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ACTION OF ELEMENTARY SULFUR ONTO CARBANIONS : A NEW ROUTE TO DIALKYLPOLYSULFIDES

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The reaction of sec-Butyllithium with elemental sulfur leads to the formation of dialkylpolysulfides.

Several methods have been used in order to incorporate sulfur into organic compounds and to prepare thiolates, thioethers, dialkylpolysulfides. Different powerful nucleophiles have been reacted either on elemental sulfur or on polysulfides.

Schönberg[1)] and Hallensleben[2)] have reacted some carbanions onto dialkylpolysulfides and obtained thiolates ; Gilman[3)] using carbanions and sulfur itself produced mercaptans ; so did Manecke and Bauerschmidt[4)]. Foss[5)] and Milligan[6)] using sulfites, cyanides and Bunte salts have prepared a variety of organic polysulfides. Industry[7)] makes use of the reaction between a dihalide and a sodium polysulfide.

We have investigated the reaction of sulfur onto monocarbanionic oligomers[8)] and observed the formation of different compounds. In this paper we present the detailed investigation carried out when sec-butyllithium is used as a model.

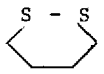
When sec-BuLi (concentration : 0.5 M) is added at room temperature to a benzene solution of S_8 sulfur (concentration : 4×10^{-2} M) a very fast reaction takes place and lithium polysulfides precipitate out. After a few minutes, the compounds are isolated and characterized. The average molecular weight of the organic compounds obtained is determined by cryometry : the results as well as those from elemental analysis correspond to coupled compounds of formula $R\text{-}S_x\text{-}R$ with $1 \leq x < 5$.

The reaction scheme proposed is the following one :

$$\text{sBu - Li} + S_8 \longrightarrow [\text{sBu-}S_8\text{-Li}] \qquad \text{non isolated}$$

$$[\text{sBu-}S_8\text{-Li}] + \text{sBu-Li} \longrightarrow \text{sBu-}S_x\text{- sBu} + \text{Li}_2S_y \qquad (x + y = 8)$$

The second step is similar to another reaction described by Hallensleben[2)].



$$+ \text{R-Li} \longrightarrow \text{R-S-(CH}_2)_4\text{-S-Li}$$

According to this scheme, we should obtain a mixture of dialkylpolysulfides which are different from one another only by the number of linked sulfur atoms. This number depends very much on one parameter : the ratio, $K = [\text{sBuLi}]/[S_8]$. For the ratio K = 2 the main products resulting from the reaction are the coupled compounds : $\text{sBu-}S_x\text{-sBu}$ with $x \simeq 3,4$ (by gel permeation chromatography and by elemental analysis). For the ratio K > 2, we observe by gel permeation chromatography the decrease of the peaks corresponding to the coupled compounds, and the appearance of a new peak corresponding to thiolate :

$$sBu-S_x-sBu + sBu-Li \longrightarrow sBu-S_y-sBu + sBu-S-Li \qquad (y < x)$$

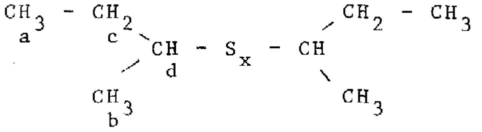
We have not separated the different alkylpolysulfides obtained, but they have been analyzed by VPC coupled with mass spectrometry. In all cases, the thiolates have been removed. Depending on the K values, we observe :

K = 8 : we obtain only one coupled compound $sBu-S_x-sBu$, and some sec-Butylthiolate ; the gas chromatography shows the presence of only one peak, and its mass spectra is identical to that of the authentic product sBu-S-sBu.

K = 4 : we obtain always coupled compounds and some thiolate. Vapour phase chromatography shows the presence of three compounds, the mass spectra of which exhibit the parent peaks at : 146 - 178 - 210 corresponding to sBu-S-sBu, sBu-S-S-sBu and sBu-S-S-S-sBu.

K = 2 : we observe -in addition to the same compounds as before with K = 8 and 4- the formation of a new polysulfide $sBu-S_4-sBu$ (mass spectra = 242).

A good linear relationship is observed between the logarithm of the retention volume and the molecular weight of the dialkylpolysulfides ; this has already been described by Hillen9) for a series of dimethylpolysulfides. By ^{1}H-NMR spectroscopy we have observed on the spectrum of the different dialkylpolysulfides (K = 2) that the protons located on the carbon α to the sulfur atom, have different chemical shifts that make them easily distinguishable. The chemical shift increases with the number of sulfur atoms linked except for the disulfide



H x	a_t	b_d	c_m	d_m
1	0.97	1.25	1.60	2.74
2	0.98	1.29	1.60	2.74
3	0.99	1.35	1.60	2.98
4	1.00	1.39	1.60	3.07

Table 1 - ^{1}H-NMR chemical shifts (CAMECA 250 MHz) of di-sec.Butylpolysulfides (solvent $CDCl_3$)

In conclusion, the reaction of carbanions with elemental sulfur leads to the formation of dialkylpolysulfides for K values ≤ 2($-S_x-$: x = 1,2,3,4). For 8 > K > 2, the number of sulfur atoms drops to 1,2,3 and for K = 8 only the dialkylmonosulfide is obtained..

References

1) A. Schönberg, A. Stephenson, H. Kaltschmitt, E. Petersen, H. Schulten, Ber.Dtsch.Chem.Ges. 66, 237 (1933)
2) M. Hallensleben, Makromol.Chem. 175, 3315 (1974)
3) H. Gilman, J.W. Morton, Org.React. 8, 258 (1954)
4) G. Manecke, E. Bauerschmidt, Makromol.Chem. 94, 84 (1966)
5) O. Foss, Act.Chem. Scand. 4, 404 (1950)
6) B. Milligan, B. Saville, J.M. Swan, J. Chem. Soc. 2608 (1963)
7) E.J. Goethals, "Topics in sulfur chemistry", Vol. 3, Edited A. Senning
8) J.F. Boscato, J.M. Catala, E. Franta, J.Brossas, Makromol.Chem. 180, 1571 (1979)
9) L.W. Hillen, R.L.Werner, J.Chromatogr. 79, 318 (1973)

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