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Syntheses and Reactions of Phenylthio- and Propylthioacetylenic Compounds

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Reactions of 2,2-dichlorovinyl sulfides and their sulfoxide and sulfone derivatives with *tert*-butoxide and with organolithium compounds have provided entries to chloroethynyl sulfides, *tert*-butoxyethynyl sulfides and their derivatives. Application of these reactions for the synthesis of several functional derivatives is also described.

Keywords——2,2-dichlorovinyl sulfide; chloroethynyl sulfide; *tert*-butoxyethynyl sulfide; ethynyl sulfide; cyclobutenone

The present work was carried out to investigate the chemical behavior of 2,2,2-trichloroethyl sulfides and dehydrochlorinated 2,2-dichlorovinyl sulfides, since little is known concenring them.

2,2,2-Trichloroethyl phenyl sulfide (**1**) was afforded in 68% yield by allowing 1,1-dichloroethylene to react with benzenesulfenyl chloride in the presence of a small amount of iodine at room temperature for 24 hr.

$$\mathrm{PhSCl} + \mathrm{CH_2{=}CCl_2} \longrightarrow \underset{\mathbf{1}}{\mathrm{PhSCH_2CCl_3}} \xrightarrow{\mathrm{NEt_3}} \underset{\mathbf{2a}}{\mathrm{PhSCH{=}CCl_2}}$$

The compound (**1**) was easily dehydrochlorinated to phenyl 2,2-dichlorovinyl sulfide (**2a**) in 83% yield by refluxing with triethylamine in benzene for 48 hr. As an aliphatic analog, propyl 2,2-dichlorovinyl sulfide (**2b**) was prepared by the previously reported method[1] starting from propanethiol and chloral.

The reactions of **2a** and **2b** with potassium *tert*-butoxide and organolithium compounds were convenient for the preparation of several functional derivatives of ethynyl sulfides, as described below.

The reaction of **2a** or **2b** with 1.1 molar equivalents of *tert*-butoxide in tetrahydrofuran (THF) at −30° afforded the corresponding chloroethynyl sulfide **3a** (in 26% yield) or **3b** (in 35% yield). Both the products **3a** and **3b** are liquids distillable at very low pressure, and their infrared (IR) spectra exhibit absorption bands at 2165—2170 cm^{-1} characteristic of their cabon–carbon triple bonds. Although several alkyl chloroethynyl sulfides were reported[2] as products in the reaction of 2,2-dichlorovinyl sulfides with alkanethiols in the presence of potassium hydroxide, we were not able to obtain details of this work.

$$\underset{\begin{array}{l}\mathbf{2a}\ (\mathrm{R{=}Ph})\\ \mathbf{2b}\ (\mathrm{R{=}C_3H_7})\end{array}}{\mathrm{RSCH{=}CCl_2}} \xrightarrow[\text{in THF}]{\textit{tert}\text{-BuOK}} \underset{\begin{array}{l}\mathbf{3a}\ (\mathrm{R{=}Ph})\\ \mathbf{3b}\ (\mathrm{R{=}C_3H_7})\end{array}}{\mathrm{RSC{\equiv}CCl}}$$

When the amount of *tert*-butoxide was increased to 2.2 molar equivalents in the above experiments, replacement of the chlorine by a *tert*-butoxy grouping proceeded to give *tert*-butoxyethynyl sulfides (**4a** and **4b**) in good yields (see Table I). I Phenyl 2,2-dichlorovinyl sulfoxide (**5**) and sulfone (**6**) were also subjected to reaction with *tert*-butoxide under the same conditions to give the corresponding *tert*-butoxyethynyl sulfoxide (**7**) and sulfone (**8**) (see Table I). Compounds **5** and **6** were obtained by oxidation of **1** with sodium metaperiodate and potassium permanganate to the corresponding sulfoxide (**9**) and sulfone (**10**), respectively,

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Table I.

$$RXCH{=}CCl_2 \xrightarrow[\text{in THF}]{\textit{tert}\text{-BuOK}^{a)}} RXC{\equiv}CO\textit{tert}\text{-Bu}$$

Substrate No.	X	R	React. temp. (°C)	React. time (hr)	Product No.	Yield[b] (%)
2a	S	Phenyl	−30	0.5	**4a**	81.6
2b	S	*n*-Propyl	−30	2.0	**4b**	84.7
5	S→O	Phenyl	−70	1.0	**7**	57.0
6	SO_2	Phenyl	−70	1.0	**8**	76.0

a) Reaction conditions: molar ratio of the substrate to *tert*-BuOK=1: 2.2; solvent, THF.
b) Based on the product isolated.

followed by dehydrochlorination with triethylamine.

The compounds **4a**, **4b**, **7** and **8**, were thermally unstable. On heating **4a** and **4b** in benzene and **7** and **8** in toluene under reflux, evolution of isobutene took place with the formation of cyclobutenones (**11a**, **b**) from **4a**, **b** and cyclobutane-1,3-dione (**12**) from **8**; however, **7** decomposed into unidentified smaller molecules. The IR spectra of **11a** and **11b** exhibit >C=O signals at 1745 and 1740 cm^{-1}, and >C=C< signals at 1585 and 1580 cm^{-1}. In cyclobutanone the carbonyl group signal appears at about 1780 cm^{-1}, but conjugation of the internal double bond may affect its position. The carbonyl signals of **11a** and **11b** are in fairly close agreement with those reported for 3-alkoxycyclobutenones.[3] The carbonyl signal of **12** appeared at 1740 cm^{-1}, which is close to those (1750—1755 cm^{-1}) of cyclobutane-1,3-diones reported previously.[3]

$$RSC{\equiv}C\text{-}OBu\text{-}\textit{tert} \xrightarrow[\text{in benzene}]{\text{reflux}} \begin{matrix} RSCH\text{-}C{=}O \\ | \quad | \\ \textit{tert}\text{-}BuO\text{-}C{=}C\text{-}SR \end{matrix}$$

4a (R=Ph), **4b** (R=C_3H_7) → **11a** (R=Ph), **11b** (R=C_3H_7)

$$PhSO_2C{\equiv}C\text{-}OBu\text{-}\textit{tert} \xrightarrow[\text{in toluene}]{\text{reflux}} \begin{matrix} PhSO_2CH\text{-}C{=}O \\ | \quad | \\ O{=}C\text{—}CHSO_2Ph \end{matrix}$$

8 → **12**

The reactions presumably proceed through ketene intermediates. As shown in Chart 1, ketene (**13**) is formed initially with elimination of isobutene, and then cycloaddition of the ketene **13** with unchanged substrate gives **14** (for the formation of **11a**, **11b** from **4a**, **4b**). Further elimination of isobutene from **14** gives **15** (from the formation of **12** from **8**).

The reactions of **2a** and **2b** with organolithium compounds were then investigated. Compound **2a** was allowed to react with 2.4 molar equivalents of butyl lithium in ether at −70°,

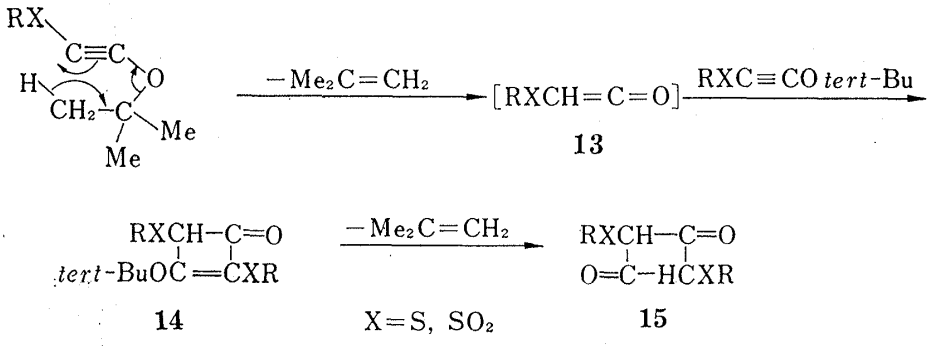

Chart 1

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and treatment of the reaction mixture with ammonium chloride solution gave ethynyl phenyl sulfide (**16a**) in 68% yield. The use of phenyl lithium and *tert*-butyl lithium in place of butyl lithium gave **16a** in 44% and 18% yields, respectively, and in the latter case phenyl 1-*tert*-butylvinyl sulfide was obtained as a by-product in 17% yield. The reaction of **2b** with butyl lithium under the same conditions gave ethynyl propyl sulfide (**16b**) in 58% yield. Although a few ethynyl alkyl sulfides[4] have appeared in the literature, the reaction with butyl lithium can be conveniently used as an alternative synthesis of aryl (or alkyl) ethynyl sulfides.

$$\underset{\textbf{2a}\ (R=Ph)\\ \textbf{2b}\ (R=C_3H_7)}{RSCH{=}CCl_2} \xrightarrow{2RLi} \underset{\textbf{17}}{[RSC{\equiv}CLi]} \xrightarrow{H_2O} \underset{\textbf{16a}\ (R=Ph)\\ \textbf{16b}\ (R=C_3H_7)}{RSC{\equiv}CH}$$

Since the lithiated intermediate **17** may be produced in the reaction mixture, *in situ* utilization of **17** for nucleophilic substitution was investigated by further reaction with carbonyl compounds. At the end of the reaction of **2a, b** with butyl lithium the addition of carbonyl compounds at −10° afforded **18** in considerable yields. The results are summarized in Table II.

$$\underset{\textbf{2a}\ (R=Ph)\\ \textbf{2b}\ (R=C_3H_7)}{RSCH{=}CCl_2} \xrightarrow[\text{in ether at } -70^\circ]{2BuLi} [RSC{\equiv}CLi] \xrightarrow[\text{at } -10^\circ]{R^1R^2C{=}O} \underset{\textbf{18}}{RSC{\equiv}CCR^1R^2\ (OH)}$$

Table II. Production[a] of Phenyl (and Propyl)thio Ethynyl Carbinols (**19**—**24**) $RSC{\equiv}CC(OH)R^1R^2$

Compound No.	R	R^1	R^2	React. time (hr)	Yield[b] (%)
19	Phenyl	Phenyl	H	0.5	46.2
20	Phenyl	Et	H	0.5	69.2
21	Phenyl	Me	Me	0.5	70.7
22	Propyl	Phenyl	H	0.5	53.3
23	Propyl	Et	H	0.5	50.6
24	Propyl	Me	Me	0.5	53.7

a) General procedures are given in "Experimental." Molar ratio $RSCH{=}CCl_2$: BuLi: $R^1R^2C{=}O$=1.0: 2.4: 1.2.
b) Based on the product isolated.

Experimental[5]

2,2,2-Trichloroethyl Phenyl Sulfide (**1**)——To a stirred solution of 6.1 g (0.05 mol) of 1,1-dichloroethylene and 0.6 g of iodine in 30 ml of benzene, 7.2 g (0.05 mol) of benzenesulfenyl chloride was added dropwise at 5—10°. After being stirred overnight at 20—25°, the reaction solution was washed with $Na_2S_2O_3$ solution and dried over $MgSO_4$. Removal of the benzene and distillation of the resulting residue gave **1**. Yield, 8.6 g (67.4%). bp 98—99°/0.1 mmHg. *Anal.* Calcd for $C_8H_7Cl_3S$: C, 39.78; H, 2.92. Found: C, 40.19; H, 2.93. NMR δ (ppm in $CDCl_3$): 4.01 (2H, s, $-SCH_2-$), 7.10—7.60 (5H, m, aromatic protons).

2,2,2-Trichloroethyl Phenyl Sulfoxide (**9**)——To a stirred solution of 12.0 g (0.05 mol) of **1** in 50 ml of methanol, an aqueous solution of 11.8 g (0.055 mol) of sodium metaperiodate was added dropwise at room temperature, and stirring was continued for 24 hr. The viscous oily material liberated was separated by decantation and dissolved in benzene. After being dried over $MgSO_4$, the benzene solution was concentrated under reduced pressure and the solid residue was recrystallized from methanol to give colorless prisms of **9**. Yield, 6.4 g (49.2%). mp 100—101°. *Anal.* Calcd for $C_8H_7Cl_3OS$: C, 37.31; H, 2.74. Found: C, 37.37; H, 2.74. IR ν_{max}^{KBr} cm^{-1}: 1045 (S→O). NMR δ (ppm in $CDCl_3$): 4.03 (2H, s, $-SOCH_2-$), 7.40—7.85 (5H, m, aromatic protons).

2,2,2-Trichloroethyl Phenyl Sulfone (**10**)——To a stirred solution of 12.0 g (0.05 mol) of **1** in 50 ml of acetic acid, 7.9 g (0.06 mol) of powdered potassium permanganate was added in small portions at room temperature, and stirring was continued overnight. Crystals of the sulfone were collected by filtration, washed with cold water and dried. The filtrate, after excess potassium permanganate had been quenched with

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$NaHSO_3$, was concentrated under reduced pressure. Additional sulfone was obtained by extraction of the resulting residue with $CHCl_3$. The combined crystals were recrystallized from methanol to give colorless prisms of **10**. Yield, 11.5 g (81.4%). mp 42—43°. *Anal.* Calcd for $C_8H_7Cl_3O_2S$: C, 35.12; H, 2.58. Found: C, 35.21; H, 2.55. IR ν_{max}^{KBr} cm^{-1}: 1340, 1160 (SO_2). NMR δ (ppm in $CDCl_3$): 4.42 (2H, s, $-SO_2CH_2-$) 7.55—8.15 (5H, m, aromatic protons).

Phenyl 2,2-Dichlorovinyl Sulfide (2a), Phenyl 2,2-Dichlorovinyl Sulfoxide (5) and Phenyl 2,2-Dichlorovinyl Sulfone (6)——A solution of 12.0 g (0.05 mol) of **1** and 10.1 g (0.1 mol) of triethylamine in 50—80 ml of benzene was refluxed for 48 hr. Triethylamine hydrochloride precipitated in the reaction solution was filtered off and the filtrate was concentrated under reduced pressure. The resulting residue was subjected to distillation under reduced pressure to give **2a**. Yield, 8.4 g (82.3%). bp 89—91°/0.1 mmHg. *Anal.* Calcd for $C_8H_6Cl_2S$: C, 46.85; H, 2.95. Found: C, 46.64; H, 2.95. IR $\nu_{max}^{liq.}$ cm^{-1}: 1580 (>C=C<). NMR δ (ppm in $CDCl_3$): 6.51 (1H, s, –SCH=), 7.30—7.55 (5H, m, aromatic protons). Compounds **5** and **6** were obtained by procedures similar to the above from **9** and **10**, respectively. **5**: reaction time, 18 hr. Yield, 6.5 g (66.8%). bp 118—119°/0.1 mmHg. *Anal.* Calcd for $C_8H_6Cl_2OS$: C, 43.45; H, 2.74. Found: C, 43.76; H, 2.88. IR $\nu_{max}^{liq.}$ cm^{-1}: 1585 (>C=C<), 1050 (S→O). NMR δ (ppm in $CDCl_3$): 6.63 (1H, s, –SOCH=), 7.10—7.50 (5H, m, aromatic protons). **6**: reaction time, 4 hr. Yield, 7.5 g (63.2%). bp 126—128°/0.1 mmHg. *Anal.* Calcd for $C_8H_6Cl_2O_2S$: C, 40.53; H, 2.55. Found: C, 40.92; H, 2.70. IR $\nu_{max}^{liq.}$ cm^{-1}: 1580 (>C=C<), 1340, 1160 (SO_2). NMR δ (ppm in $CDCl_3$): 6.91 (1H, s, $-SO_2CH=$), 7.45—8.00 (5H, m, aromatic protons).

Chloroethynyl Phenyl Sulfide (3a) and Chloroethynyl Propyl Sulfide (3b)——To a stirred solution of 10.3 g (0.05 mol) of **2a** in 30 ml of THF, a solution of 6.1 g (0.055 mol) of potassium *tert*-butoxide in 50 ml of THF was added dropwise at −30——40°. The stirring was continued for 0.5 hr at the same temperature. After removal of THF by evaporation under reduced pressure, the resulting residue was extracted with isopropyl ether (IPE). Rotary evaporation of the extract and distillation of the resulting residue under reduced pressure gave **3a**. Yield, 2.2 g (25.6%). bp 77—78°/0.1 mmHg. MS *m/e*: 168 (M^+). IR $\nu_{max}^{liq.}$ cm^{-1}: 2170 (–C≡C–). NMR δ (ppm in $CDCl_3$): 7.20—7.45 (5H, m, aromatic protons). The product **3b** was obtained by similar procedures from **2b**. Yield, 2.3 g (34.7%). bp 47—49°/13 mmHg. MS *m/e*: 134 (M^+). IR $\nu_{max}^{liq.}$ cm^{-1}: 2165 (–C≡C–). NMR δ (ppm in $CDCl_3$, J=Hz): 1.03 (3H, t, J=6, $-CH_3$), 1.56 (2H, sextet, J= 6 and 7, $-CH_2-$), 2.66 (2H, t, J=7, $-SCH_2-$).

***tert*-Butoxyethynyl Phenyl Sulfide (4a) and *tert*-Butoxyethynyl Propyl Sulfide (4b)**——To a stirred solution of 10.3 g (0.05 mol) of **2a** in 30 ml of THF, a solution of 12.3 g (0.11 mol) of potassium *tert*-butoxide in 100 ml of THF was added dropwise at −30——40°, and stirring was continued for 0.5 hr at the same temperature. When the reaction was completed, THF was evaporated off under reduced pressure and the resulting residue was extracted with IPE. Rotary evaporation of the extract gave almost pure **4a**. Yield, 8.4 g (81.6%). The product is thermally unstable and could not be purified by distillation *in vacuo*. IR $\nu_{max}^{liq.}$ cm^{-1}: 2175 (–C≡C–). NMR δ (ppm in $CDCl_3$): 1.49 (9H, s, *tert*-butoxy), 7.00—7.40 (5H, m, aromatic protons). The product **4b** was obtained by similar procedures. Yield, 7.0 g (84.7%). IR $\nu_{max}^{liq.}$ cm^{-1}: 2185 (–C≡C–). NMR δ (ppm in $CDCl_3$, J=Hz): 1.01 (3H, t, J=6, $-CH_3$), 1.38 (9H, s, *tert*-butoxy), 1.60 (2H, sextet, J=6 and 7, $-CH_2-$), 2.54 (2H, t, J=7, $-SCH_2-$).

***tert*-Butoxyethynyl Phenyl Sulfoxide (7) and *tert*-Butoxyethynyl Phenyl Sulfone (8)**——To a stirred solution of 0.05 mol of **5** or **6** in 100 ml of THF, a solution of 12.3 g (0.11 mol) of potassium *tert*-butoxide in 100 ml of THF was added dropwise at −70°. The stirring was continued for 1 hr at the same temperature. Work-up by procedures similar to those for **4a** gave **7** and **8**. The products are thermally unstanble and could not be purified by distillation even under very low pressure. **7**: Yield, 6.3 g (57.0%). IR $\nu_{max}^{liq.}$ cm^{-1}: 2165 (–C≡C–), 1080 (S→O). NMR δ (ppm in $CDCl_3$): 1.53 (9H, s, *tert*-butoxy), 7.35—7.70 (5H, m, aromatic protons). **8**: Yield, 9.1 g (76.0%). IR $\nu_{max}^{liq.}$ cm^{-1}: 2170 (–C≡C–), 1340, 1160, (SO_2). NMR δ (ppm in $CDCl_3$): 1.52 (9H, s, *tert*-butoxy), 7.30—8.00 (5H, m, aromatic protons).

3-*tert*-Butoxy-2,4-bis(phenylthio)-2-cyclobuten-1-one (11a) and 3-*tert*-Butoxy-2,4-bis(propylthio)-2-cyclobuten-1-one (11b)——A solution of 10.3 g (0.05 mol) of **4a** in 30 ml of benzene was refluxed until the evolution of isobutene ceased. The solvent was evaporated off under reduced pressure, and the resulting residue was chromatographed on silica gel (benzene) to afford **11a** as a colorless liquid. Yield, 1.8 g (20.1%). *Anal.* Calcd for $C_{20}H_{20}O_2S_2$: C, 67.38; H, 5.65. Found: C, 67.66; H, 5.89. IR $\nu_{max}^{liq.}$ cm^{-1}: 1745 (>C=O), 1585 (>C=C<). NMR δ (ppm in $CDCl_3$): 1.45 (9H, s, *tert*-butoxy), 4.34 (1H, s, –SCH–), 6.90—7.60 (10H, m, aromatic protons). The product **11b** was obtained by similar procedures. Yield, 2.5 g (34.8%). *Anal.* Calcd for $C_{14}H_{24}O_2S_2$: C, 58.29; H, 8.39. Found: C, 57.85; H, 8.13. IR $\nu_{max}^{liq.}$ cm^{-1}: 1740 (>C=O), 1580 (>C=C<). NMR δ (ppm in $CDCl_3$, J=Hz): 0.98 (3H, t, J=6, $-CH_3$), 1.05 (3H, t, J=6, $-CH_3$), 1.35—2.00 (4H, m, $-CH_2-$), 1.42 (9H, s, *tert*-butoxy), 2.43 (2H, t, J=7, $-CH_2SC(=O)-C=$), 3.09, 3.12 (2H, t, J=7, $-C=CSCH_2-$), 4.12 (1H, s, –SCH–).

2,4-Bis(phenylsulfonyl)-cyclobutane-1,3-dione (12)——A solution of 12.0 g (0.05 mol) of **8** in 30 ml of toluene was refluxed until the evolution of isobutene ceased. The solvent was evaporated off under reduced pressure and the resulting residue was chromatographed on silica gel (benzene) to afford **12** as prisms. Yield, 0.5 g (6.3%). mp 105—106°. *Anal.* Calcd for $C_{16}H_{12}O_4S_2$: C, 57.82; H, 3.64. Found: C, 57.48; H, 3.53.

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IR ν_{max}^{KBr} cm^{-1}: 1740 (>C=O), 1335, 1155 (SO_2). NMR δ (ppm in $CDCl_3$): 4.39 (2H, s, $-SO_2\overset{|}{C}H-$), 7.45—8.00 (10H, m, aromatic protons).

Ethynyl Phenyl Sulfide (16a) and Ethynyl Propyl Sulfide (16b)——To a 50 ml ethereal solution of 10.3 g (0.05 mol) of **2a**, a solution of 0.12 mol of butyl lithium in 75 ml of pentane was added dropwise at −70°. The mixture was stirred for 0.5 hr at the same temperature, then saturated NH_4Cl solution was added dropwise at −70° and the reaction mixture was allowed to stand at room temperature. The ether–pentane layer was dried over $MgSO_4$. Concentration of the solution under reduced pressure and distillation of the resulting residue under reduced pressure gave **16a**. Yield, 4.4 g (66.0%). bp 68—69°/2.7 mmHg. *Anal.* Calcd for C_8H_6S: C, 71.60; H, 4.51. Found: C, 71.16; H, 4.94. IR $\nu_{max}^{liq.}$ cm^{-1}: 3260 (≡C–H), 2045 (–C≡C–). NMR δ (ppm in $CDCl_3$): 3.22 (1H, s, ≡C–H), 7.10—7.60 (5H, m, aromatic protons). The product **16b** was obtained by similar procedures. Yield, 2.9 g (57.9%). bp 70—72°/155 mmHg. *Anal.* Calcd for C_5H_8S: C, 59.95; H, 8.51. Found: C, 59.53; H, 8.05. IR $\nu_{max}^{liq.}$ cm^{-1}: 3280 (≡C–H), 2040 (–C≡C–). NMR δ (ppm in $CDCl_3$, J=Hz): 1.03 (3H, t, J=6, $-CH_3$), 1.77 (2H, sextet, J=6 and 7, $-CH_2-$), 2.73 (2H, t, J=7, $-SCH_2-$), 2.73 (1H, s, ≡C–H). By the use of *tert*-butyl lithium and phenyl lithium in place of butyl lithium in the above procedures, **16a** was obtained in 17.5% and 43.2% yields, respectively. In the former run, phenyl 1-*tert*-butylvinyl sulfide was obtained as a by-product in 16.6% yield. bp 75—77°/0.2 mmHg. *Anal.* Calcd for $C_{12}H_{15}S$: C, 74.94; H, 8.39. Found: C, 75.10; H, 8.32. IR $\nu_{max}^{liq.}$ cm^{-1}: 1585 (>C=C<). NMR δ (ppm in $CDCl_3$): 1.08 (9H, s, *tert*-butyl), 5.95—6.05 (2H, broad, $=CH_2$), 7.00—7.50 (5H, m, aromatic protons).

Phenyl(and Propyl)thio Ethynyl Carbinols (19—24)——To a stirred solution of 0.05 mol of **2a** or **2b** in 50 ml of ether, a pentane solution of 0.12 mol of butyl lithium was added dropwise at −70°. The mixture was stirred for 0.5 hr, then 10 ml of ether solution of 0.06 mol of a carbonyl compound was added dropwise at −10°, and the stirring was continued for a further 0.5 hr at the same temperature. Then, a saturated NH_4Cl solution was added dropwise at −70° with vigorous stirring. The ether–pentane layer was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting residue was subjected to distillation under reduced pressure to give **19—24**. Yields of the products are shown in Table II, and spectral and analytical data in Table III.

Table III. Physical, Spectral and Analytical Data of Ethynylcarbinols (**19—24**) $RSC{\equiv}CC(OH)R^1R^2$

Compd. No.	bp (°C/mmHg)	IR $\nu_{max}^{liq.}$ cm^{-1} –OH	IR –C≡C–	NMR δ (ppm in $CDCl_3$, J=Hz)	Formula (M.W.)	Analysis (%) Calcd (Found) C	H
19	164—165/0.1	3310	2180	5.60 (1H, s, $-\overset{|}{C}H-$), 2.30—2.70 (1H, br, –OH) 7.05—7.60 (10H, m, aromatic protons)	$C_{15}H_{12}OS$ (240.32)	74.97 (74.80	5.03 5.24)
20	115/0.1	3360	2175	4.30—4.70 (1H, m, $-\overset{|}{C}H-$), 2.20—2.45 (1H, br, –OH), 1.80 (2H, octet, J=5 and 7, $-CH_2-$), 1.03 (3H, t, J=7, $-CH_3$), 7.00—7.50, (5H, m, aromatic protons)	$C_{10}H_{12}OS$ (180.27)	68.71 (68.88	6.29 6.35)
21	114—115/0.1	3330	2190	2.20—2.40 (1H, br, –OH), 1.59 (6H, s, $(-CH_3)_2$), 7.00—7.50 (5H, m, aromatic protons)	$C_{10}H_{12}OS$ (180.27)	68.71 (68.74	6.29 6.21)
22	121—122/0.1	3330	2180	5.43 (1H, d, J=6, $-\overset{|}{C}H-$), 2.65 (1H, d, J=6, –OH), 2.65 (2H, t, J=7, $-SCH_2-$), 1.72 (2H, sextet, J=7, $-CH_2-$), 0.96 (3H, t, J=7, $-CH_3$), 7.10—7.60 (5H, m, aromatic protons)	$C_{12}H_{14}OS$ (206.30)	69.86 (69.63	6.84 6.81)
23	105—107/13	3345	2170	4.20—4.45 (1H, m, $-\overset{|}{C}H-$), 2.10—2.40 (1H, br, –OH), 2.67 (2H, t, J=7, $-SCH_2-$), 1.40—2.00 (4H, m, $-CH_2-$ and $-CH_2-$), 1.02, 1.00 (6H, t, J=7, $-CH_3$ and $-CH_3$)	$C_8H_{14}OS$ (158.26)	60.72 (60.58	8.92 8.76)
24	102—103/13	3355	2170	2.30—2.40 (1H, br, –OH), 2.66 (2H, t, J=6, $-SCH_2-$), 1.67 (2H, m, J=6 and 7, $-CH_2-$), 1.50 (6H, s, $(-CH_3)_2$), 1.01 (3H, t, J=7, $-CH_3$)	$C_8H_{14}OS$ (158.26)	60.72 (60.32	8.92 8.65)

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