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Alkylation of Remote Non-activated δ-Carbon Atoms: Addition of δ-Carbon Radicals, Generated by 1,5-Hydrogen Transfer in Alkoxy Radical Intermediates, to Activated Olefins

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Abstract: *A free radical introduction of a functionalized alkyl chain onto remote non-activated δ-carbon atoms (Michael type alkylation) has been achieved. Photolysis of suitable alkyl nitrites involves generation of δ-alkyl radicals and in the presence of radicophilic olefins, intermolecular addition takes place and affords δ-alkylated products in 36-80% yields. δ-Alkylation is also achieved in the reaction of alkyl benzenesulfenates with tributyltin hydride (TBTH), in the presence of activated olefins and introduction of a functionalized alkyl chain involves alkoxy and δ-carbon radicals. Products with functionalized alkyl chains were obtained in 36-86% yields. δ-Alkylation of alkyl benzenesulfenates also occurs in the reaction with hexabutylditin in the presence of activated olefins.*

Sequential radical reactions are firmly established as a powerful tool for the synthesis of complex organic molecules.[1] Introduction of a functional group into remote non-activated carbon atoms is an especially prominent radical reaction applied to the functionalization of inaccessible angular methyl groups in steroid molecules and other natural products.[2] Diversity of reactions of this type offer several possibilities for the introduction of different functional groups onto non-activated carbon atoms. There are several known free radical reactions for the functionalization of remote non-activated carbon atoms such as photolysis of alkyl nitrites,[3] lead tetraacetate oxidation of saturated alcohols,[4] decomposition of alkyl hypoiodites[2a,c,e] and other related reactions involving alkoxy,[5] nitrogen[6] and other radical intermediates.[7] The key step in all of these reactions is 1,n-, preferably 1,5-hydrogen, transfer from a non-activated carbon atom to alkoxy radical and formation of the corresponding carbon radicals.[2,8] It was estimated that the rate constant is $k_{1,5\text{-H-shift}} = 8 \times 10^8$ for abstraction from a methylene group and one hundred times lower for hydrogen transfer from a methyl group.[9]

The fate of δ-carbon radicals, generated by 1,5-transposition of the radical centre, depends on the precursors of alkoxy radicals, the reagents used for their generation and the reaction conditions.[2-5,10] δ-Carbon radicals involved in the alkyl hypohalite decompositions preferably undergo halogen abstraction from alkyl hypohalites.[2,4,5] While in the Barton reaction a carbon radical is coupled with a nitroso radical thus forming δ-nitroso alcohols.[1f,2,3] In some of these reactions δ-carbon radicals were intercepted by ligand-transfer oxidations thus affording δ-substituted alcohols[10] or five-membered cyclic ethers (in the lead tetraacetate oxidations of alcohols).[2,4] However, by electron-transfer oxidations of

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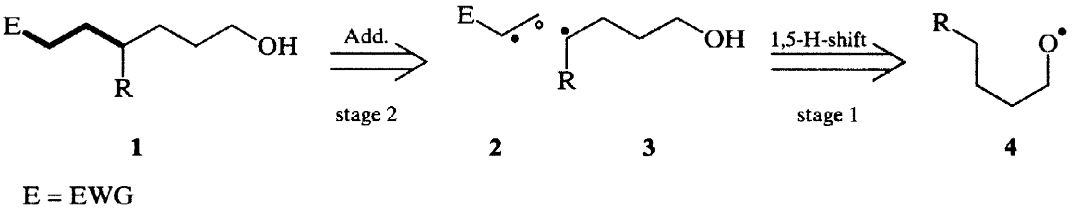
the intermediary carbon radical δ-unsaturated alcohols are formed.[10,12] Only in several cases, such as in Barton reactions, does interception of δ-carbon radicals, by intramolecular addition to the appropriately disposed olefinic bond, takes place and thus affords the corresponding cyclopentane derivatives.[13] On the other hand, δ-carbon radicals, formed by photolysis of alkyl nitrites, possessing a keto group on the appropriate position, undergo 3-*exo*-cyclization to give rearranged products.[14] δ-Alkyl radicals generated in the lead tetraacetate-iodine oxidation (hypoiodite reaction) of cyanohydrins, undergo 5-*exo*-cyclization to the cyano group to afford rearranged keto-cyanides.[2c,15] Interception of δ-alkyl radicals by carbon monoxide was observed in the lead tetraacetete oxidation of alcohols and lactones were obtained.[16]

In order to introduce a functionalized alkyl chain **1** onto remote non-activated carbon atoms we investigated the possibility of combining this methodology for generation of carbon radicals **3** (stage 1), remote from the functional group, with the well-known Giese intermolecular addition of carbon radicals **3** onto electron deficient olefinic bonds **2** (stage 2). By connecting them into one sequence, we would have one pot, radical reactions (Scheme 1).



Scheme 1.

We found that δ-alkyl radicals generated by Barton reactions are free enough to be intercepted by radicophilic olefins. Our preliminary results on this sequence of radical reactions involving δ-alkylation of non-activated carbon atoms and introduction of a functionalized alkyl chain have been reported.[17]

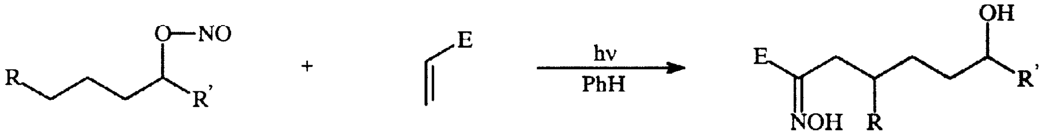
In order to achieve interception of δ-carbon radicals **3** by intermolecular addition to activated olefins **2** it was necessary to generate a really free radical and to apply reaction conditions which prevent other reactions (such as atom transfer or coupling). We found that δ-alkyl radicals, generated by photolysis of alkyl nitrites, could be quenched by radicophilic olefins, when an excess of the olefins is used to favour the addition reaction. In addition to Barton reactions, alkoxy radicals arise in the reaction of alkyl benzenesulfenates with tributyltin hydride, which undergo 1,5-hydrogen shift. These conditions also give free δ-alkyl radicals without a counterpart and could be quenched by activated olefins as Michael acceptors.[17]

The synthetic importance of this methodology is in the formation of C-C bonds with remote non-activated δ-carbon atoms and the introduction of functionalized alkyl chains. *The aim of our studies was to develop a new synthetic method for Michael type alkylation of non-activated carbon atoms remote from the original functional group and to introduce mono- and difunctional alkyl chains.*

A. δ-Alkylation of Alkyl Nitrites in the Presence of Activated Olefins

The photolysis of alkyl nitrites **5a-e**, **15**, **18** and **20** was carried out in dilute benzene solution (0.016 M or 0.2% solution) in the presence of 80 molar equivalents of activated olefins **6** (Scheme 2). A large excess of olefin **6** was used to favour intermolecular addition of the corresponding intermediary carbon radical of type **11** and to suppress coupling of δ-alkyl radicals with NO. Reactions were performed by irradiation of alkyl nitrites at room temperature in an inert atmosphere and were monitored by tlc.

Irradiation of *n*-pentyl nitrite (**5a**) in benzene solution, in the presence of acrylonitrile was completed after 3 hours, and 6-hydroxy-3-methyl-2-oximino-hexyl cyanide (**7a**) was obtained in 45% yield (Scheme 2). Lower concentrations of acrylonitrile decreased the yield of the δ-alkylated product **7** because of the competing coupling reaction of δ-alkyl radical with NO. Higher concentrations of activated olefins **6** did not improve the yields of δ-alkylated products. When methyl vinyl ketone (**6b**) and ethyl acrylate (**6c**) were used as radicophilic olefins modest yields of the corresponding alkylated products **7b** and **7c** were obtained. Secondary alkyl nitrites (entries **d** and **e**) were also successfully alkylated (Scheme 2). δ-Alkylation of secondary alkyl nitrites is not stereoselective and approximately 1 : 1 mixture of two diastereoisomers were obtained.



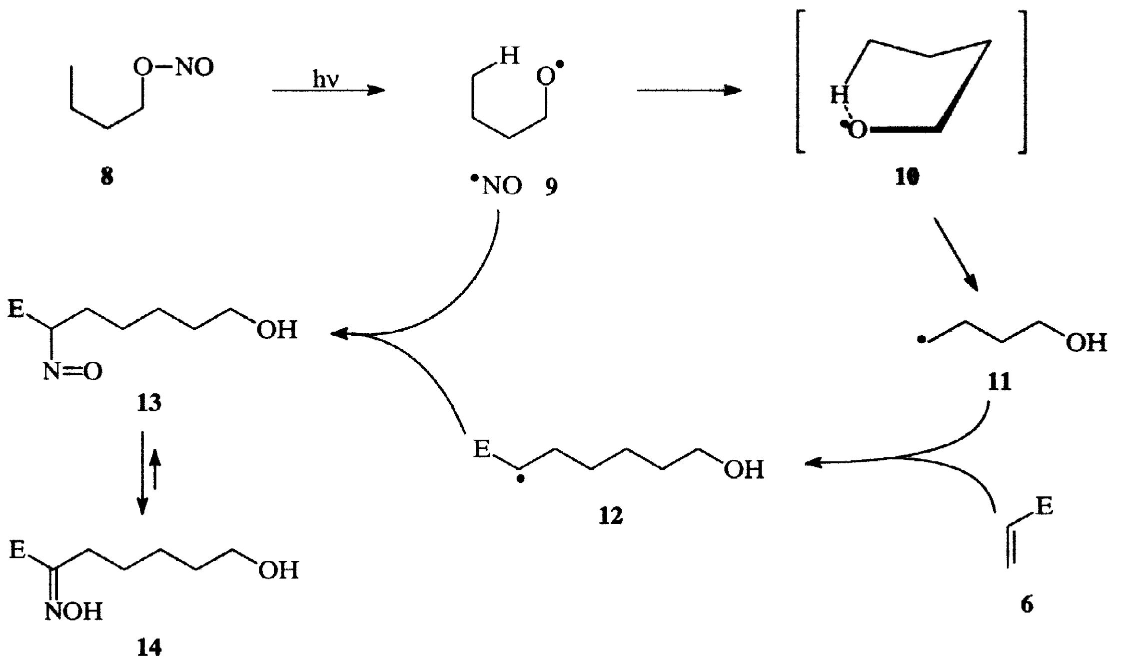
5 **6**[a] **7**[b]

	R	R'	E	Yield (%)[c]
a)	Me	H	CN	45
b)	Me	H	COMe	56
c)	Me	H	COOEt	55
d)	Me	Et	CN	80[d]
e)	Me	Et	COOEt	49[d]

a) Activated olefins were used in 80 molar equivalents.
b) Exists as a tautomeric mixture with predominantion of oxime form.
c) Isolated yields, (yields by GC-analysis were 10-20% higher).
d) A mixture of two diastereoisomers.

Scheme 2.

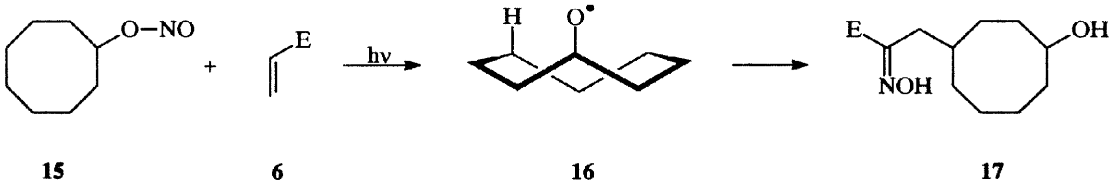
The mechanism is as follows. Alkoxy radical **9**, formed by photolytically induced cleavage of the O-N bond of alkyl nitrites **8**, undergoes intramolecular 1,5-hydrogen migration (*via* transition state **10**) by an *endo* S_H2 reaction transposing the radical centre to the δ-carbon atom **11** (Scheme 3).[2,3,8,18] By running reactions in dilute solutions of alkyl nitrites and in the presence of a high concentration of activated olefins **6**, the intermolecular addition of δ-alkyl radical **11** to the olefinic bond takes place forming an electrophilic carbon radical **12**. This is less reactive towards the electron deficient olefinic bond and preferentialy undergoes a coupling reaction with the NO radical, thus affording the alkylated nitroso compound **13**. When an 80 molar excess of activated olefins **6** is used, coupling of radical **11** with the NO radical does not occur. However, when lower concentrations of olefinic compounds are used a mixture of nitroso compounds is formed. These compounds possessing an electron withdrawing group attached to the same carbon atom easily tautomerise to give the oximino compounds **14** as final reaction products (Scheme 3).



Scheme 3.

In order to confirm our methodology for alkylation of non-activated carbon atoms δ-position, we applied it to other systems whose structure and stereochemistry permit intramolecular 1,5-transposition of alkoxy radicals to carbon radicals.

Cyclooctyloxy radical **16**, formed by irradiation of cyclooctyl nitrite **15**, undergoes to transannular reaction and the δ-carbon radical was quenched by radicophilic olefins **6** (acrylonitrile and methyl vinyl ketone) thus giving the corresponding δ-alkylated products **17a** and **17b** as essentially 1 : 1 mixture of *cis*- and *trans*-isomers (Scheme 4).



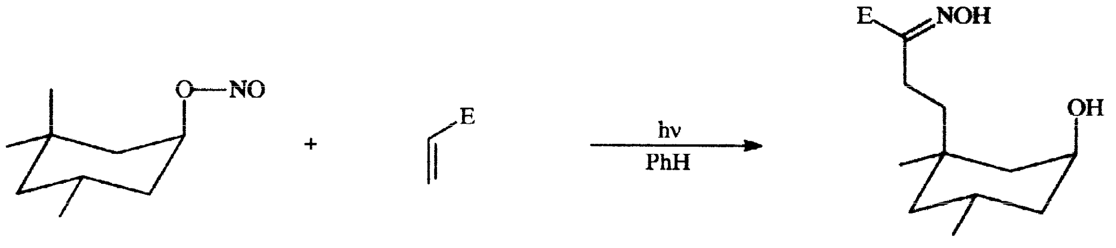
a) E = CN 43% (48 : 52)

b) E = COMe 36% (47 : 53)

Scheme 4.

Intramolecular abstraction of hydrogen by alkoxy radicals from non-activated methyl groups was also successfully achieved, especially when both of the reactive centres (alkoxy radical and carbon atom at δ-position) are fixed and possess the appropriate stereochemistry allowing chair-like conformation of the transition state **10**, necessary for 1,5-hydrogen transfer.

We found that by irradiation of 3,3,5-trimethylcyclohexyl nitrite (ONO axial) (**18**), in the presence of activated olefins **6**, Michael type alkylation of the stereochemically accessible (axial) methyl group takes place and the corresponding alkylated products **19a** and **19b** were obtained. Alkylated products, possessing a NO group at the carbon atom adjacent to an electron withdrawing group exist in a tautomeric oximino form **19** (Scheme 5). Nitroso compounds can also dimerise and nitroso-dimer was also formed as a reaction product.



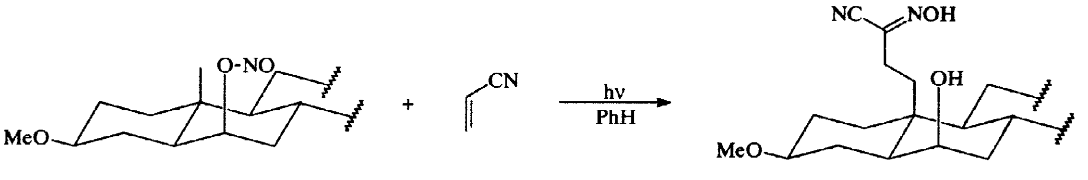
18 **6** **19**

a) E = CN 41%

b) E = COOEt 31%

Scheme 5.

This sequence of radical reactions was applied to steroid molecules, in order to introduce a functionalized alkyl chain onto an angular 19-methyl group. Thus by photolysis of 3-methoxy-6β-cholestanyl nitrite (**20**), in the presence of acrylonitrile, alkylation of the 19-methyl group occurs and nitroso compound **21** and its dimer were obtained. Since both of the reactive centres are in a 1,3-diaxial relationship the transposition of radical centre from the 6β-alkoxy to the 19-methyl group is favourable. The nitroso compound formed by intermoleculer addition and subsequent nitrosation is in an equilibrium with nitroso-dimer and oxime. The intermediary C_{19}-radical also reacts with NO radical to afford a dimer of the C_{19}-nitroso compound (15%). By refluxing of such a mixture, containing nitroso-dimers, with isopropyl alcohol, the dimers were converted into the oxime **21** (Scheme 6) and 19-hydroxyimino cholestane derivative.



20 **21**

22%

Scheme 6.

B. δ-Alkylation of Alkyl Benzenesulfenates by Activated Olefins

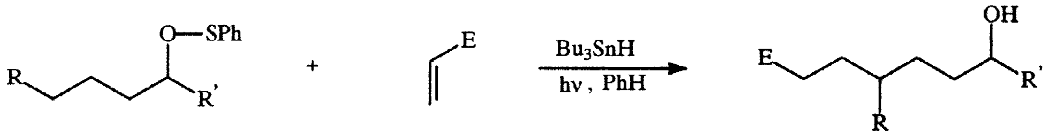
Beckwith[19] found that alkoxy radicals are generated in the reaction of alkyl benzenesulfenates with tributyltin hydride (TBTH) (Scheme 7). Alkoxy radicals undergo characteristic reactions

$$\mathrm{RO{-}SPh} \quad + \quad \mathrm{Bu_3Sn^\bullet} \quad \longrightarrow \quad \mathrm{RO^\bullet} \quad + \quad \mathrm{Bu_3Sn{-}SPh}$$

Scheme 7.

(hydrogen abstraction, fragmentation and addition).[19,20] As was pointed out in the δ-alkylation of alkyl nitrites, a large excess of activated olefins is required in order to prevent a coupling of the δ-alkyl radical with nitroso radical. By using alkyl benzenesulfenates as precursors of alkoxy radicals, we wanted to find conditions for decreasing the ratio of activated olefins to alkoxy radical precursor since in this case the δ-alkyl radical does not exist as a radical pair.

Alkyl benzenesulfenates **22** were prepared in good yield by reaction of the corresponding alcohols with benzenesulfenyl chloride in the presence of triethylamine.[20a,21] Alkylation of alkyl benzenesulfenates **22** was carried out by reductive reaction with TBTH in the presence of 10 molar equivalents of activated olefins (Michael acceptors).[17] The benzene solution was irradiated with a 125 W high pressure mercury lamp at room temperature. Thus, irradiation of *n*-pentyl benzenesulfenate (**22a**) and TBTH in the presence of acrylonitrile afforded 3-methyl-6-hydroxyhexyl cyanide (**23a**). δ-Alkylation of *n*-pentyl benzenesulfenate with ethyl acrylate, as activated olefin, give ethyl 4-methyl-7-hydroxyhexanoate (**23b**) (Scheme 8). Under the same experimental conditions 3-heptyl benzenesulfenate was successfully alkylated in the δ-position by acrylonitrile, ethyl acrylate and methyl vinyl ketone, and alkylated products **23c-e** were obtained (Scheme 8).



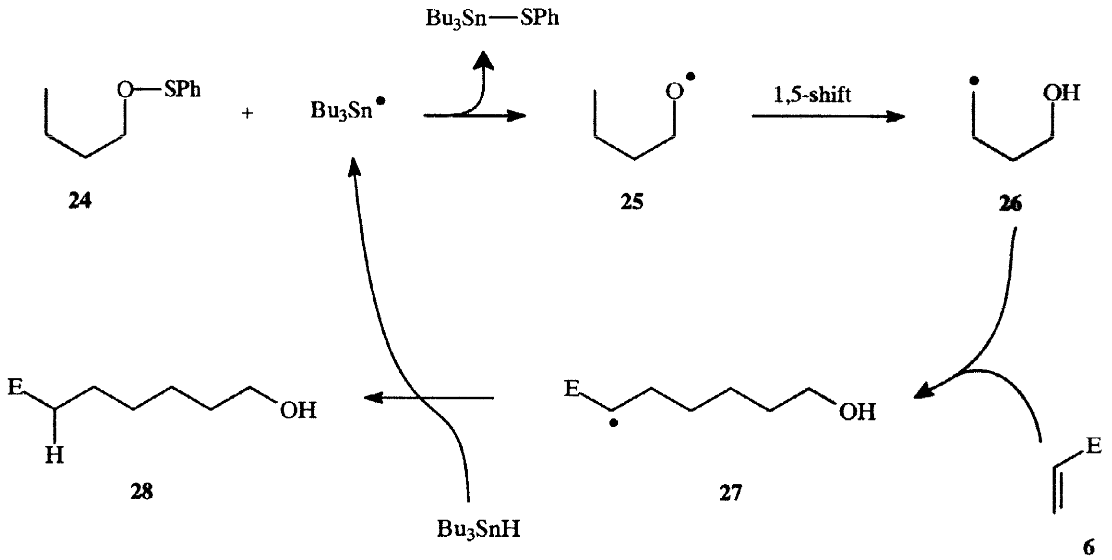
22 **6** [a] **23**

	R	R'	E	Yield (%) [b]
a)	Me	H	CN	32
b)	Me	H	COOEt	56
c)	Me	Et	CN	36 [c]
d)	Me	Et	COOEt	86 [c]
e)	Me	Et	COMe	37 [c]

a) Activated olefins were used in 10 molar equivalents.
b) Isolated yields, (yields by GC-analysis were 10-20% higher).
c) 1:1 mixture of two diastereoisomers.

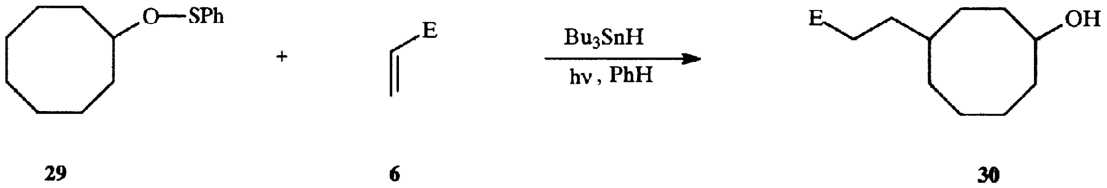
Scheme 8.

Alkyl benzenesulfenates **24** react with the thiophilic tributyltin radical to form alkoxy radicals **25** and the stable tributylthiophenyltin molecule. Alkoxy radicals generated in this way, possessing no radical counterpart, smoothly undergo a 1,5-hydrogen shift to produce δ-carbon radicals **26**. In the presence of activated olefins the δ-alkyl radicals undergo intermolecular addition to the activated olefins ($k_{add} = 3 \times 10^5\ M^{-1}s^{-1}$), rather than hydrogen atom transfer from tributyltin hydride. The intermediary radicals **27** are electrophilic species and undergo hydrogen abstraction from TBTH to give δ-alkylated products **28** and tributyltin radical (Scheme 9).



Scheme 9.

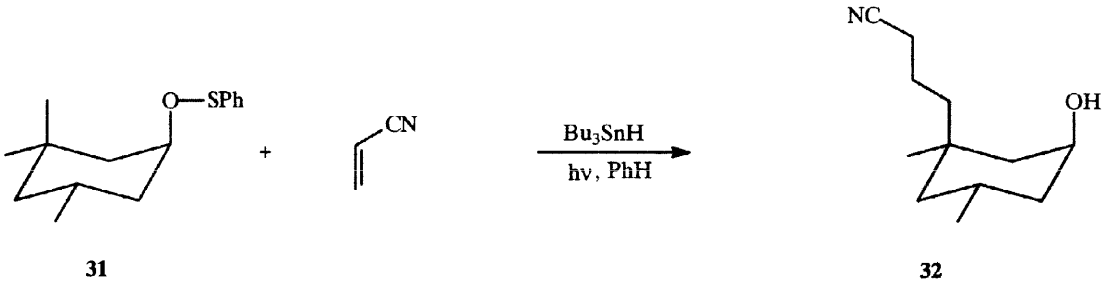
Cyclooctyl benzenesulfenate (**29**) was also alkylated in the 4-position by activated olefins (acrylonitrile and ethyl acrylate) under the same reaction conditions. Transannular hydrogen transfer occurs and in the subsequent addition reaction, δ-alkylated products **30a** and **30b** were obtained as a mixture of essentially equal amounts of *cis-* and *trans*-isomers (Scheme 10).



a)	E = CN	28% (1:1)
b)	E = COOEt	33% (1:1)

Scheme 10.

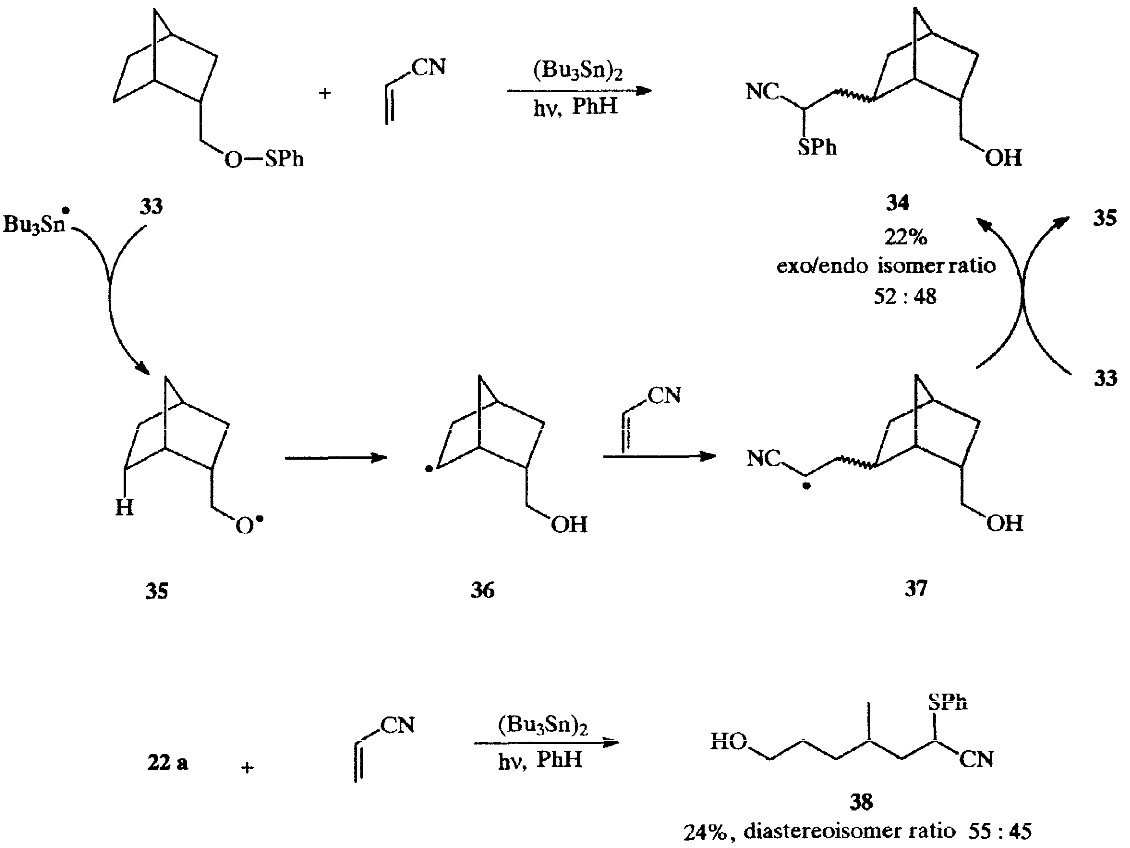
Alkyl benzenesulfenates possessing both reactive centres with fixed conformation were also successfully alkylated. For example, 3,3,5-trimethylcyclohexyl benzenesulfenate (O-SPh axial) (**31**) was alkylated by acrylonitrile at the axial methyl group and **32** was obtained (Scheme 11).



34%

Scheme 11.

Alkylation of remote non-activated carbon atoms was also achieved in the reaction of alkyl benzenesulfenate 33 with 4 molar equivalents of activated olefins in the presence of hexabutylditin. Thus by irradiation of norbornylmethyl benzenesulfenate 33 and acrylonitrile, in the presence of hexabutylditin a remote Michael type alkylation occurs and 2-(5-hydroxymethyl-2-norbornyl)-1-phenylthio-ethyl cyanide (34) was obtained as the main reaction product. Under the same conditions *n*-pentyl benzenesulfenate (22a) reacts with acrylonitrile in the presence of hexabutylditin to give δ-alkylated product 38 (Scheme 12). In this alkylation of the remote carbon atom the sequence of radical reactions (33 → 35 → 36 → 37) is terminated by intermolecular phenylthio group transfer, from the starting alkyl benzenesulfenates to the intermediary carbon radical 37 (Scheme 12).[17b] In this reaction,



Scheme 12.

an alkyl radical 36, generated by 1,5-hydrogen transfer, undergoes in the presence of acrylonitrile intermolecular addition to the olefinic bond rather than a phenylthio group transfer reaction involving starting compound 33. However, radical 37 is more electrophilic than alkyl radical 36, and since species 37 is more thiophilic, it participates in the intermolecular phenylthio group transfer to afford final reaction product 34.

The present results demonstrate a convenient method for the introduction of a functionalized alkyl chain at remote non-activated carbon atoms, especially at inaccessible angular methyl groups. This methodology offers the opportunity to introduce two carbon chains bearing different electron withdrawing groups with or without an oximino group.

EXPERIMENTAL

Solvents used in all of the experiments were distilled over calcium hydride. Purifications and separations of the reaction products were carried out by column chromatography using silica gel 70-200 mesh. IR spectra (ν_{max} in cm^{-1}) were recorded on Perkin-Elmer 457 grating instrument. ^{1} H-NMR spectra (ppm in δ-values) were run (in CDCl$_3$ if not otherwise stated) at 200 MHz, using Varian 200 at 200 MHz spectrometer. ^{13} C-NMR spectra were recorded on the same instrument at 50 MHz. Mass spectra were performed on Finningan ITDS 700 instrument.

δ-Alkylation of Alkyl Nitrites 5a-e, 15, 18 and 20 by Photolysis in the Presence of Radicophilic Olefins

Alkyl nitrites were prepared by introduction of nitrosyl chloride into the solution of alcohols in pyridine at -20 °C.[2d] *n*-Pentyl nitrite was prepared by reaction of *n*-pentanol with a saturated aqueous solution of sodium nitrite and 50% sulfuric acid.[22]

Photolytical δ-alkylation of alkyl nitrites in the presence of radicophilic olefins. General procedure.
A solution of alkyl nitrite (3 mmol) and 80 molar equivalents of an electron deficient olefin (0.24 mol) in dry benzene (200 ml) was irradiated at r.t., in an argon atmosphere, by a 125 W high pressure mercury lamp during 3 h. The solvent was evaporated under reduced pressure and the reaction products were separated by chromatography on silica gel column (using benzene/ethyl acetate = 1 : 1 as eluent).

δ-Alkylation of n-pentyl nitrite (5a) with acrylonitrile. A solution of 0.351 g (3 mmol) of *n*-pentyl nitrite and 12.7 g (0.24 mol; 80 molar equivalent excess) of acrylonitrile in 200 ml of dry benzene was irradiated during 3 h. Benzene was removed by evaporation and the oily residue was separated by chromatography on silica gel (using benzene/ethyl acetate = 1 : 1 as eluent) to give 0.18 g (45% yield) of 1-oximino-3-methyl-6-hydroxyhexyl cyanide (**7a**) as a colourless oil. IR (neat, cm^{-1}): 3259, 2230, 1708, 1664, 1462, 1377, 1277, 1047; ^{1}H-NMR (200 MHz) δ: 1.00 (d, 3H, J = 6.7 Hz), 1.25-1.80 (m, 4H), 1.98 (m, 1H), 2.38 (dd, 1H, J_{gem} = 14.5 Hz, J_{vic} = 7.7 Hz, CHCH$_A$H$_B$), 2.55 (dd, 1H, J_{gem} = 14.5 Hz, J_{vic} = 6.7 Hz, CHCH$_A$H$_B$), 3.68 (t, 2H, J = 6.3 Hz), 10-10.5 (broad s, 1H); ^{13}C-NMR (50 MHz) δ: (139.61, 115.24) C, (63.09, 34.44, 32.60) CH$_2$, 30.79 CH, 29.71 CH$_2$,19.67 CH$_3$; MS: 171 (M+1).

1-Oximino-3-methyl-6-hydroxyhexyl cyanide (**7a**) was acetylated using acetic anhydride and 1-acetoximino-3-methyl-6-acetoxyhexyl cyanide was isolated as a colourless oil by column chromatography using petrolether/ethyl acetate 9 : 1 as eluent. IR (neat, cm^{-1}): 2228, 1736, 1713, 1458, 1435, 1387, 1367, 1249, 1006; ^{1}H-NMR (200 MHz) δ: 1.02 (d, 3H, J = 6.6 Hz), 1.25-1.55 (m, 2H), 1.70 (m, 2H), 2.00 (m, 1H), 2.06 (s, 3H), 2.28 (s, 3H), 2.58 (m, 2H), 4.07 (t, 2H, J = 6.5 Hz); ^{13}C-NMR (50 MHz) δ: (171.14, 166.63, 145.84, 113.15) C, (64.08, 36.65, 32.74) CH$_2$, (30.89) CH, (25.89) CH$_2$, (20.92, 19.31, 19.23) CH$_3$; MS: 255 (M+1).

δ-Alkylation of n-pentyl nitrite (5a) with methyl vinyl ketone. A solution of 0.351 g (3 mmol) of *n*-pentyl nitrite, 16.8 g (0.24 mol) of methyl vinyl ketone in 200 ml of benzene was irradiated by the standard procedure and 5-methyl-3-oximino-8-hydroxyoctan-2-one (**7b**) was obtained as a colourless liquid (0.31 g, 56% yield). IR (neat, cm^{-1}): 3283, 1690, 1456, 1425, 1382, 1366, 1123, 1071; ^{1}H-NMR (200 MHz) δ: 0.90 (d, 3H, J = 6.7 Hz), 1.30 (m, 2H), 1.60, (m, 2H), 1.86 (m, 1H), 2.36 (s, 3H), 2.41 (dd, 1H, J_{gem} = 12.3 Hz, J_{vic} = 6.5 Hz, CHCH$_A$H$_B$), 2.51 (dd, 1H, J_{gem} = 12.3 Hz, J_{vic} = 8.1 Hz, CHCH$_A$H$_B$), 2.86 (s, 1H), 3.64 (t, 2H, J = 6.6 Hz), 10.35 (broad s, 1H); ^{13}C-NMR (50 MHz) δ: (198.22, 159.36) C, (63.04, 32.97) CH$_2$, 30.56 CH, (29,68, 29.27) CH$_2$ (25.21, 19.71) CH$_3$; MS: 188 (M+1).

δ-Alkylation of n-pentyl nitrite (5a) with ethyl acrylate. Reaction was performed with 0.351 g (3 mmol) of *n*-pentyl nitrite and 24.0 g (0.24 mol) of ethyl acrylate in 200 ml of benzene. It was isolated 0.36 g (55% yield) of colourless liquid of ethyl 2-oximino-4-methyl-7-hydroxy octanoate (**7c**). IR (neat,

cm^{-1}): 3305, 1732, 1653, 1463, 1383, 1308, 1183, 1152, 1017; ^1H-NMR (200 MHz) δ: 0.90 (d, 3H, J = 6.7 Hz), 1.20-1.50 (m, 2H), 1.35 (t, 3H, J = 7.1 Hz), 1.60 (m, 2H), 2.00 (m, 1H), 2.51 (dd, 1H, J_{gem} = 12.6 Hz, J_{vic} = 6.4 Hz, $CHCH_AH_B$), 2.65 (dd, 1H, J_{gem} = 12.6 Hz, J_{vic} = 8.1 Hz, $CHCH_AH_B$), 3.63 (t, 2H, J = 6.6 Hz), 4.29 (q, 2H, J = 7.2 Hz), 10.20-11.20 (broad s, 1H); ^{13}C-NMR (50 MHz) δ: (163.97, 152,39) C, (62.92, 61.69, 32.97, 31.61) CH_2, 30.89 CH, 29.78 CH_2, (19.76, 14.01) CH_3. MS: 218 (M + 1), 200.

Photolysis of 3-heptyl nitrite in the presence of an activated olefins.

δ-Alkylation of 3-heptyl nitrite (5d) with acrylonitrile. A solution of 0.435 g (3 mmol) of 3-heptyl nitrite and 12.7 g (0.24 mol) of acrylonitrile in 200 ml of benzene was irradiated during 3 h. The solvent was evaporated and the oily residue was purified by column chromatography on silica gel (using benzene/ethyl acetate = 1 : 1 as eluent). Pure 1-oximino-3-methyl-6-hydroxyoctyl cyanide (**7d**) was isolated as a pale yellow oil in 80% yield (0.475 g) (48 : 52 ratio of two diastereoisomers determined by ^{13}C NMR). IR (neat, cm^{-1}): 3247, 2229, 1712, 1461, 1383, 1261, 1016; ^1H-NMR (200 MHz) δ: 0.96 (t, 3H, J = 7.5 Hz), 0.98 (d, 3H, J = 6.6 Hz), 1.25-1.70 (m, 6H), 1.95 (m, 1H), 2.40 (dd, 1H, J_{gem} = 14.4 Hz, J_{vic} = 3.6 Hz, $CHCH_AH_B$), 2.52 (dd, 1H, J_{gem} = 14.4 Hz, J_{vic} = 7.9 Hz, $CHCH_AH_B$), 3.58 (m, 1H), 10.60 (broad s, 1H); ^{13}C-NMR (50 MHz) δ: (132.28, 110.58) C, (73.99, 73.48) CH, (38.72, 38.53, 33.60, 33.23, 31.93, 31.48) CH_2 , (31.13, 30.47) CH, (29.99, 29.10) CH_2, (19.33, 19.12, 9.87, 9.78) CH_3; MS: 185 (M+1).

δ-Alkylation of 3-heptyl nitrite (5e) with ethyl acrylate. Reaction was performed with 4.35 g (3 mmol) of 3-heptyl nitrite and 24.0 g (0.24 mol) of ethyl acrylate in benzene solution (200 ml). It was obtained 0.36 g (49% yield) of ethyl 2-oximino-4-methyl-7-hydroxynonanoate as a pale yellow oil (**7e**, as a mixture of diastereoisomers, 45 : 55 determined by ^{13}C NMR). IR (neat, cm^{-1}): 3386, 1733, 1462, 1300, 1260, 1186, 1132, 1027; ^1H-NMR (200 MHz) δ: 0.87 (d, 3H, J = 6.6 Hz), 0.90 (t, 3H, J = 7.2 Hz), 1.25-1.55 (m 6H), 1.30 (t, 3H, J = 7.1 Hz), 1.90 (m, 1H), 2.48 (dd, 1H, J_{gem} = 12.7 Hz, J_{vic} = 6.5 Hz, $CHCH_AH_B$), 2.61 (dd, 1H, J_{gem} = 12.7 Hz, J_{vic} = 8.1 Hz $CHCH_AH_B$), 3.50 (m, 1H), 4.25 (q, 2H, J = 5.7 Hz), 10.70 (broad s, 1H); ^{13}C-NMR (50 MHz) δ: (163.99, 163.97, 152.29) C, (73.45, 73.45) CH, (61.58, 33.83, 33.79, 32.87, 32.82, 31.62, 31.48) CH_2, (31.11, 31.06) CH, (29.94, 29.77) CH_2 , (19.78, 19.64,13.97, 9.88, 9.74) CH_3. MS: 246 (M + 1), 228. Anal. Calcd. $C_{12}H_{23}NO_4$: C, 58.77; H, 9.38; N, 5.71; Found: C, 58.61; H, 9.01; N, 5.90.

Photolysis of cyclooctyl nitrite (15) in the presence of an activated olefins.

δ-Alkylation of cyclooctyl nitrite (15) with acrylonitrile. A solution of 0.47 g (3 mmol) of cyclooctyl nitrite and 12.7 g (0.24 mol) of acrylonitrile in 200 ml of benzene was irradiated during 3 h, and by chromatography on silica gel column (using benzene/ethyl acetate = 1 : 1 as eluent) it was isolated 0.25 g (43%) of 2-(4-hydroxycyclooctyl)-1-oximinoethyl cyanide as a oil (**17a**, 48 : 52 mixture of two diastereoisomers determined by ^{13}C NMR). IR (neat, cm^{-1}): 3286, 2230, 1624; ^1H-NMR (200 MHz) δ: 1.30-2.15 (m, 13H), 2.50 (m, 2H), 3.92 (m, 1H), 10.92 (broad s, 1H); ^{13}C-NMR (50 MHz) δ: 132.61, 110.52, 72.68, 39.27, 35.56, 34.36, 32.64, 30.16, 27.41, 25.24, 23.15; MS: 211 (M+1).

δ-Alkylation of cyclooctyl nitrite (15) with methyl vinyl ketone. Reaction was performed with 0.47 g (3 mmol) of cyclooctyl nitrite and 16.8 g (0.24 mol) of methyl vinyl ketone in benzene (200 ml). After separation of the reaction mixture 0.245 g (36%) of pale yellow oil of 1-(4-hydroxycyclooctyl)-2-oximinobutan-3-on 17b was isolated as a mixture of two diastereoisomers (47 : 53, determined by ^{13}C NMR). IR (neat, cm^{-1}): 3273, 1681; ^1H-NMR (200 MHz) δ: 1.30-2.30 (m, 13H), 2.38 (s, 3H), 2.48 (m, 2H), 3.88 (m, 1H), 9.10-9.80 (s, 1H); ^{13}C-NMR (50 MHz) δ; 198.00, 159.29, 72.66, 35.85, 33.92, 32.93, 29.96, 27.74, 25.26, 25.20, 23.03, 21.26. MS: 228 (M + 1), 210. Anal. Calcd. $C_{12}H_{21}NO_3$: C, 63.43; H, 9.25; N, 6.16; Found: C, 63.35; H, 9.18; N, 6.36.

Photolysis of 3,3,5-trimethylcyclohexyl nitrite (ONO axial) (18) in the presence of radicophilic olefins.

δ-Alkylation of 3,3,5-trimethylcyclohexyl nitrite (ONO axial) (18) with acrylonitrile. By photolysis of 0.51 g (3 mmol) of 3,3,5-trimethylcyclohexyl nitrite in the presence of 12.7 g (0.24 mol) of acrylonitrile in 200 ml of benzene, according to the general procedure (3 h, r.t.) it was isolated 0.275 g (41% yield) of oily *t*-3,*t*-5-dimethyl-*c*-3-(3-oximino-3-cyanopropyl)-*r*-1-cyclohexanol (**19a**). IR (neat, cm^{-1}): 3338, 2229, 1710, 1631, 1457, 1379, 1251, 1181,1083, 1012; ^{1}H-NMR (200 MHz) δ: 0.88 (s, 3H), 0.89 (d, 3H, J = 5.1 Hz), 1.00-2.10 (m, 9H), 2.30-2.60 (m, 2H), 4.20 (m, 1H); ^{13}C-NMR (50 MHz) δ: (134.36, 110.58,) C, 68.23 CH, (47.37, 41.35, 40.96, 35.56, 32.97) CH$_2$, 29.80 CH, 27.48, CH$_2$, (22.44, 22.13) CH$_3$. MS: 225 (M + 1), 207.

*δ-Alkylation of 3,3,5-trimethylcyclohexyl nitrite (ONO axial) (**18**) with ethyl acrylate.* 3,3,5-Trimethylcyclohexyl nitrite (0.51 g, 3 mmol) was reacted with ethyl acrylate (24.0 g, 0.24 mol) using general procedure (benzene as a solvent, r.t. irradiation) to give *t*-3,*t*-5-dimethyl-*c*-3-(3-carberthoxy-3-oximinopropyl)-*r*-1-cyclohexanol 19b (0.25 g, 31% yield) as a pale yellow oil. IR (neat, cm^{-1}): 3295, 1723, 1457, 1376, 1304, 1194, 1154, 1099, 1017; ^{1}H-NMR (200 MHz) δ: 0.86 (d, 3H, J = 5.2 Hz), 0.89 (s, 3H), 1.20-2.05 (m, 9H), 1.34 (t, 3H, J = 5.7 Hz), 2.58 (m, 2H), 4.18 (m, 1H), 4.30 q, 2H, J = 5.7 Hz), 10.50 (broad s, 1H); ^{13}C-NMR (50 MHz) δ: 164.01, 153.77, 67.77, 61.67, 48.10, 41.00, 40.74, 34.67, 33.30, 29.50, 22.45, 22.09, 20.08, 13.98. MS: 272 (M + 1), 254. Anal. Calcd. $C_{14}H_{25}NO_4$: C, 61.76; H, 9.19; N, 5.14; Found: C, 61.70; H, 9.31; N, 5.08.

*Photolysis of 3-methoxy-6β-cholestanyl nitrite (**20**) in the presence of acrylonitrile.* A solution of 0.894 g (2 mmol) of 3-methoxy-6β-cholestanyl nitrite and 8.48 g (0.16 mol) of acylonitrile was irradiated according to the general procedure. The crude reaction mixture was refluxed with isopropyl alcohol and 0.22 g (22%) of 3-methoxy-6β-hydroxy-19-(2-oximino-cyanoethyl)-cholestane and 3-methoxy-6β-hydroxy-19-hydroxyimino-cholestane 0.14 g (15%) were isolated as a pale yellow oils (which crystalize after standing for several days). Compound **21** has following spectral evidences: IR (KBr, cm^{-1}): 3349, 2229, 1626, 1467, 1381, 1261; ^{1}H-NMR (200 MHz) δ: 0.80 (s, 3H), 0.90 (m, 9H), 1.00-2.30 (m, 31H), 2.54 (m, 2H), 3.30 (m, 1H), 3.42 (s, 3H), 3.85 (m, 1H), 10.60 (s, =NOH); ^{13}C-NMR (50 MHz) δ: 140.21, 115.38, 80.09, 72.23, 56.69, 56.12, 55.70, 53.80, 48.71, 42.64, 40.44, 39.71, 39.50, 38.07, 36.12, 35.74, 34.26, 33.33, 32.12, 30.56, 29.69, 28.69, 28.15, 27.99, 25.19, 24.18, 23.79, 22.80, 22.55, 18.64, 12.18. MS: 501 (M + 1), 483. Anal. Calcd. $C_{31}H_{52}N_2O_3$: C, 74.40; H, 10.40; N, 5.60; Found: C, 74.21; H, 10.52; N, 5.58. 3-Methoxy-6β-hydroxy-19-hydroxyimino-cholestane: IR (KBr, cm^{-1}): 3290, 1636, 1468, 1374, 1083, 1011; ^{1}H-NMR (200 MHz) δ: 0.60 (s, 3H), 0.86 (d, 6H, J = 6.4 Hz), 0.89 (d, 3H, J = 6.2 Hz), 0.95-2.30 (m, 29H), 3.20-3.33 (m, 1H), 3.32 (s, 3H), 3.76 (m, 1H), 7.10 (m, 1H), 7.23 (s, 1H), 10.98 (s, 1H); ^{13}C-NMR (50 MHz) δ: 154.23, 79.75, 69.72, 56.15, 55.32, 53.17, 46.19, 44.25, 42.30, 40.33, 39.73, 39.42, 36.07, 35.69, 31.43, 30.08, 28.99, 27.93, 24.18, 23.75, 22.73, 22.51, 21.58, 18.68, 11.84. It was observed that irradiation of starting compound **20** by an old UV-lamp give higher yields of compound **21**, however with a new lamp yield was decreased and increased the yield of C_{19}-hydroxyimino cholestane derivative.

δ-Alkylation of Alkyl Benzenesulfenates 22a-e, 29 and 31 by Reduuction with Bu_3SnH (TBTH) in the Presence of Radicophilic Olefins

Alkyl benzenesulfenates **22a-e**, **29** and **31** were prepared by reaction of benzenesulfenyl chloride with alcohols in anhydrous methylene chloride and in the presence of triethyl amine under argon atmosphere at -40 °C.[20,21] The colourless solution was washed successively with water, diluted hydrochloric acid and brine, dried (anh. Na_2SO_4) and the solvent was evaporated *in vacuo.* The oily residue, containing a crude alkyl benzenesulfenates were purified by distillation at reduced pressure (lower molecular weight) or by chromatograpgy on silica gel column.

Benzenesulfenyl chloride was prepared by chlorination of thiophenol with sulfuryl chloride in the presence of triethyl amine, in pentane solution and under argon atmosphere.[23]

Reaction of alkyl benzenesulfenates with TBTH in the presence of radicophilic olefins. General procedure. A solution of alkyl benzenesulfenates **22a-e**, **29**, and **31** (2.24 mmol), 22.4 mmol (10 molar equivalents) of a radicophilic olefins (Michael acceptors) and 2.5 mmol of TBTH in 200 ml of benzene was irradiated at r.t. by a 125 W high pressure mercury lamp for 2 h in an argon atmosphere. The course of reactions were monitored by TLC. Benzene was removed by evaporation, the residue was dissolved in ether, washed with aqueous saturated sodium fluoride solution (in order to remove tin compounds) and dried over anh. Na_2SO_4. Ether was evaporated and the reaction products were separated by chromatography on silica gel column (using benzene/ethyl acetaete = 7 : 3 as eluent).

*δ-Alkylation of n-pentyl benzenesulfenate **22a** with acrylonitrile in the presence of TBTH.* A solution of 0.44 g (2.24 mmol) of n-pentyl benzenesulfenate, 1.20 g (2.24 mmol) of acrylonitrile and 0.65 g (2.24 mmol) of TBTH in 220 ml of benzene was irradiated during 2 h. The crude reaction mixture was separated by column chromatography and afforded 0.10 g (32% yield) of oily 3-methyl-6-hydroxyhexyl cyanide **23a**. IR (neat, cm^{-1}): 3403, 2247; ^{1}H-NMR (200 MHz) δ: 0.94 (d, 3H, J = 6.3 Hz), 1.25-1.80 (m, 7H), 2.25-2.47 (m, 2H), 3.65 (t, 2H, J = 6.4 Hz); ^{13}C-NMR (50 MHz) δ: 119.93 C, (62.81, 32.14, 32.08) CH_2, 31.77, CH, 29.79 CH_2, 18.69 CH_3, 14.86 CH_2. MS: 142 (M + 1), 124.

*δ-Alkylation of n-pentyl benzenesulfenate **22b** with ethyl acrylate in the presence of TBTH. n*-Pentyl benzenesulfenate (0.54 g, 2.75 mmol) was reacted with 0.80 g (2.75 mmol) of TBTH in the presence of 2.75 g (27.5 mmol) of ethyl acrylate using the general procedure. By purification of crude oil on silica gel column it was isolated 0.29 g (56% yield) of ethyl 4-methyl-7-hydroxyheptanoate (23b) as a colourless liquid. IR (neat, cm^{-1}): 3408, 1736, 1262, 1184; ^{1}H-NMR (200 MHz) δ: 0.90 (d, 3H, J = 6.2 Hz), 1.26 (t, 3H, J = 7.2 Hz), 1.10 -1.80 (m, 7H), 2.20-2.40 (m, 2H), 3.63 (t, 2H, J = 6.6 Hz), 4.13 (q, 2H, J = 7.2 Hz); ^{13}C-NMR (50 MHz) δ: 174.11, 63.09, 60.21, 32.50, 32.12, 32.01, 31.72, 30.05, 19.16, 14.15; MS: 189 (M+1) 100%.

*δ-Alkylation of 3-heptyl benzenesulfenate (**22c**) with activated olefins*

*δ-Alkylation of 3-heptyl benzenesulfenate (**22c**) with acrylonitrile.* 3-Heptyl benzenesulfenate (0.62 g, 2.75 mmol) and 1.46 g (27.5 mmol) of acrylonitrile was dissolved in 220 ml of benzene and 0.80 g (2.75 mmol) of TBTH was added. The reaction mixture was irradiated during 2 h. 3-Methyl-6-hydroxyoctyl cyanide (**23c**) was isolated as a colourless liquid (0.17 g, 37% yield) (1 : 1 ratio of two diastereoisomers determined by ^{13}C NMR). IR (neat, cm^{-1}): 3436, 2247, 1462, 1427, 1382, 974; ^{1}H-NMR (200 MHz) δ: 0.92 (d, 3H, J = 1.4 Hz), 0.94 (t, 3H, J = 7.4) Hz), 1.10-1.80 (m, 9H), 2.24-2.50 (m, 2H), 3.40-3.60) (m, 1H); ^{13}C-NMR (50 MHz) δ: 119.91, 73.23, 73.07, 33.89, 33.72, 32.10, 32.03, 31.85, 30.15, 30.05, 18.74, 18.61, 14.77, 9.78, 9.73; MS: 170 (M+1) 37%, 152 [(M+1) - H_2O] 100%.

*δ-Alkylation of 3-heptyl benzenesulfenate (**22d**) with ethyl acrylate.* Irradiation of a solution of 0.62 g (2.75 mmol) of 3-heptyl benzenesulfenate, 2.75 g (27.5 mmol) of ethyl acrylate and 0.80 g (2.75 mmol) of TBTH in benzene (220 ml) for 2 h provided 0.52 g (86% yield) of colourless liquid of ethyl 3-methyl-6-hydroxynonanoate (**23d**, as a mixture of diastereoisomers, 1 : 1 determined by ^{13}C NMR). IR (neat, cm^{-1}): 3452, 1735, 1462, 1378, 1256; ^{1}H-NMR (200 MHz) δ: 0.89 (d, 3H, J = 4.6 Hz) 0.94 (t, 3H, J = 7.2 Hz), 1.25 (t, 3H, J = 7.2 Hz), 1.10-1.80 (m, 9H), 2.20-2.40 (m, 2H), 3.40-3.60 (m, 1H) 4.12 (q, 2H, J = 7.2 Hz); ^{13}C-NMR (50 MHz) δ: 174.00, 73.21, 73.07, 60.05, 34.00, 33.94, 32.32, 32.23, 31.88, 31.68, 31.54, 29.97, 29.86, 19.12, 19.03, 14.00, 9.71, 9.67; MS: 217 (M+1) 70%, 199 [(M + 1) - H_2O] 100%.

*δ-Alkylation of 3-heptyl benzenesulfenate with (**22e**) ethyl vinyl ketone.* A solution of 0.62 g (2.75 mmol) of 3-heptyl benzenesulfenate, 1.93 g (27.5 mmol) of methyl vinyl ketone and 0.80 g ((2.75 mmol) of TBTH in 220 ml of benzene was irradiated in an argon atmosphere for 2 h. The solvent was evaporated and the residual oil was separated on silica gel column (using benzene/ethyl acetate = 9 : 1 as eluent). 5-Methyl-8-hydroxydecan-2-on (**23e**) was isolated as a liquid in 37% yield (0.19 g) as a mixture of two diastereoisomers (ratio 1 : 1 determined by ^{13}C NMR). IR (neat, cm^{-1}): 3446, 2959, 1713, 1461, 1359; ^{1}H-NMR (200 MHz) δ: 0.88 (d, 2H, J = 5.2 Hz), 0.94 (t, 3H, J = 7.2 Hz), 1.10-1.70 (m, 9H), 1.90 (broad m, 1H), 2.15 (s, 3H), 2.38-2.50 (m , 2H), 3.42-3.56 (m, 1H); ^{13}C-NMR (50 MHz) δ: 209.53 C, (73.36, 73.20) CH, (41.27, 34.09, 33,99, 32.44) CH_2, 32.38 CH, 32.33 CH_2, 32.22 CH, (30.57, 30.40, 30.07, 29.96) CH_2, (29.73, 19.30, 19.20, 9.77, 9.72) CH_3; MS: 187 (M+1) 10%, 169 [(M+1) - H_2O] 100%.

*δ-Alkylation of cyclooctyl benzenesulfenate (**29**) with activated olefins.*

δ-Alkylation of cyclooctyl benzenesulfenate with acrylonitrile. Cyclooctyl benzenesulfenate (0.65 g, 2.75 mmol), 1.46 g (27.5 mmol) of acrylonitrile and 0.8 g (2.75 mmol) of TBTH was irradiated for 2 h. 2-(4-

Hydroxycyclooctyl)-ethyl cyanide (30a)was obtained as a colourless oil in 33% yield (0.15 g) as a mixture of *cis-* and *trans-*isomers (1 : 1 determined by ^{13}C NMR). IR (neat, cm^{-1}): 3402, 3019, 2927, 2252, 1216, 910, 760; ^{1}H-NMR (200 MHz) δ: 1.10-2.04 (m, 15H), 2.36 (t, 2H, J = 7.2 Hz), 3.74-4.00 (m, 1H); ^{13}C-NMR (50 MHz) δ: 119.82, (72.12, 71.52, 71.12) CH, (36.69, 36.44) CH, (35.89, 34.58, 34.40, 33.89, 33.21, 33.01, 32.79, 32.52, 32.16, 29.77, 29.63, 27.57, 27.19, 25.53, 25.20, 23.13, 22.33, 21.89, 21.11, 15.04) CH_2; MS: 182 (M+1) 10%, 164 [(M+1) - H_2O] 100%.

δ-Alkylation of cyclooctyl benzenesulfenate (29) with ethyl acrylate. A solution of 0.65 g (2.75 mmol) of cyclooctyl benzenesulfenate, 2.75 g (27.5 mmol) of ethyl acrylate and 0.8 g (2.75 mmol) of TBTH was irradiated for 2 h. From the reaction mixture it was isolated 0.21 g (34%) of ethyl 3-(4-hydroxycyclooctyl)-propanoate (**30b**, 1 : 1 mixture of *cis-* and *trans-*isomers determined by ^{13}C NMR). IR (neat, cm^{-1}): 3446, 1734, 1245, 1162; ^{1}H-NMR (200 MHz) δ: 1.26 (t, 3H, J = 7.2 Hz), 1.10-2.05 (m, 15 H), 2.25-2.35 (m, 2H), 3.75-3.85 (m, 1H), 4.13 (q, 2H, J = 7.2 Hz); ^{13}C-NMR (50 MHz) δ: 174.04, (72.52, 71.96, 71.56), CH, 60.19 CH_2, (37.33, 37.04) CH, (36.56, 36.27, 34.80, 34.65, 34.23, 33.52, 33.18, 32.98, 32.81, 32.63, 32.39, 32.03, 30.37, 30.14, 28.04, 27.77, 25.89, 25.38, 23.36, 22.69, 22.16, 21.36) CH_2, 14.19 CH_3; MS: 211 [(M+1) - H_2O] 100%.

Alkylation of axial methyl group of 3,3,5-trimethylcyclohexyl benzenesulfenate (O-SPh axial) (31) with acrylonitrile. Reaction of 0.56 g (2.24 mmol) of 3,3,5-trimetilcyclohexyl benzenesulfenate with 0.727 g (2.5 mmol) of TBTH in the presence of 1.187 g (22.4 mmol) of acrylonitrile yielded, after the standard work up procedure, 0.147 g (34%) of *t*-3,*t*-5-dimethyl-*c*-3-(3-cyanopropil)-*r*-1-cyclohexanol (**32.**) as a colourless oil. IR (neat, cm^{-1}): 3469, 2950, 2247, 1457, 1013; ^{1}H-NMR (200 MHz) δ: 0.85 (s, 3H), 0.89 (d, 3H, J = 6.6 Hz), 0.70-2.10 (m, 11H), 2.31 (t, 2H, J = 6.8 Hz), 4.15 (q, 1H, J = 3.2 Hz); ^{13}C-NMR (50 MHz) δ: 120.11, 67.89, 47.12, 41.96, 41.66, 38.51, 33.04, 29.95, 22.49, 22.23, 20.81, 17.91; MS: 196 (M+1) 10%, 178 [(M+1) - H_2O] 100%.

Alkylation of the remote carbon atom of endo*-2-norbornylmethyl benzenesulfenate (33) with acrylonitrile in the presence of hexabutylditin.* A solutioin of 0.468 g (2 mmol) of *endo*-2-norbornylmethyl benzenesulfenate and 0.212 g (4 mmol) of acrylonitrile in the presence of 0.174 g (0.3 mmol) of hexabutylditin in 40 ml of benzene was irradiated in an argon atmosphere during 15 min. Using the standard work up procedure it was isolated 0.124 g (22%) of 2-(6-hydroxymethyl-2-norbornyl)-1-phenylthio-ethyl cyanide (**34**) as a colourless oil (the ratio of *exo-* an *endo-*isomers = 52 : 48). IR (neat, cm^{-1}): 3403, 2237, 2000-1800, 749, 692; ^{1}H-NMR (200 MHz) δ: 0.50-0.70 (m, 1H), 0.80-2.00 (m, 8H), 2.00-2.30 (m, 3H), 3.55-3.80 (m, 3H), 7.34-7.46 (m, 3H), 7.58-7.67 (m, 2H). ^{13}C-NMR (50 MHz) δ: 134.64, 130.51, 129.56, 129.51, 119.53, 63.80, 63.65, 42.61, 42.43, 42.15, 41.57, 38.40, 38.29, 38.20, 37.98, 36.91, 36.76, 36.67, 35.83, 35.74, 31.97, 31.74, 31.54 (a mixture of two isomers). MS: 288 (M + 1), 270 [(M+1)-H_2O], 161.

δ-Alkylation of n*-pentyl benzenesulfenate (22a) with acrylonitrile in the presence of hexabutylditin.* A solution of 0.392 g (2 mmol) of *n*-pentyl benzenesulfenate and 0.212 g (4 mmol) of acrylonitrile in the presence of 0.174 g ((0.3 mmol) of hexabutylditin in 40 ml of benzene was irradiated during 15 and from the reaction mixture was isolated 0.12 g (24%) of 1-phenyltho-3-methyl-6-hydroxyhexyl cyanide **38** as a colourless liquid. IR (neat, cm^{-1}): 3399, 2237, 2000-1800, 751, 692; ^{1}H-NMR (200 MHz) δ: 0.96 and 0.97 (d, 3H, $J_1 = J_2 = 6.4$ Hz), 1.10-2.00 (m, 7H), 3.64 (t, 2H, J = 6.2 Hz), 3.70-3.80 (m, 1H), 7.34-7.46 (m, 3H), 7.58-7.66 (m, 2H) (55 : 45 mixture of two diastereoisomer determined by ^{13}C NMR); ^{13}C-NMR (50 MHz) δ: 134.66, 134.60, 130.55, 129.56, 129.45, 119.24, 62.82, 39.40, 39.17,35.25, 35.16, 32.63, 31.90, 30.81, 30.37, 29.72, 29.63, 19.09, 18.76. MS: 250 (M + 1), 232 [(M+1)-H_2O], 123.

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