organotin reagents cannot be used in industry. On the other hand, it is known that organosilanes have a strong affinity to heteroatoms, and can be used for the reduction of halides in the presence of an initiator, such as peroxide.[2] Thus, studies on the replacement of organotin compounds by monosilane compounds such as diphenylsilane[3] and polysilane compounds such as tris(trimethylsilyl)silane,[4] tetrakis(trimethylsilyl)silane,[5] *etc.*, have been carried out.

Reductive	$(C_2H_5)_3SiH$, Ph_2SiH_2, Ph_3SiH	Less Toxic
	$[(CH_3)_3Si]_3SiH$	
Non-reductive	$[(CH_3)_3Si]_4Si$	
Reductive	$(CH_3CH_2CH_2CH_2)_3SnH$	Toxic
Non-reductive	$[(CH_3CH_2CH_2CH_2)_3Sn]_2$	

Fig. 1 Radical Reagents of 14 Group

Dedicated to the memory of great and respectable Prof. Sir. Derek H. R. Barton.

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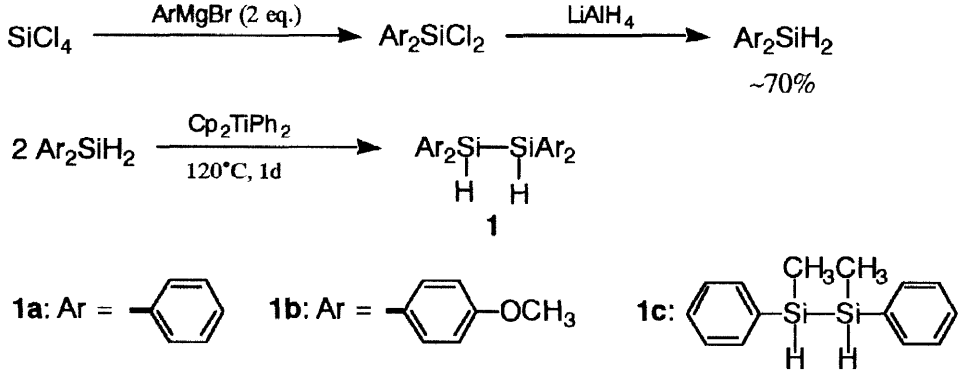
Namely, tris(trimethylsilyl)silane is effective for the reduction of alkyl bromides, reductive addition to activated olefins and alkylation onto heteroaromatic bases with alkyl bromides,[4,5] while tetrakis(trimethylsilyl)silane is effective only for the alkylation onto heteroaromatic bases with alkyl bromides.[5] However, tris(trimethylsilyl)silane is an oil and lacks stability under aerobic conditions for storage. Here, we would like to report on the utilization of tetraaryldisilanes ($Ar_4Si_2H_2$), which are stable crystals under aerobic conditions, as a novel diversified and strategic reagent for the radical reduction and carbon-carbon bond formations with alkyl bromides.[6] To date, to our knowledge, the use of organodisilanes as a radical reagent for organic synthesis has not been reported, though the preparation of disilanes has been reported.[7]

Results and Discussion

At first, tetraaryldisilanes **1** were prepared by the coupling reaction of diarylsilanes in the presence of a Ti-complex as shown below according to the literature method.[8] Here, disilanes **1a** and **1b** were obtained in 57% and 52%, respectively. Disilane **1c** was not obtained effectively by the coupling method, so, it was prepared by the reaction of phenylmethylchlorosilane and Mg in THF in 13% yield. We also tried to prepare 1,1,2,2-tetrakis(*p*-chlorophenyl)disilane by the coupling reaction of bis(*p*-chlorophenyl)silane with a Ti-complex. However, the yield was extremely poor (2%) and the obtained disilane was not so stable under atmosphere or in solution.



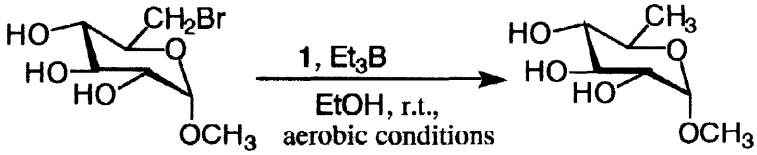
Scheme 1. Preparation of Disilanes

The radical reactivity of the present organodisilanes **1a~1c** prepared was studied in ethanol as a solvent from the environmental point of view, instead of a general organic solvent such as benzene, toluene, *etc.*, and AIBN[2,2'-azobis(isobutyronitrile)] was used as a radical initiator. Disilanes **1a** and **1b** are crystals and disilanes **1a~1c** are sufficiently stable in ethanol, and they do not decompose under atmosphere, unlike tributyltin hydride or tris(trimethylsilyl)silane. The reduction of methyl 6-bromo-6-deoxy-α-D-glucopyranoside with disilanes **1a~1c** was carried out and the reactivities were compared. Then, the reductive addition of 1-adamantyl bromide to phenyl vinyl sulfone with disilanes **1a~1c** was

studied. Finally, alkylation of lepidine salt with 1-adamantyl bromide in the presence of disilanes **1a**~**1c** were carried out. The reactivities of disilanes **1a**~**1c** in these three types of reactions are summarized in Table 1. ACVA[4,4'-azobis(4-cyanovaleric acid)], instead of AIBN works well as a radical initiator, though the yields in these three types of reactions were slightly decreased. Recently, V-70[2,2'-azobis-(2,4-dimethyl-4-methoxyvaleronitrile)] was reported as a better radical initiator than AIBN, since the radical reaction is initiated at room temperarure.[9] However, in our reactions, V-70 was not effective to carry out the reactions at room temperature.

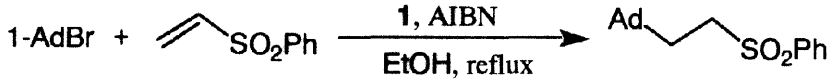
Table 1. Reactivity of Disilanes **1a**~**1c**

< Reduction >



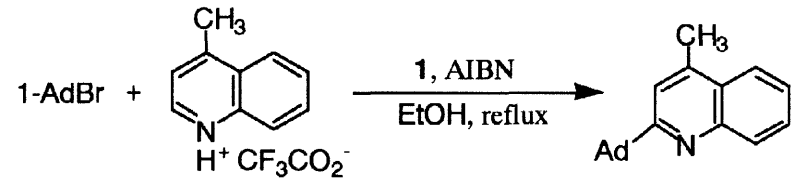
Disilane	Yield / %
1a	85
1b	63
1c	79

< Reductive addition >



Disilane	Yield / %
1a	88
1b	77
1c	52

< Substitution >

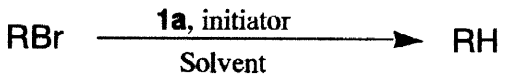


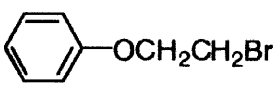
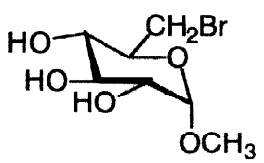
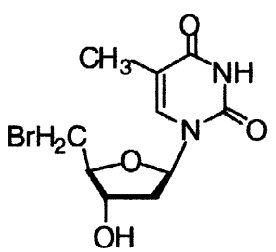
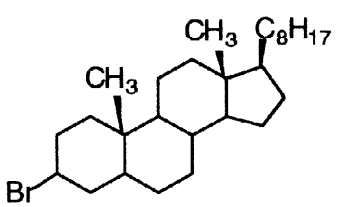
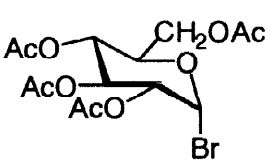
Disilane	Yield / %
1a	93
1b	68
1c	25

As shown in Table 1, 1,1,2,2-tetraphenyldisilane **1a** showed the best reactivity. Probably, the result comes from that the bond energy of Si-H in disilanes **1a** is lower than those of disilanes **1b** and **1c**. Moreover, disilane **1a** is the most convenient in the preparation of disilanes, because the yield of the coupling reaction with a Ti-complex is the best. Therefore, the extension of substrates in these three types of reactions was carried out with disilane **1a**. In the reduction of 2-bromoethyl phenyl ether with disilane **1a** and AIBN under refluxing conditions (method **A**), the yields of ethyl phenyl ether were 93% and 97%, with 1 equiv. and 2 equiv. of disilane **1a**, respectively. However, in the reduction using 0.5 equiv. of disilane **1a** under the same conditions, the yield of ethyl phenyl ether was decreased to 49%. These

results indicate that one of the two hydrogen atoms bonded to silicon atoms in disilane **1a** participates in this reaction and, therefore, this radical reduction requires more than 1 equiv. of disilane **1a** to obtain the reduction product in good yield. On the other hand, the radical reduction of 2-bromoethyl phenyl ether with 1 equiv. of Ph_2SiH_2 initiated by AIBN was carried out to form ethyl phenyl ether in only 3% yield and the starting material was recovered in 95% yield. So, there is a considerably big difference in the reactivity between disilane **1a** and Ph_2SiH_2. Thus, the reduction of other alkyl bromides at room

Table 2. Radical Reduction of Alkyl Bromides



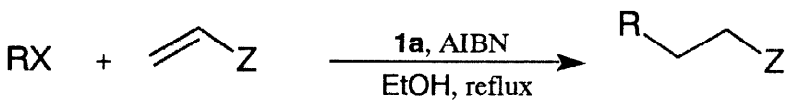
Substrate	Solvent	Method	Yield / %
	EtOH	A_1	49
	EtOH	A_2	93
	EtOH	A_3	97
	EtOH	B	89
	EtOH	B	97
	EtOH	C	88
	EtOH	B	35
	EtOH	C	99
	EtOH	C	40
	THF	C	75

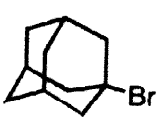
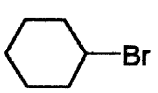
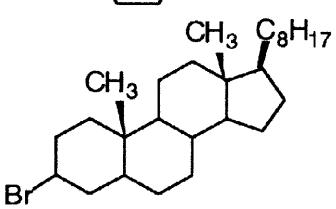
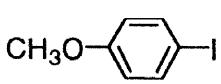
Method **A**: A_1 (**1a** 0.5 eq., AIBN 0.15 eq.), A_2 (**1a** 1.0 eq., AIBN 0.3 eq.), A_3 (**1a** 2.0 eq., AIBN 0.6 eq.). Method **B**: Triethylborane (2.4 eq.) was added twice Method **C**: Triethylborane (2.4 eq.)

temperature (Et_3B)[10] was carried out to give the reduction products in good yields as shown in Table 2.

Radical addition to activated olefins with halides to form a carbon-carbon bond was carried out in the presence of disilane **1a** and AIBN in ethanol. As shown in Table 3, the radical addition to phenyl vinyl sulfone with alkyl bromides gave the corresponding reductive addition products in moderate to good yields, and anisyl iodide gave the corresponding product in low yield together with reduction product, anisole, in 61%. The reactivity of alkyl bromides increased in the following order, primary < secondary < tertiary alkyl groups. The reactivity depends on the bond energies of the C-Br bond in alkyl bromides and the nucleophilicity of the formed carbon radical toward activated olefins. Other activated olefins such as diethyl vinylphosphonate and ethyl acrylate can be used in the addition reaction.

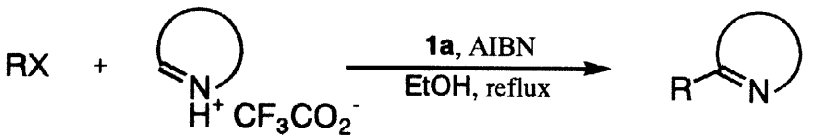
Table 3. Radical Addition to Olefin

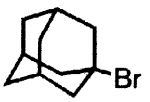
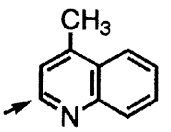
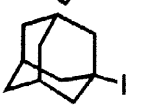
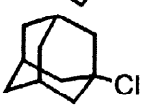
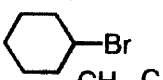
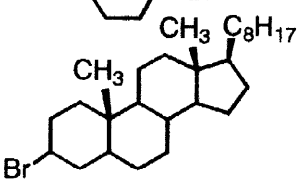
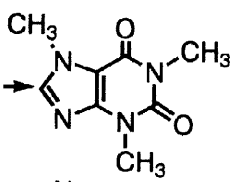
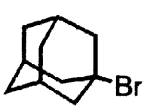
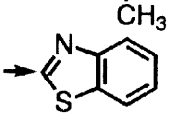
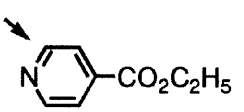
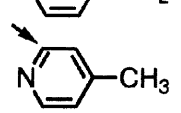
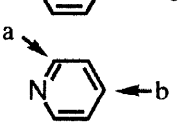
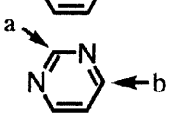


Substrate	Z Group	Yield / %
	SO_2Ph	88
	$PO(OEt)_2$	74
	COOEt	47
	SO_2Ph	78
	SO_2Ph	62
$CH_3(CH_2)_7Br$	SO_2Ph	43
	SO_2Ph	20

Finally, the radical alkylation onto heteroaromatic bases was investigated. A mixture of alkyl bromide, disilane **1a**, and a heteroaromatic base, which was activated by protonation with trifluoroacetic acid, was heated in ethanol at refluxing temperature to give the corresponding alkylated heteroaromatic bases in moderate to good yields as shown in Table 4. Here, the radical alkylation of lepidine salt gave the corresponding alkylated products in good yields with secondary and tertiary alkyl bromides while, in the alkylation of lepidine salt with primary alkyl bromides, the corresponding alkylated product was obtained in low yield. Here, alkyl iodide shows the same reactivity as alkyl bromide. However, alkyl chloride did

Table 4. Radical Alkylation of Heteroaromatic Bases

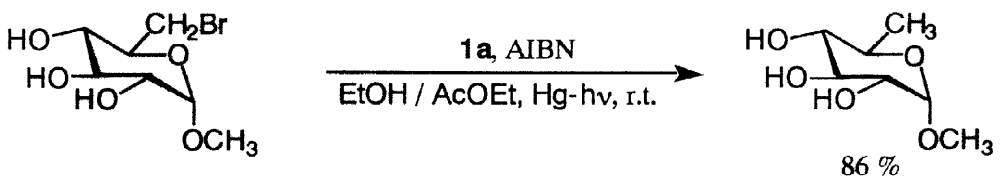


Substrate	Heteroaromatic Base	Yield / %
		93
		91
		0
		73
		63
$PhCH_2CH_2Br$		32
		55
		69
		47
		68
		79 (a : b = 50 : 29)
		54 (a : b = 13 : 41)

not react at all. Many other heteroaromatic bases such as caffeine, benzothiazole, ethyl isonicotinate, γ-picoline, pyridine, and pyrimidine were also alkylated effectively with adamantyl bromide in the presence of disilane **1a** and AIBN.

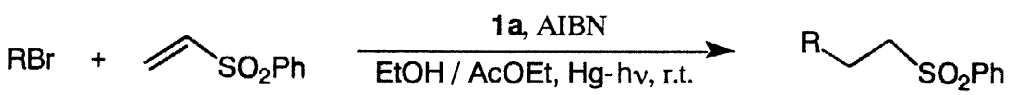
Table 5. Radical Reaction under Photochemical Conditions

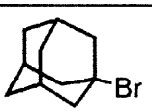
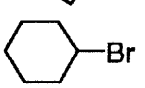
< Reduction >



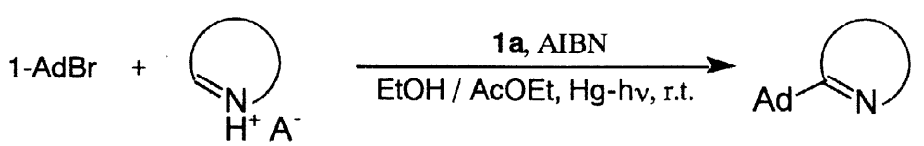
86 %

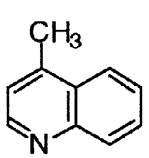
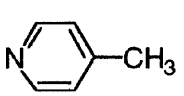
< Reductive addition >



RBr	Yield / %
	84
	64
$CH_3(CH_2)_7Br$	43

< Substitution >



Heteroaromatic Base	Yield / %
	19
	40

The present three types of reactions can be carried out under irradiation with a high pressure mercury lamp in the presence of AIBN. As shown in Table 5, in reduction and reductive addition to activated olefin, the same reactivities as in aerobic conditions and thermal conditions were observed. However, the yields in alkylation of heteroaromatic bases were low due to the UV-absorption by heteroaromatic bases.

In conclusion, $Ph_4Si_2H_2$ (**1a**) is very useful as a novel strategic and diversified radical reagent, *i.e.*, reduction of alkyl halides, reductive addition to activated olefins, and alkylation of heteroaromatic bases. Moreover, the present reactions proceed in ethanol instead of other toxic organic solvents such as benzene or toluene.

Acknowledgement: H.T. gratefully acknowledges financial support from Graduate School of Science and Technology of Chiba University. The authors thank Ms. Ritsuko Hara for measurement of HRMS and Dr. Hiroko Seki for measurement of elemental analysis in Chemical Analysis Center of Chiba University.

Experimental Section

General: ^{1}H NMR and ^{29}Si NMR spectra were obtained with JEOL-JNM-GSX400 and JEOL-JNM-GSX500 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-200 spectrometer. Microanalysis was performed with a Perkin-Elmer 240 elemental analyser at the Chemical Analysis Center of Chiba University. GC spectra was recorded on a Shimadzu GC-8A gas chromatograph with packed column (OV-17 and SE-30). Melting points were determined on a Yamato Melting Points Apparatus Model MP-21. Wakogel C-200 was used for column chromatography, and Wakogel B-5F was used for pTLC. Column JAIGEL-1HF ($CHCl_3$) and JAIGEL-345-15 (CH_3OH) were used for recycling preparative HPLC (Japan Analytical Industry Co.,HPLC-908).

Materials: Most of alkyl halides and simple organic chemicals were commercially available. The following compounds were prepared according to the procedures described in the literatures: methyl 6-bromo-6-deoxy-α-D-glucopyranoside,[11] 5'-bromo-5'-deoxythymidine,[12] and organodisilanes.[7,8] Tetraphenyldisilane: mp 76.5~80.5 °C (lit[7] mp 79~80 °C); IR, 2120 cm^{-1} (SiH); ($CDCl_3$, TMS) ^{1}H NMR δ = 5.19 (s, SiH), ^{29}Si NMR δ = -34.96; Tetra(*p*-methoxuphenyl)disilane: mp 122.1~124.3 °C; IR, 2100 cm^{-1} (SiH); ($CDCl_3$, TMS) ^{1}H NMR δ = 5.12 (s, SiH), ^{29}Si NMR δ = -36.45; Diphenyldimethyldisilane: oil; IR, 2110 cm^{-1} (SiH); ($CDCl_3$, TMS) ^{1}H NMR δ = 4.36~4.44 (m, SiH), ^{29}Si NMR δ = -36.37 and -36.80.

General Procedure for Radical Reduction with Organodisilanes: Method A; A solution of alkyl bromide (0.5 mmol), tetraphenyldisilane (0.5~2.0 mmol) and AIBN (0.3 eq. based on tetraphenyldisilane) in ethanol (6 ml) was refluxed for 14 h under an argon atmosphere. **Method B**; Triethylborane in THP (1.2 ml, 1 mol/l) was added into a mixture of alkyl bromide (0.5 mmol) and

organodisilane (1.2 mmol) in a solvent (2.5 ml) under aerobic conditions at room temperature. After stirring for 4 h, the same amount of triethylborane was added again and the obtained mixture was stirred overnight at the same temperature. **Method C**; Triethylborane in THP (1.2 ml, 1 mol/l) was added into a mixture of alkyl bromide (0.5 mmol) and organodisilane (1.2 mmol) in a solvent (2.5 ml) under aerobic conditions at room temperature, and reaction mixture was stirred for 1~4 h at the same temperature. After the reaction, the yield of ethoxybenzene was determined by GC, and the other reaction mixture was evaporated and purified by pTLC and column chromatography on silica gel.

General Procedure for Radical Addition to Olefins with Organodisilanes under Thermal Conditions: A mixture of alkyl halide (0.3 mmol), olefin (0.9 mmol), organodisilane (0.75 mmol), and AIBN (0.15 mmol) in ethanol (3.6 ml) was stirred for 14 h at refluxing temperature under an argon atmosphere. After the reaction, solvent was removed and the residue was purified by pTLC, column chromatography and recycling preparative HPLC.

General Procedure for Alkylation of Heteroaromatic Bases with Organodisilane and AIBN under Thermal Conditions: AIBN (0.45 mmol) was added 5 times over 8 h (2-h intervals) to a solution of a heteroaromatic base (1.5 mmol), alkyl halide (0.3 mmol) and organodisilane (0.45 mmol) in ethanol at refluxing temperature. Organodisilane (0.45 mmol) was added again after 4 h. The solution was stirred for 14 h (total 22 h) at the same temperature. The resulting solution was quenched with sat. aqueous sodium hydrogen carbonate. The organic layer was extracted with ethyl acetate and dried over Na_2SO_4. After removal of solvent, the residue was purified by pTLC, column chromatography and recycling preparative HPLC.

General Procedure for Radical Reduction with Organodisilanes under Photochemical Conditions: A mixture of alkyl bromide (0.3 mmol), organodisilane (0.75 mmol), and AIBN (1.0 mmol) in ethyl acetate (2.0 ml) and ethanol (2.0 ml) was irradiated with a high-pressure mercury lamp (400 W) for 7 h at room temperature. After the reaction, the residue was worked up in the usual way.

General Procedure for Radical Addition to Olefins with Organodisilanes under Photochemical Conditions: A mixture of alkyl bromide (0.3 mmol), olefin (0.9 mmol), organodisilane (0.75 mmol), and AIBN (1.0 mmol) in ethyl acetate (2.0 ml) and ethanol (2.0 ml) was irradiated with a high-pressure mercury lamp (400 W) for 7 h at room temperature. After the reaction, the residue was worked up in the usual way.

General Procedure for Alkylation of Heteroaromatic Bases with Organodisilane and AIBN under Photochemical Conditions: A mixture of alkyl bromide (0.3 mmol), heteroaromatic base (1.5 mmol), organodisilane (0.75 mmol), and AIBN (1.0 mmol) in ethyl acetate (2.0 ml) and ethanol (2.0 ml) was irradiated with a high-pressure mercury lamp (400 W) for 7 h at room temperature. After the reaction, the residue was worked up in the usual way.

Methyl 5-deoxy-α-D-glucopyranoside: mp 92.5~96.5 °C (lit[13] mp 99 °C) ; IR (Neat) 3300, 2900, 1060 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.28 (3H, d, J=6.2Hz), 3.13 (1H, td, J=9.2, 4.5Hz), 3.41 (3H, s),

3.51-3.72 (3H, m), 4.38 (1H, d, J=8.1Hz), 4.66 (1H, d, J=4.5Hz), 4.69 (1H, d, J=3.7Hz), 5.33 (1H, d, J=4.0Hz) ; MS (EI) Found: M-CH_3O=147

Cholestane: mp 77.5~79.0 °C ; IR (KBr) 2930, 2850, 1470, 1440, 1380 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=0.61-1.98 (33H, m), 0.64 (3H, s), 0.77 (3H, s), 0.85 (3H, d, J=1.7 Hz), 0.87 (3H, d, J=1.7Hz), 0.90 (3H, d, J=6.5Hz) ; Anal. Calcd for $C_{27}H_{48}$: C, 87.02; H, 12.98 %. Found: C, 86.91; H, 13.13 %.

5'-Deoxythymidine: mp 185.0~187.0 °C (lit[14] mp 188 °C) ; IR (KBr) 3390, 3190, 2965, 2930, 1725, 1660, 1480, 1440, 1270, 1085, 1060 cm^{-1} ; ^1H NMR (DMSO-d_6) δ=1.23 (3H, d, J=6.6Hz), 1.79 (3H, d, J=1.1Hz), 2.00-2.25 (2H, m), 3.95 (1H, m), 4.20 (1H, m), 5.24 (1H, d, J=4.4Hz), 6.09 (1H, t, J=7.0Hz), 7.39 (1H, d, J=1.1Hz), 11.27 (1H, s) ; HRMS (FAB+) Found: m/z 227.1021 Calcd for $C_{10}H_{15}N_2O_4$: $(M+H)^+$ =227.1031

2,3,4,6-Tetra-O-acetyl-1,5-anhydro-D-glucitol: mp 66.0~67.5 °C (lit[15] mp 71~73 °C) ; IR (KBr) 2975, 2880, 1750, 1370, 1235, 1035 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=2.03 (3H, s), 2.04 (6H,s), 2.10 (3H, s), 3.31 (1H, t, J=11.0Hz), 3.58-3.62 (1H,m), 4.04-4.23 (3H, m), 4.98-5.09 (2H, m), 5.21 (1H, t, J=9.5Hz) ; MS (FAB+) Found: $(M+H)^+$ =333

2-(1-Adamantyl)ethyl phenyl sulfone: mp 103.5~105.5 °C (lit[16] mp 101.4~103.5 °C) ; IR (KBr) 3060, 2900, 2850, 1445, 1300, 1150, 1085, 740, 690 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.40 (6H, d, J=2.4Hz), 1.45-1.50 (2H, m), 1.57 (3H, d, J=11.5Hz), 1.68 (3H, d, J=12.2Hz), 1.93 (3H, bs), 3.04-3.08 (2H, m), 7.55-7.59 (2H, m), 7.64-7.68 (1H, m), 7.89-7.92 (2H, m) ; MS (FAB+) Found: $(M+H)^+$ =305

Diethyl 2-(1-adamantyl)ethylphosphonate: Oil[16] ; IR (Neat) 2980, 2900, 2850, 1450, 1240, 1035, 960 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.31-1.39 (2H, m), 1.33 (6H, t, J=7.1Hz), 1.45 (6H, d, J=2.4Hz), 1.59-1.72 (8H, m), 1.96 (3H, bs), 4.02-4.16 (4H, m) ; MS (EI) Found: m/z 300

Ethyl 3-(1-Adamantyl)propionate: Oil[16] ; IR (Neat) 2980, 2900, 2850, 1740, 1450, 1300, 1190 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, J=7.1Hz), 1.40-1.44 (2H, m), 1.46 (6H, d, J=2.7Hz), 1.61 (6H, d, J=12.2Hz), 1.70 (3H, d, 12.2Hz), 1.95 (3H, bs), 2.23-2.27 (2H, m), 4.12 (2H, q, J=7.1Hz) ; MS (EI) Found: m/z 236

2-Cyclohexylethyl phenyl sulfone: Oil ; IR (Neat) 3060, 2920, 2850, 1445, 1310, 1150, 1085, 740, 690 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=0.81-0.90 (2H, m) 1.08-1.34 (3H, m), 1.55-1.69 (8H, m), 3.07-3.12 (2H, m), 7.55-7.59 (2H, m), 7.64-7.68 (1H, m), 7.90-7.92 (2H, m) ; MS (FAB+) Found: $(M+H)^+$ =253

2-(3-Cholestanyl)ethyl phenyl sulfone: mp 116.0~119.5 °C ; IR (KBr) 3060, 2930, 2860, 1445, 1375, 1305, 1150, 740, 690 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=0.63 (3H, s), 0.70 (3H, s), 0.85 (3H, d, J=1.8Hz), 0.87 (3H, d, J=1.8Hz), 0.89 (3H, d, J=6.6Hz), 0.75-2.00 (34H, m), 3.07 (2H, m), 7.55-7.59 (2H, m), 7,64-7.68 (1H, m), 7.89-7.92 (2H, m) ; ^{13}C NMR ($CDCl_3$) δ=12.07, 12.25, 18.67, 20.99, 22.56, 22.82, 23.83, 24.18, 28.01, 28.23, 28.43, 28.88, 29.59, 32.05, 35.11, 35.49, 35.79, 35.96, 36.17, 37.02, 38.24, 39.51, 40.04, 42.57, 46.36, 54.46, 54.50, 56.27, 56.53, 128.05, 129.25, 133.58, 139.24 ; Anal. Calcd for $C_{35}H_{56}O_2S$: C,77.72; H, 10.44 %. Found: C, 77.89; H, 10.56 %.

***n*-Decyl phenyl sulfone**: Oil ; IR (Neat) 3060, 2920, 2860, 1445, 1305, 1150, 690 cm^{-1} ; ^1H NMR

($CDCl_3$) δ=0.87 (3H, t, J=6.9Hz), 1.22-1.34 (14H, m), 1.67-1.74 (2H, m), 3.06-3.10 (2H, m), 7.56-7.58 (2H, m), 7.66 (1H, t, J=7.5Hz), 7.90-7.92 (2H, m) ; MS (FAB+) Found: $(M+H)^+$ =283

2-(4-Methoxyphenyl)ethyl phenyl sulfone: mp 38.0~40.8 °C ; IR (KBr) 2960, 2920, 2840, 1520, 1445, 1300, 1250, 1150, 800, 730, 690, 525 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=2.97-3.01 (2H, m), 3.31-3.35 (2H, m), 3.76 (3H, s), 6.79 (2H, d, J=8.7Hz), 7.03 (2H, d, J=8.7Hz), 7.56-7.60 (2H, m), 7.67 (1H, tt, J=7.4, 1.6Hz), 7.92-7.95 (2H, m) ; HRMS (FAB+) Found: m/z 277.0887 Calcd for $C_{15}H_{17}O_3$: $(M+H)^+$ =277.0898

2-(1-Adamantyl)-4-methylquinoline: mp 115.5~121.5 °C (lit[16] mp 120.3~122.0 °C) ; IR (KBr) 3060, 2900, 2850, 1595, 1445, 760 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.82 (6H, t, J=3.0Hz), 2.11 (6H, d, J=2.9Hz), 2.15 (3H, bs), 2.68 (3H, d, J=1.0Hz), 7.32 (1H, d, J=1.0Hz), 7.48 (1H, m), 7.64 (1H, m), 7.93 (1H, d, J=8.3Hz), 8.06 (1H, d, J=8.2Hz) ; MS (EI) Found: m/z 277

2-Cyclohexyl-4-methylquinoline: Oil[16] ; IR (Neat) 3060, 2920, 2850, 1600, 1450, 760 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.25-2.04 (10H, m), 2.83-2.90 (1H, m), 7.17 (1H, s), 7.49 (1H, ddd, J=8.3, 6.9, 1.0Hz), 7.66 (1H, ddd, J=8.4, 6.9, 1.2Hz), 7.95 (1H, dd, J=8.3, 1.2Hz), 8.05 (1H, dd, J=8.4, 1.0Hz) ; MS (EI) Found: m/z 225

2-(3-Cholestanyl)-4-methylquinoline: mp 186.0~187.5 °C (lit[5] mp 182.0~184.0 °C) ; IR (KBr) 2930, 2870, 2850, 1600, 1470, 1450, 760 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=0.68 (3H, s), 0.86 (3H, d, J=1.7Hz), 0.88 (3H, d, J=1.7Hz), 0.92 (3H, d, J=6.6Hz), 0.94 (3H, s), 0.71-2.05 (31H, m), 2.69 (3H, s), 2.92 (1H, m), 7.19 (1H, s), 7.49 (1H, ddd, J=8.3, 6.9, 1.0Hz), 7.66 (1H, ddd, J=8.4, 6.9, 1.2Hz), 7.94 (1H, dd, J=8.3, 1.2Hz), 8.04 (1H, dd, J=8.4, 1.0Hz) ; MS (EI) Found: m/z 513

4-Methyl-2-phenethylquinoline: Oil[16] ; IR (Neat) 3060, 3025, 2920, 2860, 1600, 1450, 760, 700 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=2.66 (3H, s), 3.12-3.17 (2H, m), 3.20-3.26 (2H, m), 7.10 (1H, s), 7.18-7.31 (5H, m), 7.49-7.58 (1H, m), 7.67-7.73 (1H, m), 7.95 (1H, dd, J=8.5, 1.0Hz), 8.08 (1H, d, J=7.7Hz) ; MS (EI) Found: m/z 247

2-(1-Adamantyl)caffeine: mp 249.0~252.0 °C (lit[5] mp 249.0~250.0 °C) ; IR (KBr) 2900, 2875, 1705, 1665, 1540, 1430, 745 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.80 (6H, bs), 2.15 (9H, bs), 3.39 (3H, s), 3.57 (3H, s), 4.17 (3H, s) ; MS (EI) Found: m/z 328

2-(1-Adamantyl)benzothiazole: mp 103.5~104.5 °C (lit[5] mp 102.3~104.2 °C) ; IR (KBr) 2900, 2850, 1510, 1440, 1000, 760, 725 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.82 (6H, bs), 2.16 (9H, bs), 7.33 (1H, ddd, J=8.1, 7.2, 1.1Hz), 7.44 (1H, ddd, J=8.3, 7.2, 1.2Hz), 7.86 (1H, dd, J=8.1, 1.2Hz), 8.0 (1H, dd, J=8.3, 1.1Hz) ; MS (EI) Found: m/z 269

Ethyl 2-(1-adamantyl)isonicotinate: Oil ; IR (Neat) 2900, 2850, 1730, 1600, 1560, 1400, 1280, 1220, 1115, 760 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.42 (3H, t, J=7.1Hz), 1.80 (6H, bs), 2.02 (6H, d, J=2.9Hz), 2.13 (3H, bs), 4.41 (2H, q, J=7.1Hz), 7.64 (1H, d, J=5.1Hz), 7.83 (1H, s), 8.71 (1H, d, J=5.1Hz) ; HRMS (FAB+) Found: m/z 286.1810 Calcd for $C_{18}H_{24}NO_2$: $(M+H)^+$ =286.1807

2-(1-Adamantyl)pyridine: mp 36.0~38.5 °C (lit[16] mp 33.0~37.0 °C) ; IR (KBr) 2905, 2850, 1590,

1465, 775, 745 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.79 (6H, d, J=2.7Hz), 2.00 (6H, d, J=3.1Hz), 2.11 (3H, bs), 7.08 (1H, ddd, J=7.7, 4.8, 1.0Hz), 7.27 (1H, dt, J=7.7, 1.0Hz), 7.62 (1H, td, J=7.7, 1.9Hz), 8.58 (1H, ddd, J=4.8, 1.9, 1.0Hz) ; MS (EI) Found: m/z 213

4-(1-Adamantyl)pyridine: mp 75.5~77.0 °C (lit[16] mp 75.0~78.0 °C) ; IR (KBr) 2905, 2845, 1595, 1410, 800 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.75 (3H, d, J=12.4Hz), 1.81 (3H, d, J=12.4Hz), 1.89 (6H, d, J=2.7Hz), 2.12 (3H, bs), 7.25 (2H, dd, J=4.6, 1.7Hz), 8.51 (2H, dd, J=4.6, 1.7Hz) ; MS (EI) Found: m/z 213

2-(1-Adamantyl)pyrimidine: mp 70.0~72.5 °C ; IR (KBr) 2900, 2850, 1570, 1560, 1420, 1100, 790 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.80 (6H, t, J=3.1Hz), 2.08 (6H, d, J=2.9Hz), 2.12 (3H, bs), 7.09 (1H, t, J=4.9Hz), 8.70 (2H, d, J=4.9Hz) ; HRMS (FAB+) Found: m/z 215.1548 Calcd for $C_{14}H_{19}N_2$: $(M+H)^+$ =215.1548

4-(1-Adamantyl)pyrimidine: mp 72.5~73.4 °C ; IR (KBr) 2900, 2850, 1580, 1540, 1470, 1390, 1300, 840, 640, 585 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.75-1.83 (6H, m), 1.97 (6H, d, J=2.7Hz), 2.13 (3H, bs), 7.26 (1H, dd, J=5.4, 1.3Hz), 8.64 (1H, d, J=5.4Hz), 9.16 (1H, d, J=1.3Hz) ; HRMS (FAB+) Found: m/z 215.1548 Calcd for $C_{14}H_{19}N_2$: $(M+H)^+$ =215.1548

2-(1-Adamantyl)-4-methylpyridine: mp 107.5~108.5 °C ; IR (KBr) 3040, 2900, 2850, 1600, 1560, 1450, 810 cm^{-1} ; ^1H NMR ($CDCl_3$) δ=1.78 (6H, d, J=2.9Hz), 1.99 (6H, d, J=3.1Hz), 2.10 (3H, bs), 2.33 (3H, s), 6.90 (1H, d, J=5.0Hz), 7.08 (1H, s), 8.42 (1H, d, J=5.0Hz) ; MS (EI) Found: $(M+H)^+$ =227 ; Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16 %. Found: C, 84.32; H, 9.09; N, 6.33 %.

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