

HETEROCYCLIC AZALLYL RADICALS

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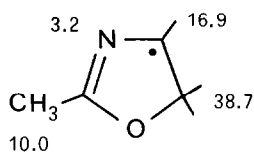
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Methylthiyl radical selectively abstracts allylic hydrogens from oxazolyn and thiazolin derivatives, yielding nitrogen centered azallyl radicals.

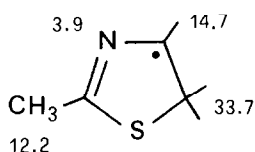
Allyl radicals have long been studied<sup>1</sup> by esr, whereas only recently esr detection of a triazallyl has been achieved.<sup>2</sup> The only nitrogen centered azallyl radical observed by esr in solution is a large, conjugated, hence persistent, radical.<sup>3</sup> Simpler azallyl radicals have been observed only in solids.<sup>4</sup>

Since it was shown that methylthiyl radical (MeS·) not only adds to double bonds but also abstracts hydrogen atoms,<sup>5</sup> we used this process as a suitable tool to produce simple nitrogen centered azallyl radicals, starting from appropriate heterocyclic derivatives.

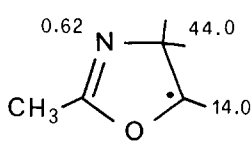
Photolysis of MeSSMe in cyclopropane containing 2-methyloxazolin or 2-methylthiazolin, yields the azallyl radicals (1) and (2): their hfs constants are given in gauss. Methylthiyl radical abstracts only the methylenic hydrogen in position 4 (allylic) and not that in position 5 ( $\alpha$  to heteroatom), thus indicating a selective behaviour in the hydrogen abstraction. On the contrary, when t-butoxyl radical (t-BuO·) is employed, both molecules produce complex and asymmetric esr spectra since hydrogens from both methylenic groups (positions 4 and 5) are abstracted. Therefore, in addition to (1) and (2), also radicals (3) and (4) are simultaneously produced.



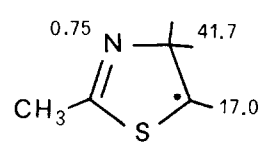
(1)



(2)



(3)

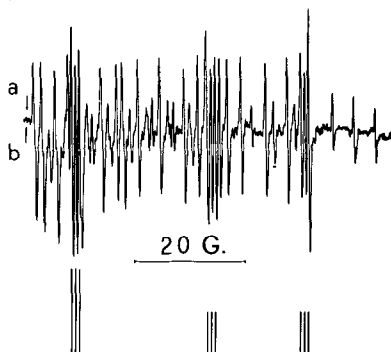


(4)

The esr spectrum obtained from 2-methylthiazolin with t-BuO·, i.e. the mixture of (2) and (4), is reported in the Figure. By taking advantage of the selectivity of MeS·, we could subtract from the lines of this spectrum those of the spectrum of (2); the interpretation of (4), as well as of (3), could thus be achieved.

The hfs constants of H $\alpha$  (14.0 G) in radical (3) is smaller than in (4)

( $a_{H\alpha} = 17.0$  G). This trend is common to other oxygen and sulphur containing radicals and attributed to a distortion from planarity of the  $sp^2$  carbon due to the oxygen atom.<sup>6</sup> As a consequence the corresponding sulphurated radicals, where such a deformation either does not occur or is less efficient, have larger  $a_H$  splittings, despite the greater ability of sulphur in delocalizing the unpaired electron.<sup>7</sup>



**Figure.** Half esr spectrum (upfield) of radicals (2) and (4) simultaneously obtained by hydrogen abstraction from 2-methyl thiazolin by means of  $t\text{-BuO}\cdot$  at  $-100^\circ$  in cyclopropane. The center of the spectrum of the allylic radical (2) is indicated by letter *a*, that of (4) by letter *b*. Underneath the stick diagram of the spectrum of (4), obtained by subtraction, is reported. The spectrum of (2) also shows second order effects.

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