

SOLVATION AND REARRANGEMENT OF A CARBANION

J.F. BIELLMANN and J.L. SCHMITT

Laboratoire associé au C.N.R.S., Institut de Chimie,
Université Louis Pasteur, 1 rue Blaise Pascal, 67008 STRASBOURG.

(Received in UK 19 September 1973; accepted for publication 8 October 1973)

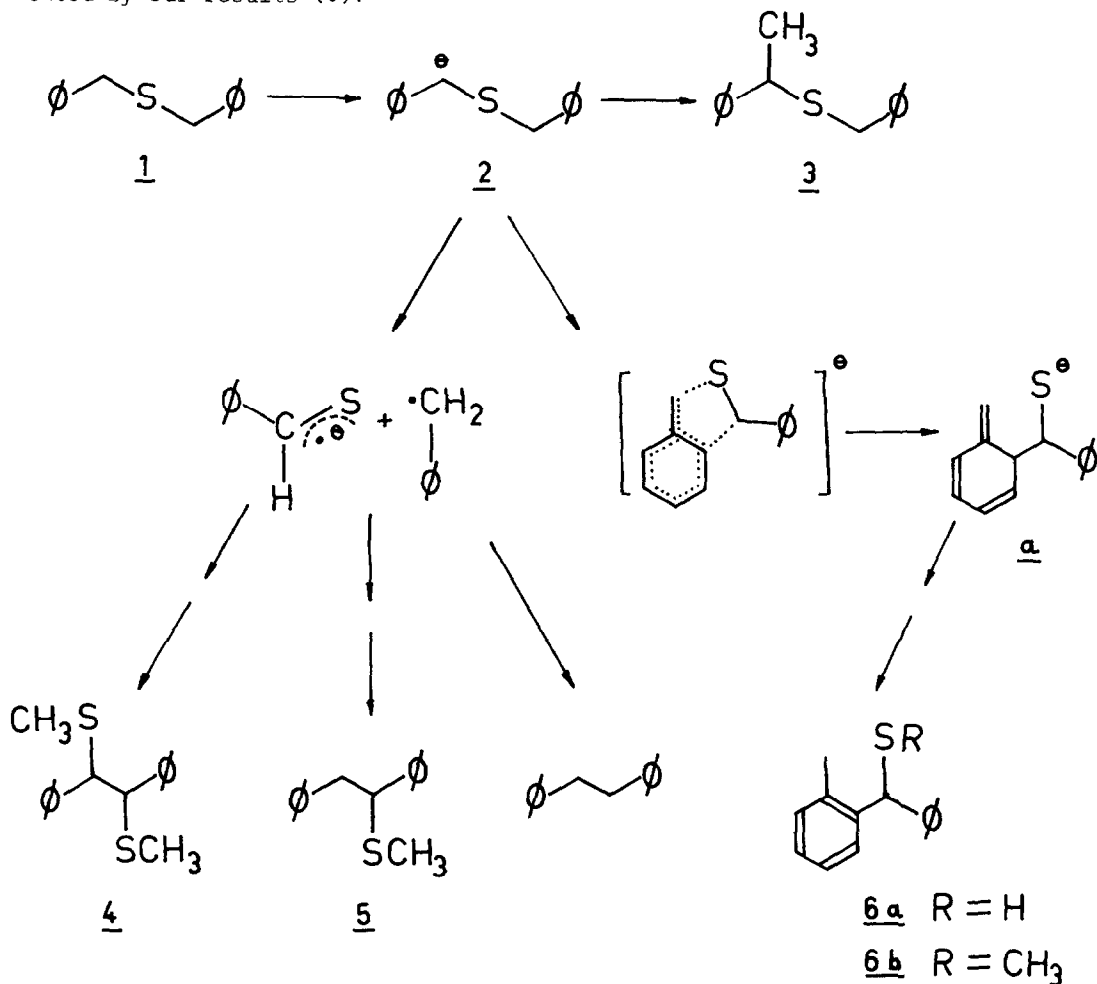
The rearrangement of dibenzylthioether 1 to a Sommelet type product 6a under basic conditions has been described (1). Following our interest in carbanions derived from sulphides, we undertook a new study of this system (2).

At low temperature (-78°C), using n-butyllithium as a base and tetramethylethylene diamine (TMEDA) as a solvating agent in tetrahydrofuran (THF), the carbanion 2 seems stable, at least for the period studied (one hour) : after addition of methyl iodide, the methylated thioether 3 is isolated (3) ; by increasing the temperature, the derivative 6b is isolated. Quite clearly this product arises from a Sommelet type rearrangement. At higher temperatures, the product 5 appears together with 6b (3) ; simultaneously products like dibenzyl and (1,2-dimethylthio)dibenzyl 4 appear (3). These latter products and 5 come from a Stevens type rearrangement.

The Sommelet type rearrangement, which may be a concerted sigmatropic [2,3] shift on the carbanion 2 (4), gives, in a highly ordered transition state, the thiolate a which is rapidly converted by proton shift to the thiolate of 6a.

The Stevens type rearrangement may be a dissociative process (5) : dissociation of carbanion 2 to the radical-anion of thiobenzaldehyde and the benzyl radical ; the recombination of these radicals gives the thiolate precursor of 5. The escape of the radicals from the solvation cage and their recombination leads to the dibenzyl and the dithiolate precursor of 4.

Due to the highly ordered transition state of the Sommelet type rearrangement compared to the dissociation process of the Stevens type rearrangement, the former path is preferred at lower temperature, as indicated by our results (6).



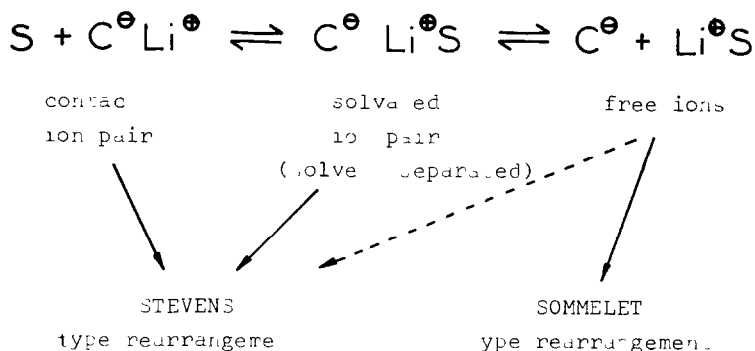
However the temperature is not the only important factor for the competition control of the two rearrangements. Our study shows that the nature of the ion-pair present is of crucial importance. The results were obtained at +11°C by addition of the n-butyllithium to the medium, and after 2 minutes the dibenzylthioether in equivalent ratio; after 45 minutes methyl iodide is added. The yields of the products are determined by gaschromatography.

| Medium | Yield | | | Ratio |
|----------------------------------|------------|------------|-------------|------------------------|
| | % <u>1</u> | % <u>5</u> | % <u>6b</u> | % <u>6b</u> / <u>5</u> |
| Hexane/TMEDA 1eq. +) | 0 | 0 | 100 | 0 |
| THF | 0 | 2 | 98 | 0,02 |
| THF/TMEDA 1eq. | 0 | 7 | 93 | 0,07 |
| THF/HMPT(50/1)/TMEDA 1eq. +) ++) | 20 | 23 | 57 | 0,4 |
| THF/(2,2,2) 1eq. +) ++) | 50 | 29 | 21 | 1,3 |
| THF/TMEDA 1eq./LiBr 9eq. | 0 | 2 | 98 | 0,02 |
| THF/TMEDA 15eq./LiBr 14eq. | 0 | 0 | 100 | 0 |

+) TMEDA : tetramethylethylene diamine
 1eq. : one equivalent to n-butyllithium
 HMPT : hexamethylphosphorus triamide
 (2,2,2) : cryptate (2,2,2) (7).

++) Under these conditions, part of the n-butyllithium is destroyed by reaction with the medium (8).

The solvation of the cation is in favour of the Sommelet reaction. We propose the following explanation : the carbanion 2 is present, according to the solvent, as an intimate ion pair, a solvated ion pair (solvent separated) and a free ion (9). The more dissociated species give raise to the Sommelet - and probably to the Stevens type rearrangement, the less dissociated species only the Stevens type. The less dissociated ion pairs may be present as aggregates.



The cryptate (2,2,2), which complexes strongly with the lithium cation, increases the distance between the anion and the cation and gives at least the solvent separated ion pair, if not the free anion : the Sommelet type rearrangement is the most important. The lithium bromide suppresses almost completely the Sommelet type rearrangement. Which proves that the free ions, whose concentrations are decreased by lithium bromide as a common salt, give the Sommelet type rearrangement.

From our results, intimate ion pairs and solvated ions give at this temperature mostly, if not exclusively, the Stevens type rearrangement.

Consideration of the structure of the intermediates of the two rearrangements confirms this conclusion. The transition state of the Sommelet type rearrangement has a delocalised negative charge ; the delocalisation of a charge is disfavoured by a strong interaction with the counterion, which is important in poorly solvating solvents. For the Stevens type rearrangement, the charge is not necessarily delocalised in the homolytic process leading to the radical anion.

In conclusion, the competition of both rearrangements is affected not only by the temperature, but also by the nature of the ions present. Care should be taken in comparing data for the rearrangement of different carbanions that the nature of the ions are similar.

References

- (1) C.R. Hauser, S.W. Kantor and W.R. Brasen, J. Amer. Chem. Soc., **75**, 2660 (1953).
- (2) J.F. Biellmann and J.B. Ducep, Tetrahedron Letters, **33** (1971) ; ibid. 5871 (1971).
J.F. Biellmann and J.B. Ducep, Tetrahedron, **27**, 5861 (1971).
- (3) Identification of these products has been carried out by synthesis (to be described in the full paper).
- (4) Nguyen Trong Anh, Les règles de Woodward-Hoffmann, Ediscience, Paris, 1970, p. 75 and 82.
- (5) By analogy with the mechanism proposed for the Wittig rearrangement :
U. Schoellkopf, Angew. Chem., **82**, 795 (1970).
S.H. Pine, J. Chem. Education, **48**, 99 (1971).
- (6) To be discussed in the full paper.
- (7) B. Dietrich, J.M. Lehn and J.P. Sauvage, Tetrahedron, **29**, 1647 (1973).
- (8) S.C. Honeycutt, J. Organometal. Chem., **29**, 1 (1971).
H. Gilman and G.J. Bernard, J. Org. Chem., **22**, 1165 (1957).
- (9) M. Szwarc, Ions and ion pairs in organic reactions, Wiley-Interscience, New-York, 1972.