scribed as octahedral, even though the average Br–Mg–O, O–Mg–O, and H–Mg–H angles [97.0 (5), 92 (2), and 73 (1)°, respectively] show significant deviations from ideal values. The assignment of octahedral symmetry for Mg is also supported by the fact that the trans L–Mg–L angles are roughly linear [average 162 (3)°] and the fact that the H_3Mg and MgO_2Br moieties are staggered (Figure 3).

It is difficult to tell from the structural results if the Mg···H interaction is ionic or covalent. Our feeling is that it is largely ionic, partly because the average Mg–H distance in our compound [2.06 (3) Å] is significantly longer than that in MgH_2 (1.95 Å).[15] However, the possibility that there is a substantial covalent contribution to the Mg···H interaction cannot be entirely dismissed.

Perhaps the best known example of a single-crystal study of a binary transition-metal hydrido anion is that of ReH_9^{2-}.[16,17] Here also, a variety of earlier formulations (Re^-, ReH_4^-, and ReH_8^{2-}) were suggested for the "rhenide" species before a single-crystal neutron diffraction analysis finally established the complex as the tricapped trigonal prismatic ReH_9^{2-} anion.[17] To our knowledge, the only other single-crystal investigation reported is that of the related ternary complexes Li_4RhH_4 and Li_4RhH_5.[18] Although the analysis of the former compound revealed the presence of square-planar RhH_4 units (Rh–H = 1.90 Å), the proposed structures were interpreted in terms of ionic bonding between hydrogen and both the lithium and rhodium atoms. In contrast, the solid-state structure of $FeH_6Mg_4X_4(THF)_8$ consists of well-defined molecular units built on discrete covalently bound FeH_6^{4-} species more analogous with ReH_9^{2-}.

The second and third row analogues of the title compound are as yet unknown. However, the particularly intriguing ternary hydrides M_2RuH_6 (M = Ca, Sr, Eu, Yb) have been reported.[19–21] These compounds are typically prepared by reaction of an alkaline-earth or lanthanide hydride with ruthenium metal at elevated temperatures and under a hydrogen atmosphere. They are insoluble in all common solvents, and attempts to synthesize single crystals of these materials have, as far as we know, been unsuccessful. Nevertheless, powder X-ray and neutron studies of the deuterium analogues of these materials have indicated a remarkably similar lattice structure consisting of octahedral RuD_6 units (Ru–D = 1.69 Å), with each face of the octahedron of deuterium atoms capped by alkaline-earth or lanthanide ions.[19] Also described in that paper is the powder neutron diffraction analysis of Sr_2IrD_5, whose structure could be interpreted to contain square-pyramidal IrD_5 units (Ir–D = 1.70 Å).[22]

In summary, an X-ray structural investigation of $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ has fully established the existence of the binary metal hydrido anion FeH_6^{4-}, which is isoelectronic with the well-known ReH_9^{2-} anion. A neutron diffraction analysis of the title compound is in progress. Finally, it should be noted that, in the original study of Weichselfelder,[1] analogous reactions of PhMgBr with $NiCl_2$, $CoCl_2$, $CrCl_3$, and WCl_6 were also reported, leading to similarly intriguing products. It would be interesting to see if other binary metal hydride anions (e.g., NiH_4^{4-}) could be isolated from such reactions.

Acknowledgment. Financial support from Grant CHE-79-26479 from the National Science Foundation and Grant PRF-12442-AC3 from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Listings of final positional and thermal parameters (Tables A and B, 2 pages). Ordering information is given on any current masthead page.

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Carbenoid Insertion Reactions: Formation of [4.1.1]Propellane[1]

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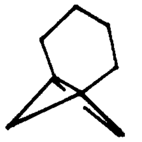
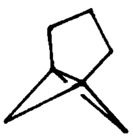
Received April 2, 1981

In 1978 we observed[1] the probable formation of [4.1.1]propellane (**1**). The recent acquisition of a microprobe for ^{13}C NMR determinations has enabled us to obtain further evidence supporting this claim. In view of the current interest in [*n*.1.1]propellanes,[2–4] we offer our observations at this time. In particular, we find chemical shift values in the ^{13}C NMR spectrum which are remarkably different from those reported earlier[4] for the closely related homologue [3.1.1]propellane (**2**) or its derivative.[3]


1


2

Following an earlier observation[5] that 2,2,4,4-tetramethylbicyclo[1.1.0]butane is formed in the pyrolysis of the salt of the tosylhydrazone of 2,2,4-trimethylpent-3-enal, we sought to extend this methodology[3] as a means of preparing 1,3-bridged bicyclobutanes, i.e., [*n*.1.1]propellanes. From a consideration of the geometry of bicyclobutane derivatives[6] it seemed likely that the introduction of a four-carbon bridge to such a molecule would add the least additional strain, and therefore this system was chosen to test the methodology.

An outline of the route by which 3-methylenecycloheptanone (**3**) was synthesized is given in Scheme I. Pyrolysis, at 180–200 °C, of the dry sodium salt of the tosylhydrazone derivative **4** gives an evolution of nitrogen, and a volatile component distills from the reaction vessel (ca. 20% yield). This component is mainly a mixture of 3-methylenecycloheptene (**5**), 4-methylenecycloheptene (**6**), and [4.1.1]propellane (**1**). The evidence which supports this contention is as follows. The mixture can be separated into two major components by preparative GC (15% SE30, base-washed Chrom. A, 140 °C). The first component to elute is 4-methylenecycloheptene (**6**),[7] as established by the synthesis of an authentic sample by the route outlined in Scheme II. The second component is a mixture of 3-methylenecycloheptene (**5**) and another very reactive compound. For a long time this component

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(1) V. C. Trenerry, Ph.D. Thesis, Adelaide, 1978. An alternative name for this compound is tricyclo[4.1.1.$0^{1,6}$]octane.

(2) U. Szeimies-Seebach, J. Harnish, G. Szeimies, M. V. Meerssche, G. Germain, and J.P. Declerq, *Angew. Chem. Int. Ed. Engl.*, **17**, 848 (1978); U. Szeimies-Seebach and G. Szeimies, *J. Am. Chem. Soc.*, **100**, 3966 (1978).

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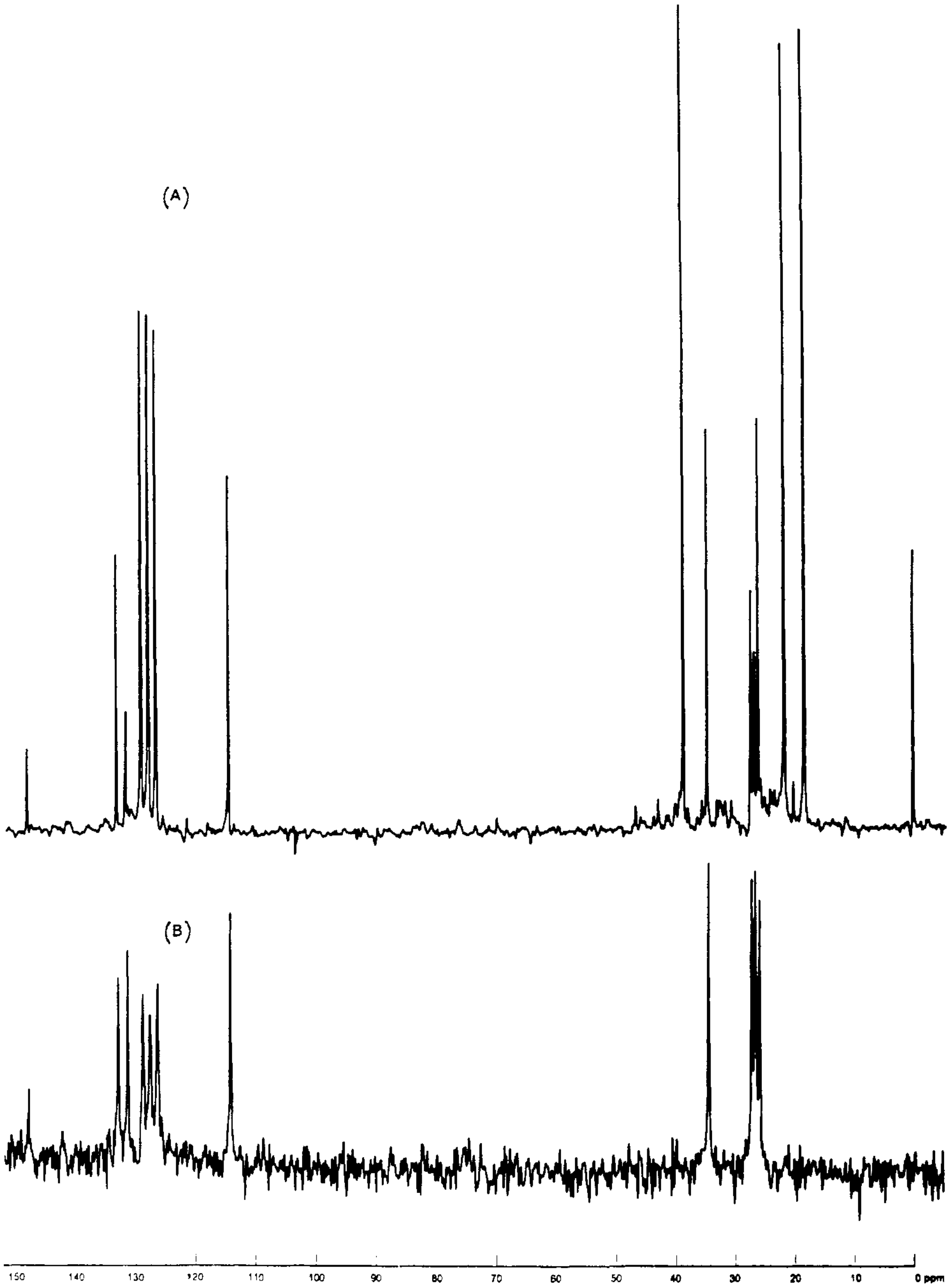

Figure 1. ^{13}C microprobe NMR spectra at 20.1 MHz, in ca. 0.1 mL of benzene-d_6 containing 0.1% 2,6-di-*tert*-butyl-4-methylphenol: (A) [4.1.1]-propellane (**1**) and 3-methylenecycloheptene (**5**) (5 s interval between pulses), (B) 3-methylenecycloheptane (auto recall).

could not be prepared in a reproducible manner until it was found that the propellane was stabilized in solution by the addition of the radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol (ca. 1 mg/mL).

Treatment of the crude product of the pyrolysis with potassium *tert*-butoxide in Me_2SO (room temperature, 24 h) rearranges the olefins **5** and **6** to 1-methylcyclohepta-1,3-diene (**7**)[8] but, as shown by NMR, leaves the propellane intact. The retention time differences of the diene **7** and the propellane were sufficient to allow a GC–MS determination of the molecular ions of each. They were isomeric compounds. An authentic sample of the diene **7** was prepared by the route outlined in Scheme II.

Samples of 3-methylenencycloheptene[9] (**5**) were prepared by the route outlined in Scheme II or, more conveniently, by a Wittig reaction on cyclohept-2-enone. The NMR spectra of diene **5** and the second component from the preparative GC are reproduced in Figure 1 and 2. The differences between the ^{13}C NMR spectra (Figure 1A, B) show that the other compound in the mixture contains only four different types of carbon atom.[10a] By continuous wave (CW) off-resonance decoupling the peaks at δ 39.9, 23.3, and 20.0[10b] can be considered to be triplets (they are not all strictly first order), but both by CW and by broad-band (BB) off-resonance decoupling the peak at δ 2.0 (5) remains a sharp singlet. This data is consistent with the proposed [4.1.1]propellane (**1**) structure but differs markedly from that reported for [3.1.1]propellane (**2**).[11]

The ^1H NMR spectra of the second component (Figure 2A, B) also add strong support for the presence of the propellane **1**. The spectrum (Figure 2A), which is the difference spectrum obtained by electronically substracting the resonances due to the olefin **5** from the original spectrum (Figure 2B), is particularly informative. The sharp resonances at δ 0.82 and 1.43 can be

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[9] M. R. Short, *J. Org. Chem.*, **37**, 2201 (1972).

[10] (a) The ^1H NMR spectrum was run before and after the 24-h period required to accumulate this spectrum to ensure that the propellane was still present; (b) relative to center peak of C_6D_6 triplet at 128.0 ppm (20.1 MHz); (c) relative to the C_6D_5H signal at 7.1 (5) ppm (80 MHz).

[11] (a) Reported[4] as δ 53.27 (t), 42.46 (t), 30.92 (t), 24.88 (s), at 10 °C in toluene-d_8; (b) the ^1H NMR spectrum is described as "very complex".

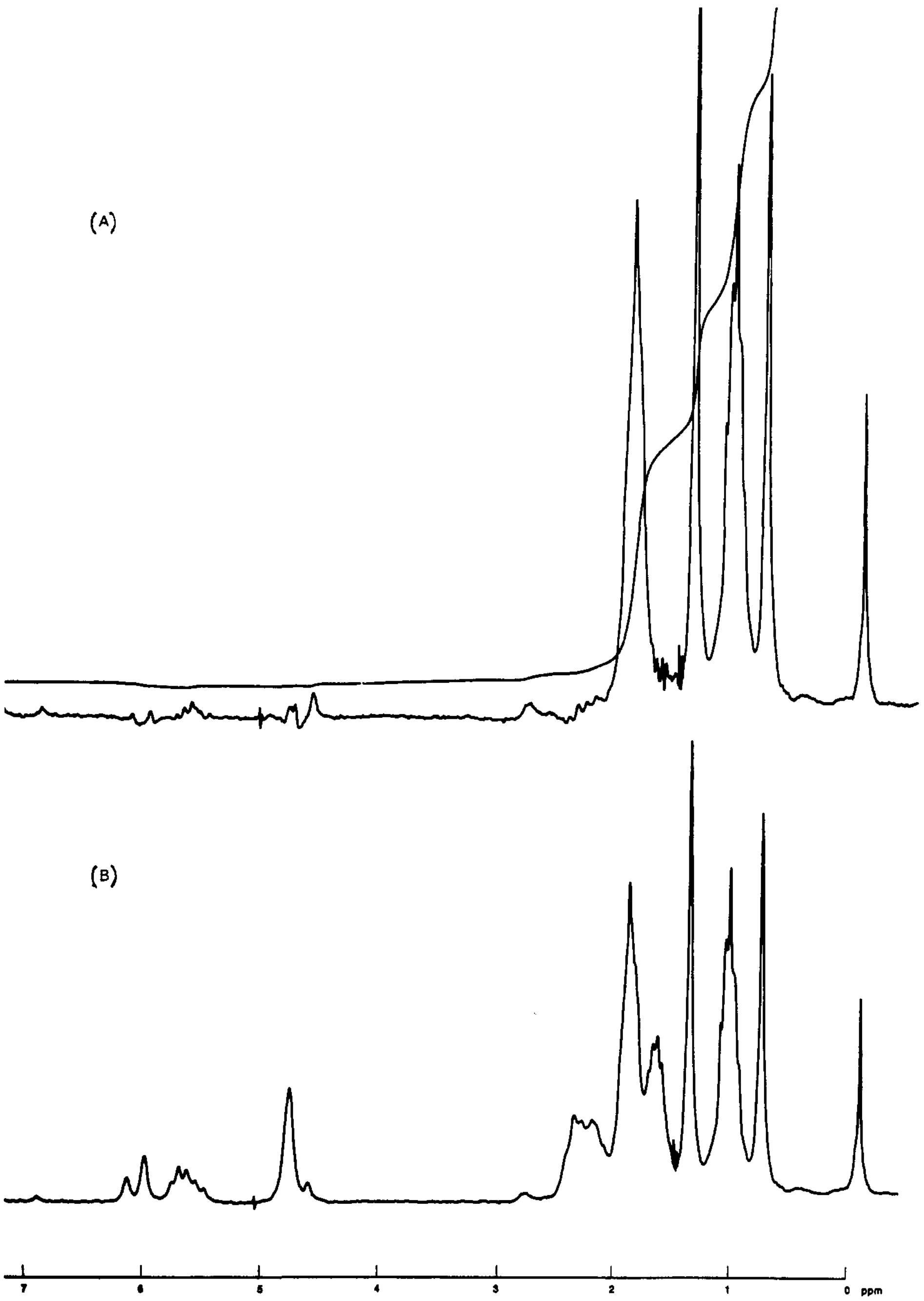

Figure 2. ^1H NMR spectra at 80 MHz in ca. 0.1 mL of CCl_4-$CDCl_3$ (1:1) (containing Me_4Si and 0.1% inhibitor). (A) Electronically generated difference spectrum of [4.1.1]propellane (**1**). (B) Original mixture containing both compounds **1** and **5**.

ascribed to the endo and exo protons[12] of the bicyclobutane portion of the molecule, whereas the broader signals at δ 1.1 and 1.9 are consistent with the two pairs of nonequivalent methylene groups of the bridge. In benzene-d_6 there are some shifts of the resonances[10c] [δ 1.8, 0.8 (5), bridge CH_2's; 0.86, 1.33, endo, exo H's].

In the ^{13}C NMR spectrum of the crude pyrolysis product it is possible to recognize the peaks due to the two dienes **5** and **6** and the propellane **1**. After this solution is treated with a drop of formic acid, GC analysis shows that the peak for the second component is immediately reduced to about half its original area. Redetermination of the ^{13}C NMR spectrum shows that the peaks at δ 39.9, 20.0 and 2.0 (5) have gone and are replaced by other resonances elsewhere in the spectrum (there only appears to be a very small displacement of the peak at δ 23.3); the peaks for the olefins remain.

We contend that the above evidence is strongly supportive for the existence and observation of [4.1.1]propellane (**1**). The question arises, therefore, as to why there should be such large differences in the ^{13}C NMR spectrum from that reported for [3.1.1]propellane (**2**).[11] It has been established[13] that the ^{13}C chemical shift of ring carbon atoms generally moves to higher field with decreasing ring size for carbocyclic compounds. Therefore one might have expected the quaternary carbon atoms in [3.1.1]propellane to absorb at even higher field than those in [4.1.1]propellane. There has been a report[14] of the strong deshielding of carbon atoms in a hydrocarbon containing carbon atoms with "inverted" tetrahedral geometry.[15] Perhaps, therefore, what has been discovered is differences in the spectra of propellanes which have changed from "normal" to "inverted" tetrahedral

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(12) The exo and endo protons of 1,3-dimethylbicyclo[1.1.0]butane resonate as singlets. W. von E. Doering and J. F. Coburn Jr., *Tetrahedron Lett.*, 991 (1965).

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(14) H. Duddeck and H. Klein, *Tetrahedron Lett.*, 1917 (1976); however, see also R. E. Pincock and F.-N. Fung, *ibid.*, 19 (1980).

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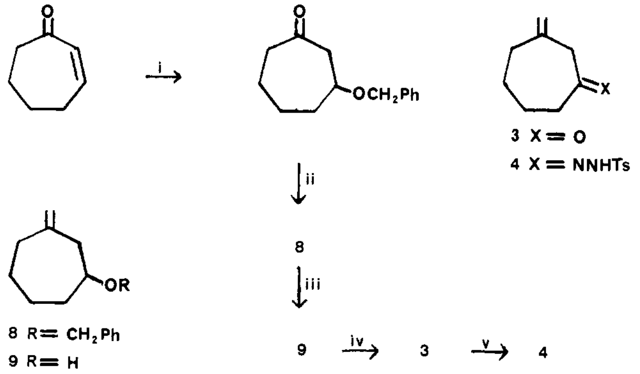
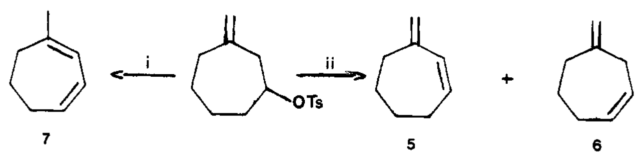
Scheme I[a]



[a] (i) Catalytic $PhCH_2ONa$, $PhCH_2OH$, room temperature, 12 h (62%). (ii) $Ph_3P{=}CH_2$, THF, room temperature, 15 h (76%). (iii) Na, NH_3 (l) (73%). (iv) PCC, NaOAc, CH_2Cl_2, room temperature, 4.5 h (85%). (v) NH_2NHTs, 1:1 MeOH-H_2O (90%)

Scheme II[a]



[a] (i) t-BuOK, Me_2SO, room temperature, 1 h. (ii) K_2CO_3, Me_2SO, 80 °C, 5 h.

geometry.[16] With such highly reactive species, there, of course, remains the possibility that the spectra reported[11b] for [3.1.1]-propellane are those of a decomposition product since toluene cannot be considered a particularly effective radical trap.

Acknowledgment. We thank Dr. E. H. Williams for help in obtaining the NMR spectra.

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A Search for Singlet Oxygen in the Disproportionation of Superoxide Anion

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Received March 30, 1981
Revised Manuscript Received June 10, 1981

A number of biological processes have been claimed to generate singlet oxygen $^1O_2$ ($^1\Delta_g$) which is harmful to biological molecules. Several explanations for the formation of $^1O_2$ in these enzymatic systems refer to superoxide anion $O_2^-\cdot$; they include reaction of $O_2^-\cdot$ with H_2O_2[1] (Haber-Weiss reaction), $OH\cdot$,[2] or itself[3] according to the elementary reaction 1 where $HO_2\cdot$ is the conjugate acid of $O_2^-\cdot$.

$$O_2^-\cdot + HO_2\cdot \xrightarrow{H^+} H_2O_2 + O_2(^1\Delta_g \text{ or } ^3\Sigma_g^-) \qquad (1)$$

In view of the biological implications of this reaction, many research workers have tried to determine whether disproportionation of $O_2^-\cdot$ yields O_2 in its $^1\Delta_g$ or $^3\Sigma_g^-$ state. On the basis of thermodynamic[4] or molecular orbital[5] considerations, it appears that $^1O_2$ could be generated by reaction 1. On the other hand, experimental determinations, using chemical[6] or radiolytic[7] sources of $O_2^-\cdot$, have led to contradictory results. The main difficulty in these studies arises probably from the very efficient quenching of $^1O_2$ by $O_2^-\cdot$ in water:[8]

$$O_2^-\cdot + {}^1O_2 \rightarrow {}^3O_2 + O_2^-\cdot \qquad (2)$$

To avoid this reaction, a low steady-state concentration of $O_2^-\cdot$ must be used; as a consequence, the catalyzed disproportionation of $O_2^-\cdot$ by impurities of water becomes the major pathway for the scavenging of $O_2^-\cdot$ unless highly purified water is used.[9] Another problem concerns the detection of $^1O_2$; the trap must react specifically with $^1O_2$ or at least it should lead to an oxidation product different from those obtained with other species present in the solution, namely, $^3O_2$, H_2O_2, $O_2^-\cdot$, $HO_2\cdot$. Finally, $O_2^-\cdot$ production must be homogeneous, and the $^1O_2$ trap must be water soluble to allow convincing kinetic treatment of experimental results. As far as we know, none of the preceding published works[6,7] fulfilled the above conditions. Consequently we designed a new technique for the detection of $^1O_2$, and we report that *reaction 1 does not produce* $^1O_2$.

The potassium salt of rubrene-2,3,8,9-tetracarboxylic acid (RTS) is water soluble in neutral and basic medium, giving a red solution which fades when reacting with $^1O_2$, yielding only the endoperoxide ($RTSO_2$):[10]

$$RTS + {}^1O_2 \rightarrow RTSO_2 \qquad (3)$$

To check the specificity of RTS toward $^1O_2$, it was shown that neither $^3O_2$ (1.2×10^{-3} M) nor H_2O_2 (0.1 M) reacted with an aqueous solution of RTS (2×10^{-4} M, pH 7.6), even after several days. In the same way, when a large excess of KO_2 (more than 100 times the stoichiometric amount) was added to an aqueous solution of RTS (2×10^{-4} M), no reaction occurred with the substrate.

In order to study the dismutation of $O_2^-\cdot$ at low steady-state concentrations, a buffered solution (phosphate 3×10^{-3} M, pH 7.6) saturated with oxygen or air containing sodium formate (0.16 M) and RTS (2×10^{-4} M) was irradiated by using a ^{60}Co γ source. The disappearance of RTS was monitored by its absorbance at 539 nm and HPLC.[10] Under such conditions, H· and

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