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2. Ene-sulfides as Reaction Partners of Organometallic Compounds

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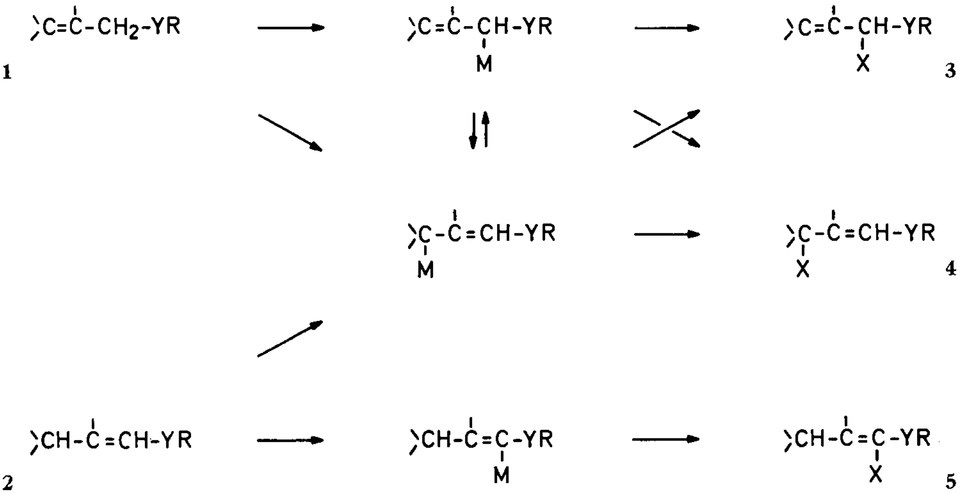
(24. X. 75)

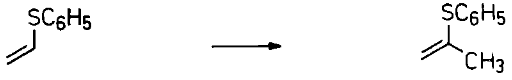
Summary. A comparison of the reactivity of ene-sulfides and en-ethers towards organometallic reagents reveals some remarkable differences. With the thio compounds metallation at the olefinic site next to the hetero atom dominates clearly over the alternative deprotonation of an allylic position. Only with propenyl phenyl sulfide both exchange modes were observed simultaneously, whereas with all higher homologues of it as well as vinyl phenyl sulfide the metal was exclusively attached to the olefinic α-carbon atom.

While allyl ethers **1** [1–3] (as well as thio allyl ethers [1] [4]) are only metallated at the one position, which is flanked by the double bond and the hetero atom, en-ethers **2** were found to exhibit ambipositional reactivity. They may undergo hydrogen/metal exchange at an allylic position [1] [5] or at the olefinic position next to the oxygen atom [5] [6–9]. Thus, it results in either a mixture of α-substituted allylic compounds **3** and γ-substituted alkenyl derivates **4** or, respectively, α-substituted alkenyl derivates **5**.



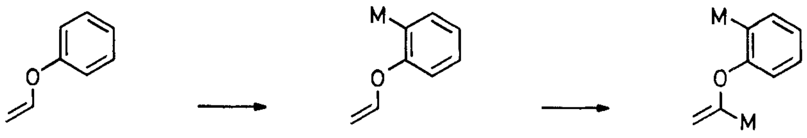
Y = O or S

Which one of the two competing types of organometallic attack would predominate, if the en-ether oxygen was replaced by sulfur? In order to examine whether metallation of olefinic CH groups next to sulfur is feasible at all, our first choice was a substrate without any allylic positions, namely the vinyl phenyl sulfide[1]) (**2a**). Indeed α-carbon alkylation was achieved in satisfactory yield (52%) after treatment with butyllithium in the presence of potassium *t*-butoxide followed by addition of methyl iodide. While this work was in progress, quite similar results have been reported in literature [10].



2a **5a**

In order to evaluate the sulfur effect on substrate reactivity somewhat more quantitatively, rate comparison with an oxygen analogue, that is the vinyl phenyl ether (**6**), became desirable. It turned out, however, that a direct comparison was not possible, since en-ether **6** would react in a different way than the corresponding ene-sulfide **2a**. Initially it is attacked at a ring position, affording **7**, and may only in an eventual consecutive step be converted into the dimetallated species **8**, in which also the olefinic site next to the hetero atom has undergone hydrogen/metal exchange.



6 **7** **8**

Nevertheless, the superiority of the sulfide is clearly demonstrated. Upon treatment with *n*-butyllithium and potassium *t*-butylalcoholate in hexane or *s*-butyllithium in tetrahydrofuran it is roughly 5 and, respectively, 20 times more rapidly consumed than its oxygen analogue. If one would only consider the attack at olefinic α-positions, these competition rate factors had to be enhanced by at least one order of magnitude. Thus at least a qualitative conclusion can be drawn: Sulfur as a second row element acidifies an adjacent CH bond more strongly than does its lower isologue oxygen. This reactivity sequence holds even if the hetero atom is attached to an olefinic carbon (our example; but *cf.* [11]), provided that ring strain effects do not interfere[2]).

The intriguing question now is, whether the homologous 1-propenyl phenyl sulfide (**2b**; *Z* + *E*) would follow the example of the vinyl compound **2a** by undergoing proton abstraction at the α-carbon atom or behave like the isomeric allyl phenyl sulfide [1] and react at the γ-position. Actually both processes occurred concurrently. Thus, after quenching with methyl iodide, 1-but-3-enyl phenyl sulfide

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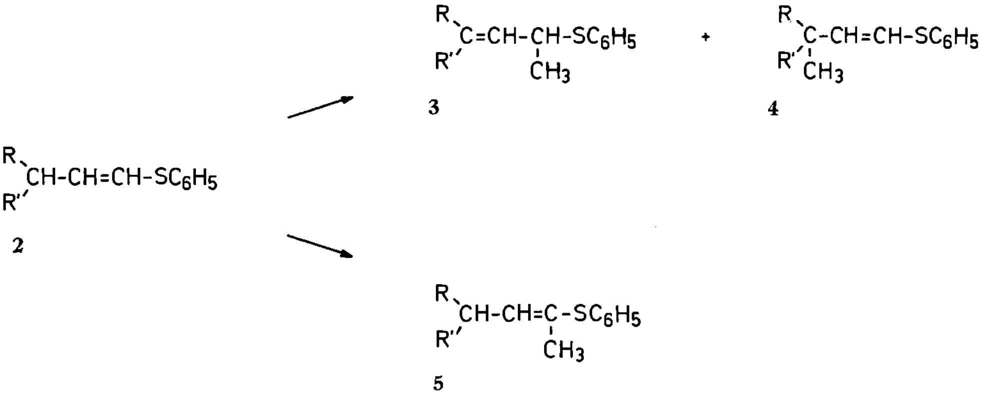
[1]) For sake of clarity, in this text the structural designation of compounds belonging to the class of ene-sulfides does not follow the IUPAC recommendations in every respect: the 'variable' ligand (alkenyl, including vinyl) will always precede the 'invariable' one (phenyl).

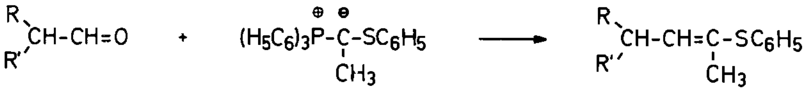
[2]) Benzofurane is (in cyclohexylamine) slightly more acidic than benzothiophene [12].

(**3b**; 1%), 1-but-1-enyl phenyl sulfide (**4b**[3]); 12%) and 2-but-2-enyl phenyl sulfide (**5b**; 32%) were obtained side by side.



b R = H, R′ = H
c R = CH_3, R′ = H
d R = CH_3, R′ = CH_3

Ene-sulfide **5b** and, later on, also the homologous members of this series, were identified by comparison with samples prepared by a different route, namely by means of *Wittig* reaction.



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$$RR'CH{-}CH{=}O + (H_5C_6)_3\overset{\oplus}{P}{-}\overset{\ominus}{C}(CH_3){-}SC_6H_5 \longrightarrow RR'CH{-}CH{=}C(CH_3){-}SC_6H_5$$

Replacement of the methyl group in **2b** by a bigger alkyl side-chain renders the allylic γ-position less readily accessible. Attack at the olefinic site, leading to 2-pent-2-enyl phenyl sulfide (**5c**; 20%) thus remains the only attractive route, if 1-but-1-enyl phenyl sulfide (**2c**; *Z*/*E*-mixture) serves as a substrate. A steep decrease of the amount of γ-deprotonation had to be anticipated on the basis of earlier findings: 2-alkenes such as 2-hexene are metallated exclusively (or essentially so) at the terminal methyl group [13]. α-Selective metallation of a longer straight-chain ene-sulfide (1-dec-1-enyl methyl sulfide; **2**: R = C_8H_{17}; R′ = H; CH_3 instead of C_6H_5) had already been observed previously [10]. In 1-(3-methyl-but-1-enyl) phenyl sulfide (**2d**; *Z*/*E*-mixture) the allylic position is, of course, even more hindered due to the alkyl branching and again only products resulting from α-attack were detected, namely 2-(4-methyl-pent-2-enyl) phenyl sulfide (**5d**; 34%).

As indicated above, most reactions, especially when carried out in petroleum ether solution, gave only moderate yields. Probably this is due to competing side reactions such as *Michael*-type addition of the organometallic reagent [14] or elimination [15] leading to thiophenolate (which indeed always is found) and an acetylene. These side reactions seem to prevail entirely, if (*E*)-1-(3,3-dimethylbut-2-enyl)

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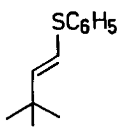
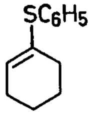
[3] Note that formula **4b** is identical with formula **2c**.

phenyl sulfide (*E*-**2e**) or 1-cyclohexenyl phenyl sulfide (**9**) are submitted to the usual metallation/alkylation procedure. None of the expected products could be identified.



2e



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The ene-sulfides **2b**–**2e** undergo *cis/trans* isomerisations with surprising ease, if an acid or free halogen is present in trace amounts (impure halomethane solvents!). The same happens if they are allowed to stand at daylight, which may generate traces of diphenylsulfide [16] photolytically. Whereas both *Z*- and *E*-isomers are almost equally represented in the equilibrium composition of **2b**, **2c** and **2d**, compound **2e** is, as one would suppose, thermodynamically destabilized in the hindered *Z*-form and goes over into the more favorable *E*-isomer to the extent of > 95%.

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Experimental Part

General remarks: *cf.* [17].

1. Starting materials and samples for comparison. – a) *Phenylthiomethyltriphenylphosphonium chloride.* The compound was prepared according to [18] [19]; 82% yield; m.p. 211–213° (dec.) (after crystallisation from dichlormethane and ethyl acetate; lit. [18] m.p. 232–234° (dec.), from nitromethane).

$C_{25}H_{22}ClPS$ (420.9) Calc. C 71.33 H 5.27% Found C 70.90 H 5.36%

b) *1-(1-Phenylthioethyl)-triphenylphosphonium iodide.* Over a period of 20 min a solution (32 ml) of butyllithium (50 mmol), 1.6M in hexane, was added dropwise to a suspension of phenylthiomethyltriphenylphosphonium chloride (21.0 g; 50 mmol) in tetrahydrofuran (100 ml) at −78°. The reaction mixture gave a negative *Gilman* test [20], after being allowed to reach room temp. Methyl iodide (7.1 g; 50 mmol) was added and slowly a precipitate settled out. After 3 h it was filtered off, washed with ether, crystallized from 400 ml acetone/water = 3:1 (*v/v*) and carefully dried (5 h, 100°); m.p. 166–168° (dec.); 85% yield.

$C_{26}H_{24}IPS$ (526.4) Calc. C 59.32 H 4.60% Found C 59.31 H 4.97%

For the corresponding chloride see [21].

c) *1-But-enyl phenyl sulfide* (**2c**). The compound was readily accessible following a patent prescription [22]; attempts failed to prepare it by base-catalyzed isomerisation [23] of crotenyl phenyl sulfide, because only an equilibrium mixture between product **2c** and starting material was formed.

d) (Z)- *and* (E)-*3-methyl-but-1-en-1-yl phenyl sulfide* ((*Z*)- and (*E*)-**2d**). To the phenylthiomethyltriphenyl-phosphonium chloride (21.0 g, 50 mmol) in tetrahydrofuran (100 ml) at —78° an hexane solution 1.6M in *n*-butyllithium (32 ml, 50 mmol) was added dropwise over a period of 20 min. The dark red reaction mixture was allowed to reach room temp. during 50 min. After 1.5 h isobutyraldehyde (3.6 g, 50 mmol) was added and afterwards the reaction mixture was warmed up at 50° for 2 h. Then it was cooled, diluted with ether (3 × 50 ml) and the adduct formed from triphenylphosphine oxide and lithium chloride was filtered off. After washing with water (3 × 50 ml), the combined organic phases were dried and then evaporated. The residue distilled under reduced pressure to furnish 6.8 g of crude product which, according to GC. (50 m, XF-1105*, 100°) was a mixture of two compounds. On the basis of spectral evidence the one with the shorter retention time was recognized to be the *Z*-**2d** and the other one was the *E*-isomer; ratio 36:64; 77% yield. – MS.: 178 (100%, M^+); 163 (65%). Careful fractionation[4] afforded several samples of which the lowest boiling one (0.6 g; b.p. 98–99/5 Torr) was rich (90% isomeric purity) in the component with the shorter retention time, which proved to posses the *Z*-configuration. The highest boiling fraction (1.4 g; b.p. 101–105°/5 Torr) mainly contained the other component with the *E*-configuration (93% isomeric purity) and longer retention time.

$C_{11}H_{14}S$ (178.3) Calc. 74.10 H 7.91% Found 73.93 H 7.87%

(*Z*)-**2d**[5]. IR.: 1590*s*, C=C; 1300*m*, —CH=CH—, *cis* (in-plane?); 745*s* and 695*s*, C_6H_5. – ^{1}H—NMR.: 7.2 (*m*, aromatic H); 6.06 (*d*, *J* = 9, olefinic H next to sulfur); 5.61 (*t*, *J* = 9, other olefinic H); 2.83 (*m*, *octet*-like, *J* = 9, with fine structure, methine H) and 10.3 (*d*, *J* = 6,5, 2 methyl groups).

(*E*)-**2d**[5]. IR.: 1590*s*, C=C; 1335*w* + 1315*w*, —CH=CH—, *trans* (in-plane?); 1230*w*; 955*s*, —CH=CH—, *trans* (out-of-plane); 815*w*; 745*s* and 695*s*, C_6H_5. – ^{1}H—NMR.: 7.2 (*m*, aromatic H); 6.0 (*m*, 2 olefinic H); 2.42 (*m*, *octet*-like, *J* = 9, methine H) and 1.03 (*d*, *J* = 6, 2 methyl groups).

e) (Z)- *and* (E)-*3,3-dimethyl-1-but-1-enyl phenyl sulfide* ((*Z*)- and (*E*)-**2e**): A tetrahydrofuran suspension of phenylthiomethyl-triphenyl-phosphonium chloride (21.0 g; 50 mmol) was converted into the ylid and treated with pivalaldehyde (4.3 g; 50 mmol). Filtration, extraction and evaporation of the organic solvents furnished a crude reaction mixture, which was submitted to vacuum distillation. In the boiling range 106–107°/2 Torr, 6.2 g of a clear liquid were collected, which according to GC. (2 m, 20% Ap-L, 200°) consisted of two substances present in a ratio 1:3. Obviously they were the two isomers (*Z*)- and (*E*)-**2e**; 65% yield. – MS.: 192 (55%, M^+); 177 (100%). $C_{12}H_{16}S$ (192.3) Calc. C 74.94 H 8.39% Found C 74.72 H 8.21%

Prep. GC. (6m, 15% Ap-L, 200°) permitted separation of the mixture. The major component with the longer retention time was found to have the *Z*-configuration.

(*Z*)-**2e**. IR.[5]: 1610 sh; 1580*s*, C=C; 1390*w*; 1360*m* + 1345*m*, —CH=CH—, *cis* (in-plane?); 1215*s*; 900*s* + 795*s*, —CH=CH—, *cis* (out-of-plane?) and 745*s* + 695*s*, C_6H_5. – ^{1}H—NMR.[5]: 7.3 (*m*, *s*-like, 5 aromat. H); 6.02 (*d*, *J* = 10.5, olefin. H next to S); 5.63 (*d*, *J* = 10.5, other olefin. H) and 1.21 (*s*, three methyl groups).

(*E*)-**2e**. IR.[5]: 1710*m*; 1580*s*, C=C; 1360*m*; 1265*m*; 955*s*, —CH=CH—, *trans*; 830*m* and 735*s* + 685*s*, C_6H_5. – ^{1}H—NMR.[5]: 7.20 (*m*, *s-like*, 5 aromat. H); 5.99 (*s*, 2 olefin. H) and 1.08 (*s*, three methyl groups).

f) (Z)- *and* (E)-*2-but-2-enyl phenyl sulfide* ((*Z*)- and (*E*)-**5b**. 1-(1-phenyl-thioethyl)-triphenyl-phosphonium iodide (3.6 g; 5.7 mmol) was suspended in 20 ml of tetrahydrofuran at – 78° and a 1.6M solution (3.7 ml) of butyllithium (5.9 mmol) was added dropwise within 10 min. After addition of freshly distilled acetaldehyde (0.25 g; 5.7 mmol) to the so formed ylid, the reaction mixture was allowed to warm up, was put into a water bath and stirred for 1 h at 40°. Petroleum ether (45 ml), added to the cooled solution, caused the precipitation of a solid, which was filtered off. The mixture was poured into saturated aqueous sodium chloride solution (50 ml) and vigorously shaken. The organic layer was decanted, the aqueous phase exhaustively extracted (3 × 20 ml petroleum ether) and the combined organic phases were washed (2 × 15 ml brine), dried and evaporated. Vacuum distillation afforded 0.41 g of *Z*- and *E*-**5b**; ratio 57:43; b.p. 84–87°/11 Torr; yield 44%. Prep. GC. (6 m, 20% Ap-L*, 190°) gave an analytically pure sample. – ^{1}H—NMR.: 7.2 (*m*, *s*-like, 5 aromat. H); 5.86 (*m*, *q*-like, *J* ~ 7.5, fine splitting, olefin. H) and 1.9 (*m*, two different methyl groups at allylic positions, two stereoisomers).

$C_{10}H_{12}S$ (164.3) Calc. C 73.12 H 7.36% Found C 73.21 H 7.52%

g) (Z)- *and* (E)-*2-pent-2-enyl phenyl sulfide* ((*Z*)- and (*E*)-**5c**). As described above (section 1f), a mixture of *Z*- and *E*-**5c** was prepared on a 5,0 mmol scale; 0.23 (26%) yield; b.p. 82–86°/5 Torr and purified by prep. GC. (3 m, 20% SE-30*, 200°). MS.: 178 (79%, M^+); 110 (100%). – ^{1}H—NMR. 7.2 (*m*, *s*-like, 5 aromat. H); 5.8 (*m*, olefin. H, two stereoisomers); 2.3 (*m*, methylene group); 1.87

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[4] Equipment: *Fischer Labor- und Verfahrenstechnik*, D–532 Bonn-Bad Godesberg, column type HMS 500.

[5] Spectra are corrected for mutual isomeric impurities in the sample.

(*m*, narrow, methyl group in allylic positions of two stereoisomers) and 1.03 (*t*, br., *J* ∼ 7.5, other methyl group.)

$C_{11}H_{14}S$ (178.3) Calc. C 74.10 H 7.91% Found C 74.10 H 8.01%

h) (Z)- *and* (E)-*2-(4-methylpent-2-enyl) phenyl sulfide* ((*Z*)- and (*E*)-**5d**). The preparation was carried out on a 20 mmol scale; addition of butyllithium to the phosphonium salt during 20 min. Distillation gave 1,7 g (*Z*)- and (*E*)-**5d**; isomeric ratio 30:70 (GC. analysis on 50 m, XF-1105*, 100°); b.p. 86–88°/2 Torr; 45% yield. – MS.: *m/e* = 192 (84%, M^+); 177 (100%). – IR.[6]: 1585*m*, C=C; 1375*w*; 735*s* and 685*s*, C_6H_5.

$C_{12}H_{15}S$ (192.3) Calc. C 74.94 H 8.38% Found C 74.94 H 8.46%

GC. (3 m, 30% DEGS, 190°) afforded the two isomers in 70% and 80% isomeric purity. To the predominant one, with the longer retention time, the *E*-configuration was assigned.

(*Z*)-**5d**[5]. ^{1}H—NMR.: 7.2 (*m*, *s*-like, aromat. H); 5.58 (*d*, *J* = 9, fine splitting, olefin. H); 2.9 (*m*, *octet*-like, *J* ∼ 7, fine structure, methine group); 1.86 (*s*-like, br., methyl group in allylic position) and 1,00 (*d*, *J* = 6.5, other methyl groups).

(*E*)-**5d**[5]. ^{1}H—NMR.: 7.2 (*m*, *s*-like, aromat. H); 5.67 (*d*, *J* = 9, fine splitting, olefin H); 2,6 (*m*, *octet*-like, *J* ∼ 7, fine structure, methine group); 1.85 (*d*, *J* ∼ 2, methyl group in allylic position) and 1.01 (*d*, J = 6.5, other methyl groups).

Upon acid catalysed isomerization a *Z/E* ratio of about 65:35 was established.

1-Cyclohexenyl phenyl sulfide (**9**). To a suspension of diphenyldisulfide (27,6 g; 126 mmol), kept at – 78°, a 1.3 M solution (95 ml) of 1-cyclohexenyl lithium [24] (126 mmol) in ether was added dropwise. After warming up to 25° in the course of 1 h and standing for another 2 h the reaction mixture was poured into water (75 ml) and extracted with ether (4 × 50 ml). The combined organic layers were washed (4 × 50 ml water), dried and evaporated. At 107–109°/1 Torr 17.6 g (73%) **9** distilled over as a colourless liquid. – MS.: 190 (79%, M^+); 81 (100%). – IR.: 1715*m*; 1585*s*, C=C; 925*m* + 915*m*; 845*w* + 800*w* and 745*s* + 695*s*, C_6H_5. – ^{1}H—NMR.: 7.2 (*m*, 5 aromat. H); 6.0 (*m*, olefin. H); 2.1 (*m*, 2 allylic methylene groups) and 1.6 (*m*, 2 other methylene groups).

$C_{12}H_{14}S$ (190.3) Calc. C 75.76 H 7.41% Found C 75.60 H 7.54%

2. Metallation Reactions: ene-sulfides as substrates. – a) *Vinyl phenyl sulfide* (**2a**). To a solution of **2a**[7] (1.35 g; 10 mmol) in petroleum ether (20 ml), potassium *t*-butoxide (1,2 g; 11 mmol) was added followed by dropwise treatment with butyllithium (1.6 M in hexane; 6.2 ml; 10 mmol) at 25° over a period of 10 min. After 3.5 h stirring, methyl iodide (1.4 g; 10 mmol) was added, while cooling in an ice bath. 30 min later it followed hydrolysis (60 ml water) and extraction (2 × 50 ml). From the organic layers, after drying, the solvent was removed using a *Widmer* column. Distillation under reduced pressure gave 1.5 g of a product mixture, which upon GC. analysis (50 m, XF-1105*, 70°; 2 m, 20% Ap-L, 150°; decane as an internal standard) was found to contain 16% starting material **2a**, 21% thioanisole and 53% 2-propenyl phenyl sulfide **5a**. The first two mentioned compounds were identified by retention time comparison with authentic materials; the main product was isolated by GC. (6 m, 15% Ap-L, 150°). – MS.: *m/e* = 150 (100%, M^+); 135 (95%). – IR.: 1710*s*; 1585*m*, C=C; 910*w*, br. and 745*s* + 695*s*, C_6H_5. – ^{1}H-NMR.: 7.3 (*m*, 5 aromat H); 5.05 (*m*, *s*-like with fine structure, olefin. H *cis* to sulfur); 4.84 (*s*, br., other olefin. H) and 1.95 (*m*, *s*-like with fine structure, methyl group).

$C_9H_{10}S$ (150.2) Calc. C 71.95 H 6.71% Found C 71.85 H 6.77%

b) (Z)- *and* (E)-*1-Propenyl phenyl sulfide* ((*Z*)- and (*E*)-**2b**). **2b** (0.77 g; 5.1 mmol; *Z/E* = 53:47 [28]), petroleum ether (10 ml) and potassium *t*-butoxide (0.67 g; 6 mmol) were mixed and butyllithium (1.6 M solution in hexane; 37 ml; 6 mmol) was added dropwise at 25°. As described above, the reaction was quenched with methyl iodide (6 mmol) and the product mixture isolated

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[6] Isomeric mixtures of varying composition did not show any characteristic differences in their IR. spectra.

[7] Prepared from 2-chloroethyl phenyl sulfide [25] applying a dehydrohalogenation procedure originally elaborated for en-ether formation [26]. Alternatively according to [27].

by extraction. GC. (50 m, XF-1105*, 90°) indicated the presence of the following compounds: 33% starting material ((*Z*)- and (*E*)-**2b**, *Z*/*E* = 54:46), 1% 3-But-1-enyl phenyl sulfide **3b** [1], 12% (*Z*)- and (*E*)-1-but-1-enyl phenyl sulfide ((*Z*)- and (*E*)-**4b**, *Z*/*E* = 44:56), 32% (*Z*)- and (*E*)-2-but-2-enyl phenyl sulfide ((*Z*)- and (*E*)-**5b**, 57:43) and 6% thioanisole. Prolongation of the reaction time to 24 h increased the amount of thioanisole (15%) at the expense of the starting material (16% (*Z*)- and (*E*)-**2b**) as well as the product mixture (7% **3b** (!); 11% (*Z*)- and (*E*)-**4b**; 12% (*Z*)- and (*E*)-**5b**[8])).

c) (Z)- *and* (E)-*1-But-1-enyl phenyl sulfide* ((*Z*)- and (*E*)-**2c**). In the same way, as outlined in the preceding paragraph, **2c** (2.5 mmol, *Z*/*E* = 44:56) was treated with the butyllithium/potassium *t*-butoxide mixture and subsequently, after 2,5 h stirring, with methyl iodide. GC. comparison (50 m, XF-1105*, 100°) with authentic samples revealed the presence of 37% starting material and 20% methylated product **5c** (isomeric mixture, *Z*/*E* = 57:43[8])).

d) (Z)- *and* (E)-*1-(3-Methyl-but-1-enyl) phenyl sulfide* ((*Z*)- and (*E*)-**2d**): Analogously, **2d** (*Z*/*E* = 36:64) underwent the metallation and methylation sequence. Working on a 20 mmol scale, the crude mixture was isolated by distillation; 2.1 g; b.p. 82–88°/2 Torr. The product composition was evaluated by GC. (50 m, XF-1105*, 100°; dodecane as an internal standard): 28% starting material **2d** recovered (*Z*/*E* = 39:61) and 34% methylated derivative **5d** (*Z*/*E* = 29:71[8])).

3. Metallation reactions: vinyl phenyl ether as a substrate. – a) *Vinyl phenyl ether* (**6**). To a solution of **6** [29] (1,34 g; 20 mmol) in tetrahydrofuran (20 ml) were added dropwise *s*-butyllithium (22 mmol) in hexane (1,05 M, 21 ml) and, after 2 h stirring at 0°, methyl iodide (2,8 g; 20 mmol). The reaction mixture was allowed to warm up at 25° during a period of 1 h and was poured into water (80 ml). The organic layer was separated, the aqueous phase extracted with ether (3 × 25 ml), the combined solution washed with water (3 × 20 ml), dried and evaporated.

Distillation of the residue furnished 1,23 g of a fraction in the boiling range 76–78°/14 Torr. It was recognized by GC. (2m, 20% Ap-L, 150°; nonane as an internal standard) to consist of starting material (33%), vinyl *m*-tolyl ether (3%) and vinyl *o*-tolyl ether (20%). The latter compound was isolated by prep. GC. (6m, 15% Ap-L, 150°) and identified by comparison with an authentic sample [30] as well as on the basis of spectral evidence. – MS.: 134 (86%, M^+); 91 (100%). – IR.: 1645*s*; 1590*s*; 1495*s*; 1240*s* + 1190*s* + 1160*s*; 965*s*; 850*m* br. and 750*s*, *ortho*-substitution. – ^{1}H–NMR.: 7,0 (*m*, aromat. H); 6.58 (*d* × *d*, *J* = 14 and 6.5, olefin. H next to oxygen); 4.53 (*d* × *d*, *J* = 14 and 2, olefin. H at a terminal position, *cis* to oxygen); 4.27 (*d* × *d*, *J* = 6.5 and 2, other olefin. H) and 2.23 (*s*, methyl group).

For a similar reaction en-ether **6** (5.1 mmol), *s*-butyllithium (10 mmol, hexane solution), potassium *t*-butoxide (10 mmol) and tetrahydrofuran (20 ml) were mixed at – 78° and stirred at 0° for 2 h. After quenching with methyl iodide the following products were discovered by GC.: 19% starting material, 1% vinyl *o*-tolyl ether and 30% of a $C_{10}H_{12}O$ fraction, the main component of which was isolated by prep. GC. and identified as 2-propenyl *o*-tolyl ether on the basis of spectral evidence and comparison with an authentic sample [31]. – MS.: 148 (97%, M^+); 108 (100). – IR.: 1680*m* + 1640*m* + 1600*m*; 1500*s*; 1270*s* + 1240*s* + 1200*s*; 1120*s* + 1115*s*; 975*s*; 830*m*, br. and 750*s*, *ortho*-substitution. – ^{1}H–NMR.: 7.0 (*m*, aromat. H); 3.96 (*m*, *s*-like with fine structure, olefin. H at a terminal position, *cis* to oxygen); 3.65 (*d*, *J* = 2, other olefin. H) and 2.2 (*m*, two different methyl groups).

b) *Reactivity comparison*[9]). At – 78° 5.3 ml of a 0.94 M solution of *s*-butyllithium (5.0 mmol) in pentane were added to a mixture of 6.8 g (5.0 mmol) **2a** and 6.0 g (5.0 mmol) **6**. After 2 h at 0° 2.8 g (20 mmol) methyl iodide were poured into the colorless solution which after being kept 3 h at 25° was diluted with 20 ml hexane, washed with water (3 × 20 ml) and dried. The concentrations of **2a** and **6**, before and after the reaction, were determined by GC. (2 m, 20% Ap-L, 100° → 160°; 50 m XF-1105*, 70°) relative to the concentration of an internal standard (nonane, approximately 1 mmol). The rate ratio (or, more precisely, consumption ratio) followed from the equation for second-order competition reactions [32] [33].

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[8]) The assumption being made, that all (*Z*)-ene-sulfides investigated in this work, except **2e**, are more rapidly eluted from carbowax or silicon rubber columns than the corresponding *E*-isomer (see also [1], p. 2270).

[9]) Work carried out by *M. Stähle*.

In a second, similar experiment *n*-butyllithium and potassium *t*-butoxide (5.0 mmol each) in 20 ml hexane were employed instead of *s*-butyllithium in tetrahydrofuran.

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