Tetrahedron Vol. 44, No 19, pp. 6095 to 6106, 1988
Printed in Great Britain

0040-4020/88 $3.00+.00

PREPARATION AND NUCLEOPHILIC SUBSTITUTION OF (E)-1-BROMO-2-PHENYLSULFONYL-2-ALKENES AND 3-ACETOXY-2-PHENYLSULFONYL-1-ALKENES

P. AUVRAY, P. KNOCHEL*[1], and J.F. NORMANT

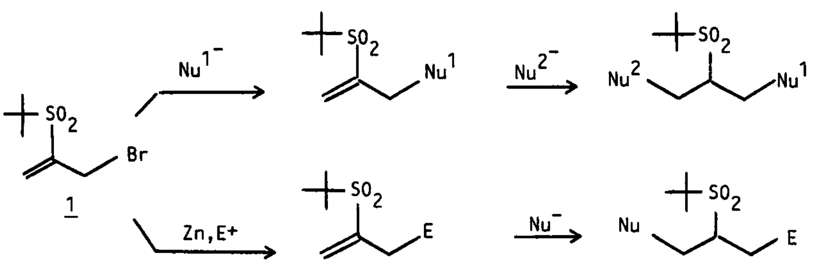
Laboratoire de Chimie des Organo-éléments, tour 44-45
Université P. et M.· Curie, 4 place Jussieu F-75252 PARIS Cédex 05

(*Received in Belgium* 8 *July* 1988)

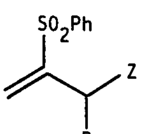
Summary - Vinylphenylsulfone reacts with aldehydes to yield sulfonylated secondary allylic alcohols which are converted to either primary allylic bromides, or secondary allylic acetates. Both react highly regioselectively with lithium cyanocuprates, or enolates.

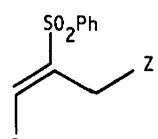
We have recently reported the multicoupling ability of 3-bromo 2-ter-butylsulfonyl propene, which may be used either as an $a^2/a^{2'}$ synthon[2], or as a $d^2/a^{2'}$ synthon[3,4] (in the presence of Zinc) (Scheme 1)

Scheme 1



It was of great interest to test the generality of this synthetic approach by extending this study to the case of higher homologs of substrate 1, namely compounds of type 2 and 3

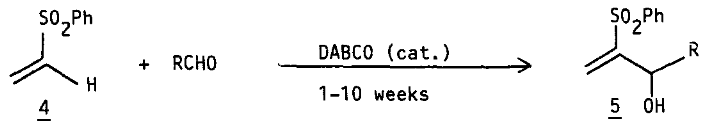
2 

3 

where regioselectivity of attack has to be accounted for, since nucleophilic attack of 2 or 3 may follow a S_N2 or S_N2' pathway.
In this paper[5], we report the preparation of substrates of type 2 and 3, and their regioselective use as multicoupling reagents.

Preparation of 2-Phenylsulfonyl-1-alken-3-ols

The starting alcohols can be prepared easily by the basic treatment of a vinyl sulfone in the presence of an aldehyde . We used the commercially available phenyl vinyl sulfone, instead of tert-Butyl vinyl sulfone .
This scheme has been disclosed[6] in the case of α,β-ethylenic ketones, esters, nitriles, using 10% of 1,4-diazabicyclo [2.2.2] octane (DABCO) and we have checked that it may apply in our case.



57-84%

At 25°, the reaction is slow, the more so if the aldehyde is α-substituted (pivalaldehyde reacts to the extent of 10% after 150 days) but in a number of cases the reaction can be used preparatively (see table 1). The yield depends mainly on the rate competition between the hydroxy alkylation, and the degradation of the aldehyde (aldols, polymers). With propionaldehyde, the hydroxy sulfone could not be entirely separated from such oligomers, by column chromatography. Among the various catalysts that we tried, DABCO proved to be the best, 1,8-diazabicyclo-[5,4,0] undec-7-ene(DBU) is too basic and leads to polymerisation. Heating (130°, sealed tube) speeds up the reaction but yields are lower by 10-20%. Extension of this reaction to vinyl phenyl sulfoxide led to no reaction.

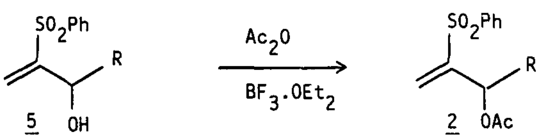
Table 1 - Synthesis of allylic alcohols from 4, RCHO, and 10% DABCO at 25°C

RCHO	Product	Reaction time (weeks)	Yield %
MeCHO	5a	2	84
EtCHO	5b	2	a
PrCHO	5c	4	75
BuCHO	5d	10	79
iBuCHO	5e	11	81
Ph-CHO	5f	3	57

a : see text

Crotonaldehyde gave no isolable product, and furfural led to 20% of product after 3 weeks. The allylic alcohols are readily converted to the corresponding acetates by acetic anhydride in the presence of a catalytic amount of BF_3-Et_2O[7] (0°, 10 min), (Scheme 2)

Scheme 2



R=Me, 2a : 94%
R=n.Pr, 2c : 95%

and to the corresponding bromides (only the E isomer) by N.Bromosuccinimide-dimethyl sulfide in dichloromethane[8] (12 h at 25°C) in high yield (see Scheme 3 and Table 2)

Scheme 3

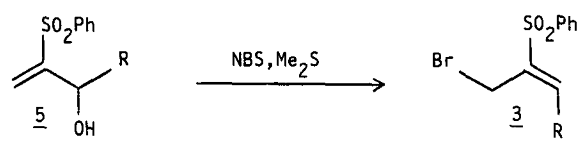


Table 2 - Synthesis of 2-phenylsulfonyl 1-bromo-2-alkenes 3 from alcohols 5 a-c-d-e (Scheme 3)

Alcohol	R	Product	Yield %
5a	Me	3a	85
5c	Pr	3c	87
5d	n.Bu	3d	87
5e	i.Bu	3e	82

Nucleophilic attack of the allylic acetates (2) and bromides (3)

These allylic bromides and acetates have been reacted with ketone enolates and cyanocuprates[9], with the assumption that in both cases, an addition-elimination pathway should direct the incoming nucleophile so that an overall "S_N2'" reaction should take place. This proved to be the case. Moreover, the bulky sulfonyl moiety promotes not only a good regio- but also stereoselectivity, so that compounds 6 are exclusively of E configuration (see scheme 4 and table 3).

Scheme 4

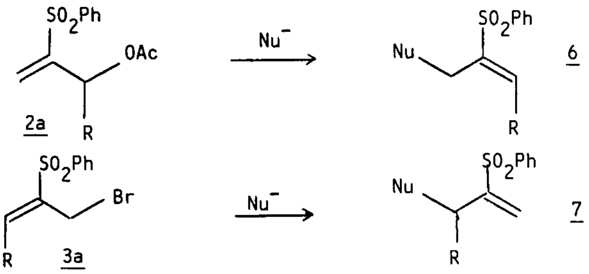
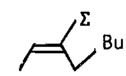
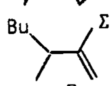
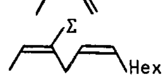
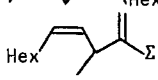
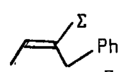
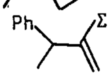
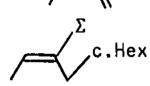
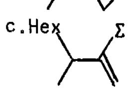
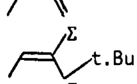
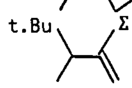
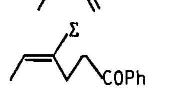
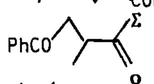
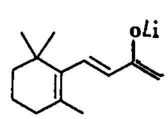
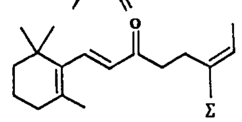
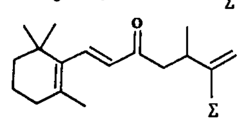


Table 3 - Nucleophilic substitution of allylic acetates 2a and bromides 3a

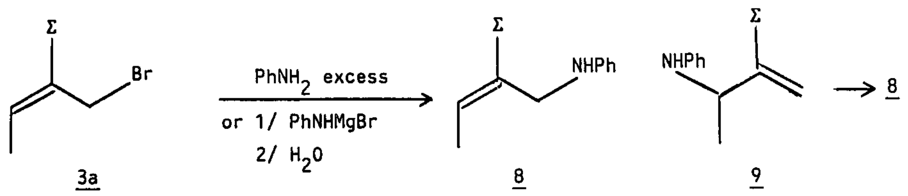
Entry	Substrate	Nucleophile	Product[a]		Yield %
1	2a	BuCuCNLi		6a	82
2	3a	BuCuCNLi		7a	89
3	2a	(Z)-C_6H_{13}-CH=CHCuCNLi		6b	78
4	3a	(Z)-C_6H_{13}-CH=CH-CuCNLi		7b	77[b]
5	2a	PhCuCNLi		6c	84
6	3a	PhCuCNLi		7c	96
7	2a	Cyclo-C_6H_{11}-CuCNMgCl		6d	95
8	3a	Cyclo-C_6H_{11}-CuCNMgCl		7d	94
9	2a	ter-BuCuCNLi		6e	98
10	3a	ter-BuCuCNLi		7e	35[c]
11	2a	Ph-C(OLi)=CH_2		6f	80
12	3a	Ph-C(OLi)=CH_2		7f	56
13	2a			6g	89
14	3a			7g	78

a/ Σ stands for SO_2Ph; b/ with 10% of 6b in the presence of BF_3-OEt_2-see text; c/ with 64% of 6e

Thus starting from either the allylic acetate or bromide, one can get the corresponding vinylsulfone, either linear or branched. Such high regio- and stereoselectivity has been described in the case of Phenyl sulfonyl cyclo pentenol derivatives[10]. However in the case of a bulky nucleophile (table 3 entry 10) such as a ter-Butyl cyanocuprate, the primary bromide 3a leads to 65% of 6e via S_N2, together with 7e (35%). With (Z)-1-octenyl cyanocuprate (table 3 entry 4) 3a gives a 50/50 mixture of 6b and 7b, but in the presence of BF_3,OEt_2[11], the S_N2'/S_N2 ratio raises to 88/12.

Amines can also be used as nucleophiles : in this case, our results are in good accordance with those of Doomes et al[12] who studied analogous nucleophilic substitutions of 1-bromo (and 1-amino)-2-(methylsulfonyl)-3-phenyl-2-propenes . We observed that anilin in excess, or its chloromagnesium amide (made from butylmagnesium chloride), both give a mixture of S_N2 and S_N2' products (8 and 9) which slowly equilibrate to give the S_N2 derivative 8 (scheme 5) in yield of 78%.

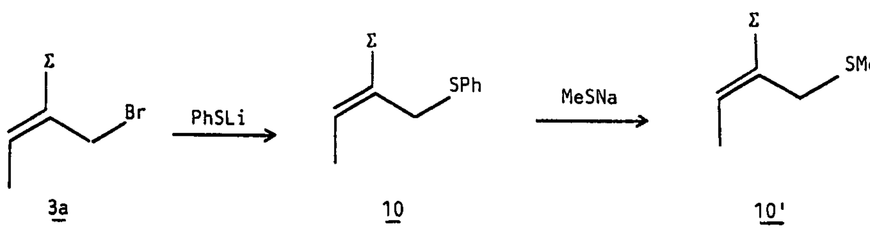
Scheme 5



A similar trend is observed in the case of thiolates : lithium phenyl thiolate gives exclusively the primary thiol ether 10 corresponding to an overall S_N2 reaction.

When allowed to react with one equivalent of sodium methyl thiolate (a more nucleophilic reagent than phenyl thiolate) 10 leads to a 20:80 mixture of 10 and 10', thus either an S_N2 isoperative, or two S_N2' substitutions eventually lead to the thermodynamically more stable sulfide 10', the latter pathway bring more probable (scheme 6).

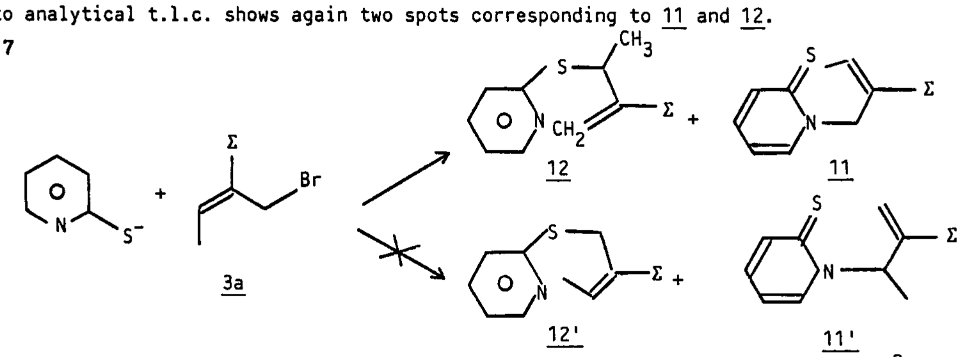
Scheme 6



A further proof of the latter hypothesis is brought by the reaction of 3a with lithium pyridine-2-thiolate, which should react first by the more nucleophilic thiolate moiety, and then could undergo an intramolecular nucleophilic attack by nitrogen : from the four possible educts, only two are formed, namley one colorless (12) showing a methylene unit in NMR, and the yellow 11, showing an allylic methyl group.

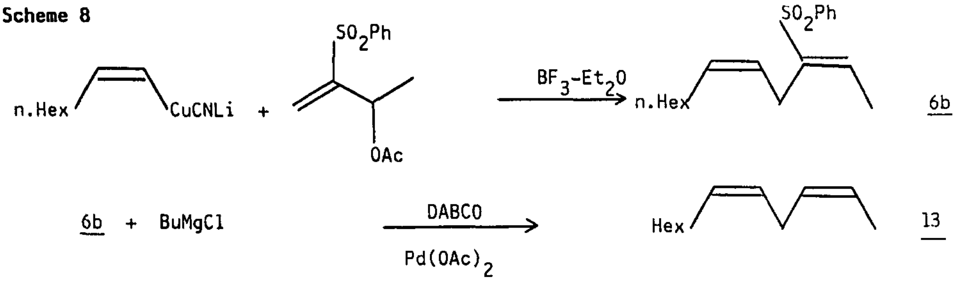
Each of them, isolated by preparative t. l.c. dissolved in ether, and submitted after a short time, to analytical t.l.c. shows again two spots corresponding to 11 and 12.

Scheme 7



These results also point to an exclusive attack by an S_N2' pathway.
Finally, as an illustration of the preceding stereo- and regioselective synthese, we have prepared a skipped (Z-Z) diene according to Scheme 8 :

Scheme 8



sulfone 6b being reductively desulfonylated, according to Julia's procedure[13], to (Z,Z)-2,5-dodecadiene 10.

In conclusion, due to the presence of the phenylsulfonyl moiety, the easily available acetates of type 2, or bromides of type 3 can be substituted regioselectively, leading to (Z)-1-2 disubstituted alkenes, or to 3-substituted terminal alkenes, once the sulfonyl moiety is discarded.

EXPERIMENTAL PART -

THF and ether were distilled from sodium/benzophenone. Infrared spectra were recorded on a Perkin Elmer 457G spectrometer. Proton NMR spectra were obtained at 100MHz with a Jeol MH100 and at 250MHz with a Bruker AM250. ^{13}C-NMR spectra were obtained with a Jeol FX90.
Chemical shifts in $CDCl_3$ solution are reported in ppm relative to tetramethylsilane as an internal standard. Gas chromatography was carried out with a Carlo Erba 2150 model equiped with an OV101 (20 m) column. Merck 60 (70-230 mesh) silica gel was used for the fash chromatography[14].

General procedure for the preparation of 2-ter-butylsulfonyl-1-alken-3 ols 5
In a dry erlenmeyer, flushed with Argon are placed 3 g (17.8 mmol) of vinylphenyl sulfone in 7 ml of the freshly distilled aldehyde. 0.2 g (1.78 mmol) of dry DABCO are then added (dissolution). The erlenmeyer is stoppered and left at room temeperature. Reaction is followed by T.L.C. After disappearance of the phenylvinyl sulfone, the mixture is taken up by 100 ml CH_2Cl_2 and successively washed with a 1N HCl solution (30 ml). The organic layer is dried over $MgSO_4$. Solvent and excess aldehyde are evaporated under vacuum, and the resulting oil is chromatographed on silica. In the case of 5a we operated on a 1 mole scale, and in this case, a careful evaporation of solvent and remaining acetaldehyde under high vacuum led to a product readily used for further transformations. Spectroscopic data are collected in table 4.

2-Phenylsulfonyl-1-buten-3-ol 5a
Yield (from 17.8 mmol of vinyl sulfone) : 3.17 g (84%). Chromatography with ether : CH_2Cl_2 : hexane/ 8:70:30 gives an oil.
Found : C, 56.30 ; H, 5.65%. Calcd. for $C_{10}H_{12}SO_3$: C, 56.58 ; H, 5.70%.

2-Phenylsulfonyl-1-hexen-3-ol 5c
See general procedure. From n-butanal. Obtained 3.20 g (75%) of 5c as an oil. Eluent ether : CH_2Cl_2 : hexane/ 8:70:30.
Found : C, 60.50 ; H, 6.52%. Calcd. for $C_{12}H_{16}SO_3$: C, 59.97 ; H, 6.71%.

2-Phenylsulfonyl-1-hepten-3-ol 5d
See general procedure. From n-pentanal 3.57 g (79%) of 5d are obtained as an oil. Same eluent as for 5c.

2-Phenylsulfonyl-5-Methyl-1-hexen-3-ol 5e
See general procedure. From isovaleraldehyde. 3.66 g of 5e are obtained as an oil (same eluent as for 5c).

2-Phenylsulfonyl-3 phenyl-1-propen-3-ol 5f
See general procedure. From benzaldehyde. 2.79 g of 5c are obtained as an oil (same eluent as for 5c). M.p. 78°C.
Found : C, 65.58 ; H, 5.10%. Calc. for $C_{15}H_{14}SO_3$: C, 65.67 ; H, 5.14%.

Preparation of the secondary allylic acetates 2

5 mmol of the preceding alcohols are dissolved in 4 ml acetic anhydride, and to the solution maintained at 0°C, are added 0.1 ml BF_3-OEt_2O (0.8 mmol). The mixture turns organge progressively, and the reaction is over after 10-15min. The solution is then poured in CH_2Cl_2 (150 ml). After washing successively with a saturated solution of sodium hydrogencarbonate (30 ml) and brine (30 ml), the organic layer is dried over $MgSO_4$ and evaporated in two steps, to remove the solvent, and then under a 10^{-2} mmHg pressure to remove the acetic acid-acetic anhydride. The oil is then chromatographed on silica. Spectroscopic data are collected in table 4.

Acetate of 2-phenylsulfonyl-1-buten-3-ol 2a
From 5a. 1.19 g (94%) of 2a are obtained as an oil. Eluent : ether : CH_2Cl_2 : hexane/3:70:30. Found : C, 56.28 ; H, 5.60%. Calcd. for $C_{12}H_{14}SO_4$: C, 56.68 ; H, 5.55%.

Acetate of 2-phenylsulfonyl-1-hexen-3-ol 2c
From 5c. 1.34 g (95%) of 2c are obtained as an oil. Same eluent as for 2a.

Preparation of 2-phenylsulfonyl-3-bromo-1-alkenes 3

from alcohols 5 a, c, d, e.
A solution of 1.8 ml dimethylsulfide in 14 ml CH_2Cl_2 is added dropwise to a stirred suspension of 3.58 g (0.02 mol) of N-bromosuccinimide in 45 ml CH_2Cl_2 maintained at -20°C. The temperature is allowed to raise up to 0°C and the pale yellow suspension is stirred for 15 min. A solution of 19 mmol of the alcohol 5 in 18 ml CH_2Cl_2 is then added. The mixture is stirred at 25° for 12 h whereby a yellow solution is obtained, which is successively washed with a saturated solution of sodium hydrogenocarbonate (2 x 20 ml) then brine (20 ml) and dried over magnesium sulfate. Solvents are evaporated under vacuum and the residue is either recrystallized, or flash chromatographed on silica. Spectroscopic data are collected in table 4.

(E)-1-Bromo-2-phenylsulfonyl-2-butene 3a
From 5a are obtained 4.44 g (85%) of 3a, first chromatographed eluent ether : CH_2Cl_2 : hexane/5:70:30, then recrystallized From ether. m.p. : 73°C.
Found : C, 43.55 ; H, 3.95%. Calcd. for $C_{10}H_{11}SO_2Br$: C, 43.65 ; H, 4.03%.

(E)-1-Bromo-2-phenylsulfonyl-2-hexene 3c
From 5c. 5.00 g of 3c are obtained as an oil. Same eluent as for 3a.

(E)-1-Bromo-2-phenylsulfonyl-2-heptene 3d
From 5d. 5.24 g (87%) of 3d are obtained as an oil. Same eluent as for 3a.

(E)-1-Bromo-2-phenylsulfonyl-5-methyl-2-hexene 3e
From 5e. 4.94 g (82%) of 3e are obtained as an oil. Same eluent as for 3a.

General procedure for the reaction of cyanocuprates with allylic-acetates 2 or bromide 3

To a stirred suspension of 358 mg (4 mmol) of copper cyanide in 15 ml THF at -80°, is added slowly a solution of 4 mmol of the lithium- or magnesium organometallics 1N in ether or THF. The mixture is then stirred for 30 min at temperatures in the -30,-10°C range, according to each case. A solution of 2 mmol of the acetate 2 or bromide 3 in 5 ml THF is then added slowly at -80°C. In the case of 3a and Z octenylcyanocuprate, a solution of 4 mmol BF_3-OEt_2 (0.5 ml) in 2 ml ether is added at -80°C before introducing reagent 3. The mixture is allowed to warm slowly and is followed by T.L.C. When no more starting 2 or 3 is detected, the mixture is hydrolyzed with a saturated solution of NH_4Cl (20 ml) and 1 ml concentrated ammonia. The aqueous phase is extracted with ether (2 x 20 ml). The organic phase, washed with a sat. solution of NH_4Cl (20 ml) is dried over $MgSO_4$. Solvents are evaporated under vacuum, and the residue is chromatographed on silica. Spectroscopic data are collected in table 5.

(E)-3-Phenylsulfonyl-2-octene 6a
From butyl lithium and 2a. Reaction time 1 hr at -60° → -15°C.
0.41 g (82%) of sulfone 6a are obtained as an oil. Eluent : CH_2Cl_2 : cyclohexane/70:30.
Found : C, 66.70 ; H, 7.90%. Calcd. for $C_{14}H_{10}SO_2$: C, 66.63 ; H, 7.99%.

2-Phenylsulfonyl-3-methyl-1-hexene 7a
From butyllithium and 3a. Reaction time 0.5 hr at -60°C. 0.45 g (89%) of 7a are obtained as an oil. Same eluent as for 6a.

3-Phenylsulfonyl-2(E),5(Z) dodecadiene 6b
From 2a and (Z)1-octenyl-lithium cyanocuprate. The latter reagent, prepared from (Z)-1- iodo-1-octene[15] by lithium/iodine exchange[16], and then following the general procedure, with a reaction time of 1.5 hr at -15°C, led to 0.48 g (78%) of sulfone 6b, separated from isomer 7b during chromatography (eluent ether : CH_2Cl_2 : cyclohexane/1:70:30.

(Z)-2-Phenylsulfonyl-3-methyl-1,4 undecadiene 7b
From 3a and (Z):1 octenyl cuanocuprate (prepared as above) in the presence of 2 equivalents of BF_3-Et_2O added prior to the bromide 3a. Reaction time 2 hr at -60° → -10°C. 0.47 g of 7b are obtained (77%) as an oil; Same eluent as for 6b.

(E)-2-Phenylsulfonyl-1-phenyl-2-butene 6c
From 2a and lithium phenyl cyanocuprate. Reaction time : 1 hr at -60° → -45°C. 0.46 g (84%) of 6c are obtained as an oil. Same eluent as for 6b.

2-Phenylsulfonyl-3-phenyl-1-butene 7c
From 3a and lithium phenyl cyanocuprate. Reaction time 0.25 hr at -60°C. 0.52 g (96%) of 7c are obtained (oil). M.p. : 48°C.
Found : C, 70.49 ; H, 5.88%. Calcd. for $C_{16}H_{16}SO_2$: C, 70?56 ; H, 5.92%.

(E)-2-Phenylsulfonyl-1-cyclohexyl-2-butene 6d
From 2a and lithium cyclohexyl cuanocuprate. Reaction time 2 hr at -80° → -30°C. 0.53 g (95%) of 6d are obtained as an oil. Eluent CH_2Cl_2 : hexane/70:30.

2-Phenylsulfonyl-3-cyclohexyl-1-butene 7d
From 3a and lithium cyclohexyl cyanocuprate. Reaction time 1 hr at -60°C. 0.52 g (94%) of 7d are obtained as an oil. Same eluent as for 6d.

(E)-4-Phenylsulfonyl-2,2-dimethyl-4-hexene 6e
From 2a and lithium ter-butyl cyanocuprate. Reaction time 2.2 hr at -60° → -45°C. 0.49 g (98%) of 6e are obtained as an oil. Eluent : CH_2Cl_2 : cyclohexane/70:30.
Found : C, 67.00 ; H, 8.05. Calcd. for $C_{14}H_{20}SO_2$: C, 66.63 ; H, 7.99%.

2-Phenylsulfonyl-3,4,4 trimethyl-1-pentene 7e
From 3a and lithium ter-butyl cyanocuprate. Reaction time 0.25 hr at -60°C. 0.17 g of 7e (35%) are obtained as an oil, separated from 0.32 g 6e. Eluent CH_2Cl_2 : cyclohexane/70:30.

General procedure for the reaction of lithium enolates with acetate 2a and bromide 3a

To a stirred solution of 361 mg (3.6 mmol) of diisopropylamine in 7 ml THF at -80°C is added 3.2 ml of a 1N solution of n-Butyl lithium and the temperature is raised up to -40°C. After 15 min, the solution is cooled to -80°C and 3 mmol of the ketone in 2 ml THF are added. The solution is then stirred at -60°C for 0.5 hr and a solution of 2 mmol of 2a or 3a in 3 ml THF is added at -80°C. The reaction is followed bu t.l.c. while temperature is allowed to raise. The mixture is then hydrolyzed with a saturated NH_4Cl solution (20 ml). After extraction of the aqueous layer by ether 20 ml, the organic phase is washed with sat. NH_4Cl (20 ml), dried over $MgSO_4$ and solvents are evaporated under vacuum. The residue is chromatographed by flash chromatography. See spectroscopic data in table 5.

(E)-3-Phenylsulfonyl-6-phenyl-2-hexen-6-one 6f
From 2a and acetephenone. Reaction time 2.5 hr at -60° → -10°C. 0.5 g of 6f (80%) are obtained. Eluent CH_2Cl_2 : cyclohexane/80:20. m.p. : 86°C (CH_2Cl_2/pentane).

4-Phenylsulfonyl-3-methyl-1-phenyl-4-penten-1-one 7f
From 3a and acetophenone. Reaction time 2.5 hr at -60° → -10°C. Obtained : 0.35 g (56%) of 7f. Eluent CH_2Cl_2 : cyclohexane/80:20. m.p. : 133°C (CH_2Cl_2/pentane).
Found : C, 68.50 ; H, 5.70%. Calcd. for $C_{18}H_{18}SO_3$: C, 68.76 ; H, 5.77%.

(E,E)-6-Phenylsulfonyl-1-(2,6,6-trimethyl-1-cyclohexenyl)-1,6-octadien-3-one 6g
From -ionone and 2a. Reaction time 3.5 hr at -60° → -25°C. 0.69 g (89%) of 6g are obtained as an oil. Eluent ether : CH_2Cl_2 : cyclohexane/2:70:30.
Found : C, 71.38 ; H, 7.75%. Calcd. for $C_{23}H_{30}SO_3$: C, 71.46 ; H, 7.82%.

(Z)-6-Phenylsulfonyl-1-(2,6,6-trimethyl-1-cyclohexenyl)-5-methyl-1,6-heptadien-6-one 7g
From -ionone and 3a. Reaction time 1.5 hr at -60° → -20°C. 0.60 g of 7g are obtained as an oil. Same eluent as for 6g.

2-Phenylsulfonyl-3-(N-phenylamino)-1-butene 8 and
(E)-2-Phenylsulfonyl-1-(N-phenylamino)-2-butene 9
A solution of 0.40 g (4.3 mmol) of anilin in 5 ml THF is added to a stirred solution of 0.55 g of sulfone 3a (2 mmol) in 5 ml THF at -78°C. The mixture is warmed up to -50°C, and the reaction, followed by t.l.c., is over after 30 min. 10 ml of saturated NH_4Cl solution and 25 ml CH_2Cl_2 are added. The organic phase is washed with brine (20 ml), dried over $MgSO_4$ and evaporated under vacuum. Chromatography of the residue (ether : CH_2Cl_2 : hexane/2.70:30) gives 0.48 g (85%) of a 57/43 mixture of 8 (oil) and 9 (solid, m.p. : 88°C).
9 found : C, 66.50 ; H, 6.00%. Calcd. for $C_{16}H_{17}NSO_2$: C, 66.88 ; H, 5.96%.

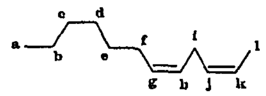
2-Phenylsulfonyl-1-phenylthio-prop-2-ene 10
Same general procedure as for the reaction of enolates, from 2a and lithium phenyl thiolate (prepared from thiophenol and n-butyllithium at - 80° in THF) reaction time 1 h at -40°. 0.596 mg of 10 are obtained (98%).

m.p. : 52°C.
Found : C,63.06 ; H, 5.27%. Calcd. for $C_{16}H_{16}S_2O_2$: C,63.12 ; H, 5.30%.
This compound is reacted with 2 mmol MeSNa in 20 ml THF. The raw product isolated as above is only studied by ^1H and ^{13}C NMR and shows a mixture of 20% of 10 and 80% of 10' : the latter is characterized by the following parameters : $PhSO_2-\overset{c}{C}(=\overset{b}{C}H-CH_{3a})-\overset{d}{C}H_2-S-\overset{e}{C}H_3$

^1H RMN δ,$CDCl_3$: 1.89(d,3H,J=7.5Hz(a), 1.92(s,3H((e)), 3.45(s,2H,d), 7.20(q,1H,J=7.5Hz,(b)), 7.40 to 8.11(m,5H(phenyl))
^{13}C RMN δ,$CDCl_3$: 27.85(d), 14.29 and 13.93 (a and e)

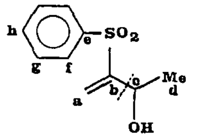
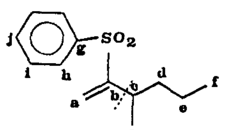
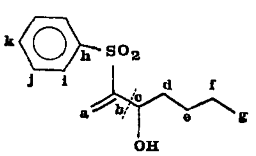
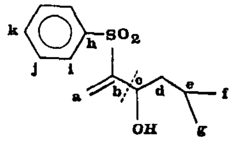
3(2-pyridylthio)-2-phenylsulfonylbut-1-ene 12 (and thione 11)
Same procedure as for 10. Preparative T.L.C. with ether : CH2Cl2 : cyclohexane/10:70:30 allows the isolation of 11 (yellow) and 12 (colorless) (oils). As they equilibrate rapidly, the NMR spectra show the caracteristic following signals :
12 : ^1H RMN ($CDCl_3$,δ) : 1.62(d,3H, J=7.5Hz(CH_3-CH), 4.89(q,1H,J=7.5Hz, (CH-CH_3)), 6.3(s,1H, H-C=trans to SO_2), 6.5 to 8.1(m,10H)
The 13C NMR spectrum shows no signal above 160 ppm.
11 : ^1H RMN δ : 2.04(d,3H,J=7,5Hz,CH_3-CH=), 5.43(s,2H,(-CH_2-CH=)), 6.51 to 8.10 m, 10H)
^{13}C RMN ($CDCl_3$,δ) : 180.8 (C=S)
mixture 11 + 12 : found : C, 59.06 ; H, 5.00%. Calcd. for $C_{15}H_{15}S_2O_2N$: C, 58.99 ; H, 4.95%

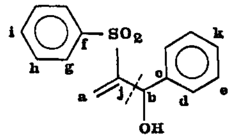
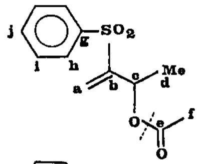
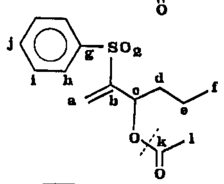
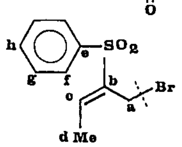
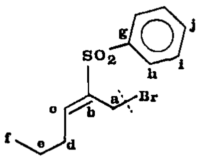
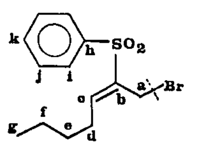
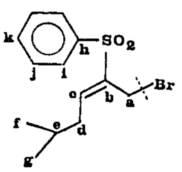
(Z,Z)-2,5-dodecadiene 13
According to Julia's procedure [13], 1 mmol of 6b (0.306 g) gave 0.121 g (73%) of 10 (oil).



IR : (neat) 3010,2960,2920,2860,1650,1585,1465,1455,1440,1400,1380,1365,1305,1270,1225,1150,1090, 1025,965,900,740,700
^{13}C NMR : ($CDCl_3$,δ) 130.32, 129.14, 127.90, 123.91, 31.89(i), 29.74(f), 29.07, 27.34, 25.40, 22.71, 14.07(l), 12.71(a)
1H NMR : (CDCl3,δ) 0,86(m,3H,(a)),1.3(la,8H,(b-e), 1.6(dxd,3H,J_1=5.8Hz),J_2=0.6Hz,(l)), 2.05 (m, 2H,(f)), 2.75(m,2H,(i)), 5.48(m,4H,(g,h,j,k)).

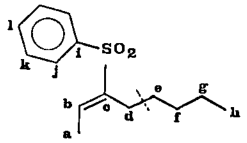
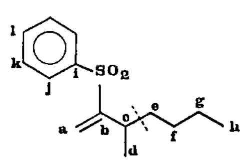
Table 4 - Spectroscopic data of alcohols 5, acetates 2, bromides 3

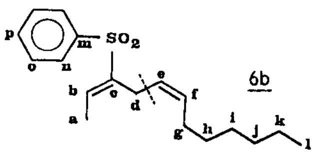
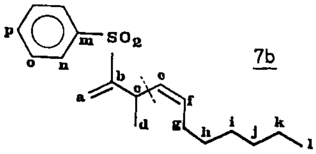
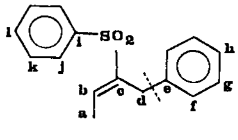
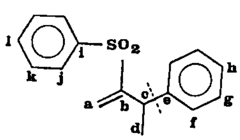
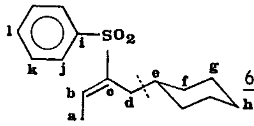
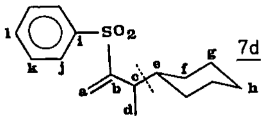
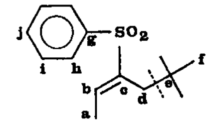
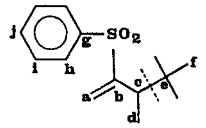
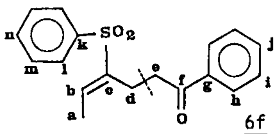
Compound		^1H NMR $CDCl_3$-δ from TMS	^{13}C RMN($CDCl_3$,δ from TMS	I.R.[a]
	5a	1.22(d,3H,J=6.4Hz(d)), 3.30,s,1H,(OH),4.45(m, 1H,(c)),6.05(s,1H,(Ha trans/SO_2)),6.29(s,1H, (Ha cis/SO_2)),7.4 to 8.35,m,5h(Ph)	154.44(b),139.26(e), 133.40(h),129.08(f), 127.89(g),123.78(a), 64.47(c),22.62(d)	3480,2975,2930, 1580,1445,1375, 1300,1175,1135, 1100,1075,1035, 955,915,835,750, 685,620
	5c	0.78(t,3H,J=6.8Hz,(f)) 1.11 to 1.68(m,4H,(d,e)) 3.39(d,1H,OH),4.44(m,1H, (c)),6.18(s,1H(Ha trans/SO_2)),6.45(s,1H, (Ha cis/SO_2),7.5-8.4(m, 5H,phenyl)	153.68(a),139.26(g), 133.69(j),129.28(i), 128.00(h),124.81(b) 68.05(c),38.46(d),18.35 (e),15.55(f)	3500,2960,2925, 2870,1580,1445, 1380,1300,1170, 1140,1115,1080, 1025,970,915,775, 755,695
	5d	0.78(t,3H,J=7Hz,(g)), 1.0 to 1.6(m,6H,(d,e,f)) 3.68(d,1H,J=4.8Hz,OH), 4.49(m,1H(c)),6.12(s,1H, Ha trans/SO_2)),6.50(s, 1H,Ha cis/SO_2)),7.45-7.85(m,5H,phenyl)	153.68(b),139.29(h), 133.66(k),129.25(j), 128.00(i),124.84(a), 68.32(c),36.08(d),27.23 22.17	3500,2950,2925, 2865,1580,1445, 1375,1300,1165, 1135,1075,955, 750,685
	5e	0.78(larged,6H,(f,g)), 1.08-1.92(m,3H,(d,e)), 3.42(d,1H,J=5Hz,OH), 4.47(m,1H,(c)),6.12(s, 1H(Ha trans/SO_2)),6.33 (s,1H,Ha cis/SO_2)),7.35-7.95(m,5H,phenyl)	154.16(b),139.11(h), 133.63(k),129.19(i), 127.97(j),124.45(a), 66.53(c),47.73(e),24.37 (d),23.12 and 21.36(f,g)	3490,2960,2875, 1585,1465,1435, 1385,1370,1305, 1170,1145,1080, 960,920,770,750, 690

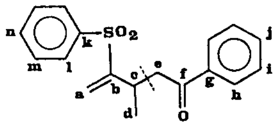
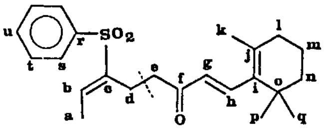
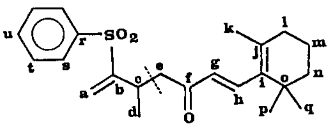
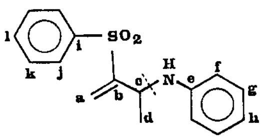
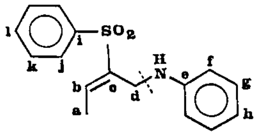
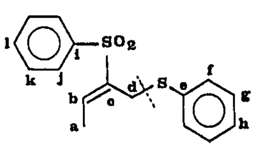
	5f	3.45(d,1H,J=4.5Hz,OH), 5.7(m,1H(b)),6.09(s,1H, (Ha trans/SO_2)),6.6(s, 1H,Ha cis/SO_2)),7.14-7.95(m,10H,phenyls)	152.80(j),139.20(f) 138.99,133.21(i),128.86, 128.71,128.26,127.82, 126.81(a)., 120.09,71,15 (b)	3500,3060,2920, 2850,1580,1450, 1300,1130,1080, 1040,965,910,780, 750,700,685,650
	2a	1.45(d,3H,J=6.5Hz,(d)), 1.8(s,3H,(f)),5.48(q, 1H,J=6.5Hz,(c)),6.07(s, 1H,(Ha trans/SO_2)),6.50 (s,1H,(Ha cis/SO_2)), 7.45-7.90(m,5H,phenyl)	168.85(e),150.88(b), 139.71(g),133.69(j), 133.69(j),129.28-128.09 (h,i),126.30(a),66.35(c), 20.44-20.17(d,f)	3060,2890,2930, 1740,1700,1580, 1440,1370,1310, 1230,1180,1140, 1070,1040,950,870, 845,740,680
	2c	0.81(t,3H,J=7Hz,(f)), 1.23(q,2H,(d)),1.73(s, 3H,(l)),5.48(t,1H,J=6Hz, (c)),6.11(s,1H,Ha trans/ SO_2),6.53(s,1H,Ha cis/ SO_2),7.48-7.88(m,5H, phenyl)	168.99(k),150.19(b), 139.79(g),133.66(j), 129.22-128.29(h,i), 126.42(a),69.81(c),36.23 20.35(l),18.44,13.46(f)	2960,2930,2870, 1740,1580,1445, 1370,1315,1305, 1225,1140,1020, 970,750,685
	3a	1.95(d,3H,J=7.5Hz,(d)),, 4.20(s,2H(a)),7.29(q, 1H,J=7.5Hz,(c)),7.56-8.15(m,5H,phenyl)	143.82,139.71(e),139.32, 133.69(h),129.28(g), 128.26(f),20.94(a),14.89 (d)	3025,3010,1640, 1580,1445,1305, 1290,1210,1195, 1135,1080,1010, 1000,855,765,740, 685,650
	3c	0.96(t,3H,J=7.5Hz,(f)), 1.59(m,2H,(e)),2.34(m, 2H,(d)),4.23(s,2H,(a)), 7.29(t,1H,J=7.5Hz,(c)), 7.5-8.15(m,5H,phenyl)	148.35,139.77(g),138.36, 133.51(j),129.16(i), 128.09(h),30.84(d),21.03 (e),13.76(f)	3060,2960,2930, 2870,1630,1585, 1445,1370,1305, 1210,1185,1140, 1080,755,725,685, 655
	3d	0.9(t,3H,J=7.5Hz,(g)), 1.44(m,4H,(e,f)),2.34 (q,2H,J=7.5Hz,(d)),4.23 (s,2H(a)),7.23(t,1H, J=7.5Hz(c)),7.45-8.04 (m,5H,(phenyl))	148.59,139.95(h),138.25, 133.45(k),129.13(j), 128.06(i),29.67,28.69, 22.56,21.21,13.73(g)	3060,2950,2920, 2850,1630,1580, 1445,1300,1210, 1180,1140,1080, 760,730,685,655
	3e	0.93(d,6H,J=7.5Hz,(f,g)) 1.87(m,1H,(e)),2.25(t, 2H,J=7.5Hz(d)),4.26(s, 1H,(a)),7.29(t,1H, J=7.5Hz(c)),7.5-8.1(m, 5H,phenyl)	147.48,139.95(h),138.78, 133.45(k),129.10(j), 128.00(i),37.60(e),27.68 (d),22.31(f,g),21.24(a)	3030,2980,2960, 2935,1630,1585, 1465,1445,1385, 1370,1310,1215, 1190,1145,1085, 1000,760,735,690, 660

a/ as film (neat) for liquids, or KBr plates (solids)

Table 5 - Spectroscopic data of products 6 and 7, from nucleophilic addition of cuprates and enolates to 2a and 3a

Compound		^{1}H NMR spectra	^{13}C NMR spectra	I.R.^{a}
	6a	0.75-2.5(m,11H,(d-h)), 1.85(d,3H,J=7.5Hz,(a)), 7.05(q,1H,J=7.5Hz(b)), 7.5-8.1(m,5H,phenyl)	142.50,140.32(c and i), 136.99,133.05(b and l), 129.09,128.08(k and j), 36.69,28.32,26.30,22.18, 14.11, 13.90	3060,2950,2920, 2860,1640,1580, 1445,1300,1155, 1130,1080,755, 720,690
	7a	0.75(t,3H,J=7.0Hz,(h)), 1.02(d,3H,J=7.5Hz,(d)), 1.35(m,6H,(e,f,g),2.49 (m,1H,(c)),5.88(s,1H(Ha trans/SO_2)),6.51(s,1H, (Ha cis/SO_2)),7.5-8.15 (m,5H,phenyl)	156.27(a),139.05(i), 133.39(l),129,10(k), 128.29(j),122.19(b), 36.47,33.46,28.87, 22.28,21.75(d),13.85(h)	2960,2920,2850, 1445,1380,1300, 1175,1148,1125, 1080,950,840, 750,690,630

 6b	0.9(t,3H,J=7.0Hz,(l)), 1.32(m,8H(h,i,j,k)), 1.89(d,3H,J=7.5Hz,(a)), 3.09(d,2H,J=7.0Hz,(d)), 4.89-5.58(m,2H,(e,f)), 7.14(q,1H,J=7.5Hz,(b)), 7.45-8.1(m,5H,(phenyl))	141.08,140.01,137.71 133.06(p),131.66,129.01,(o),128.09(n),124.48, 31.73(d),29.29,28.99, 27.29,24.46,22.61,14.06 (l)	2960,2925,2855, 1640,1585,1450, 1380,1315,1305, 1155,1135,1085, 1000,970,900,785, 725,690
 7b	0.87(t,3H,J=7.0Hz,(l)), 1.2(m,11H,d,h,i,j,k), 1,70(m,2H,(g)),3.45(m, 1H,(c)),5.15(m,2H(e,f)), 5.86(s,1H(Ha trans/SO_2), 6.40(s,1H,Ha cis/SO_2); 7.40-8.0(m,5H,phenyl)	155.56(b),139.62(m), 133.30(p),131.34,130.89, 129.01(o),128.24(n), 123.14(a),32.06(c),31.67, 29.23,28.90,27.05,22.58, 22.14(d),14.06(l)	2920,2850,1580, 1440,1310,1300, 1165,1140,1080, 745,685
 6c	1.77(d,3H,J=7.5Hz,(a)), 3.72(s,2H,(d)),7.11(m, 5H,(f,g,h)),7.30(q,1H, J=7.5Hz,(b)),7.5-8.1(m, 5H,(j,k,l))	140.90,139.91,139.20, 136.55,132.83,128.80, 128.18,127.97,127.82, 126.18,31.61(d),14.51(a)	3060,3030,2920, 1640,1595,1580, 1490,1480,1445, 1300,1285,1145, 1125,1080,735, 700,685,630
 7c	1.34(d,3H,J=7.13Hz,(d)), 3.83(q,1H,J=7.13Hz,(c)), 5.82(s,1H,(Ha trans/ SO_2)),6.5(s,1H,Ha cis/ SO_2)),6.85-7.10(m,5H, (f,g,h)),7.2 à 7.7(m,5H, (j,k,l))	155.14(b),141.94,139.35, 133.04(l),120.80,128.27, 127.94,127.05,126.54, 124.51,39.48(c),22.05(d)	3060,3015,,2970, 2930,1600,1580, 1490,1445,1300, 1160,1130,960, 905,740,690,645
 6d	1.0 to 1.80(la,11H,(e,f, g,h)),1.86(d,3H,J=7.5Hz, (a)),2.19(d,2H,J=7.0Hz, (d)),7.2(q,1H,J=7.5Hz, (b)),7.5-8.1(m,5H, phenyl)	140.93,140.42,138.28, 132.94(l),128.95(k), 127.88(j),36.97(e),33.64 33.10,26.21,26.13(h), 14.66(a)	3030,2920,2850, 2260,1640,1585, 1480,1305,1215, 1180,1160,1140, 1120,1085,1000, 910,760,735,690, 620
 7d	0.93(d,3H,J=7.5Hz,(d)), 0.90 à 1.98(la,m,11H, (e,f,g,h)),2.34(m,1H, (c)),5.82(s,1H,(Ha trans/SO_2)),6.48(s,1H, (Ha cis/SO_2)),7.5-8.1(m 5H,(phenyl))	155.53(b),139.14(i), 133.36(l),129.04(k), 128.36(j),122.67(a), 41.98(c),39.15(e),31.10, 28.96,26.13,18.44	2915,2825,1450, 1390,1315,1305, 1175,1150,1120, 1080,1025,1000, 950,895,865,840, 765,750,690,650
 6e	0.99(s,9H,(f)),1.86(d, 3H,J=7.5Hz,(a)),2.31(s, 2H,(d)),7.14(q,1H, J=7.5Hz,(b)),7.5-8.1(m, 5H,(phenyl))	142.21,141.22,141.14, 132.76d(j),128.94(i), 127.70(h),38.52(e),33.44 (d),30.54(f),16.12(a)	3060,2950,1640, 1580,1475,1445, 1300,1195,1080, 760,750,735,685
 7e	0.87(s,9H,(f)),0.90(d, 3H,J=7.5Hz,(a)),2.55(q, 1H,J=7.5Hz,(c)),6.0(s,1H, (Ha trans/SO_2),7.5-8.10 (m,5H,(phenyl))	155.53(b),139.35(g), 133.30(j),129.04, 128.47(h,i),123.98(a), 42.25(c),33.96(e), 27.71(f),18.20(d)	3060,2950,1640, 1580,1475,1445, 1300,1145,1120, 1080,1065,750, 685,620
 6f	1.87(d,3H,J=7.5Hz,(a)), 2.73(m,2H,(d)),3.21(m, 2H,(e)),7.14(q,1H, J=7.5Hz(b)),7.30-8.05 (m,5H,(phenyl))	198.12(f),140.61,139.45 (k),138.38,136.17,133.04 (n),129.05(m),128.40, 127.77,37.13(d),20.47(e), 13.92(a)	3060,2960,2930, 2910,2850,1970, 1895,1815,1725, 1700,1585,1575, 1480,1445,1405, 1375,1360,1340, 1300,1290,1275, 1215,1200,1185, 1150,1130,1085, 1015,1005,970, 940,925,860,850, 780,765,755,730, 690,650

	7f	1.12(d,3H,J=6.8Hz,(d)), 3.24(m,3H,(e,c)),6.03 (s,1H,(Ha trans/SO_2)), 6.57(s,1H,(Ha cis/SO_2)), 7.40-8.10(m,10H, (phenyls))	197.48(f),154.99(b), 138.87(k),133.51,133.18, 129.22,128.59,128.24, 128.03,123.71,45.41(c), 30.06(e),20.38(d)	3100,2960,1675, 1595,1580,1445, 1405,1365,1300, 1290,1210,1160, 1125,1080,960, 850,800,750,685, 635
	6g	250MHz,)1.04(s,6H, (p,q)),1.48(m,2H,(m)), 1.59(m,2H,(n)),1.75(s, 3H,(k)),1.88(d,3H, J=7.10Hz,(a)),2.07(t,2H, J=6.30Hz(l)),2.58(t,2H, J=7.20Hz,(d)),2.78(t,2H, J=7.20Hz,(e)),6.08(d,1H, J=16.4Hz,(h)),7.03(q,1H, J=7.10Hz,(b)),7.28(d,1H, J=16.4Hz,(g)),7.53(m,3H, (t,u)),7.84(m,2H,(s))	198.32(f),142.33,140.84, 139.62,138.13,136.37, 135.81,133.09(u),129.94, 129.07(t),127.85(s),39.68, 38.70,33.94,33.49,28.72, 21.66,20.65,18.77,14.00(a)	b
	7g	1.08(s,6H,(p,q)),1.15(d, 3H,(d)),1.71(s,3H,(k)), 1.23-2.16(m,6H,(l,m,n)), 2.43 to 3.34(m,3H,(e,c)) 5.91(s,1H,(Ha trans/SO_2)) 6.09(d,1H,J=17Hz,(h)), 6.48(s,1H,(Ha cis/SO_2)), 7.35(d,1H,J=17Hz,(g)), 7.45-8.10(m,5H,(phenyl))	197.30(f),155.05(b),142.27 139.05(r),136.49,135.83, 133.54(u),130.06,129.19, 128.15(s),123.50,47.05, 39.75,33.99,33.55,30.00, 28.78,21.72,20.38,18.83	2960,2935,2870, 1690,1660,1605, 1585,1450,1365, 1310,1165,1145, 1085,1030,980, 955,850,750,690, 630
	8	1,41(d,3H,J=7.0Hz,(d)), 3.9(La,1H,NH),4.19(q, 1H,J=7.0Hz,(c)),6.00(s, 1H,(Ha trans/SO2),6.24 (s,1H,(Ha cis/SO2),6.12-7.90(m,10H,phenyls)	152.99(b),145.07,141,25, 138.87,133.27,128.92, 128.54,127.94,123.97(a), 117.51,112.95,48.4(c), 22.4(d)	3390,2970,2860, 1600,1500,1445, 1375,1300,1255, 1180,1150,1080, 1065,745,685
	9	1.89(d,3H,J=7.0Hz,(a)), 3.60(s,2H,(d)),3.80(la, 1H,NH),6.20-7.72(m,11H, (b,phenyls))	147.34,141.21,133.31, 129.20,127.88,118.31, 113.4,39.78(d),14.47(a)	3390,3040,2860, 1640,1595,1595, 1580,1510,1470, 1440,1430,1315, 1300,1130,1070, 760,740,685,605
	10	1.59(d,3H,J=7.5Hz),(a), 3.84(s,2H(d)),7.14(q,1H, J=7.5Hz(b)),7.23(la,s, 5H(f,g,h)),7.45 to 8.10 (m,5H,(j;k;l))	140.80,140.08,138.24, 134.48,132.88,131.27, 128.64,128.55,127.78, 126.98,30.02(d),13.93(a)	3050,2925,2840, 1635,1580,1475, 1440,1300,1140, 1080,730,680

(a) as film (neat) for liquids, or KBr plates for solids
(b) not recorded

Acknowledgements -

We thank the C.N.R.S. for financial support (U.A. 473) and the Rhône-Poulenc Company for a grant to one of us (P. Auvray). We also thank Mrs F. Grosjean and Mrs M. Baudry for the synthesis of several starting materials, and Mrs Mathé for typing the manuscript.

Bibliography -

1. New address: Dept of Chemistry, The University of Michigan, ANN ARBOR - Michigan 48109-1055 (U.S.A.)
2. P. Auvray, P. Knochel and J.F. Normant, Tetrahedron Lett. 26, 425 (1985)
3. P. Auvray, P. Knochel and J.F. Normant, Tetrahedron Lett. 26, 4455 (1985)
4. a/ P. Auvray, P. Knochel and J.F. Normant, Tetrahedron Lett. 26, 2329 (1986)
   b/ P. Knochel and J.F. Normant, J. Organomet. Chem. 309, 1 (1986)
5. For a preliminary communication see :
   P. Auvray, P. Knochel and J.F. Normant, Tetrahedron Lett. 27, 5095 (1986)
6. **a/** R. Oda, T. Kawabata and S. Tanimoto, Tetrahedron Lett. 1653 (1964) ; **b/** H. Morita, Z. Suzuki and H. Hirose, Bull. Chem. Soc. Japan, 2815 (1968) ; **c/** A.B. Baylis and M.E. Hillman, German Patent 2155113 (May 1972) C.A. 77 34174 (1972) ; **d/** S.E. Drewes and N.D. Emslie, J. Chem. Soc. Perkin Trans. 1, 2079 (1982) ; **e/** P. Perlmutter and C.C. Teo, Tetrahedron Lett. 25, 5951 (1984) ; **e/** H.M.R. Koffmann and J. Rabe, J. Org. Chem. 50, 3849 (1985) ; **g/** O. Basaviah and V.V.L. Gowriswari, Tetrahedron Lett. 27, 2031 (1986) ; **h/** H. Amri and J. Villieras, Tetrahedron Lett. 27, 4307 (1986)
7. D. Seebach, G. Calderari and P. Knochel, Tetrahedron 41, 4861 (1985)
8. E.J. Corey, C.U. Kim and M. Takeda, Tetrahedron Lett. 4339 (1972)
9. J.P. Gorlier, L. Hamon, J. Levisalles and J. Wagnon, J. Chem. Soc. Chem. Commun. 88 (1973), L. Hamon and J. Levisalles, J. Organomet. Chem. 251, 133 (1983)
   In our case, the organocyanocuprates gave much better results than the lithium dialkylcuprates
10. R.E. Donaldson, J.C. Saddler, S. Byrn, A.T. Mac Kenzie and P.L. Fuchs, J. Org. Chem. 48, 2167 (1983) ; D.K. Hutchinson and P.L. Fuchs, J. Amer. Chem. Soc. 107, 6137 (1985) ; D.K. Hutchinson, S.A. Hardinger and P.L. Fuchs, Tetrahedron Lett. 27, 1425 (1986)
11. K. Maruyama and Y. Yamamoto, J. Amer. Chem. Soc. 99, 8068 (1977)
12. a/ E. Doomes, P.A. Thiel, M.L. Nelson, J. Org. Chem. 41, 248 (1976)
    b/ E. Doomes, U. Clarke and J.J. Neitzel, J. Org. Chem. 52, 1540 (1987)
    c/ E. Doomes and B. Overton, J. Org. Chem. 52, 1544 (1987)
13. a/ J.L. Fabre, M. Julia and J.N. Verpeaux, Tetrahedron Lett. 23, 2469 (1982)
    b/ J.L. Fabre and M. Julia, Tetrahedron Lett. 24, 4311 (1983)
14. W.C. Still, M. Kahn, M. Mitra, J. Org. Chem. 43, 2923 (1978)
15. Prepared in the same way as (Z)-1-iodo-1-hexene :
    A. Alexakis, G. Cahiez and J.F. Normant, Org. Syntheses, F. Semmelhack editor 62, 1 (1984)
16. G. Cahiez, D. Bernard and J.F. Normant, Synthesis (1976) 26.