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2,2′-Binaphthylene phosphorochloridite (BINOL-PCl) as a bulky and efficient reagent for the conversion of primary and secondary alcohols into iodides, and tertiary alcohols stereo- and/or regioselectively into olefin(s)

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Primary and secondary alcohols were transformed in high yield to corresponding iodides by 4-chloro-3,5-dioxaphosphacyclohepta [2,1-α; 3,4-α'] dinaphthalene (BINOL-PCl) at room temperature. The tertiary alcohols formed corresponding alkenes by stereo- and/or regioselective elimination reactions. (*E*)-1,2-Diphenyl-1-propene and 2,3-diphenyl-1-propene were stereoselectively obtained from 1,2-diphenyl-2-propanol, as representative. No (*Z*)-1,2-diphenyl-1-propene was observed. 2-Methyl-1-phenylcyclopentene and 3-methyl-2-phenylcyclopentene were regioselectively obtained from 2-methyl-1-phenylcyclopentanol. ^{13}C chemical shifts for the α-methylene carbon of some alkyl iodides empirically calculated through a very simple additive relationship lead to similar or even better values than the reported values. All primary alkyl iodides showed the iodine heavy atom effect on the α-methylene carbon chemical shift.

Key Words: Alkyl iodide, 2,2′-dihydroxy-1,1′-dinaphthalene (BINOL), 2,2′-binaphthylene phosphorochloridite (BINOL-PCl), stereoselective, anti-E2 elimination reaction, heavy atom effect.

Introduction

Halogen-containing compounds are very useful intermediates in organic synthesis.[1] Alkyl iodides are an important class of compounds used extensively in such organic syntheses as the radical-mediated synthesis of

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trifluoroethyl amines and trifluoromethyl ketones,[2] the asymmetric synthesis of alpha-functionalized primary sulphonamides,[3] and the coupling reaction of alkyl iodide electron-deficient alkenes using nickel boride (Cat.)-borohydride exchange resin (BER) in methanol.[4] Recently, a new application of alkyl iodides was reported for photo-initiated carbonylation with carbon monoxide, using amines for the preparation of carbonyl C-labeled amides.[5]

Alcohols are also easily transformed into deoxy derivatives via halides.[6] The most common precursors to alkyl halides are alcohols, and their conversion into halides is one of most frequently used functional group transformation reactions.[7] Although alkyl iodides are less stable than chlorides and bromides and iodide is the most expensive of the common halogens, they are far more reactive than other corresponding halogens, and in some cases iodides are the only reactive halides.[8] Among the different routes to such derivatives are the use of alcohols as readily available starting materials and a substitution reaction for the iodine atom.[9]

The conversion of alcohols to alkyl halides with tertiary phosphines and different sources of halogens has been studied extensively.[10–18] The first preparation method for the conversion of alkanes into their corresponding iodo compounds was developed in Germany using a multiphase system.[19] To perform iodination of hydroxyl groups, several methods have been described that use a variety of reagent systems, such as $Al(HSO_4)_3$/KI in nonaqueous solution,[20] $CeCl_3.7H_2O$/NaI,[21] silicaphosphine (Silphos),[22] and KI/silica sulfuric acid (SSA),[23] and use of triphenylphosphine/iodine under solvent-free conditions using microwave irradiation.[24] Corey et al. reported the formation of some alkyl iodides upon treatment of alkyl *o*-phenylene phosphites with iodine.[25]

2,2′-Dihydroxy-1,1'-dinaphthalene (BINOL), a bulky compound, is an efficient, applicable, and important chiral compound used in a wide variety organic syntheses; as a ligand in organometalics,[26] enantioselective syntheses,[27] etc. In the present study we introduced racemic BINOL as a mediate for the conversion of primary and secondary alcohols into their corresponding iodides, and a stereo- and/or regioselective elimination reaction on tertiary alcohols in excellent yields.

Experimental

General

Melting points were measured with a digital melting point apparatus (Electrothermal) and are uncorrected. IR spectra were determined in the 4000-400 cm^{-1} region with a NEXUS 670 FT IR spectrometer by preparing KBr pellets (Urmia University, Urmia, Iran). The ^{1}H-NMR spectra were measured at 90 MHz using a Varian NMR EM 390 spectrometer (Isfahan University of Technology, Isfahan, Iran), at 300 MHz using a Bruker 300 FT-NMR spectrometer (Urmia University, Urmia, Iran), and at 400 MHz using a JEOL JNM-Al 400 spectrometer (Osaka Prefecture University, Osaka, Japan) in CCl_4 or $CDCl_3$ as solvents and using TMS as the internal standard. All alcohols (except **3w-y**), triethylamine, phosphorus trichloride, and solvents were obtained from Merck and Aldrich, and were used without further purification. 2,2′-Dihydroxy-1,1'- dinaphthalene (BINOL) **1**[28] and tertiary alcohols **3w-y**[29] were synthesized and purified in our laboratory, as previously described in the literature.

General procedure for the preparation of iodides from related primary and secondary alcohols

Compound **2** (1.50 g, 4.30 mmol) was dissolved in dry toluene (20 mL) in a 2-necked round bottom flask equipped with an ice-bath, magnetic stirrer, and nitrogen and/or argon atmosphere. The solution of benzyl alcohol (0.46 g, 4.30 mmol) and triethylamine (0.87 g, 8.60 mmol) in dry toluene (20 mL) was added dropwise into the round bottom flask at 0 °C, and then stirred at room temperature in a nitrogen and/or argon atmosphere for 48 h. Progress of the reaction was monitored by TLC. The salt of triethylammonium hydrochloride precipitate was then filtered. The solvent was removed from the crude mixture at reduced pressure. Dry CH_2Cl_2 (20 mL) was added to dissolve the crude mixture. Iodine (0.60 g, 4.73 mmol) was added to the solution of CH_2Cl_2 in small portions via magnetic stirring. The color of the iodine disappeared and then turned dark violet with additional excess iodine. The solution was washed with 10% sodium thiosulfate (20 mL). After drying the organic phase over anhydrous sodium sulfate, the solvent was removed at reduced pressure. A colorless oily liquid was obtained (caution! benzyl iodide and its derivatives are lachrymators that can damage eye and lung tissues).[30] The iodides **5a**, **k**, **l**, **m**, **n**, **o**, **p**, and **q** were separated using a Kugelrohr apparatus,[31] and other iodides were separated by silica gel column chromatography. Spectroscopic, and physical data for the products are shown below, as representative.

Benzyl iodide (5a). (lit.[22,24]), Colorless oily liquid (90%). IR (KBr) ν_{max}/cm^{-1}: 3082.58 (m), 3060.71 (m), 3027.44 (m), 2963.76 (w), 1599.06 (w), 1493.05 (s), 1453.36 (s), 1157.41 (s), 1059.67 (w), 754.09 (s), 692.82 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.29-7.44 (m, 5H), 4.50 (s, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 139.3, 128.9, 128.8, 128.0, 6.0.

4-Chlorobenzyl iodide (5b). (lit.[22,24]), Yellow solid (90%), mp 52-56 °C. IR (KBr) ν_{max}/cm^{-1}: 3020.00 (w), 2923.92 (m), 2852.45 (w), 1701.79 (m), 1593.08 (m), 1489.60 (s), 1407.44 (m), 1154.64 (m), 1089.51 (s), 832.29 (s), 806.24 (s), 554.64 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.33 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 4.43 (s, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 137.9, 133.6, 130.1, 129.0, 4.2.

2-Chlorobenzyl iodide (5c). (lit.[24]), Yellow solid (85%), mp 108-110 °C. IR (KBr) ν_{max}/cm^{-1}: 3059.65 (w), 2921.84 (m), 2850.38 (m), 1589.64 (w), 1474.80 (m), 1442.60 (m), 1215.17 (w), 1158.23 (m), 829.77 (w), 752.87 (s), 679.76 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.21-7.44 (m, 4H), 4.55 (s, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 136.8, 133.8, 130.6, 130.2, 129.4, 127.3, 2.3.

3-Nitrobenzyl iodide (5e). (lit.[23,24]), Amber yellow solid (80%), mp 66-68 °C. IR (KBr) ν_{max}/cm^{-1}: 3084.03 (w), 3061.97 (w), 2866.35 (w), 1516.18 (s), 1475.34 (w), 1438.54 (w), 1351.86 (s), 1313.38 (m), 813.05 (m), 682.91 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 8.25 (s, 1H), 8.13 (dt, J_3 = 8.1, J_4 = 1.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 8.1 Hz, 1H), 4.51 (s, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 141.4, 134.7, 129.9, 123.5, 122.8, 2.1.

2-Phenyl-1-iodoethane (5g). (lit.[22,24]), Light brown liquid (90%). IR (KBr) ν_{max}/cm^{-1}: 3084.16 (w), 3061.48 (m), 3026.58 (m), 2958.79 (w), 1601.20 (w), 1494.83 (s), 1453.38 (s), 1236.07 (m), 1169.26 (s), 750.54 (s), 734.21 (s), 697.62 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.23-7.41 (m, 5H), 3.40 (t, J = 7.8 Hz, 2H), 3.23 (t, J = 7.8 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 140.7, 128.7, 128.4, 126.9, 40.4, 5.7.

3-Phenyl-1-iodopropane (5h). (lit.[32]), Yellow oil (90%). IR (KBr) ν_{max}/cm^{-1}: 3083.76 (m), 3061.15 (m), 3025.31 (s), 2926.86 (s), 2852.39 (m), 1602.68 (m), 1495.74 (s), 1453.37 (s), 1213.25 (s), 741.93 (s), 698.90

(s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.21-7.32 (m, 5H), 3.20 (t, J = 6.9 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H), 2.16 (quin, J = 7.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 140.4, 128.6, 128.5, 126.2, 36.2, 34.9, 6.4.

Cinnamyl iodide (5i). (lit.[24]), Colorless solid; (80%). mp 54-56. (lit. 56-57 °C). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.23-7.50 (m, 5H), 6.71 (m, 1H), 6.34 (d, J = 15.6, 1H), 4.27 (dd, J_3 = 7.2 Hz, J_4 = 1.2 Hz, 2H).

Piperonyl iodide (5j). (lit.[23]), Light green solid (20%). IR (KBr) ν_{max}/cm^{-1}: 3050.60 (w), 2955.58 (m), 2923.33 (s), 2852.46 (m), 1502.46 (m), 1487.92 (s), 1444.36 (s), 1377.12 (w), 1284.63 (s), 1039.34 (s), 848.41 (s), 808.12 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 6.86-6.93 (m, 2H), 6.72 (d, J = 8.4 Hz, 1H), 5.97 (s, 2H), 4.46 (s, 2H).

Allyl iodide (5k). (lit.[22]), Colorless liquid (80%). IR (KBr) ν_{max}/cm^{-1}: 3085.37 (s), 3046.70 (w), 2978.40 (s), 2960.44 (s), 1642.68 (s), 1437.24 (s), 1403.30 (s), 670.10 (s), 490.42 (m).^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 6.01-6.16 (m, 1H), 5.23-5.30 (m, 1H), 4.97-5.00 (m, 1H), 3.86-3.90 (ddd, J_3 = 8.1, J_4 = 1.5, J_4 = 1.2 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 135.6, 117.7, 5.4.

n-Amyl iodide (5l). (lit.[29,33]), Colorless liquid (80%). IR (KBr) ν_{max}/cm^{-1}: 2957.75 (s), 2928.64 (s), 2871.21 (m), 1464.18 (m), 1426.66 (w), 1378.69 (w), 1229.35 (s), 1174.66 (s), 915.81 (w), 726.28 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 3.21 (t, J = 7.05 Hz, 2H), 1.85 (quin, J = 7.2 Hz, 2H), 1.27-1.42 (m, 4H), 0.926 (t, J = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 33.3, 32.7, 21.7, 13.9, 7.0.

iso-Amyl iodide (5m). (lit.[29]), Colorless liquid (70%). IR (KBr) ν_{max}/cm^{-1}: 2958.91 (s), 2928.10 (s), 2870.12 (s), 2827.56 (w), 1466.49 (s), 1384.90 (m), 1249.56 (s), 1179.65 (s), 730.32 (s), 694.56 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 3.22 (t, J = 7.2 Hz, 2H), 1.71-1.76 (m, 3H), 0.92 (d, J = 6.3 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 42.5, 29.0, 21.7, 5.1.

n-Hexyl iodide (5p). (lit.[24,33]), Colorless liquid (80%). IR (KBr) ν_{max}/cm^{-1}: 2956.87 (s), 2927.74 (s), 2856.41 (s), 1465.37 (m), 1426.62 (w), 1378.30 (w), 1217.89 (m), 1172.83 (m), 811.89 (w), 722.24 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 3.20 (t, J = 6.9 Hz, 2H), 1.83 (quin, J = 6.9 Hz, 2H), 1.29-1.40 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 33.5, 30.7, 30.2, 22.5, 14.0, 7.3.

Cyclohexyl iodide (5q). (lit.[22,24]), Colorless liquid (80%). IR (KBr) ν_{max}/cm^{-1}: 2930.94 (s), 2853.47 (s), 1447.24 (s), 1331.09 (w), 1252.07 (m), 1243.74 (m), 1172.82 (s), 1094.20 (m), 986.88 (m), 654.69 (s), 639.04 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 4.38 (m, 1H), 2.17 (m, 2H), 1.93-2.04 (m, 2H), 1.61-1.71 (m, 3H), 1.39-1.48 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 39.6, 32.7, 27.3, 25.2.

2-Octyl iodide (5s). (lit.[22]), Light brown liquid (85%). IR (KBr) ν_{max}/cm^{-1}: 2957.47 (s), 2926.16 (s), 2856.46 (s), 1457.40 (s), 1377.38 (m), 1135.77 (m), 724.20 (w). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 4.14-4.23 (m, 1H), 1.93 (d, J = 6.6 Hz, 3H), 1.53-1.88 (m, 2H), 1.29-1.65 (m, 8H), 0.87-0.90 (t, J = 6.9 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 42.9, 31.7, 30.8, 29.7, 29.0, 28.4, 22.6, 14.1.

1-phenyl cyclohexene (6w). (lit.[33]), Colorless oily liquid. IR (KBr) ν_{max}/cm^{-1}: 3029.69 (w), 2927.40 (m), 2856.86 (m), 1598.93 (w), 1493.39 (w), 1445.44 (w), 908.52 (s), 734.32 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.20-7.41 (m, 5H), 6.13-6.15 (m, 1H), 2.41-2.44 (m, 2H), 2.21-2.24 (m, 2H), 1.66-1.84 (m, 4H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 142.7, 136.6, 128.2, 126.5, 124.9, 124.8, 27.4, 25.9, 23.1, 22.2.

2-Methyl-1-phenylcyclopentene (6x). (lit.[34]), Colorless oily liquid. IR (KBr) ν_{max}/cm^{-1} 3055.52

(m), 2928.34 (m), 2840.05 (m), 1686.01 (m), 1598.34 (m), 1494.85 (s), 1444.77 (s), 761.05 (s), 698.72 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.20-7.40 (m, 5H), 2.74-2.81 (m, 2H), 2.53 (t, J = 7.8 Hz, 2H), 1.92 (t, J = 7.2 Hz, 2H), 1.89 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 138.8, 135.2, 128.6, 128.0, 127.6, 126.0, 40.1, 37.3, 21.9, 15.5.

3-Methyl-2-phenylcyclopentene (7x). (lit.[34]), Colorless oily liquid. IR (KBr) ν_{max}/cm^{-1}: 3040.00 (w), 2924.06 (m), 2852.33 (m), 1666.58 (w), 1454.81 (m), 1155.76 (m), 1069.73 (m), 840.21 (w). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.19-7.43 (m, 5H), 6.12 (s, 1H), 2.42-2.56 (m, 2H), 2.08-2.31 (m, 2H), 1.61-1.71 (m, 1H), 1.10 (d, J = 6.9 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 139.1, 128.3, 126.7, 126.1, 125.9, 123.4, 45.7, 29.7, 19.7, 8.6.

(*E*)-2-Phenyl-2-pentene (8y). Colorless oily liquid. IR (KBr) ν_{max}/cm^{-1}: 3058.48 (s), 3029.88 (m), 2960.58 (w), 2928.81, (m), 2871.48 (m), 1687.17 (w), 1599.56 (m), 1494.05 (m), 1377.72 (m), 1069.92 (w), 698.06 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.13-7.39 (m, 5H), 5.80 (td, J_3 = 7.2 Hz, J_4 = 1.2 Hz, 1H), 2.16 (m, 2H), 2.05 (d, J = 1.2 Hz, 3H), 1.08 (t, J = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 144.0, 130.3, 128.2, 126.5, 125.6, 112.2, 22.1, 15.6, 14.7.

2-Phenyl-1-pentene (9y). Colorless oily liquid. IR (KBr) ν_{max}/cm^{-1}: 3080.91 (w), 2872.00 (m), 1627.00 (w), 1450.00 (m), 1379.10 (m), 1068.72 (w), 859.71 (w), 756.63 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.25-7.50 (m, 5H), 5.34 (m, 1H), 5.13 (m, 1H), 2.56 (td, J_3 = 7.2, J_4 = 1.2 Hz, 2H), 1.57 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ = 148.6, 141.5, 130.3, 128.3, 126.2, 112.2, 37.5, 21.4, 14.4.

(*E*)-1,2-Diphenyl-1-propene (8z). (lit.[35,36]), IR (KBr) ν_{max}/cm^{-1}: 3100.18, (w), 3059.69 (m), 3018.14 (w), 2900.23 (w), 2853.24 (w), 1601.72 (s), 1571.61 (s), 1494.08 (s), 1359.07 (s), 1208.18 (s), 806.10 (s), 764.99 (s), 691.36 (s). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.52-7.54 (m, 4H, *o*-Ph-H), 7.21-7.44 (m, 6H, *m*,*p*-Ph-H), 6.84 (q, J = 1.2 Hz, 1H), 2.28 (d, J = 1.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 143.9, 138.3, 137.3, 129.1, 128.3, 128.1, 127.6, 127.1, 126.4, 125.9, 17.6.

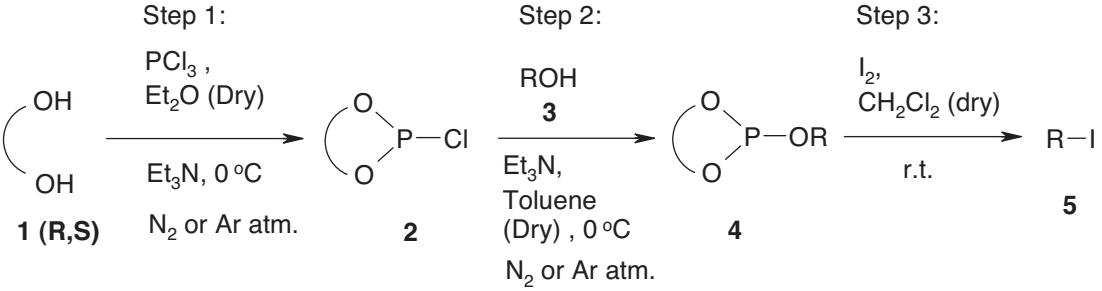
Results and discussion

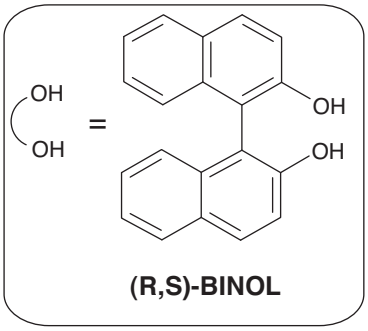
Herein we introduced a convenient method for converting alcohols to their related alkyl iodides using 4-chloro-3,5-dioxaphosphacyclohepta [2,1-α; 3,4-α'] dinaphthalene (BINOL-PCl) (**2**), which can be used as a cheap, easy to prepare new source of reagent (Scheme 1). Racemic 2,2′-dihydroxy-1,1'-dinaphthalene (BINOL) (**1**) is readily available and was prepared according to the literature.[28] In order to select the best conditions for the preparation of **2**, compound **1** was first reacted with PCl_3 in dry diethyl ether under a nitrogen and/or argon atmosphere, according to a previously reported method.[29] This reagent system appears to be bulky, reactive, and versatile, and easily converted to alkyl-2,2′-dinaphthylene phosphite (**4**) in the presence of primary, secondary, and tertiary alcohols in step 2 (Scheme 1). Reaction between **4** (phosphites of primary and secondary alcohols) and iodine in dry CH_2Cl_2 afforded the related alkyl iodides (**5**) in high yield in step 3.

We then applied the optimized condition to the reaction of structurally different alcohols. With this method, primary and secondary alcohols were converted into their iodides in excellent yield, and tertiary alcohols (3°) (see later) were stereo- and/or regioselectively converted to the corresponding olefin(s) (Table 1). Reaction of **2** with 2-methylbenzyl alcohol (**3d**), furyl alcohol (**3f**), and other benzylic alcohol derivatives

that contain electron-donating substituents failed (Table 1). Exceptionally, the reaction of **2** with piperonyl alcohol (**3j**) afforded piperonyl iodide (**5j**) in low yield. It seems, presumably, that the formation of their more stable benzyl and/or furyl cations via an electron-donating substituent was prevented in CH_2Cl_2 as a nonpolar solvent. Nonpolar solvents cannot stabilize carbocations, which can favor the S_N2 reaction mechanism in step 3 (Scheme 1). Instead, **2** reacted with 3-nitrobenzyl alcohol (**3e**) as an electron-withdrawing substituent on benzyl alcohol, and then reacted with iodine through steps 2 and 3, affording 3-nitrobenzyl iodide (**5e**) in high yield, according to ^{1}H-NMR and ^{13}C-NMR data (Table 1).

In order to gain more insight into the applicability of this method, some competitive reactions were performed between structurally different alcohols (Table 1). We examined *endo*-(1S)-(**-**)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-ol (borneol) (**3r**) as a bulky secondary alcohol and no bornyl iodide (*endo* and/or *exo*) was obtained. It seems that the hindrance effect of bulky bornyl moiety prevented progression of the reaction with bulky reagent **2**, according to thin layer chromatography (TLC) monitoring. Instead, secondary alcohols cyclohexanol (**3q**), 2-octanol (**3s**), 1-phenyl-1-propanol (**3t**), and 1-phenylethanol (**3u**) afforded corresponding iodides in high yield, as representative. The primary and secondary alkyl iodides obtained are shown in Table 1.





Scheme 1.

The stereoselective synthesis of olefins via elimination reaction of some tertiary alcohols was investigated in the presence of triphenylphosphine in carbon tetrachloride,[35] and in the presence of semi-heterogeneous polystyryl diphenylphosphine in carbon tetrachloride.[37] Reaction of **2** with tertiary alcohols and then with iodine gave the related olefins. No tertiary alkyl iodides were obtained in the reaction with tertiary alcohols via reagent **2**. It seems that the adduct phosphites of the tertiary alcohols stereo- and/or regioselectively converted to corresponding olefin(s). 1-Phenylcyclohexanol (**3w**) in reaction with **2** in the presence of triethylamine and then with iodine afforded 1-phenylcyclohexene (**6w**) in high yield. 1-Phenyl-1-iodocyclohexane (**5w**) was not observed (Scheme 2 and see Experimental). The reaction of 2-methyl-1-phenylcyclopentanol (**3x**) with reagent

2 afforded a mixture of both alkenes, 2-methyl-1-phenylcyclopentene (**6x**) and 3-methyl-2-phenylcyclopentene (**7x**), as thermodynamic and kinetic products, respectively. Possible pathways for the formation of **6x** and **7x** from **4x** are E2 elimination reactions through pathways *a* and *b*, respectively (Scheme 2). Interestingly, the amount of kinetic product (**7x)** was greater than that of the thermodynamic product (**6x)** in the reaction mixture. The isomeric ratio of **7x**:**6x** was first 96.7:3.3 in the crude reaction mixture after removing toluene as the reaction solvent. No phosphite **4x** was observed after working up. Dissolving the reaction mixture in dichloromethane and then evaporation increased the ratio of **7x**:**6x** after working up (69.4:30.6). Finally, the ratio of the 2 isomeric alkenes (**7x**:**6x**) was 3.2:96.8 (Scheme 2, Figure 1). According to the literature, kinetic alkenes isomerize to thermodynamic alkenes in acidic conditions.[38] These experimental observations indicate that the kinetic alkene **7x** isomerized to the thermodynamic alkene **6x**. The steric hindrance around H-1 was greater than that around H-2 on phosphite **4x**, so that triethylamine primarily captured H-2 on the cyclopentyl ring moiety on **4x** via pathway *b* with a regioselective E2-elimination reaction (Scheme 2). This was experimentally confirmed, as the spectrum of **7x** contained triethylammonium salt (Figure 2). This spectrum showed a triplet at δ 1.40 ($\approx$9H), a quartet at δ 3.11 ($\approx$6H), and a broad singlet at δ 12.1 ppm (1H), indicating the formation of triethylammonium salt.

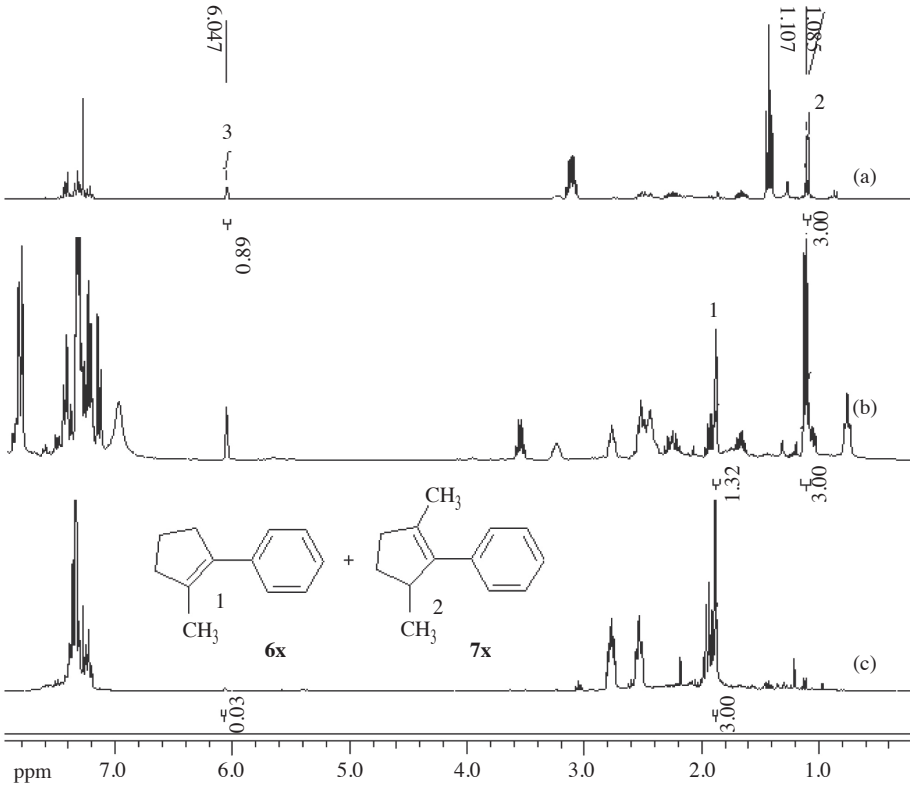


Figure 1. Expanded ^{1}H-NMR spectrum of the various ratios of **6x** and **7x** obtained from **4x** and continuous isomerization of **7x** to **6x**.

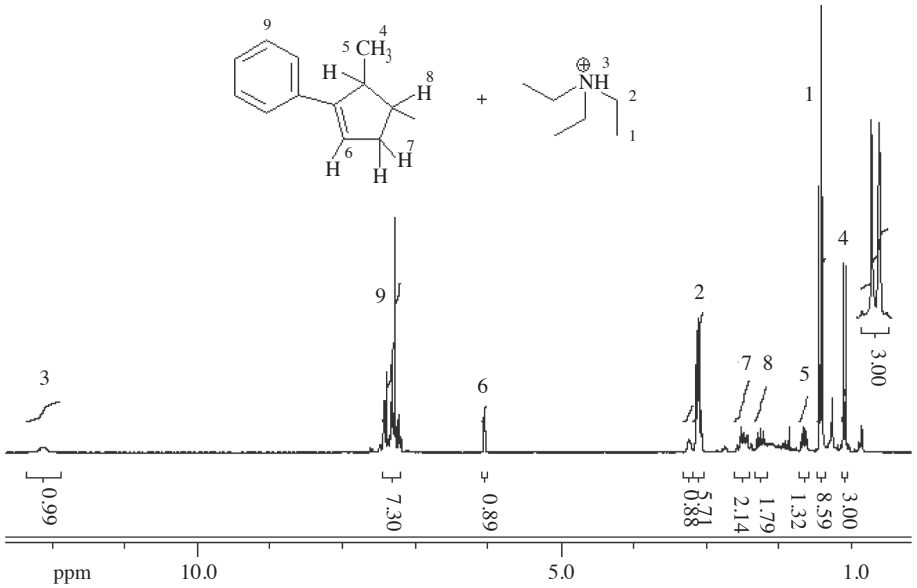
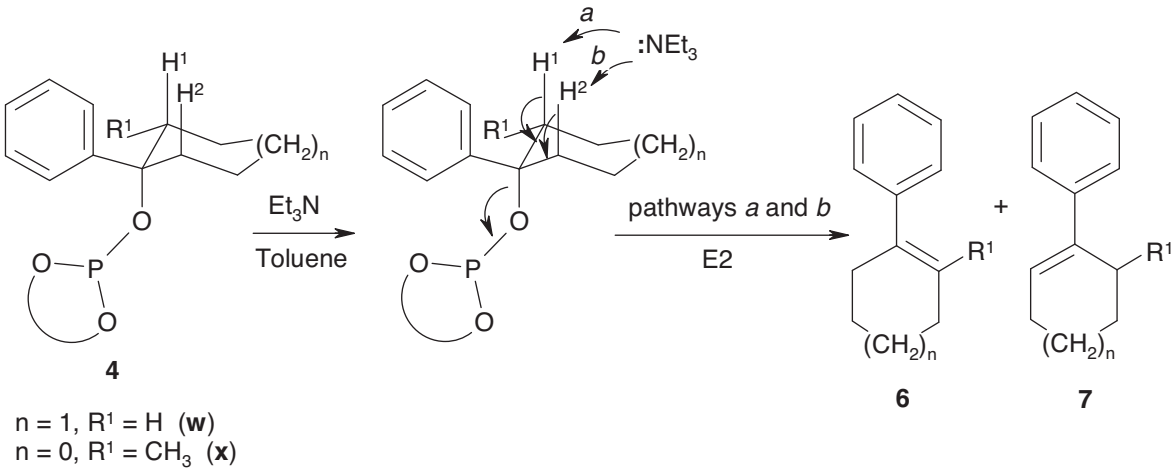


Figure 2. ^{1}H-NMR spectrum of crude **7x**, containing triethylammonium salt.



Scheme 2.

2-Phenyl-2-pentanol (**3y**) and 1,2-diphenyl-2-propanol (**3z**) in the presence of **2** afforded BINOL-phosphites **4y** and **4z**, respectively. The stereoselective second order E2 elimination reaction of **4y** gave a mixture of alkenes: (*E*)-2-phenyl-2-pentene (**8y**) and the *terminal*-alkene, 2-phenyl-1-pentene (**9y**) (Scheme 3 and Figure 3). The allylic coupling constant between the methyl's protons and the olefinic proton in **8y** and **8z** is 1.2 Hz, indicating *E*-isomers. Moreover, stereoselective E2 elimination of **4z** afforded (*E*)-1,2-diphenyl-1-propene (**8z**) and 2,3-diphenyl-1-propene (**9z**) (Scheme 3 and Figure 4). Interestingly, no (*Z*)-2-phenyl-2-pentene (**10y**) or (*Z*)-1,2-diphenyl-1-propene (**10z**) was observed. A possible mechanism for the anti-elimination reaction of phosphites **4y** and **4z** was described (Scheme 3). Rotamers **4y(i)** and **4z(i)** are anti-forms and are more stable than gauche forms **4y(ii)** and **4z(ii)**. The ethyl and phenyl ring in **4y** and the 2 phenyl rings in **4z** are anti- and gauche forms in corresponding **4y(i)** and **4z(i)**, and **4y(ii)** and **4z(ii)**, respectively. The hindrance effect

is significant in the gauche form and caused repulsion of the ethyl and phenyl groups in **4y(ii)** and the 2 phenyl groups in **4z(ii)**, respectively. According to Scheme 3, there are 2 pathways for the capture of protons from **4y** and **4z**. The isomeric ratio of **8y**:**9y** obtained was 74.07:25.93, based on peak integrations in the mixture of the 2 alkenes. The ratio became 94.34:5.66 for **8y** and **9y**, after working up (Figure 3).

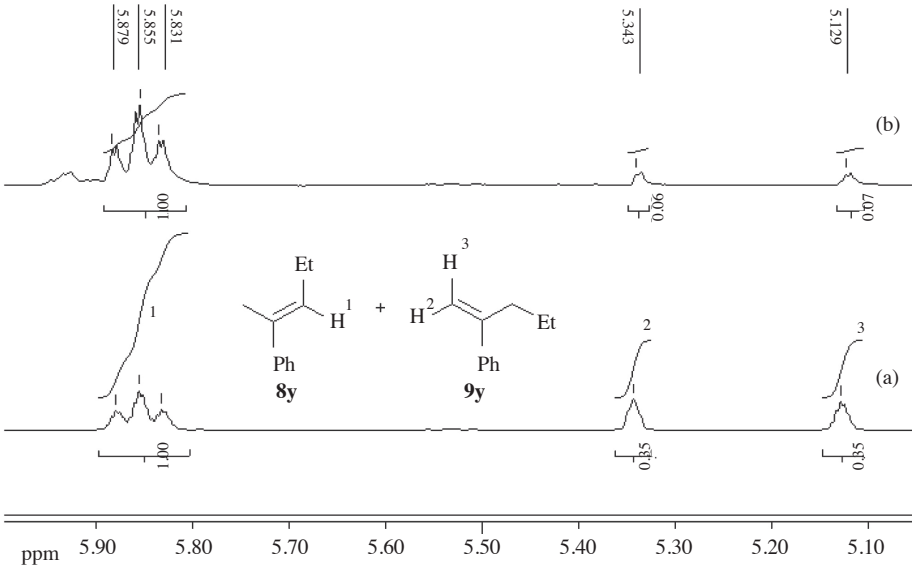


Figure 3. Expanded ^{1}H-NMR spectrum of the mixture of **8y** and **9y** in a crude reaction mixture (a) and after working up (b).

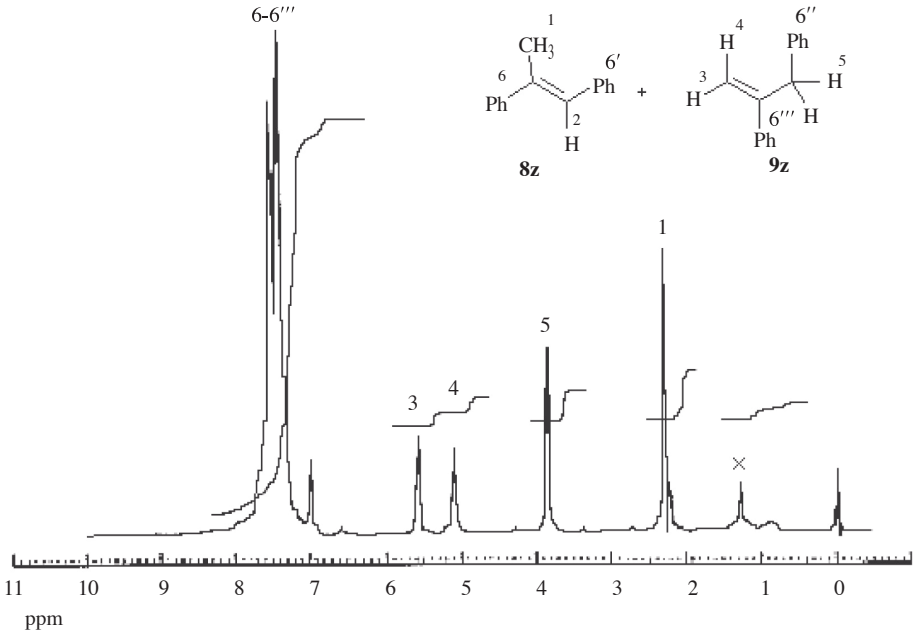
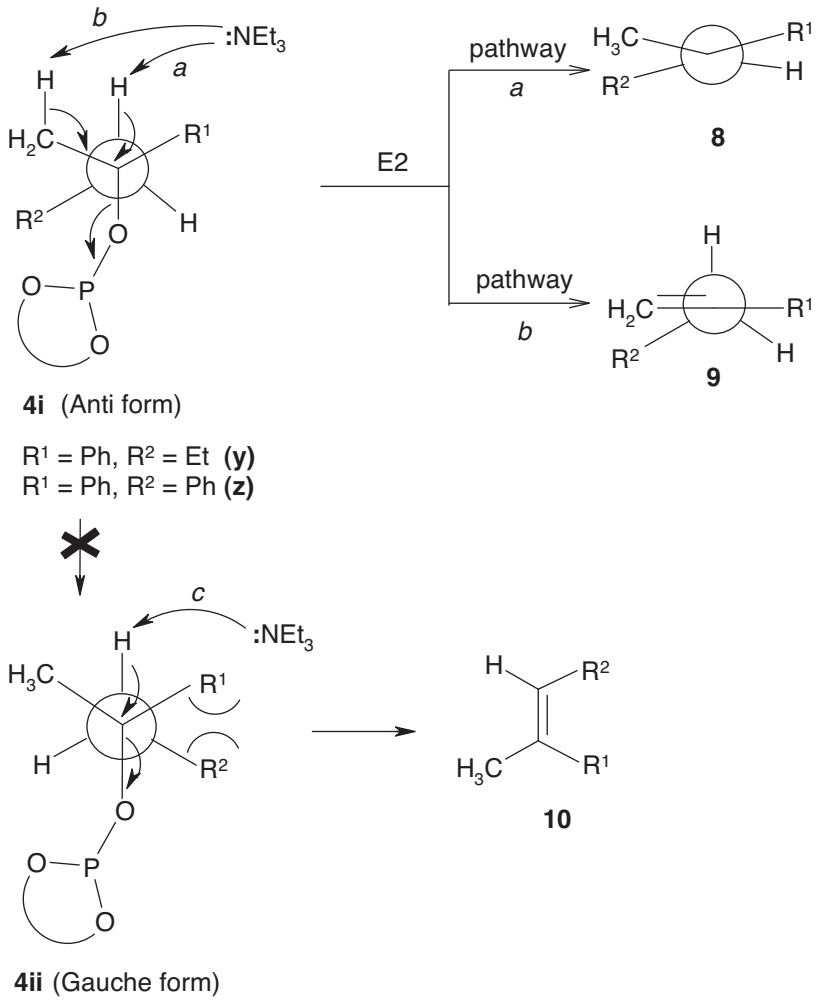


Figure 4. ^{1}H-NMR spectrum of the mixture of alkenes **8z** and **9z** in CCl_4 at 90 MHz.



Scheme 3.

Figure 4 shows the ^{1}H-NMR spectrum of the mixture of 2 alkenes (**8z** and **9z)**. All the assigned integrations have good relations with each of the corresponding protons. The peak of methyl protons in the ^{1}H-NMR spectrum of **8z** shows a doublet ($^4J_{CH}$ = 1.2 Hz) and has allylic coupling with the H-2 olefin proton. Furthermore, the peak of the H-2 proton also shows a doublet ($^4J_{CH}$ = 1.2 Hz) due to allylic coupling with methyl protons. The ^{13}C-NMR spectrum of alkene **8z** showed 11 different chemical shift values for its carbon atoms. The carbon atom of the methyl group has a peak at δ 17.54 ppm and other carbon atoms have chemical shift values ranging from δ 125.93 to 143.88 ppm at the aromatic region (see Experimental).

Distinguishing between (*E*)-alkene **8z** and corresponding (*Z*)-alkene **10z** is not a trivial matter. The NOE difference spectrum is needed as a powerful tool for this purpose.[39] Figure 5 shows the NOE spectrum for **8z** and the NOE results of irradiating methyl protons. We irradiated methyl protons and observed that H-2 was not noticeably enhanced and had equal positive and negative peaks, whereas *ortho*-protons 6 and 6' on the 2 phenyl rings were definitively enhanced. These results indicate that the methyl group and H-2 protons are on opposite sides of the carbon-carbon double bond (C=C) in **8z**. On the other hand, the geminal protons, H-3 (δ

= 5.44 ppm) and H-4 (δ = 5.10 ppm) with the phenyl group, are on the same and opposite sides of the C=C double bond in **9z**, respectively.[36]

Table 1. Preparation of primary and secondary alkyl iodides from related alcohols.

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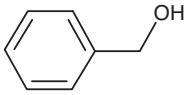
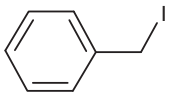
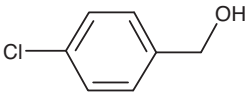
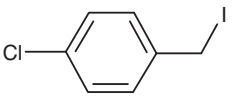
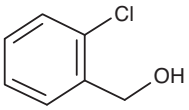
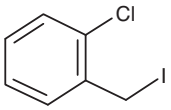
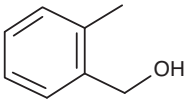
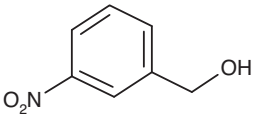
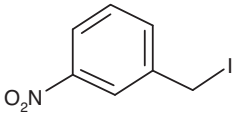
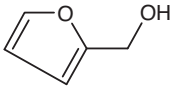
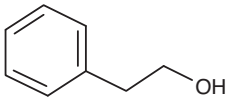
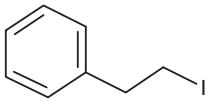
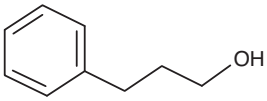
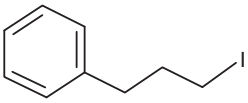
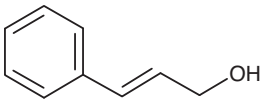
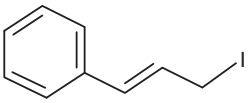
a			90
b			90
c			85
d		*ii*	-
e			80
f		*ii*	-
g			90
h			90
i			80

Table 1. Contunied.

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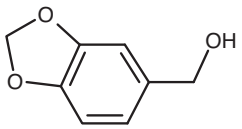
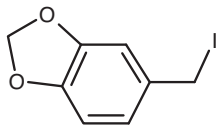
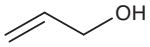
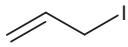
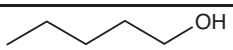
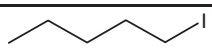
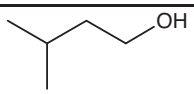
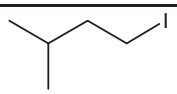
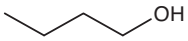
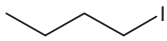
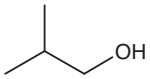
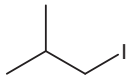
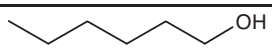
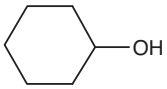
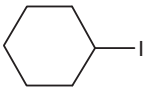
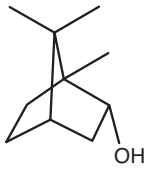
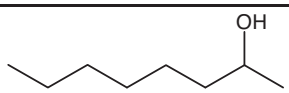
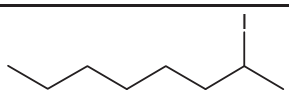
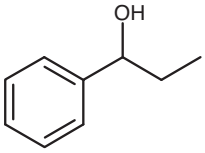
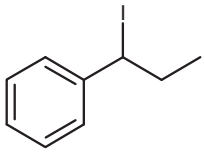
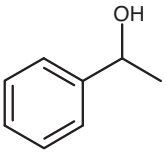
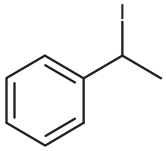
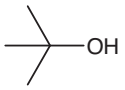
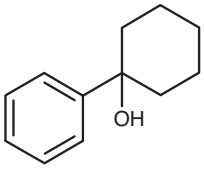
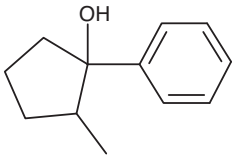
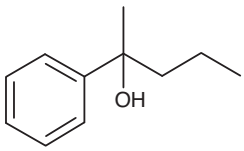
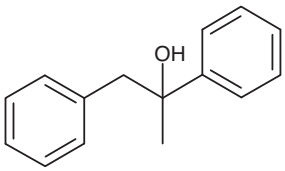
j			20
k			80
l			80
m			70
n			75
o			70
p			80
q			80
r		*ii*	-
s			85
t			80

Table 1. Contunied.

ROH (**3**)	ROH (structure)	RI (structure) (**5**)	Yield of **5** (%)[i]
u			70
v		*iii*	-
w		*iv*	-
x		*v*	-
y		*v*	-
z		*v*	-

[i] Yields are for pure isolated products of column chromatography. The yield of iodides **5a**, **k**, **l**, **m**, **n**, **o**, **p**, and **q** are based on Kugelrohr distillation (see Experimental section). [ii] No corresponding iodides were obtained. [iii] No *tert*-butyl iodide was obtained. [iv] 1-Phenylcyclohexene was obtained. [v] Results were obtained by stereo- and/or regioselective elimination reaction (see Results).

Table 2. Experimentally (δ_{exp}) and empirically calculated α-methylene carbon chemical shifts, and ICS values for some α-substituted and some primary alkyl iodides (from Table 1). The substituent α-effect (α_Y) is also shown.

Compound	Y	Alkyl iodides (**5**)				
		α_Y^i	δ_{exp}	δ_{calc}^{ii}	ICS	SCS
5a	Ph	23	5.99	14.5	−8.51	26.69
5b	4-Cl-Ph	21.0	4.18	12.5	−8.32	24.88
5c	2-Cl-Ph	23.2	2.33	14.7	−12.37	23.03
5e	3-NO_2-Ph	23.9	2.13	15.4	−13.27	22.82
5g	$PhCH_2$	18.1	5.71	9.6	−3.89	26.41
5h	$PhCH_2CH_2$	10.5	6.37	8.0	−1.63	27.07
5k	CH_2=CH	20	5.38	11.5	−6.12	26.08
5l	$CH_3(CH_2)_3$	16.3	7.03	7.8	−0.77	27.73
5m	$(CH_3)_2CHCH_2$	13.5	5.05	5.0	0.05	25.75
5p	$CH_3(CH_2)_4$	16.4	7.28	7.9	−0.62	27.98

[i]Calculation based on Refs.[40−42] [ii] Calculated by Eq. (1).

The ^{13}C-NMR spectra of all the obtained primary alkyl iodides show the iodine heavy atom effect on the α-methylene carbon chemical shift (Table 2). All experimentally and empirically calculated ^{13}C chemical shifts of the α-methylene carbon atoms of some primary alkyl iodides are summarized in Table 2. Table 2 shows results in increasing up field effects for α-methylene carbon atoms bonded to iodine atoms in primary alkyl iodides. In fact, the observed deviations for the α-methylene carbon are related to the iodine heavy atom effect.

For the empirical calculation of the ^{13}C-NMR chemical shift (δ_{calc}) of a disubstituted methylene carbon (Y–CH_2–I), the α-effect of I (α_I) and Y (α_Y) is added to the methane carbon chemical shift (-2.3), according to Eq. (1). The α-methylene carbon chemical shift depends on the effect of Y and iodine substituents in primary iodides; therefore, a simple prediction can be made by summing up both effects through the application of Eq. (1):[39]

$$\delta_{calc} = -2.3 + \sum nA \tag{1}$$

where δ is the predicted shift for a carbon atom, A is the additive shift parameter, and n is the number of carbon atoms for each shift parameter (-2.3 is the shift of the ^{13}C of methane). Yet, further work on ^{13}C-NMR chemical shifts of a disubstituted methylene or methine carbon have shown that they may deviate from additivity, and that this non-additivity is a powerful and sensitive tool for detecting any kind of intramolecular interaction due to the simultaneous presence of both substituents at the same carbon atom.[40,41] This non-additivity has been defined according to Eq. (2), and is referred to as intramolecular interaction chemical shift (ICS) by analogy to the well-established substituent-induced chemical shifts (SCS), as Eq. (3):[40]

$$ICS = \delta_{exp} - \delta_{calc} \tag{2}$$

$$SCS_\alpha = \delta_{exp}(Y - CH_2 - I) - \delta_{exp}(H - CH_2 - I) \tag{3}$$

In summary, a novel and convenient route was developed for the conversion of primary and secondary alcohols to their corresponding iodides (**5a-u**, except **3d** and **f,** and hindered bulky alcohol **3r**). Tertiary alcohols stereo- and/or regioselectively converted to their corresponding alkene(s) in the presence of bulky **2**. The iodine heavy atom effect was observed in the obtained primary alkyl iodides.

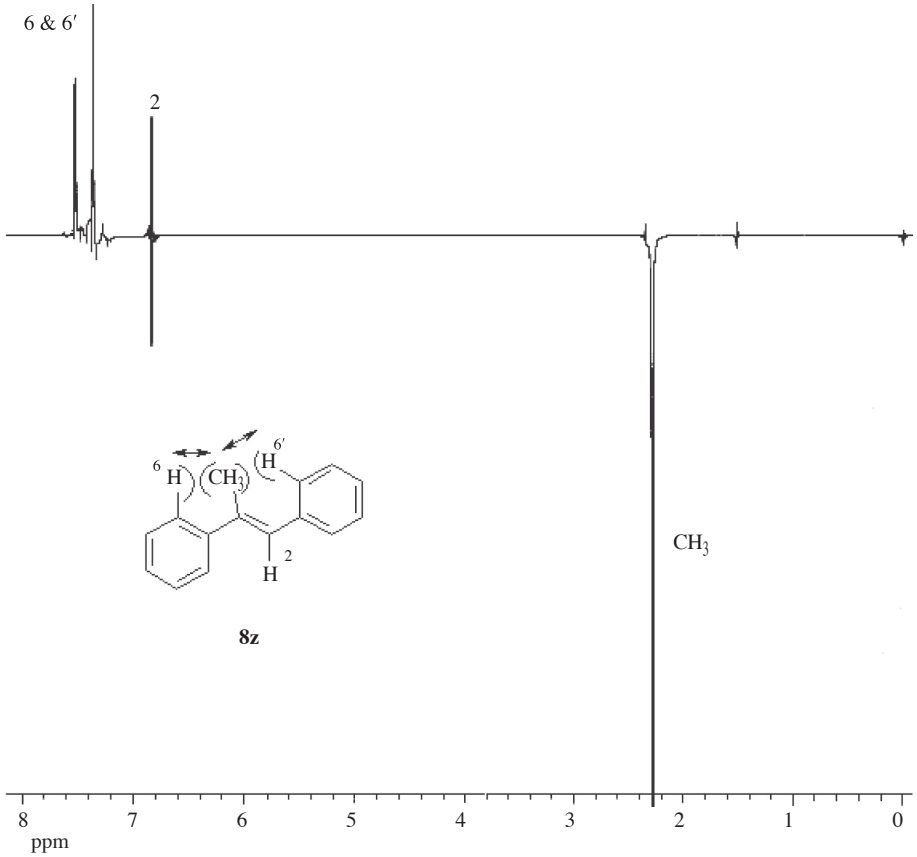


Figure 5. NOE difference spectrum of alkene **8z** in $CDCl_3$ at 400 MHz.

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