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Restricted Rotation in (Methyldithio)methyl Radical

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It is known that alkylthiyl radicals (RS·) not only add to double bonds but also abstract hydrogens from allylic-like systems;[1-3] we have recently shown that the corresponding radicals can be detected by ESR spectroscopy.[4-6] Under the usual photolytic conditions MeS· seems incapable of abstracting hydrogens from non allylic moieties, and therefore the self-reaction to give $MeSS\dot{C}H_2$ was not observed.[6] However, we observed that when a freshly prepared sample of MeSSMe in cyclopropane is photolyzed, an ESR signal gradually develops and reaches the steady state in about 20 min. On the contrary, in already-photolyzed samples the appearance of the radical is instantaneous.

The feature of the ESR spectrum at −50 °C (see Figure 1) as well as its a_H splitting (17.1 ± 0.1 G at −60 °C) points to a radical of the type[7,8] $X{-}S\dot{C}H_2$; the lack of additional splittings[9] and the g factor ($2.0041_5 \pm 0.0001$) indicate that the radical is of the type $RSS\dot{C}H_2$.[9] Sulfide radicals ($R{-}S\dot{C}H_2$) have different g factors (2.0048) and large splittings at the γ-hydrogens of R.[7,8]

The large amount of time required to generate the $RSS\dot{C}H_2$ radical indicates that we are not dealing with a hydrogen abstraction but with a more complex process that requires the formation of relatively stable byproducts from which the radical is actually generated. Once the photolysis has built up a sufficient amount of byproducts, the radical does not need a delay time when subsequent photolyses are carried out on the same sample.[10] To check the nature of R in $RSS\dot{C}H_2$, we examined the reaction products. Although we could not identify all the reaction products, we did observe, by mass spectroscopy, that the product with the highest molecular weight (186) is $MeSSCH_2CH_2SSMe$ (see Experimental Section). This seems to indicate that the observed radical is $CH_3SS\dot{C}H_2$: one of its possible ways of decaying is, in fact, the dimerization.

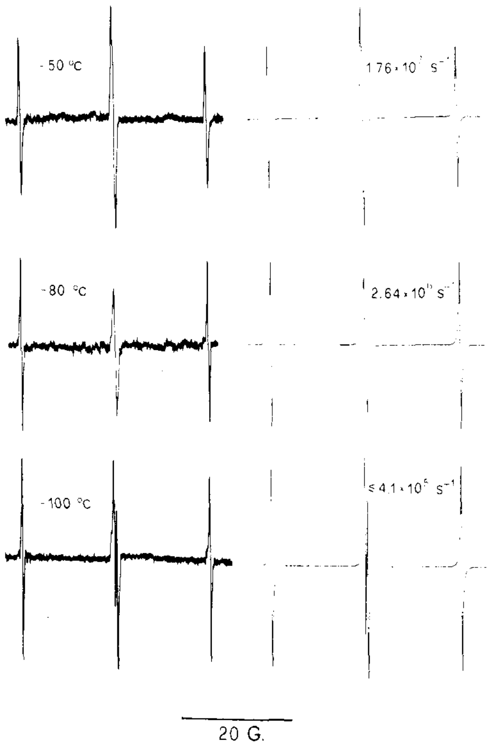

Figure 1. Temperature dependence (left) of the ESR spectrum of $MeSS\dot{C}H_2$: on the right-hand side is shown the computer simulation obtained with the rate constants indicated.

An additional check of the radical structure can be obtained by producing it in an independent way. Photolysis of *t*-BuOO-*t*-Bu in presence of MeSSMe is known to abstract hydrogen to give $CH_3SS\dot{C}H_2$.[13,14] This reaction, however, also gives the radical $(t\text{-BuO})_2\dot{S}Me$ whose ESR signal interferes[14] with those of $MeSS\dot{C}H_2$. Despite this fact we measured the g factor (2.0041) and the a_H splitting (17.0 ± 0.1 G) of $CH_3SS\dot{C}H_2$ at −50 °C and found values identical with those of the radical obtained by photolysis of MeSSMe alone. This confirms that we are dealing with the same radical; however, the $CH_3SS\dot{C}H_2$ obtained from MeSSMe alone also shows, at −100 °C, that the two hydrogens are not equivalent (a_H splitting of 16.95 ± 0.1 and 17.45 ± 0.1 G). When the temperature is raised, the two central lines broaden and eventually coalesce into a single signal that sharpens again above −80 °C (Figure 1). On the contrary, the $CH_3SS\dot{C}H_2$ obtained via *t*-BuOO-*t*-Bu was reported not to give such an effect.[13,14] Owing to this circumstance, the two hydrogens of $MeSS\dot{C}H_2$, as well as those of other similar radicals,[9] were reported to be equivalent.[13,16] This led a proposal of a symmetric con-

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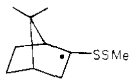
[10] For instance one could propose a mechanism such as eq 1-3.

$$MeSSMe \rightarrow 2MeS\cdot \qquad (1)$$

$$MeS\cdot + MeS\cdot \rightarrow CH_2{=}S + MeSH \qquad (2)$$

$$MeS\cdot + CH_2{=}S \rightarrow MeSS\dot{C}H_2 \qquad (3)$$

Formation of thioaldehydes from thiyl radicals have been reported,[11] and addition of thiyl radicals to thiocarbonyls is a known process.[12] We in fact observed the ESR spectrum due to addition of MeS·, produced by photolysis of MeSSMe, to thiocamphor.



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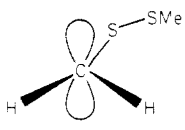
formation[14,16] for MeSS$\dot{C}H_2$, as opposed to that of the corresponding sulfide MeS$\dot{C}H_2$ that has two different H_α splittings (16.7 and 17.5 G).[8,14]

Taking advantage of our observations, we proved, however, that the same nonequivalence is present even when MeSS$\dot{C}H_2$ is produced by hydrogen abstraction with t-BuO·. At −50 °C the spectrum of the radical is a triplet with a 1:2:1 ratio, and its central line is symmetrically spaced with respect to the outer lines ($a_{H_\alpha} = 17.0 \pm 0.1$ G); on the contrary, at −110 °C there are three lines with equal intensity, and the "central" line is separated by $16.9_5 \pm 0.1$ G from the outer line on the left but by $17.3_5 \pm 0.1$ G from that on the right. This indicates that a fourth line is now missing, covered by the signals of $(t\text{-BuO})_2\dot{S}Me$.

This observation thus modifies the current ideas upon the conformation of disulfide radicals. The asymmetry we have observed requires the existence of an asymmetric conformation, and two possibilities have to be taken into account. (i) If free S–S rotation is assumed, then the SS bond cannot be, as proposed,[14,16] parallel to the direction of the p_z orbital bearing the unpaired electron (eclipsed conformation). (ii) On the other hand, if the S–S rotation is slow[17] on the ESR time scale at this temperature, then one can have nonequivalence even with an eclipsed conformation.

A choice between these two situations cannot be easily made: we wish to point out that in case i the observed barrier must be that of C–S rotation whereas in case ii the barrier is that of the faster motion between C–S and S–S rotation.



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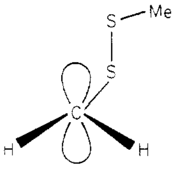

ii

Computer simulation of the line shape yields a $\Delta G^{\ddagger} = 5.5 \pm 0.3$ kcal/mol^{-1}, a value smaller than that estimated[8] for the corresponding S–$\dot{C}H_2$ rotation in MeS$\dot{C}H_2$ (7 kcal/mol^{-1}). If we are dealing with a CS rotation, the difference might depend on the smaller steric hindrance, due to the longer SS bond with respect to the SMe bond, or to electronic effects, due to substitution of a Me with a MeS group. Obviously the difference could simply depend on the fact that the restricted motion we observed is S–S rotation (case ii) rather S–C rotation.

Experimental Section

Photolysis of MeSSMe and of MeSSMe with t-BuOO-t-Bu was carried out in cyclopropane solutions sealed in Suprasil quartz tubes within the cavity of the spectrometer. Addition of a certain amount of benzene intensifies the ESR signal of MeSS$\dot{C}H_2$ produced by direct photolysis of MeSSMe.

Since the photolysis of MeSSMe, under the very same conditions required to detect the ESR signal (low concentration and low temperature), has a very low yield, the amount of reaction products was too small for a complete analysis. However, since our aim was to obtain indications for the structure of the observed radical, rather than to study the reaction pathway, mass spectroscopy was of sufficient help for our purpose. The white solid that precipitates after photolysis at −60 °C turns out to be composed by at least two (and possibly three) products. That with the highest molecular weight (186, M^+) was identified as $CH_3SSCH_2CH_2SSCH_3$ from its fragmentation pathway: m/e 139 (M − CH_3S), 107 (M − CH_3SS), and 93 (M − CH_3SSCH_2). Line-shape simulation was carried out on the computer facilities of the University of Bologna.

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Registry No. MeSSMe, 624-92-0; MeSS$\dot{C}H_2$, 80641-42-5; $CH_3SSCH_2CH_2SSCH_3$, 80641-43-6.

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Synthesis and Structural Verification of Novel Olefinic Derivatives of Bicyclo[2.2.2]octane. Intermediates in the Synthesis of Bridged Morphinan-Like Compounds

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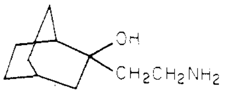
In the attempt to synthesize suitable intermediates for the preparation of novel C-ring-bridged morphinan derivatives, we have discovered, and now report, a set of reaction conditions which will provide 2-(2-aminoethyl)bicyclo[2.2.2]oct-2-ene hydrobromide (**2**) at the expense of the exocyclic isomer **3** from the starting alcohol, 2-(2-aminoethyl)bicyclo[2.2.2]octan-2-ol (**1**).



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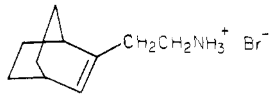

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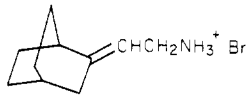

3

A priori, it appeared that for successful generation of the bicyclooctene derivative from this alcohol two criteria should be met. First, reaction conditions that favor a concerted elimination mechanism were assumed to be required in order to maintain the structural integrity of the ring system. Of the three commonly interconvertible bicyclooctane isomers, the [2.2.2] skeleton, while no more strained than the [3.2.1] or the [3.3.0] systems, is the least stable due to its low entropy.[2a] When exposed to strong ionizing conditions, derivatives of 2-substituted bicyclo[2.2.2]octane and octene capable of forming carbonium ions will often undergo Wagner–Meerwein and related types of rearrangements[3-6] to the aforementioned isomeric forms.

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