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THE REACTION BETWEEN DIMETHYLOXOSULPHONIUM METHYLIDE AND BENZONITRILE OXIDE

A. Umani-Ronchi, P. Bravo and G. Gaudiano

Istituto di Chimica del Politecnico di Milano

Milano, Italy

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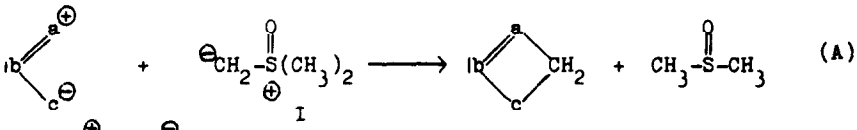
Dimethyloxosulphonium methylide (I) is known to behave as a nuclephile, and as such it has been used, mostly in the last years, to react with electrophilic double bonds such as $\rangle C{=}O$, $\rangle C{=}S$, $\rangle C{=}N-$ and $\rangle C{=}C\langle$. In most cases the reaction consists in a methylene transfer to the double bond, to form three-membered rings(1).

We are now investigating the reactivity of (I) towards 1,3-dipoles in order to test the possibility of obtaining four-membered heterocyclic rings, as follows:



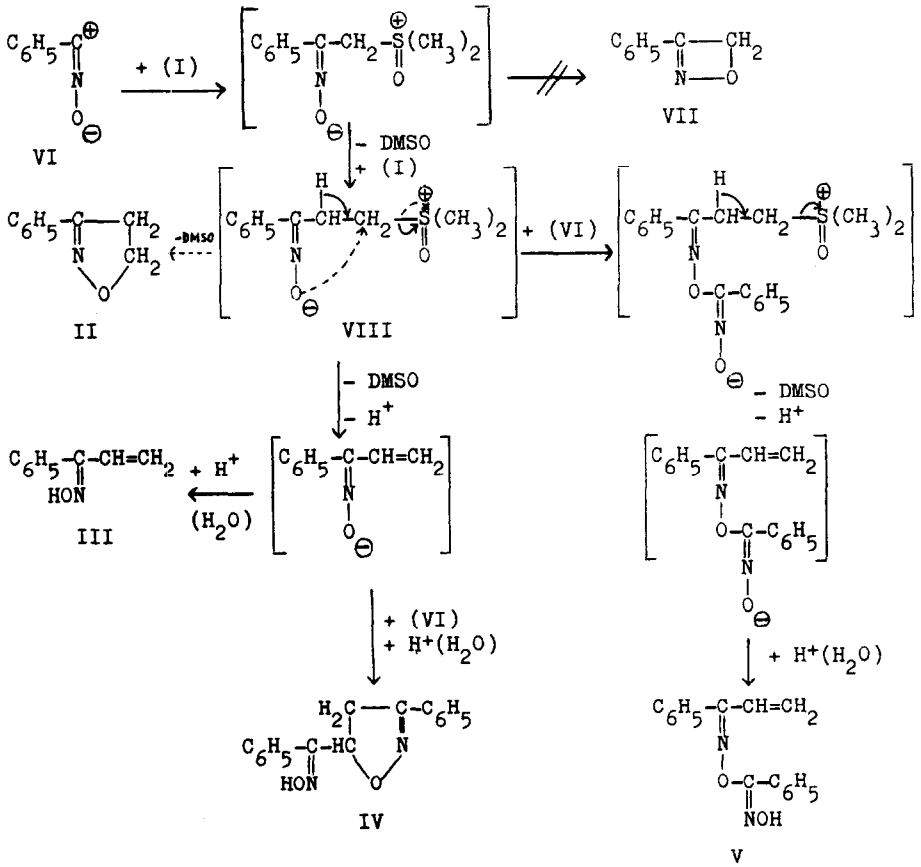
(A)

where $^{\oplus}a{=}\underline{b}{-}c^{\ominus}$ is a dipole in which b is nitrogen (2).

We have first investigated benzonitrile oxide (VI) as 1,3-dipole (2,3,4), by letting it react, in a cold DMSO solution, with the ylide (I) obtained *in situ*, according to the literature (5), from trimethyloxosulphonium iodide or chloride and NaH.

Actually the reaction affords a complex mixture of pro-

ducts among which we have been able to isolate the 3-phenyl-2-isoxazoline (II), the phenylvinylketoxime (III), the oxime of the 3-phenyl-5-benzoyl-2-isoxazoline (IV) and the hydroxamic ester of



the phenylvinylketoxime (V), whereas we have been unable to isolate, possibly because of its unstability, the 3-phenyl-oxazetidine (VII) that should have been obtained if the scheme (A) had been operating. In other words the ylide (I) is able to bring about two consecutive transfers of methylene to the

substrate, probably through the zwitterionic intermediate (VIII) from which the above-mentioned compounds can be easily derived (see the schema in the preceding page).

As shown in the schema, the intermediate (VIII) could give rise either to a direct closure to isoxazoline (II) or, by a β-elimination, to a double bond, as in the compounds (III) and (V). These last products, of course, can undergo further reaction with (VI), as shown by the presence of the isoxazoline (IV) in the reaction mixture.*

To our knowledge, so far no similar reaction of the ylide (I) has been reported. Once more, as previously observed by other Authors (8), this ylide in its behaviour reminds diazomethane (9).

The identity of (II) has been prooved by its analysis, NMR spectrum and other physicochemical characteristics, compared with the data from the literature (10).

The oxime (III) is the major product (yields up to 30%) when two moles of (I) are used per mole of (VI). It is a solid of m.p. 85° (λ_{max} 222 mμ, ε_{max} 16.200, in ethanol), whose structure▲ has been prooved mainly by its analysis and NMR spectrum in $CDCl_3$ ($-\underset{\text{II}}{C}-\underset{X}{CH}=C<^{H_A}_{H_B}$ shows an ABX pattern with δ_A= 5.4, δ_B= 5.2, δ_X= 6,65; $J_{gem.}$ 1.0, $J_{AX(cis)}$ 10.5, $J_{BX(trans)}$ 17.5; C_6H_5- multiplet at 7-7.8δ; OH at 9.8δ).

An isomeric acrylophenone oxime [λ_{max} 215 mμ, ε_{max} 12.500, in ethanol (10b)], obtained by a different method, has been reported in the literature (10b,c) as a solid of m.p. 109-110°,

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* The formation of the compounds (II),(III),(IV) and (V) can not be explained, to our opinion, by the possible formation of ethylene from the ylide, both because ethylene should only give rise (6,7), by reaction with (VI), to the isoxazoline (II), and also because the ylide (I) is known to be stable in the cold (5).

▲ The NMR spectra have been determined with a Varian A 60 spectrometer. The chemical shifts are in p.p.m. (TMS as internal reference). The J values are in c/s.

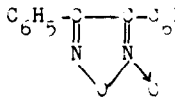
whose NMR spectrum in part reported by F.L.Scott (10c) shows an ABX pattern for the system $-\underset{\|}{C}-CH_X=C\begin{matrix}H_A\\H_B\end{matrix}$ with δ_A= 5.53, δ_B= 5.71, δ_X= 7.25 (in part overlapped with the aromatic protons signal at 7.2-7.7); $J_{gem.}$ 1.5, $J_{AX(trans)}$ 17.5, $J_{BX(cis)}$ 11.0; and a broad signal at ~9.5 δ due to the OH.

It seems clear that the two oximes are syn-anti isomers. From the data of their NMR spectra we can safely deduce (11) that the low-melting oxime (III) from the ylide, whose vinyl protons absorb at higher field than the high-melting isomer, is the syn-phenyl isomer.

The structure of (IV), solid of m.p. 136°, has been established on the basis of its analysis and NMR spectrum in $CDCl_3$ ($-\underset{\|}{C}-CH_2-\underset{|}{C}H-O-$ AX_2 pattern, δ_A= 5.6, δ_X= 3.5; 2 C_6H_5- multiplet at 7.0-7.8δ; OH broad at 7.8-8.5δ), as well as by its synthesis from the vinyl oxime (III) by reaction with benzonitrile oxide.

The structure of (V), solid of m.p. 126°, has been established by its analysis and NMR spectrum in $CDCl_3$ ($-\underset{\|}{C}-CH_X=C\begin{matrix}H_A\\H_B\end{matrix}$ ABX pattern, δ_A= 5.4, δ_B= 5.6, δ_X= 6.2; $J_{gem.}$ 1.5, $J_{AX(cis)}$ 10.0, $J_{BX(trans)}$ 17.0; 2 C_6H_5- multiplet at 7.1-8.0δ; OH at 4.9δ). This compound has been also obtained in very small amount, together with (IV), in the reaction between (III) and (VI).

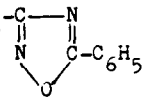
Beside these four compounds (II, III, IV and V), many side-products have been obtained in small amounts; among them we have been able to isolate benzonitrile ,benzamide, benzoic acid, the diphenylfuroxane (IX), the amidobenzoate (X) and the diphenyl-1,2,4-oxadiazole (XI). The first three products take



IX

$C_6H_5-CO-NH-O-CO-C_6H_5$

X



XI

their origin from (VI) by a reductive and/or hydrolitic process.

(IX) is the normal product of dimerisation of (VI); (X) is a compound which has been found also among the decomposition products of the benzohydroxamyl chloride (12) as well as of the benzonitrile oxide itself, under acidic conditions; (XI) represents the product of the reaction between (VI) and benzonitrile, firstly reported by G. Leandri(13).

Further investigations on the reactivity of (I) and other ylides on both benzonitrile oxide and other 1,3-dipoles are in progress.

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