Trigonal Configuration of Disulphonyl Carbanions

A. Berlin, S. Bradamante, R. Ferraccioli, and G. A. Pagani

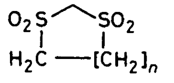
Dipartimento di Chimica Organica e Industriale dell'Università, and CNR, Centro Speciali Sistemi Organici, Via C. Golgi 19, 20133 Milano, Italy

One-bond C–H coupling constants of the anionic carbon of anions derived from disulphones (**1**)—(**3**) provide unequivocal evidence for the trigonal hybridization of the charged carbon, previously assigned as tetrahedral; it is shown that the 1,3-dithiolane 1,1,3,3-tetroxide undergoes ring opening upon treatment with strong bases.

Analysis of the quoted[1] acidity variation found along the series of sulphones (**1**)—(**4**) and evaluation of non-bonding interactions in the conjugate anions of the same led Cram[2] to propose a pyramidal configuration for the carbanionic carbon of anions derived from (**1**)—(**3**) and a trigonal configuration for the anion of (**4**). We present herein definitive evidence that all the α,α'-disubstituted disulphonyl carbanions have a trigonal configuration and that the carbanion of the *S,S'*-tetroxide (**4**) is unstable, thus challenging one of the basic arguments for the previous configurational assignment. Substrates (**1**)—(**3**) were easily deprotonated by dimsyl sodium in Me_2SO; ^{13}C chemical shifts of the anionic carbon are reported in Table 1, together with the $^1J_{CH}$ coupling constants, and the respective variations relative to the neutral precursors. The value of the one-bond coupling constant $^1J_{CH}$ for a certain carbon atom is diagnostic of its hybridization state. In fact, the equation[3] $0.2\Delta(^1J_{CH}) = \Delta(\%\ s)$ relates the variation of $^1J_{CH}$ to the variation of the s character of the carbon orbitals [for $sp^3 \rightarrow sp^2$, $\Delta(\%\ s) = 8$, $\Delta(^1J_{CH})$ is *ca.* 40 Hz]. On this basis the variation of $^1J_{CH}$ between the neutral precursor carbon acid and the carbanion provides information whether a tetrahedral to trigonal configurational rehybridization is occurring in the anion. We find that the increase of the one-bond coupling is a maximum for the anion of (**1**) and a minimum for the anion of

$MeS(O_2)—CH_2—S(O_2)Me$

(**1**)

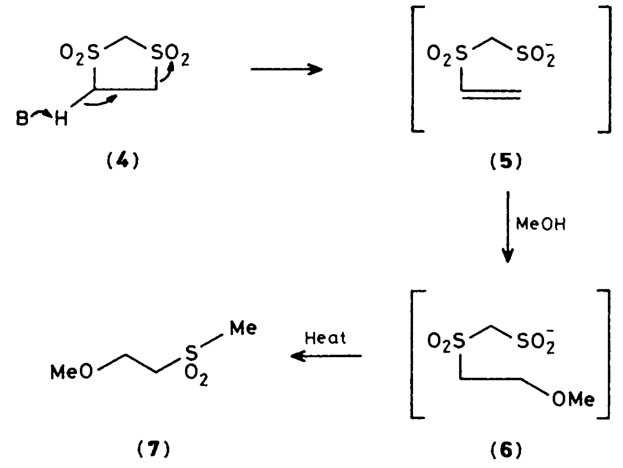


(**2**) *n* = 3
(**3**) *n* = 2
(**4**) *n* = 1

Table 1. N.m.r. data of the anionic carbon atom of disulphonyl carbanions and their variation relative to the precursors.[a]

Carbanion	δ_{CH}	$^1J_{CH}$/Hz
(1)	63.94	176.58
	(−6.21)	(30.68)
(2)	63.10	165.9
	(−8.47)	(20.2)
(3)	68.03	157.1
	(−2.03)	(9.6)

[a] Chemical shifts are referred to external $SiMe_4$ for 0.33 M solutions of substrate in Me_2SO at 35 °C. Numbers in parentheses are the differences between the data for the anion subtracted from the data for the neutral species; a negative variation of shift means an upfield displacement of the anion relative to the neutral compound.



Scheme 1

(**3**). There is unequivocal evidence[4] that the presence of the negative charge on the anionic carbon greatly reduces the expected enhancement of the $^1J_{CH}$. Despite this, the variations we report and the absolute sizes of the $^1J_{CH}$ cannot be assigned other than to trigonal carbon atoms in the carbanions. Even the smallest value and increment found for the anion of dithiane *S,S'*-tetroxide must be assigned to a trigonalized carbon since it is of the same size as the one found for the acetylacetonate anion in the same solvent.[4] We believe that the reasons that cause the limited increment of the coupling constant in the anion (**3**) are essentially conformational in nature. This conclusion is also suggested by a close inspection of the variation of the ^{13}C resonances in the anions. Relative to the neutral precursors, the carbon shifts suffer a small upfield displacement [with the exception of (**3**)]; this should be considered the result of the low-field shift (*ca.* 87 p.p.m.) due to tetrahedral → trigonal rehybridization, competitive with the high-field shift due to the intense localization of the negative charge on the anionic carbon (160 p.p.m. per unit negative charge).

The disulphone (**4**) did not lead to a stable carbanion by deprotonation at C-2 upon treatment with dimsyl sodium. In a series of parallel experiments we could isolate the β-methoxyethyl methyl sulphone (**7**) after treatment of the sulphone (**4**) with equimolar amounts of sodium methoxide in MeOH, under nitrogen, at room temperature, followed by short reflux. ^1H N.m.r. monitoring of the initial room temperature treatment in Me_2SO offered evidence for the formation of an ABX system (Me_2SO: 90 MHz: δ_A 6.06, δ_B 6.1, δ_C 7.1, J_{AX} 10, J_{BX} 16.5 Hz) assigned to the vinylic moiety of the intermediate non-isolated salt (**5**); subsequent heating probably promoted the Michael addition of methanol to give (**6**) and the thermal loss of SO_2 to give the final compound (**7**). All these results are in accord with the ring fission of the dithiolane disulphone as depicted in Scheme 1. The ring fission of (**4**) appears to be fast under strong base conditions so that the pK_a reported by Corey is composite and does not represent a simple ionization.

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