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Lithiation of 1-Phenylsulfenyl-4-penten-1-ynes and Reactions with Electrophiles

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Abstract: 1-Phenylsulfeny-4-penten-1-yne **1a**, upon treatment with n-butyllithium , gave **2a** that could be trapped with H_2O, D_2O and MeI leading regioselectively to the allene derivatives **3**, **4** and **5** respectively. Also regioselective was the reaction of **2a** with ketones furnishing very high yields of the allenic alcohols **6**, **7** and **8**. Similarly regioselective was the coupling of **2b** with acetone affording allenic alcohol **18**. Less regioselective were the reactions with aldehydes, leading to mixtures of allenic and propargylic alchools. Allenic alcohols **8** and **18** can be cyclized to dihydrofurans **19** and **20**.

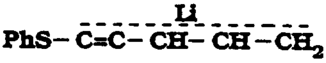
Dienyl and polyenyl sulfides[1] are of some synthetic importance. Skipped sulfenyl, sulfinyl and sulfonyl enynes too appear to have synthetic potential for the preparation of unsaturated systems. Metallation and subsequent reactions with electrophiles of dienyl sulfides and derivatives have been studied in some detail[2,3] emphasizing the synthetic potential of the relevant metallated species. Metallation of enynyl sulfides and reaction of the resulting delocalized carbanionic species have not been investigated so far, apart from the isomerization of some alkylsulfenyl enynes under basic conditions (sodium methoxide or sodium amide[4]) and the butyllithium promoted dimerisation reaction.[5] In the present paper we report on the lithiation of 1-phenylsulfenyl-4-penten-1-ynes **1** and reactions with electrophiles.

Sulfides **1** were prepared by cross-coupling of phenylsulfenylethynylmagnesium bromide with the appropriate allylic bromide in the presence of nickel dichlorodiphenylphosphinoethane ($NiCl_2$(dppe)) (see experimental part). Lithiation of **1a** with n-BuLi in THF at -78°C afforded a dark red solution of lithiated species **2a**, as proved by trapping it with D_2O to give deuterated allene **4**, and with MeI to furnish allene derivative **5** with complete α-regioselectivity. Moreover, quenching of **2a** with aq. sat. NH_4Cl gave sulfenyl allene **3**. Completely α-regioselective was also the coupling reaction of **2a** with cyclohexanone,[6] cyclopentanone and acetone providing very high yields of allenic alcohols **6**, **7** and **8** respectively. It is worth

$PhSC \equiv CCH_2CH{=}CH_2$

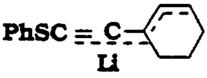
1a

1b

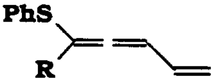


$PhS-\overset{Li}{\overline{C{=}C-CH-CH-CH_2}}$

2a



2b

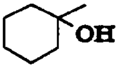


3 : R = H

4 : R = D

5 : R = Me

6 : R =



7 : R =

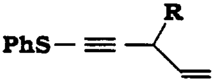
8 : R = Me_2COH

9 : R = $PhC(CH_3)OH$

11 : R = MeCHOH

13 : R = nPrCHOH

16 : R = PhCHOH



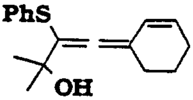
10 : R = $PhC(CH_3)OH$

12 : R = MeCHOH

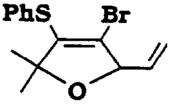
14 : R = n-PrCHOH

15 : R = $PhCH_2CHOH$

17 : R = PhCHOH



18



19

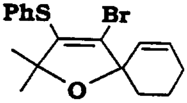


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Table. Reaction of **2a** - **b** with electrophiles (E) in THF at - 78° C

E	Reaction Product (Ratio)	% Overall[a] yield		E	Reaction Product (Ratio)	% Overall[a] yield
H_2O	**3**	95		$PhCOCH_3$	**9** +**10** (7/3)	40
D_2O	**4**	88		MeCHO	**11** +**12** (3/1)	45
MeI	**5**	97		Pr^nCHO	**13** +**14** (3/2)	45
Cyclohexanone	**6**	81		$PhCH_2CHO$	**15**	50
Cyclopentanone	**7**	81		PhCHO	**16** + **17** (2/3)	63
Me_2CO	**8**	55		Me_2CO[b]	**18**	40

a) Yields calculated on isolated products and not optimized. b) Reaction with **2b**

emphasizing such a complete α-regioselectivity when compared with that of lithiated phenylthioacetylene[7] where the produced α-lithioallene underwent α-regioselective coupling with ketones in satisfactory yields only in the presence of hexamethylphosphoric triamide (HMPA). Moreover, condensation with aromatic ketones gave low yields with poor α/γ ratios and perhaps the coupling with aldehydes was unsuitable. The α-regioselectivity of the reaction of **2a** with ketones might be explained with the higher charge density in the α-position of **2a**, as reported for allenic-α-acetylenic carbanions.[8] The Pearson's "hard and soft acid and base" (HSAB) principle[9,10] could be invoked to explain such a α-regioselectivity considering that the allenic end of **2a** is harder than the propargylic and the allylic ones. Less regioselective was the reaction of **2a** with acetophenone that furnished allenic and propargylic alcohols **9** and **10** in a 7/3 ratio. Much less regioselective was the reaction of **2a** with aldehydes. Indeed, the reaction of **2a** with acetaldehyde and butyraldehyde led in satisfactory yield to a mixture of the allenic and acetylenic alcohols **11** and **12**, and **13** and **14** respectively, that could be easily separated by column chromatography and fully characterized by IR and NMR spectroscopy (See Table), while the reaction with phenylacetaldehyde turned out to be completely γ-regioselective to give propargylic alcohol **15**. Moreover, poor regioselectivity was observed in the reaction of **2a** with benzaldehyde that furnished a 2 to 3 mixture of the alcohols **16** and **17**.

Lithiation of phenylsulfenyl enyne **1b** furnished the sulfur stabilized carbanion **2b**, that reacted smoothly with acetone leading regioselectively to the allenic alcohol **18**.

The abovementioned allenic alcohols are suitable for the synthesis of substituted dihydrofurans.[11] Indeed, we have found that allenic alcohol **8** can be easily cyclized to dihydrofuran **19** upon treatment with N-bromosuccinimide (NBS) and alcohol **18** gives almost quantitative yield of spirodihydrofuran **20**.[12]

Thus, we have shown in the present paper that sulfur stabilized delocalized carbanions **2**, which are rather stable at low temperature, can be used for the introduction of the allenenyl and the enynyl unit onto several carbon frames upon treatment with the appropriate electrophiles, often regioselectively.[13] Work is in progress for a better control of the regiochemistry of the coupling reactions of **2** and derivatives.

EXPERIMENTAL.

^{1}HNMR spectra were recorded on a Varian EM 360A and a Varian XL-200 spectrometers; chemical shifts are reported in parts per million (δ) from internal standard using $CDCl_3$ as solvent. IR spectra were recorded on a Perkin-Elmer spectrometer model 598 and refer to films. GC analyses were carried out with a Hewlett-Packard MP-5890 series II gaschromatograph (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.); GC-MS spectrometry analyses were performed on a HP-5890 series II gaschromatograph equipped with HP-5971 Mass Selective Detector operating at 70 eV (E.I.). Boiling points were uncorrected. Flash chromatographies were performed with Merck 230-400 mesh silica gel.

Materials: Tetrahydrofuran (THF) and diethyl ether of commercial grade were purified by distillation (twice) from sodium wire in N_2 atmosphere. Petroleum ether refers to the 40-60°C boiling fraction. **Phenylthioacetylene**[14] was prepared as reported from **(Z)-1-bromo-2-phenylthioethene**.[15] Allylic halides and all other chemicals were of commercial grade and used without further purification or eventually distilled prior to use. All the new compounds gave satisfactory elemental analysis ($^+$ 0.3% for C, H, N) and were performed on Carlo Erba C,H,N analyser.

Preparation of **1-phenylsulfenylpent-4-en-1-yne 1a**. To a stirred THF (25 ml) solution of phenythioacetylene (5.6 g, 41.7 mmol) was added dropwise a THF solution of 0.83 N n-BuMgBr (55.0 ml, 45.6 mmol) at 0°C under nitrogen. After 15 min. the reaction mixture was allowed to warm at room temperature and added with $NiCl_2$(dppe) (0.66 g, 1.2 mmol). To the resulting mixture was added dropwise a THF (25 ml) solution of allyl bromide (7.05 g, 83.4 mmol). Quenching of the reaction mixture after 50 min. with aq. sat. solution of NH_4Cl, extraction with ether (100 ml x 3), drying over Na_2SO_4 and evaporation of the solvent under reduced pressure left an oily residue (7.5 g) that was distilled under vacuum to give **1-Phenylthio-pent-4-en-1-yne 1a:** 72% yield; oil, bp 63-64°C/0.4 torr. ^{1}HNMR δ: 3.2-3.4(m,2H), 5.1-6.3(m,3H), 7.2-7.9(m,5H). IR(neat) ν: 3080, 3060, 3020, 1640, 1410, 920 cm^{-1}. MS m/e : 174(M^+,100), 173(48), 147(22), 121(11), 109(9), 77(38), 65(27).

Preparation of **3-(2-Phenylthioethynyl)cyclohexene 1b.** This compound was prepared according to the procedure described for **1a**: 48% yield, oil, bp 106-8°C $7.0x10^{-2}$ torr. ^{1}HNMR(60 MHz) δ: 1.6-2.3(m,6H), 3.2-3.6(m,1H), 5.85(s,2H), 7.2-7.7(m,5H). IR(neat) ν: 3060, 3020, 2070, 1650, 685 cm^{-1}, MS m/e: 216(M^+,4), 215(13), 186(100), 185(50), 137(78), 109(69), 105(30), 77(91).

Lithiation of 1-phenylsulfenyl-4-penten-1-yne 1a and trapping with H_2O, D_2O or MeI.

To a stirred THF (5 ml) solution of **1a** (0.18g, 1.03 mmol) at -78°C under N_2 was added dropwise a hexane solution of 2.5N n-BuLi (0.40 ml, 1.24 mmol). The resulting dark red solution of **2a** was kept at -78°C for 30 min and then quenched with an aqueous sat solution of NH_4Cl. Extraction with Et_2O (3x25 ml), drying over Na_2SO_4 and evaporation of the solvent under reduced pressure left an oily residue that was purified by column chromatography using petroleum ether as eluent to give **1-phenylsulfenyl-1,2,4-pentatriene** 3: oil, 95% yield. ^{1}HNMR(60 MHz) δ: 5.0-5.4 (m, 2H); 5.8-6.5 (m,3H); 7.3-7.7 (m, 5H). IR (neat): 3060, 1940, 1580, 1440, 905 cm^{-1}. Similarly the quenching of **2a** with D_2O (1 ml) gave **1-phenylsulfenyl-1-deutero-1,2,4-pentatriene 4:** oil, 88% yield. ^{1}HNMR(60 MHz) δ: 5.0-5.4 (m, 2H); 6.0-6.4 (m, 2H); 7.3-7.7 (m, 5H). IR (neat) ν: 3060, 1940, 1580, 1440, 905 cm^{-1}. Trapping of **2a** with MeI gave **2-phenylsulfeny-2,3,5-hexatriene 5:** oil, 97% yield: ^{1}HNMR(200 MHz) δ: 2.00 (d, 3H, J= 2.9 Hz); 5.00-5.35 (m, 2H); 5.80-6.25 (m, 2H); 7.2-7.6 (m, 5H). IR (neat) ν: 3060, 2960, 1940, 1580, 1440, 905 cm^{-1}. MS m/e : 188(M^+,18), 173 (43), 161 (13), 109 (16), 79 (34), 77 (100).

Reaction of lithiated 1-phenylsulfenylpentenyne 2a with carbonyl compounds. Typical Procedure. The example of the reaction of **2a** with cyclohexanone is here described. To a stirred solution of **2a** (2.0 mmol) prepared as above was added dropwise a THF (10 ml) solution of cyclohexanone (0.39g, 4.0 mmol) at -78°C and under N_2. The reaction mixture was kept at low temperature for 30 min and then allowed to warm to RT. Quenching with aq. sat NH_4Cl solution and usual work up gave an oily residue tha was purified by column chromatography (silica gel, ether/petroleum ether: 1.5/8.5 as eluent) to give 0.81g of **1-phenylsulfenyl-1-(1-hydroxycyclohexyl)-1,2,4-pentatriene 6:** oil, 81% yield. ^{1}HNMR(60 MHz) δ: 1.2-2.0 (m, 10H); 2.5 (brs, 1H, exchange with D_2O); 4.9-5.5 (m, 2H); 5.85-6.4 (m, 2H); 7.3-7.7 (m, 5H). IR (neat) ν: 3440 (broad), 3060, 2920, 1940, 1580, 1440, 905 cm^{-1}. MS m/e: 272 (M^+, 29), 173 (100), 121 (9), 109 (7), 99 (61), 81 (65), 77 (15).

The reaction of **2a** with cyclopentanone, carried out as with cyclohexanone, gave **1-phenylsulfenyl-1-(1-hydroxycyclopentyl)-1,2,4-pentatriene 7:** oil, 81% yield. ^{1}HNMR(200 MHz) δ: 1.5-2.0 (m, 8H); 2.15 (brs, 1H, exchange with D_2O); 4.9-5.2 (m, 2H); 5.9-6.15 (m, 2H); 7.2-7.6 (m, 5H). IR (neat) ν: 3440 (broad), 3060, 2980, 1940, 1580, 1440, 905 cm^{-1}. MS m/e: 258 (M^+, 7); 173 (100); 109 (16.1), 85 (59); 77 (52).

The reaction of **2a** with acetone led to: **2-hydroxy-2-methyl-3-phenylsulfenyl-3,4,6-heptatriene 8:** oil, 55% yield. ^{1}HNMR(60 MHz) δ: 1.45 (s, 6H); 2.78 (s,1H, exchange with D_2O); 4.9-5.45 (m, 2H); 5.8-6.3 (m, 2H); 7.2-7.7 (m, 5H). IR (neat) ν : 3390 broad, 2980, 2920, 1940, 1580, 1440, 910 cm^{-1}. MS m/e: 232 (M$^+$, 3.8), 217 (27), 199 (5), 173 (100), 121 (8), 109 (65), 77 (10), 59 (46).

The reaction of **2a** with acetophenone, carried out as above, gave a mixture of two regioisomeric alcohols that were separated by column chromatography (silica gel, ether/petroleum ether: 1/9 as eluent) and characterized as **1-(1-hydroxy-1-phenylethyl)-1-phenylsulfenyl-1,2,4-pentatriene 9:** oil, 28% yield. ^{1}HNMR(60 MHz) δ: 1.7 (s, 3H), 3.15 (brs,1H, exchange with D_2O), 5.0-6.5 (m, 4H), 7.2-7.8 (m, 10H). IR (neat) ν :3450 (broad), 3060, 3020, 2980, 1940, 1620, 1585, 1480, 1440, 905, 700 cm^{-1}. MS m/e: 294 (M$^+$, 5), 279 (3), 261 (3), 185 (10), 174 (45), 173 (82), 121 (100), 110 (6), 109 (5.5), 77 (20) and **1-phenylsulfenyl-3-(1-hydroxy-1-phenylethyl)pent-4-en-1-yne 10:** oil, 12% yield. ^{1}HNMR(60 MHz) δ: 1.68+1.78 (s + s, diastereomeric CH_3, 3H), 2.55 (brs, 1H, exchange D_2O), 3.8 + 3.9 (s + s, diastereomeric H, 1H), 5.0-6.3 (m, 3H), 7.2-7.8 (m, 10H). IR (neat) ν : 3560 (broad), 3460 (broad), 3060, 3020, 2980, 2180, 1620, 1580, 1480, 1440, 920,700 cm^{-1}. MS m/e: 294 (M$^+$, 8), 185 (15), 174 (53), 173 (38), 121 (100) 110 (5) 109 (7), 77 (23).

Reaction of 2a with aldehydes. The reaction of **2a** with acetaldehyde, carried out as with ketones, led a mixture of regioisomeric alcohols that were separated by column chromatography (silica gel, ether/petroleum ether : 1/1) and characterized as **2-hydroxy-3-phenylsulfenyl-3,4,6-heptatriene 11:** oil, 34% yield. ^{1}HNMR60 MHz) δ: 1.41 (d, 3H, J=7Hz); 2.7 (brs, 1H, exchange with D_2O); 4.2-4.7 (m, 1H); 5.05-5.6 (m, 2H); 5.8-6.7 (m, 2H); 7.2-7.8 (m, 5H). IR (neat) ν : 3390 (broad), 3050, 2920, 1940, 1440, 905 cm^{-1}. MS m/e: 218(M$^+$, 5), 203 (48), 185 (21), 173 (100), 121 (14), 97 (27), 77 (13) and **1-phenylsulfenyl-3-(1-hydroxyethyl)-pent-4-en-1-yne 12:** oil, 11% yield. ^{1}HNMR(60 MHz) δ: 1.30 (d, 3H, J=7Hz); 1.9 (brs, 1H, exchange with D_2O); 3.48 (t, 1H, J=7 Hz); 3.7-4.2 (m, 1H); 5.2-5.9 (m, 3H); 7.3-7.7 (m, 5H). MS m/e: 218 (M$^+$, 12), 203 (1.5), 173 (100), 121 (16), 109 (6), 97 (21), 77 (12).

The reaction of **2a** with butanal gave **4-hydroxy-5-phenylsulfenyl-5,6-8-nonatriene 13:** oil, 27% yield. ^{1}HNMR(60 MHz) δ: 0.8-1.0 (m, 3H); 1.1-1.9 (m, 4H); 2.8 (brs, 1H, exchange with D_2O); 4.1-4.4 (m, 1H), 5.0-5.6 (m, 2H); 5.9-6.6 (m, 2H); 7.2-7.7 (m,5H). IR (neat) ν : 3400 (broad), 3060, 2960, 1940, 1610, 1440, 905 cm^{-1}. MS m/e: 246 (M$^+$, 6), 231 (1), 203 (55), 185 (8), 173 (100), 137 (2), 121 (9), 109(9), 77 (10) and **1-phenylsulfenyl-3-(1-hydroxybutyl)-pent-4-en-1-yne 14:** oil, 18% yield. ^{1}HNMR(60 MHz) δ: 0.7-1.1 (m, 3H), 1.2-1.9 (m,4H), 2.0 (brs, 1H, exchange with D_2O) 3.4-4.0 (m, 2H), 5.2-5.7 (m, 2H), 5.8-6.5 (m,1H), 7.3-7.8 (m, 5H). IR (neat) ν : 3380 (broad), 3080, 2960, 2880, 1640, 1585, 1480, 685 cm^{-1}. MS m/e: 246 (M$^+$, 82), 203 (67), 185 (23), 173 (100), 137 (7), 121 (21) 109 (17), 77 (26).

The reaction of **2a** with phenylacetaldehyde gave **1-phenylsulfenyl-3-(1-hydroxy-2-phenylethyl)-pent-4-en-1-yne 15:** oil, 50 yield. ^{1}HNMR(200 MHz) δ: 1.89 (brs, 1H, exchange with D_2O); 2.96 (ddd, 2H, J=7.76, 13.67 and 5.80 Hz); 3.46-3.54 (m, 1H); 3.94 (ddd, 1H, J=4.01, 5.80 and 7.76 Hz); 5.32 (dd, 1H, J=10.01 Hz); 5.50 (dd, 1H, J=17.04 Hz); 5.91 (ddd, 1H, J=10.01, 17.04 and 5.86 Hz); 7.10-7.50 (m, 10H). IR (neat) ν : 3420 (broad), 3060, 2920, 1580, 1480, 910 cm^{-1}. MS m/e: 294 (M^+, 41), 203 (5), 173 (100), 121 (43), 109 (6), 103 (36), 91 (36), 77 (23).

The reaction of **2a** with benzaldehyde furnished **1-phenylsulfenyl-1-hydroxybenzyl-1,2,4-pentatriene 16:** oil, 25% yield. ^{1}HNMR(60 MHz) δ: 2.6 (brs, 1H, exchange with D_2O); 5.0-5.2 (m, 1H); 5.2-5.6 (m, 4H); 7.5-7.9 (m, 10H). IR (neat) ν : 3390 (broad), 3060, 2920, 1940, 1580, 1440 910 cm^{-1} and **1-phenylsulfenyl-3-hydroxybenzyl-pent-4-en-1-yne 17:** oil, 38% yield. ^{1}HNMR(60 MHz) δ: 2.8 (brs, 1H, exchange with D_2O); 3.7 (dd, 1H, J=7 and 8 Hz); 4.8-5.1 (m, 1H); 5.3-6.3 (m, 3H); 7.3-7.8 (m, 10H). IR (neat) ν : 3420 (broad), 3060, 2980, 2190, 1580, 1440, 920 cm^{-1}. MS m/e: 280 (M^+, 9), 174 (93), 173 (100), 110 (21), 109 (17), 107 (61), 77 (73).

Lithiation of 3-(2-phenylthioethynyl)-cyclohexene 1b and reaction with acetone. To a stirred hexane solution of 1.6N n-BuLi (1.23 ml, 1.9 mmol) at -78°C and under N_2 was added dropwise a THF (10 ml) solution of **1b** (0.28g, 1.3 mmol). The resulting dark brown solution was kept at -78°C for 20 min and then added with acetone (0.19 ml, 2.6 mmol) in 2 ml of THF. Quenching with aq. sat .NH_4Cl solution after 1h and usual workup furnished a residue that was chromatographed (silica gel, ether/petroleum ether : 2/8) to give **2-hydroxy-2-methyl-3-phenylsulfenyl-4-(cyclohex-2-enyliden)-3-butene 18:** oil, 40% yield. ^{1}HNMR(60 MHz) δ :1.5 (s, 6H); 1.6-1.85 (m, 2H); 1.85-2.45 (m, 4H); 2.50 (brs, 1H, exchange with D_2O); 5.7-6.1 (m, 2H); 7.2-7.8 (m, 5H). IR (neat) ν : 3460, 3020, 2980, 1940, 1580, 1440, 690 cm^{-1}. MS m/e: 272 (M+, 4.5), 257 (12), 254 (17), 239(12), 214 (82), 213 (46), 186 (100), 137 (60), 121 (12), 109 (14), 105 (39), 77 (28).

Cyclisation of allenic alcohols 8 and 18 to dihydrofurans 19 and 20. To a stirred solution of allenic alcohol 18 (0.14g, 0.5 mmol) in 10 ml of 1,4-dioxane/water(7/3) was added N-bromosuccinimide (0.11g, 0.6 mmol) at room temperature. After 20 min the reaction mixture was poured into water and extracted with ether(3x20 ml) and worked up as usual to give a residue that was purified by a short column chromatography (silica gel, ether/petroleum ether: 7/93) and identified as **2,2-dimethyl-3-phenylsulfenyl-4-bromo-5-spirocyclohexen-2-yl)-2,5-dihydrofuran 20:** mp 69-71°C(ethanol), 94% yield. ^{1}HNMR(60 MHz) δ: 1.37 (s, 6H, CH_3), 1.98 (brs, 6H, CH_2) 5.65 (d, 1H, J=10 Hz cis), 5.9-6.6 (m, 1H), 7.2-7.7 (m, 5H). IR (nujol) n: 3060, 1640, 1580, 1440, 685 cm^{-1}. MS m/e: 352 (M^+ 2, 9.6), 350 (M^+ , 9.3), 337 (6), 335 (6), 324 (100), 322 (99), 309 (22), 307 (21), 215 (9), 213 (11), 109 (4), 77 (7). Similarly was prepared **2,2-dimethyl-3-phenylsulfenyl-4-bromo-5-ethenyl-2,5-dihydrofuran 19**: oil, 45% yield. ^{1}HNMR(60 MHz) δ: 1.45 (s, 3H), 1.70 (s, 3H), 4.8-5.5 (m, 2H) 6.2-6.7 (m, 2H), 7.3-8.0 (m, 5H). IR (neat) ν: 3060, 3000, 2960, 2920, 1630, 1440, 910, 690 cm^{-1}. MS m/e: 312 (M$^+$ 2, 2.5), 310 (M$^+$, 2.6), 231 (24), 203 (13), 201 (11), 173 (71), 110 (100), 109 (19), 77 (23).

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