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Reactions of 2,2-Dichlorovinyl and 2,2-Dichlorovinylidene Sulfides with Butyllithium

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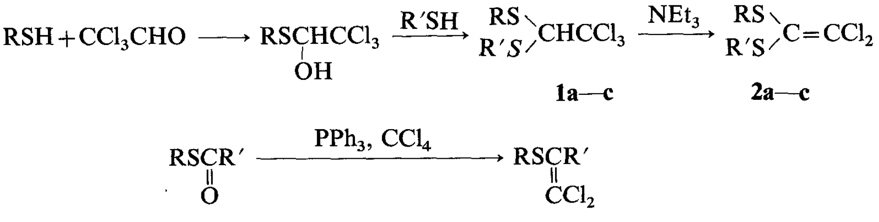
The present paper describes the reactions of two series of compounds, ${}^{RS}_{R'S}\!\!>\!C{=}CCl_2$ and ${}^{RS}_{R'}\!\!>\!C{=}CCl_2$, with butyllithium. The former gives 1,2-dithio-substituted acetylenes by rearrangement, whereas the latter gives cumulenes by dimerization.

Keywords——2,2-dichlorovinylidene sulfide; rearrangement; dimerization; 1,2-dithio-substituted acetylene; cumulene; butyllithium

In an earlier paper we reported the reaction of 2,2-dichlorovinyl sulfides with *tert*-butoxide and alkyl(or phenyl)lithium leading to thioacetylenic compounds.[1] We now wish to report the reactions of analogs such as $Cl_2C{=}C\!<\!{}^{SR}_{SR'}$ (**2**) and $Cl_2C{=}C\!<\!{}^{SR}_{R'}$ (**3**) with butyllithium; these reactions proceed in new fashions, rearrangement in the former case and dimerization to cumulenes in the latter.

The substrate compounds **2a**—**c** were prepared by dehydrochlorination of the thioacetals obtained by the previously reported method[2] from chloral and thiols. The compounds **3a**—**c** were first prepared by the reaction of thioesters of carboxylic acids with triphenylphosphine and carbon tetrachloride by a method similar to that reported previously[3] for 2,2-dichlorovinyl ethers.



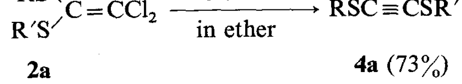
$$RSH + CCl_3CHO \longrightarrow \underset{OH}{RSCHCCl_3} \xrightarrow{R'SH} \underset{\mathbf{1a—c}}{{}^{RS}_{R'S}\!\!>\!CHCCl_3} \xrightarrow{NEt_3} \underset{\mathbf{2a—c}}{{}^{RS}_{R'S}\!\!>\!C{=}CCl_2}$$

$$\underset{\overset{\|}{O}}{RSCR'} \xrightarrow{PPh_3,\ CCl_4} \underset{\mathbf{3a—c}}{\underset{\overset{\|}{CCl_2}}{RSCR'}}$$

1a, **2a** : R, R′=Ph, Ph
1b, **2b** : R, R′=Ph, Amyl
1c, **2c** : R, R′=Amyl, Amyl

3a : R, R′=Ph, Ph
3b : R, R′=Ph, Pr
3c : R, R′=Amyl, Pr

Reaction of **2a**—**c** with butyllithium in ether resulted in the formation of rearranged acetylenic compounds, which indicates the occurrence of migration of the phenylthio or amylthio grouping from C-1 to C-2.

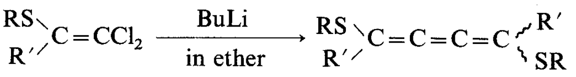


$${}^{RS}_{R'S}\!\!>\!C{=}CCl_2 \xrightarrow[\text{in ether}]{BuLi} RSC{\equiv}CSR'$$

2a	**4a** (73%)
2b	**4b** (62%)
2c	**4c** (71%)

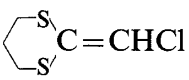
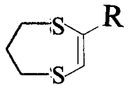
We then carried out the reaction with an equimolar mixture of **2a** and **2c**. In this reaction no cross-product was detected by means of gas chromatography. Consequently, the reaction is established as an intramolecular rearrangement.

Under the same conditions, compounds **3a**—**c** reacted with butyllithium in a different fashion to give cumulenes by dimerization.



$$\begin{matrix}RS\\R'\end{matrix}\!\!>\!C{=}CCl_2 \xrightarrow[\text{in ether}]{BuLi} \begin{matrix}RS\\R'\end{matrix}\!\!>\!C{=}C{=}C{=}C\!<\!\begin{matrix}R'\\SR\end{matrix}$$

3a **5a** (83%)
3b **5b** (62%)
3c **5c** (71%)

At that time a search of the literature revealed only two prior papers describing such a rearrangement. Cyclic chloroketene dithioacetal,  gave  (R = iso-Pr and Bu) as minor products on reaction with iso-PrMgCl and BuLi,[4] and a ${}^{R}_{R'}{>}C{=}CHCl$, in which R = *tert*-Bu and R′ = PhS, gave *tert*-BuC≡CSPh.[5] In addition, cumulene formation has been reported in the reaction of ${}^{R}_{R'}{>}C{=}CHX$, where R, R′ = alkyl and X = halogen, with alkyllithium.[6]

Mechanistically both the reactions of rearrangement and cumulene formation can be postulated to be initiated by lithiation of one of the chlorines, followed by rearrangement of the alkylthio group and by dimerization, respectively, as shown in Chart 1. The rearrangement appears to proceed through an intermediary carbene, as postulated in the previous paper.[4,7] Despite the previously reported rearrangement of ${}^{tert\text{-}Bu}_{PhS}{>}C{=}CHCl$ as mentioned above, the use of the compounds **3a**—**c** has significantly extended the scope of the rearrangement reaction and the cumulene formation to sulfides of 2,2-dichlorovinylidene and 2,2-dichlorovinyl structures.

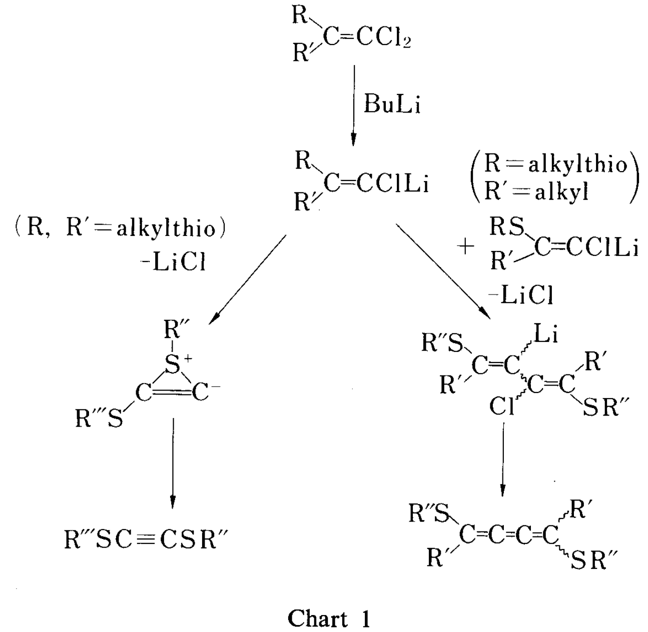


Chart 1

Experimental

All melting points are uncorrected. Carbon magnetic resonance spectra were recorded on a JEOL JNM-FX90Q instrument and all chemical shifts are given in ppm downfield from tetramethylsilane. The following abbreviations are used; s = singlet and d = doublet. Mass spectra were measured with a JEOL JMS-D100 machine.

1,1-Bis(alkylthio)-2,2-dichloroethenes (2a—c)——General Procedures: The starting **1a—c** were prepared from the corresponding thiols and chloral according to the previously reported method.[2] A solution of **1a—c** (0.1 mol) and triethylamine (0.2 mol) in benzene (200 ml) was refluxed for 3 h. Triethylamine hydrochloride deposited was filtered off and the filtrate was concentrated under reduced pressure. Distillation of the resulting residue under reduced pressure gave **2a—c**. **2a**: yield, 95%, bp 178—180 °C/0.45 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 122.88 (s), 132.20 (s) ($>C=C<$). *Anal.* Calcd for $C_{14}H_{10}Cl_2S_2$: C, 53.68; H, 3.22. Found: C, 53.46; H, 3.10. **2b**: yield, 93%, bp 155—157 °C/0.3 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 122.88 (s), 133.61 (s) ($>C=C<$). *Anal.* Calcd for $C_{13}H_{16}Cl_2S_2$: C, 50.81; H, 5.25. Found: C, 50.77; H, 5.40. **2c**: yield, 96%, bp 138—140 °C/0.3 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 120.98 (s), 132.25 (s) ($>C=C<$). *Anal.* Calcd for $C_{12}H_{22}Cl_2S_2$: C, 47.83; H, 7.36. Found: C, 47.99; H, 7.34.

Alkyl 1-Alkyl-substituted-2,2-dichlorovinyl Sulfides (3a—c)——General Procedures: A solution of the corresponding carboxylic acid thioester (0.2 mol) and triphenylphosphine (0.5 mol) in CCl_4 (300 ml) was refluxed for 10 h. After removal of the CCl_4 under reduced pressure, the resulting residue was triturated with petr. ether. The petr. ether was removed under reduced pressure and distillation of the resulting residue under reduced pressure gave **3a—c**. **3a**: yield, 54%, bp 152—154 °C/0.2 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 117.41 (s), 135.99 or 135.78 (s) ($>C=C<$). *Anal.* Calcd for $C_{14}H_{10}Cl_2S$: C, 59.80; H, 3.58. Found: C, 60.21, H, 3.70. **3b**: yield, 30%, bp 120—122 °C/0.2 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 118.38 (s), 135.18 (s) ($>C=C<$). *Anal.* Calcd for $C_{11}H_{12}Cl_2S$: C, 53.45; H, 4.89. Found: C, 53.70; H, 4.92. **3c**: yield, 35%, bp 105—107 °C/0.4 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 116.06 (s), 135.29 (s) ($>C=C<$). *Anal.* Calcd for $C_{10}H_{17}Cl_2S$: C, 50.00; H, 7.13. Found: C, 50.45; H, 7.31.

1,2-Dithio-substituted Acetylenes (4a—c)——A 1.6 M pentane solution (23 ml, 0.033 mol) of butyllithium was added dropwise to a stirred solution of **2a—c** (0.03 mol) in ether (50 ml) at −70 °C. The stirring was continued for 1 h at −30 °C, then excess of butyllithium was quenched with aqueous ammonium chloride. The ether–pentane layer was dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, distillation of the resulting residue under reduced pressure gave **4a—c**. **4a**: yield, 73%, bp 155—157 °C/0.4 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 87.99 (s, $-C\equiv C-$). *Anal.* Calcd for $C_{14}H_{10}S_2$: C, 69.38; H, 4.16. Found: C, 69.12; H, 4.11. **4b**: yield, 62%, bp 120—122 °C/0.01 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 81.54 (s), 92.76 (s) ($-C\equiv C-$). *Anal.* Calcd for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82. Found: C, 66.01; H, 6.81. **4c**: yield, 71%, bp 141—142 °C/0.4 mmHg. ^{13}C-NMR ($CDCl_3$) δ: 85.87 (s, $-C\equiv C-$). *Anal.* Calcd for $C_{12}H_{22}S_2$: C, 62.55; H, 9.62. Found: C, 62.39; H, 9.58.

1,4-Dialkyl-substituted-1,4-bis(alkylthio) butatrienes (5a—c)——A 1.6 M pentane solution (23 ml, 0.033 mol) of butyllithium was added dropwise to a solution of **3a—c** (0.03 mol) in ether (50 ml) at −70 °C with stirring. The stirring was continued for 1 h at the same temperature. In the run with **3a**, **5a** was deposited as a precipitate, which was collected by filtration and washed. Recrystallization from ethanol gave **5a**. Yield, 83%, mp 167.5—168 °C (prisms). ^{13}C-NMR ($CDCl_3$) δ: 116.97 (s, C-1 and C-4), 148.83 (s, C-2 and C-3). MS *m/z*: 420 (M^+). *Anal.* Calcd for $C_{28}H_{20}S_2$: C, 79.96; H, 4.79. Found: C, 79.49; H, 4.65. In the run with **3b** or **3c**, the reaction solution was washed with aqueous ammonium chloride and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave **5b** or **5c**, which was purified by silica gel column chromatography using hexane as an eluent. **5b**; yield, 68%. ^{13}C-NMR ($CDCl_3$) δ: 114.54 (s, C-1 and C-4), 147.42 (s, C-2 and C-3). MS *m/z*: 352 (M^+). *Anal.* Calcd for $C_{22}H_{24}S_2$: C, 74.95; H, 6.86. Found: C, 74.58; H, 6.76. **5c**: yield, 62%. ^{13}C-NMR ($CDCl_3$) δ: 115.62 (s, C-1 and C-4), 143.36 (s, C-2 and C-3). MS *m/z*: 340 (M^+). *Anal.* Calcd for $C_{20}H_{36}S_2$: C, 70.52; H, 10.65. Found: C, 70.33; H, 10.24.

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References and Notes

1) E. Nagashima, K. Suzuki, and M. Sekiya, *Chem. Pharm. Bull.*, **29**, 1274 (1981).
2) G. Schrader, Ger. Patent 1063152 (1959) [*Chem. Abstr.*, **55**, 13378*g*].
3) M. Suda and A. Fukushima, *Tetrahedron Lett.*, **1981**, 759.
4) N. H. Andersen, D. F. Duffy, A. D. Denniston, and D. B. Grotjahn, *Tetrahedron Lett.*, **1978**, 4315.
5) S. Y. Delavarenne and H. G. Viehe, *Chem. Ber.*, **103**, 1198, 1209, 1216 (1970).
6) *a*) S. Patai (ed.), "The Chemistry of Ketenes, Allenes, and Related Compounds," John Wiley & Sons, New York, 1980, p. 863; *b*) G. Köbrich, H. Heinemann, and W. Zündorf, *Tetrahedron*, **23**, 565 (1967); *c*) G. Köbrich and W. Prischel, *ibid.*, **22**, 2621 (1966); *d*) G. Köbrich and H. Trapp, *Chem. Ber.*, **99**, 670, 680 (1966).
7) R. A. Moss and M. Jones, Jr., "Carbenes," Vol. II, John Wiley & Sons, New York, 1975, p. 56.