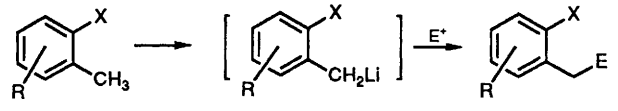
Sulphur-based Directed Benzylic Metallations: Lithiations of Alkylarenesulphonates

Babajide I. Alo * and Oluwole B. Familoni
Department of Chemistry, University of Lagos, Nigeria
Francis Marsais and Guy Queguiner *
Laboratoire de chimie Organique Heterocyclique de L'IRCOF, Institut National des Sciences Appliqueés, B.P. 08, 76130 Mont-St-Aignan, France

Benzylic anions (**6**) are obtained by regio-specific lithiations of ethyl 2-methylbenzenesulphonates. Evidence for the presence of the ethyl 2-lithiomethylbenzenesulphonates was obtained by efficient quenching studies with a range of electrophiles. Lithiations of the 2,4-dimethyl compound (**9**) gave the 2-lithiomethyl anion only, indicative of a predominant co-ordination mechanism in the lithiations.

Organolithium intermediates continue to occupy a prime position in synthetic chemistry [1] since they may facilitate a large variety of transformations. In the elaboration of homo- and hetero-aromatic [2] systems, their use is increasing owing to the continuing development of substituents capable of directing the introduction of the metal in a predictable manner.[3–6] Sulphur-based directed metallation groups have attracted particular attention. Substituents on homo- and hetero-aromatic systems including a sulphur atom such as sulphides,[7] sulphones,[8] sulphonamides,[9] and especially sulphonates [10] have proved to be excellent *ortho*-directing groups for metallation. Recently,[10b] alkyl sulphonates have been used as sulphur-based directed aromatic metallation groups. Their relatively facile reactions gave product yields ranging from good to excellent on trapping of the organolithium reagent with a variety of eletrophiles. Snieckus *et al.*[11] have demonstrated the use of sulphur groups for regioselective construction of polysubstituted aromatic compounds, providing novel and varied methodological possibilities.

Benzylic anions from the *ortho*-methyl substituent of aromatic systems containing various directed metallation groups have been used in synthesis. Deprotonation of the methyl group has been achieved in a variety of ways: Bu^nLi has been used either alone [12] (1 or 2 equiv.) or with an appropriate complexing agent as promoter,[12e,13] and lithium dialkylamides (e.g. Pr^i_2NLi) [14] or other bases [15] have also been used (Scheme 1).



(1) (2) (3)

Scheme 1. Directed metallation group X = $CONR_2$,[12a] SO_2NHR,[12b] CONHR,[12c] CSNHR,[12d] NR_2,[12e] CH_2NR_2,[12f] dihydro-oxazolyl,[12g] OMe,[6] NHCOR,[12h] SR,[12i] CO_2H,[14a] CO_2R,[14b] $OCONR_2$,[14c] or CN.[15] *Conditions:* Bu^nLi, Bu^nLi–complexing agent, Pr^i_2NLi, or other base.

Products of the reactions of such anions with electrophiles are not usually obtainable by classical methods.

In some cases, competing ring lithiation has been observed during benzylic anion generation, but the use of a complexing agent or a suitable change in metallation conditions seems to eliminate this competition.[12e,13] We have now explored the use of alkyl sulphonates as directed metallation groups in benzylic anion-forming processes as an extension of their synthetic utility. Sulphur-based directed metallation groups in general have the advantage that they are easily removed.

Table. Reaction of the lithio compounds (**6**), (**9**), and (**12**) with electrophiles.

Entry	Reactant	Electrophile	Product	R	% Yield
1	(**6**)	EtCHO	(**7a**)	EtCH(OH)	75
2	(**6**)	Me_2CO	(**7b**)	$Me_2C(OH)$	50
3	(**6**)	PhCHO	(**7c**)	PhCH(OH)	65
4	(**6**)	Ph_2CO	(**7d**)	$Ph_2C(OH)$	91
5	(**6**)	$ClCO_2Et$	(**7e**)	EtO_2C	50
6	(**6**)	CO_2	(**7f**)	HO_2C	70
7	(**6**)	PhNCO	(**7g**)	PhNHC(:O)	78
8	(**6**)	$PhSO_2Cl$	(**7h**)	$PhSO_2$	50
9	(**9**)	PhCHO	(**10a**)	PhCH(OH)	60
10	(**9**)	Ph_2CO	(**10b**)	$Ph_2C(OH)$	90
11	(**9**)	CO_2	(**10c**)	HO_2C	85
12	(**12**)	$\overline{OCH_2CHCH_2Me}$	(**13**)	—	40

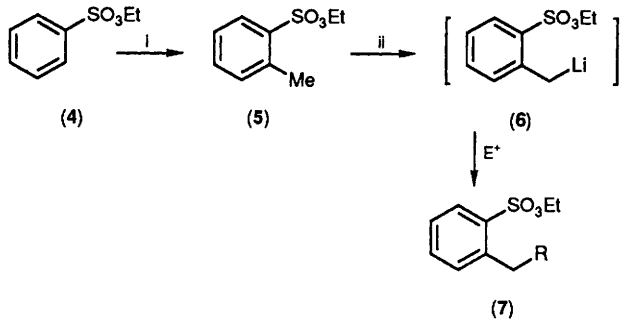
Results and Discussions

Ethyl 2-methylbenzenesulphonate (**5**)* was obtained *via* treatment of ethyl 2-lithiobenzenesulphonate with methyl iodide according to Bonfiglio's reported procedure [10b] and unambiguously characterized. The lithiation of the 2-methyl compound (**5**) with Bu^nLi (1.1 equiv.) at −78 °C proceeded rapidly to give a deep red benzylic anion species rather than the ring metallation product, as expected since the more acidic methyl proton should be removed more readily than the nuclear protons. The anion generated reacted smoothly (with the loss of the red colour) with a range of electrophiles leading to benzyl substituted products in good to excellent yields (see Table). No competing ring metallation giving the 2-lithio-6-methyl-benzenesulphonate was observed. As reported previously,[12e,13] a complexing agent may be necessary to enhance the ratio of side chain to ring metallation.

Exposure of the anion to aliphatic aldehydes gave the expected phenyl alcohols without any accompanying lactonization even on flash chromatography.

Since the use of sulphonyl chlorides as electrophiles has received relatively little attention, and new benzyl sulphones are required, we attempted to trap the anion with benzenesulphonyl chloride. Such anion trapping with sulphonyl chlorides should provide a better method for preparation of sulphones than the cumbersome classical protocol of formation of a sulphide

* Ethyl benzenesulphonate was used as earlier reported [10b] rather than the methyl ester to avoid the possibility of competition from the easy methyl group displacement reaction initially observed.

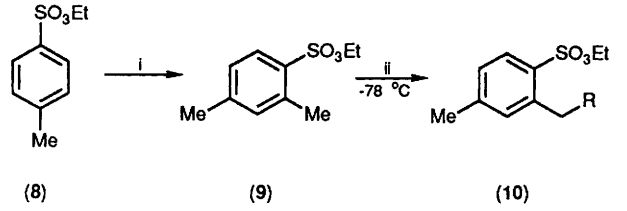


Scheme 2. *Reagents:* i, Bu^{n}Li, MeI, NH_4Cl; ii, Bu^{n}Li, −78 °C.

followed by oxidation.[8] A good yield of the sulphone was obtained in the representative example (entry 8).

The benzylic anions are presumably generated by the initial co-ordination of the Bu^{n}Li with the heteroatom of the directing group to form a monolithio complex from which the methyl proton is then abstracted. Similarly the success of the present *ortho*-metallation presumably depends on the possible co-ordination of the lithio anion with the sulphonate group at low temperatures.

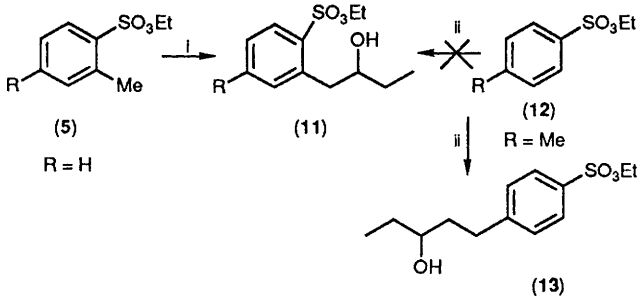
Corroborative evidence for a predominant co-ordination mechanism for these alkyl benzenesulphonate-directed metallations was obtained from lithiation experiments with ethyl 2,4-dimethylbenzenesulphonate (**9**) in which regiospecific 2-methyl lithiation was obtained. [The sulphonate (**9**) was obtained by



Scheme 3. *Reagents:* i, Bu^{n}Li, MeI, NH_4Cl; ii, Bu^{n}Li, E^+; H_3O^+.

ortho-metallation from ethyl 4-methylbenzenesulphonate (**8**)]. Lithiation of (**9**) was performed with 1.1 equiv. of Bu^{n}Li during 1.5 h to give quantitatively the benzylic anion which was trapped with various electrophiles. Product analysis by NMR spectroscopy indicated exclusive formation of the 2-substituted methyl compounds with no trace of any 4-substituted methyl compounds.

Of special interest is the use of oxiranes as electrophiles in reactions of products derived from *ortho*-lithiation of ethyl 4-methylbenzenesulphonate. The 4-methyl substituted compound (**13**) was isolated rather than the product (**11**) from the 2-lithio species.



Scheme 4. *Reagents:* i, Bu^{n}Li, EtCHO, H^+; ii, Bu^{n}Li, $EtCHCH_2O$, H_3O^+.

As quenching of the oxirane was slow at low temperatures, the reaction required warming to room temperature during 24 h for completion. This observation was therefore rationalized on the basis of a migration of the initially formed kinetic product (the 2-lithio species as previously shown) to the thermodynamic product (4-lithio-methyl species) at higher temperatures. The thermodynamically stable 4-benzyl anion predominates at room temperature wherein the epoxide formed the 4-(3-hydroxypentyl)sulphonate (**13**). Such 4-tolyl anions were previously formed only by addition of the Bu^{n}Li complexing agent tetramethylethylenediamine.[10b]

The present strategem furnishes a convenient means not only for homologations of 2-alkylbenzenesulphonates but also for the construction of sulphur-containing heterocycles (thiazines or sultones) on cyclisation of the appropriate products from quenching with electrophiles. The benzylic lithiations should also provide access to aromatic compounds bearing unusual methyl substituents.

Experimental

General.—^{1}H NMR spectra were obtained using Varian EM360L or Bruker 400 MHz spectrometers and are reported in ppm downfield of the internal standards Me_4Si in $CDCl_3$ or hexamethyldisilazane (HMDS) in $(CD_3)_2SO$. IR spectra were recorded on a Beckman IR 4250 spectrometer (films for liquids; KBr dispersions for solids). Elemental analyses were performed on a Carlo Erba 1106 instrument. M.p.s were obtained on a Kofler hot-stage apparatus and are uncorrected. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl before use and the water content of the solvent was estimated by a modified Karl–Fisher method[16] to be <45 ppm. Metallations were performed under dry deoxygenated argon. The n-butyllithium content of the commercial hexane solution was estimated by the Gilman double titration method.

Ethyl Benzenesulphonate (**4**).—Aqueous sodium hydroxide (50 g; 25% solution) was added dropwise to a stirred solution of benzenesulphonyl chloride (50 g) in ethanol (50 ml) with the temperature below 20 °C. The alkaline mixture was then stirred for 3 h. The crude product was washed several times with 5% hydrochloric acid, 5% aqueous $NaHCO_3$, and then with water. The resulting oil was vacuum distilled at 151 °C/10 mmHg (lit., [10b] 156 °C/15 mmHg) and the sulphonate (**4**) stored under argon, yield 46.5 g (95%); ^{1}H NMR, ($CDCl_3$) δ 1.3 (3 H, t), 4.2 (2 H, q), 7.6 (3 H, m), and 8.0 (2 H, m).

Ethyl 2-Methylbenzenesulphonate (**5**).—To a solution of ethyl benzenesulphonate (**4**) (0.05 mol, 9.3 g) in dry THF (120 ml), Bu^{n}Li (0.055 mol, 1.1 equiv.) in hexane (37 ml) was added at −78 °C, and the solution stirred at −78 °C for 5 h. The solution became red. Methyl iodide (0.055 mol, 7.81 g) in dry THF (30 ml) was then slowly injected at −78 °C. After 1 h at −78 °C, the mixture was allowed to warm to 0 °C, and stirred for 1 h at 0 °C, when the reaction was quenched with cold saturated aqueous NH_4Cl. The organic portion was separated and the aqueous portion extracted (×2) with dichloromethane. The combined organic portions were washed with 5% aqueous K_2CO_3 solution and brine, and dried over $MgSO_4$. Evaporation *in vacuo* gave a pale yellow oil. TLC gave one spot in ether–hexane (1:1), R_f 0.75; yield 8.0 g (80%); ^{1}H NMR ($CDCl_3$) δ 1.3 (3 H, t), 2.7 (3 H, s), 4.1 (2 H, q), 7.5 (3 H, m, ArH), and 8.0 (1 H, dd, ArH).

General Metallation Procedure.—n-Butyl-lithium (0.0137 mol. 1.12 equiv.) in hexane (10 ml) was added slowly to ethyl 2-methylbenzenesulphonate (**5**) (0.0125 mol, 2.5 g) in dry THF (50 ml) at −78 °C and the mixture stirred at −78 °C for 1.5 h. The ester lithio species gave a deep red solution.

The appropriate electrophile (0.0137 mol) in THF (30 ml) was then added at −78 °C. The mixture was stirred at −78 °C

for a further 1 h, allowed to warm to 0 °C, and stirred at 0 °C for 1 h. Water was then added at 0 °C followed by 5% HCl. The organic portion was separated and the aqueous layer extracted (×2) with dichloromethane. The combined organic portions were washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*.

Ethyl 2-(2-*Hydroxybutyl*)*benzenesulphonate* (**7a**). The crude oil obtained from the use of propionaldehyde as electrophile was purified by flash chromatography on silica gel with diethyl ether–hexane (1:1) as eluant to give the *alcohol* (**7a**) as an analytically pure colourless oil (75%) (Found: C, 56.2; H, 7.3. $C_{12}H_{18}O_4S$ requires C, 55.8; H, 7.0%); IR (film) ν_{max} 3 530br, 2 980, 2 940, 1 600, 1 480, 1 450, 1 350, 1 180, 1 010, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.6 (8 H, m), 2.2 (1 H, OH, exchangeable with D_2O), 3.1 (2 H, t), 3.8 (1 H, m), 4.1 (2 H, q), 7.5 (3 H, ArH, m), and 8.0 (1 H, dd, *J* 9 Hz, ArH).

Ethyl 2-(2-*Hydroxy*-2-*methylpropyl*)*benzenesulphonate* (**7b**). The crude oil obtained from the use of acetone as electrophile was purified by flash chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant to give *compound* (**7b**) as a colourless oil (50%) (Found: C, 56.1; H, 7.3%); IR (film) ν_{max} 3 560br, 2 980, 2 950, 1 600, 1 470, 1 350, 1 180, 1 010, and 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (9 H, m), 2.8 (1 H, s, OH, exchangeable with D_2O), 3.2 (2 H, s), 4.0 (2 H, q), 7.6 (3 H, m, ArH), and 8.0 (1 H, dd, ArH).

Ethyl 2-(2-*Hydroxy*-2-*phenylethyl*)*benzenesulphonate* (**7c**). The crude oil obtained solidified after 24 h. Recrystallization from light petroleum gave *compound* (**7c**) as white needles, m.p. 56–58 °C (Found: 62.6; H, 5.9. $C_{16}H_{18}O_4S$ requires C, 62.7; H, 5.9%); IR (KBr) ν_{max} 3 520br, 3 080, 3 020, 2 990, 1 600, 1 475, 1 455, 1 355, 1 185, 1 100, and 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (3 H, t), 2.7 (1 H, br, OH), 3.4 (2 H, m), 4.1 (2 H, q), 5.0 (1 H, q), 7.4 (8 H, m), and 8.1 (1 H, dd).

Ethyl 2-(2-*Hydroxy*-2,2-*diphenylethyl*)*benzenesulphonate* (**7d**). The crude solid obtained from the use of benzophenone as electrophile was crystallized from ether–light petroleum to give the *tertiary alcohol* (**7d**) as white needles, m.p. 130–132 °C (91%) (Found: 69.2; H, 5.3. $C_{22}H_{22}O_4S$ requires C, 69.1; H, 5.7%); IR (KBr) ν_{max} 3 460br, 1 600, 1 450, 1 345, 1 175, 1 100, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (3 H, t), 3.1 (1 H, br, OH, exchangeable with D_2O), 4.05 (2 H, s), 4.1 (2 H, q), 6.3 (1 H, d), 7.2–7.3 (8 H, m), 7.5 (4 H, m), and 8.0 (1 H, d).

Ethyl 2-(*Ethoxycarbonylmethyl*)*benzenesulphonate* (**7e**). The crude oil obtained from the use of ethyl chloroformate as electrophile was purified by flash chromatography using light petroleum–diethyl ether (1:1) as eluant to give the *acetate* (**7e**) as a colourless oil (50%) (Found: C, 53.0; H, 6.1. $C_{12}H_{16}O_5S$ requires C, 52.9; H, 5.9%); IR (film) ν_{max} 2 980, 1 730, 1 600, 1 570, 1 470, 1 440, 1 370, 1 220, 1 180, 1 030, 1 000, and 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (6 H, m), 4.1 (6 H, m), 7.6 (3 H, m, ArH), and 8.1 (1 H, dd).

Ethyl 2-(*Carboxymethyl*)*benzenesulphonate* (**7f**). The crude solid obtained from using solid CO_2 as electrophile was recrystallized from diethyl ether–light petroleum furnishing the *acid* (**7f**) as white plates, m.p. 106–108 °C (70%) (Found: C, 49.2; H, 4.75. $C_{10}H_{12}O_5S$ requires C, 49.2, H, 4.9%); IR (KBr) ν_{max} 3 300–2 500, 1 710, 1 600, 1 450, 1 350, 1 180, 1 000, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (3 H, t), 4.1 (2 H, q), 4.2 (2 H, s), 7.6 (3 H, m), 8.1 (1 H, dd), and 9.3 (1 H, br).

Ethyl 2-(N-*Phenylcarbamoylmethyl*)*benzenesulphonate* (**7g**). The crude solid obtained from using phenyl isocyanate as electrophile was recrystallized from dichloromethane–light petroleum to give the *amide* (**7g**) as pale yellow needles, m.p. 124–126 °C (78%) (Found: C, 57.15; H, 5.4; N, 4.45; $C_{16}H_{17}NO_4S$ requires C, 56.95; H, 5.8; N, 47%); IR (KBr) ν_{max} 3 360s, 2 990, 1 680, 1 600, 1 550, 1 450, 1 350, 1 180, 1 000, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (3 H, t), 4.1 (4 H, q and s), 7.1–7.6 (8 H, m), 8.0 (1 H, dd), and 8.35 (1 H, NH).

Ethyl 2-(*Phenylsulphonylmethyl*)*benzenesulphonate* (**7h**). The crude oil obtained with benzenesulphonyl chloride as electrophile was purified by flash chromatography with diethyl ether–cyclohexane (1:1) as eluant to give the *sulphone* (**7h**) as a pale yellow oil (50%) (Found: C, 52.5; H, 4.95. $C_{15}H_{16}O_5S_2$ requires C, 52.9; H, 4.7%); IR (film) ν_{max} 3 000, 1 600, 1 450, 1 350, 1 180, 1 000, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (3 H, t), 4.1 (2 H, q), 5.5 (2 H, s), 7.6 (6 H, m), and 8.1 (3 H, dd).

Ethyl 2,4-*Dimethylbenzenesulphonate* (**9**).—Lithiation of ethyl 4-methylbenzenesulphonate (**8**) with Bu^nLi at −78 °C followed by reaction with methyl iodide and quenching with aqueous NH_4Cl gave an oil which was purified by flash chromatography with hexane–diethyl ether (1:1) as eluant to give the sulphinate (**9**) as a clear white gum (83%); ^1H NMR ($CDCl_3$) δ 1.3 (3 H, t), 2.45 (3 H, s), 2.7 (3 H, s), 4.2 (2 H, q), 7.2 (2 H, m, ArH), and 7.9 (1 H, d, ArH). The sulphonate (**9**) was lithiated and treated with electrophiles as for the sulphonate (**5**).

Ethyl 2-(2-*Hydroxy*-2-*phenylethyl*)-4-*methylbenzenesulphonate* (**10a**).—The oil obtained from the reaction with benzaldehyde as electrophile was purified by flash chromatography with diethyl ether–cyclohexane (1:1) as eluant giving the 4-*methyl compound* (**10a**) as a white solid, m.p. 49–51 °C (65%) (Found: C, 63.65; H, 6.2. $C_{17}H_{20}O_4S$ requires C, 63.75; H, 6.25%); IR (KBr) ν_{max} 3 650s, 2 990, 1 600, 1 480, 1 450, 1 350, 1 180, 1 000, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (3 H, t), 2.3 (3 H, s), 3.4 (2 H, m), 4.1 (2 H, q), 5.0 (1 H, q), 7.3 (7 H, m), and 7.9 (1 H, d).

Ethyl 2-(2-*Hydroxy*-2,2-*diphenylethyl*)-4-*methylbenzenesulphonate* (**10b**). The crude solid obtained from the reaction with benzophenone as electrophile was recrystallised from diethyl ether–light petroleum to give the *alcohol* (**10b**) as white needles, m.p. 114–116 °C (90%) (Found: C, 69.9; H, 6.2. $C_{23}H_{23}O_4S$ requires C, 69.9, H, 5.0%); IR (KBr) ν_{max} 3 500s, 3 060, 1 600, 1 490, 1 450, 1 340, 1 180, 1 000, and 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (3 H, t), 2.0 (3 H, s), 4.1 (5 H, including OH), 6.0 (1 H, s), 7.4 (1 H, m), and 7.9 (1 H, d).

Ethyl 2-(*Carboxymethyl*)-4-*methylbenzenesulphonate* (**10c**). The crude product obtained from the reaction with solid CO_2 was recrystallized from light petroleum–diethyl ether to give the *acid* (**10c**) as colourless plates, m.p. 108–110 °C (85%) (Found: C, 51.4; H, 5.6. $C_{11}H_{14}O_5S$ requires C, 51.2; H, 5.4%); IR (KBr) ν_{max} 3 300–2 500, 1 710, 1 600, 1 460, 1 350, 1 180, 1 110, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 (3 H, t), 2.55 (3 H, s), 4.2 (4 H, q with s), 7.4 (2 H, m), 8.0 (1 H, d), and 8.35 (1 H, br, OH).

Ethyl 4-(3-*Hydroxypentyl*)*benzenesulphonate* (**13**).—Metallation was carried out as for ethyl benzenesulphonate. 1,2-Epoxybutane in THF was then added at 0 °C and the mixture was allowed to warm to room temperature during 24 h. Standard work-up gave a crude oil which was purified by flash chromatography with diethyl ether–cyclohexane (1:1) as eluant giving the *sulphonate* (**13**) as a colourless oil (40%) (Found: C, 57.6; H, 7.5. $C_{13}H_{20}O_4S$ requires C, 57.35; H, 7.35%); IR (film) ν_{max} 3 540s, 3 050, 1 600, 1 490, 1 450, 1 340, 1 180, 1 000, and 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.2 (6 H, m), 1.4 (4 H, m), 2.3 (1 H, OH, exchangeable with D_2O), 3.2 (2 H, m), 3.8 (1 H, m), 4.1 (2 H, q), 7.3 (2 H, d, *J* 10 Hz), and 7.8 (2 H, d, *J* 10 Hz).

Acknowledgements

We thank the C.I.E.S. French Ministry of Foreign Affairs, for the award of a Scholarship to O. B. F.

References

1 H. W. Gschwend and H. R. Rodriguez, *Org. React.*, 1979, **26**, 1; V. Snieckus and P. Beak, *Acc. Chem. Res.*, 1982, **15**, 305.
2 F. Marsais and G. Queguiner, *Tetrahedron*, 1983, **39**, 2009; V. Snieckus, *Bull. Soc. Chim. Fr.*, 1988, 67; A. Turck, L. Mojovic, and G. Queguiner, *Synthesis*, 1988, 881.
3 S. O. deSilva, J. N. Reed, and V. Snieckus, *Tetrahedron Lett.*, 1978, 5099.
4 J. M. Muchowski and M. C. Venuti, *J. Org. Chem.*, 1980, **45**, 4798.
5 C. A. Townsend and L. M. Bloom, *Tetrahedron Lett.*, 1981, 3923.
6 M. R. Winkle and R. C. Ronald, *J. Org. Chem.*, 1982, **47**, 2101.
7 N. S. Narasimhan and P. S. Chanrachood, *Synthesis*, 1979, 589; D. Babin, D. J. Fourneron, L. M. Harwood, and M. Julia, *Tetrahedron*, 1981, **37**, 325; L. Horner, A. J. Lawson, and G. Simons, *Phosphorus Sulphur*, 1983, **12**, 729.
8 F. M. Stoyanovich and B. P. Fedorov, *Angew. Chem.*, 1966, **78**, 116; F. M. Stoyanovich, R. G. Karpenko, and Y. Goldfab, *Tetrahedron*, 1971, **27**, 433; F. M. Stoyanovich, R. G. Karpenko, G. I. Gorushkina, and Y. Goldfarb, *ibid.*, 1972, **28**, 5017.
9 H. Watanabe, R. A. Schwarz, C. R. Hauser, J. Lewis, and D. W. Slocum, *Can. J. Chem.*, 1969, **47**, 1543; J. G. Lombardino, *J. Org. Chem.*, 1971, **36**, 1843; P. Breant, F. Marsais, and G. Queguiner, *Synthesis*, 1983, 822; F. Marsais, A. Cronnier, F. Trecourt, and G. Queguiner, *J. Org. Chem.*, 1987, **52**, 1133.
10 (*a*) G. D. Figuly and J. C. Martin, *J. Org. Chem.*, 1980, **45**, 3729; (*b*) J. N. Bonfiglio, *ibid.*, 1986, **51**, 2833.
11 M. Iwao, T. Iihama, K. K. Mahalanabis, H. Perrier, and V. Snieckus, *J. Org. Chem.*, 1989, **54**, 24.
12 (*a*) M. Watanabe, M. Sahara, M. Kubo, S. Fukuwara, R. J. Billedeau, and V. Snieckus, *J. Org. Chem.*, 1984, **49**, 743; (*b*) H. Watanabe, C. Mao, I. T. Barnish, and C. R. Hauser, *ibid.*, 1968, **33**, 4278; (*c*) V. Snieckus, *J. Heterocycl. Chem.*, 1984, **22**, 95; (*d*) J. I. Fitz and H. W. Gschwend, *J. Org. Chem.*, 1976, **41**, 4029; (*e*) R. E. Ludt, G. P. Crowther, and C. R. Hauser, *ibid.*, 1970, **35**, 1288; (*f*) R. L. Vaulx, F. N. Jones, and C. R. Hauser, *ibid.*, 1964, **29**, 1387; (*g*) H. W. Gschwend and A. Hamdan, *ibid.*, 1975, **40**, 2008; (*h*) W. Fuhrer and H. W. Gschwend, *ibid.*, 1979, **44**, 1133, (*i*) S. Cabiddu, S. Melis, P. P. Piras, and F. Sotgiu, *J. Organomet. Chem.*, 1979, **178**, 291.
13 R. E. Ludt, J. S. Griffith, K. N. McGrath, and C. R. Hauser, *J. Org. Chem.*, 1973, **38**, 1668.
14 (*a*) P. L. Greger, *J. Am. Chem. Soc.*, 1970, **92**, 1396; (*b*) G. A. Kraus, *J. Org. Chem.*, 1981, **46**, 201; (*c*) M. P. Sibi and V. Snieckus, *ibid.*, 1983, **48**, 1935.
15 C. K. Bradsher and T. G. Wallis, *J. Org. Chem.*, 1978, **43**, 38.
16 J. Bizot, *Bull. Soc. Chim. Fr.*, 1967, 151.

Paper 9/04980K
Received 23rd *November* 1989
Accepted 9th *January* 1990