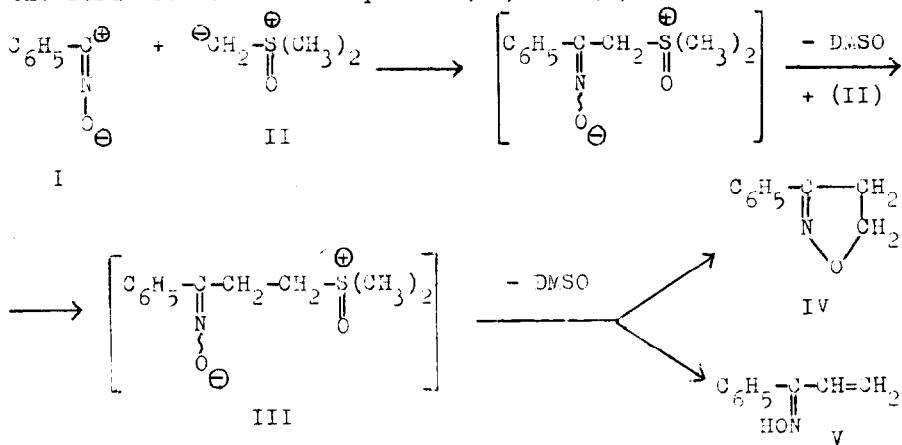# DIMETHYLOXOSULPHONIUM METHYLIDE :

A TOOL FOR THE SYNTHESIS OF FIVE-MEMBERED HETEROCYCLES

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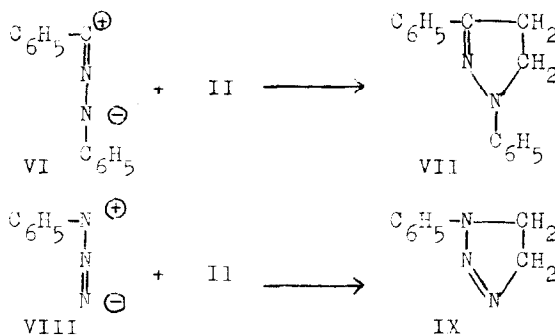
Milano, Italy

In a recent note (1) three of us reported the results of the reaction between benzonitrile oxide (I) and dimethyloxosulphonium methylide (II). This latter was shown to cause two consecutive transfers of methylene to the former, giving rise either to 3-phenyl-Δ^2-isoxazoline (IV), by ring closure, or to syn-phenylvinylketoxime (V), by a β-elimination. For this reaction we proposed the following mechanism which accounts for the formation of both compounds (IV) and (V) :

The zwitterionic intermediate (III) can clearly exist in two different configurations, syn and anti, the syn-phenyl isomer giving rise to (V), the anti isomer affording the isoxazoline (IV).[*]

Although the yields of the reaction between (I) and (II) were rather low, we felt it to be interesting to investigate the reaction between ylide (II) and other 1,3-dipoles (2) whose reactivity, in some aspects, resembles that of nitrile oxides (2,3). Actually only two $\left[(VI) \text{ and } (VIII)\right]$ of the six dipoles investigated gave satisfactory results, affording five-membered heterocycles by the following schema, presumably with the same mechanism that affords (IV) from (I) :

$$C_6H_5-\overset{\oplus}{C} \quad \quad N \quad \quad \overset{\ominus}{N} \quad \quad VI \quad C_6H_5 \quad + \quad II \quad \longrightarrow \quad C_6H_5-C{-\!\!-}CH_2 \quad N \quad CH_2 \quad N \quad VII \quad C_6H_5$$

$$C_6H_5-\overset{\oplus}{N} \quad N \quad \overset{\ominus}{N} \quad VIII \quad + \quad II \quad \longrightarrow \quad C_6H_5-N{-\!\!-}CH_2 \quad N \quad CH_2 \quad N \quad IX$$

The reaction between nitrile imine (VI) and ylide (II) was run by adding N-(α-chlorobenylidene)-N'-phenylhydrazine, as precursor of (VI), to a cold solution of the ylide (three moles) obtained from trimethyloxosulphonium iodide and NaH (4). The yield was 45%. The fluorescent pyrazoline so obtained, m.p.153° (5), was identified chiefly by its N.M.R. spectrum in $CDCl_3$ which shows the

[*] In principle the anti isomer of (III) could also give rise, through elimination, to the anti isomer of (V). Actually we did not find any trace of this anti oxime among the reaction products. This would indicate that cyclization of the anti isomer of (III) occurs much faster than elimination.

two non equivalent methylenes as two multiplets, at 2.9-3.4 δ
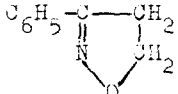and 3.5-4.1 δ. Its structure was confirmed by analysis, I.R.
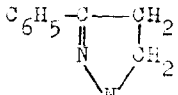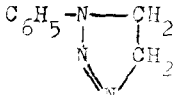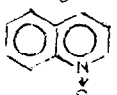and U.V. spectra.

More interesting, also because of the better yield, appears
the reaction of phenyl azide (VIII) with the ylide (II). Δ^2-Tri-
azoline (IX), m.p. 90° (6),was obtained in 80% yield, at room
temperature, in DMSO. Its identity was confirmed by its N.M.R.
spectrum in CDCl$_3$ which , as in the case of (VII), shows the two
methylenes as two multiplets, at 3.1-3.7 δ and 4.0-4.7 δ .

1-Phenyl-Δ^2-1,2,3-triazoline was first obtained by H.W.
Heine and D.A.Tamalia (6) from 1-phenylazoaziridine by an iso-
merization that appears to be general for 1-arylazoaziridines.
Only two other methods to obtain Δ^2-1,2,3-triazolines are known,
one starting from azides by addition to some activated olefinic
double bonds (7), the other involving the addition of diazometha-
ne to anils (7,8). The method of the ylides here reported could
be an useful alternative for the synthesis of these compounds
which, because of their thermal instability, require a synthesis
in the cold. At the present we are studying the possible develop-
ments and limits of this method.

As for the other 1,3-dipoles that we examined (see Table I),
azoxybenzene and N-oxyquinoline failed to react with ylide (II),
whereas diphenyldiazomethane and diphenylnitrone did not give
the expected heterocycles. In fact the only products we could
isolate from the reaction between diphenyldiazomethane and (II)
were benzophenone and diphenylketazine, and the main product
from diphenylnitrone was azobenzene together with small amounts
of azoxybenzene and other minor products not identified. The
results are summarized in Table I.

TABLE I

The reaction between $\overset{\ominus}{C}H_2-\overset{\oplus}{\underset{\parallel}{S}}(CH_3)_2$ and 1,3-dipoles
$\quad\quad\quad\quad\quad\quad\quad\quad\quad O$

Reactant	Compounds obtained (yield)
C_6H_5CNO (1) I	$C_6H_5-\overset{}{\underset{}{C}}\text{---}CH_2$ (10%) + $C_6H_5-\overset{}{C}-CH=CH_2$ (30%) $\quad\quad N\quad CH_2\quad\quad\quad\quad\quad HON$ $\quad\quad\quad O$
$C_6H_5CN_2C_6H_5$ VI	$C_6H_5-C\text{---}CH_2$ (45%) $\quad\quad N\quad CH_2$ $\quad\quad N$ $\quad\quad C_6H_5$
$C_6H_5-N_3$	$C_6H_5-N\text{---}CH_2$ (30%) $\quad\quad N\quad CH_2$ $\quad\quad N$
$C_6H_5-\overset{}{\underset{N_2}{C}}-C_6H_5$	$C_6H_5-CO-C_6H_5$ (n.d.) + $(C_6H_5)_2C=N-N=C(C_6H_5)_2$ (n.d.)
$C_6H_5-CH=N-C_6H_5$ $\quad\quad\quad\downarrow$ $\quad\quad\quad O$	$C_6H_5-N=N-C_6H_5$ (n.d.) + $C_6H_5-N=N-C_6H_5$ (n.d.) $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O$
$C_6H_5N=N-C_6H_5$ $\quad\quad\downarrow$ $\quad\quad O$	no reaction
(quinoline N-oxide structure)	no reaction

Further investigations in this field are in progress.

The N.M.R. spectra were determined with a Varian A 60 spectrometer. The chemical shifts are in p.p.m. (TMS as internal reference).

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