

SULFONYL-1,3-DICARBANIONS. EVIDENCE CONCERNING THE SCOPE AND LIMITATION OF FORMATION.

OXIDATION WITH COPPER SALTS TO FORM ALKENES.

(Received in UK 14 June 1974; accepted for publication 26 June 1974)

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The placement of carbanionic centers in close proximity is often surprisingly easy. Examples of 1,1-<sup>1a</sup>, 1,2-,<sup>1b</sup> and 1,3-dicarbaniions<sup>1c</sup> (or their respective covalent organometallic compounds) are now available. Most investigations of the chemistry of such compounds has hitherto been restricted to their ability to be alkylated or to undergo condensation reactions.

We have been interested for some time in developing general methods for the preparation of a variety of sulfonyl-1,3-dicarbaniions in order to investigate their synthetic utility. We report here the development of methodology applicable for sulfonyl-1,3-dicarbaniion formation from a variety of sulfones as well as evidence that the dicarbaniions can be oxidized, leading ultimately to olefins. Pertinent results are collected in the Table.

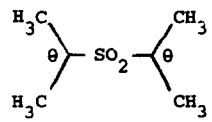
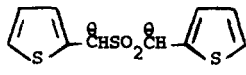
Method A, used for generating dicarbaniions from sulfones not possessing base-sensitive groups, involved treatment of sulfone (usually 1 mmol) dissolved in dry 1,2-dimethoxyethane under N<sub>2</sub> at 0°, or below, with ca. 5 mmol *n*-butyllithium for 1 and 2 and ca. 2.2 mmol *n*-butyllithium for 3 and 4.<sup>1c</sup> The dianions were generally colored, usually yellow.

Method B is a modification of a procedure originally suggested by Hauser.<sup>2</sup> The sulfone in dry 1,2-dimethoxyethane was added to a solution containing 1.1 eqv. lithium diisopropylamide at -40° C. The monoanion thus formed could thereafter be treated with 2.2 eqv. *n*-butyllithium (one equivalent reacts with diisopropylamine) to generate the dianion without observable addition of *n*-butyllithium to the carbonyl group.

In the case of 1,3, and 5 the dianions were quenched with large excesses of methyl iodide.

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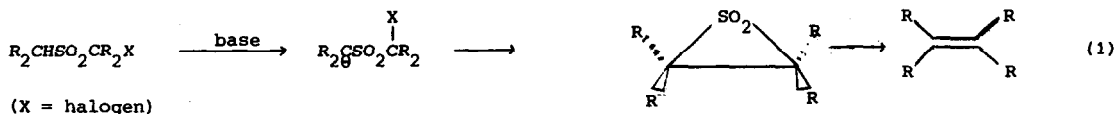
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1,3-Dicarbanion <sup>a</sup>	Method of Generation <sup>b</sup>	Oxidation <sup>c</sup> Product (% yield and method of determination)
$n\text{-C}_3\text{H}_7\overset{\ominus}{\text{C}}\text{HSO}_2\overset{\ominus}{\text{C}}\text{HC}_3\text{H}_7\text{-n}$ (1)	A	<u>cis</u> , <u>trans</u> -4-octene (45, glc) <sup>d</sup>
 (2)	A	2,3-dimethylbutene-2 (12, glc)
$\text{C}_6\text{H}_5\overset{\ominus}{\text{C}}\text{HSO}_2\overset{\ominus}{\text{C}}\text{HC}_6\text{H}_5$ (3)	A	<u>cis</u> , <u>trans</u> -stilbene (39, glc, pmr) <sup>e</sup>
 (4)	A	1,2-di(2-thienyl)ethene (23, pmr) <sup>f</sup>
$\text{C}_2\text{H}_5\text{O}_2\overset{\ominus}{\text{C}}\text{HSO}_2\overset{\ominus}{\text{C}}\text{HCO}_2\text{C}_2\text{H}_5$ (5)	B	diethylfumarate (54, isolated) <sup>g</sup> $\alpha$ -chloro-diethylfumarate (16, isolated) <sup>h</sup>
$\text{C}_2\text{H}_5\text{O}_2\overset{\ominus}{\text{C}}\overset{\text{CH}_3}{\text{C}}\text{SO}_2\overset{\ominus}{\text{C}}\overset{\text{CH}_3}{\text{C}}\text{CO}_2\text{C}_2\text{H}_5$ (6)	B	<u>cis</u> , <u>trans</u> -1,2-dimethyl-1,2-dicarboethoxyethene (35, isolated) <sup>i</sup>
$\text{C}_6\text{H}_5\overset{\ominus}{\text{C}}\overset{\text{O}}{\parallel}\text{HSO}_2\overset{\ominus}{\text{C}}\overset{\text{O}}{\parallel}\text{HC}_6\text{H}_5$ (7)	B	dibenzoyl ethylene (11, glc) <sup>j</sup> $\alpha$ -chlorodibenzoyl ethylene (5, glc) <sup>k</sup>

a) In all cases prepared from the respective sulfones; b) See text for procedure; c) See text for oxidation method; d) cis, trans ratio is ca. 1:2; e) cis, trans ratio is ca 1:6; f) only trans-isomer isolated; g) not more than trace diethylmaleate formed; h) carboethoxy groups presumed, but not proven, to be E; i) cis, trans-ratio is ca 1:1; j) only trans-isomer isolated; k) stereochemistry unknown.

Good yields of 1,3-dialkylated products were obtained as a result of a rapid reaction with the methyl iodide. The monoanions formed by treatment of the sulfone with one equivalent of base failed to give any 1,3-dimethylated products. In no case could gem-dimethyl compounds be identified suggesting that formation of 1,3-dilithio compounds is more favorable than formation of gem-dilithio derivatives.<sup>3</sup>

The oxidation reactions of the dianions (see Table) are, to the best of our knowledge, unique. The thought was to develop an alternative to the Ramberg-Bäcklund rearrangement (schematically illustrated in eq. 1)<sup>4</sup> wherein, instead of the extra step involved in the preparation of the



$\alpha$ -halosulfone, the dianion would suffer (formal) two-electron oxidation to afford a thirane-S,S-dioxide, which would subsequently decompose thermally to an olefin.

In our hands, anhydrous copper(II) chloride provided the best results. Oxidations were carried out by adding 4-5 moles of dry  $\text{CuCl}_2$  to the solution of dianion.<sup>5</sup> After warming up to room temperature the solutions (usually essentially neutral pH) were worked up by washing with  $\text{NH}_4\text{Cl}/\text{NaHCO}_3$  solution to complex the residual copper ions. In all cases the starting sulfone was not recovered in more than 5% yield. In some cases iodine was successfully used as an oxidizing agent although the yields were poor. Copper(I) chloride or iodide (with or without subsequent oxygen treatment), tetrakis [iodo(tri-*n*-butylphosphine)copper (I)]<sup>6</sup>, N-chlorosuccinimide, bromine, and chlorine all failed as oxidizing agents. The monoanions formed by treatment of the sulfone with one equivalent of base failed to undergo reaction with  $\text{CuCl}_2$ .

The chief complication encountered is with 5 and 7, where there is a pronounced tendency for introduction of chlorine at a vinylic position of the alkene formed on oxidation. This complication seems to be restricted to dicarbanions that must be formed by method B. It has been found possible to suppress the vinylic chlorination by the use of  $\text{Li}_2\text{CuCl}_4$ <sup>7</sup> as oxidant of these dianions. However, the overall yield of olefin was then also reduced.

No mechanistic details concerning the oxidation step are available. In particular, we have not thus far been able to isolate any thirane-S,S-dioxide intermediates; these may, however, be too unstable to survive the work-up conditions.

Work to improve yields and mass balances, to establish the stereochemical details, and to broaden the scope of these reactions is now in progress.

#### References

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  - (b) An interesting example of a 1,2-dicarbanion formed on reduction of cis-stilbene with sodium

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(c) A wide variety of carbonyl-containing compounds can serve as precursors of 1,3-dicarbani-  
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5414 (1973).

2. C. Mao, C.R. Hauser, and M.L. Miles, J. Amer. Chem. Soc., 89, 5303 (1967).
3. Little, if any information is available in the literature concerning the possible competitive formation of gem as opposed to 1,3-diorganometallic compounds formed by exchange of acidic hydrogens.
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