Norcaradiene intermediates in mass spectral fragmentations of tropone and tropothione †

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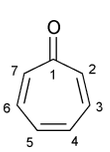
The fragmentation of mass spectroscopy of tropone (**1**) was compared with that of tropothione (**2**). The electron-impact mass spectroscopy of **1** afforded almost exclusively the benzene cation radical (*m*/*z* = 78). Mass spectroscopy of **2** gave similarly the *m*/*z* = 78 base peak along with an unusual ($M^+ - 1$) peak. This hydrogen elimination was found to occur at the C(α)–H bond by the use of a ^{2}H-labeled analogue of **2**. *Ab initio* calculations (UB3LYP/6-31G*) showed that a π cation radical of **1** and a σ cation radical of **2** were converted to norcaradiene intermediates. Their further isomerizations led to [the benzene cation radical (*m*/*z* = 78) + CO] and [(*m*/*z* = 78) + CS], respectively. The fragmentation channel of **1** was calculated to have sufficiently small activation energies of intervening transition states to give almost exclusively the *m*/*z* = 78 peak. For a σ radical of **2**, an α hydrogen moved to the sulfur atom. The resultant thiol was isomerized to a second norcaradiene and its further isomerization led to a thioketene like cation and a hydrogen atom corresponding to the unusual ($M^+ - 1$) peak. The difference in fragmentation patterns of **1** and **2** is discussed in terms of their electronic structures.

Introduction

Tropone (**1**)[1] and its sulfur analogue tropothione[2] (**2**) are simple and representative novel (nonbenzenoid) aromatic compounds.[3] The structural similarity between the two compounds allows an intriguing comparison with respect to their chemical reactivities[4,5] and physical properties.[6,7] The potential instability[8,9] of **2** has precluded obtaining substantial information about it. Our synthesis and isolation as pure crystals of tropothione[2] prompted us to investigate a detailed analysis on mass spectral (MS) fragmentations. We have performed the MS analysis of **1** and **2** with the aid of that of the ^{2}H-labeled analogues. In this study, the fragmentation of tropothione (**2**) will be compared experimentally and theoretically with that of tropone (**1**).



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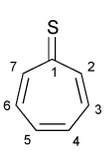
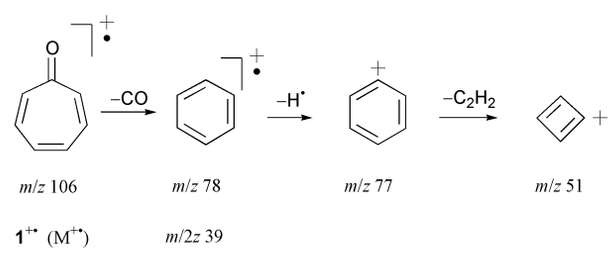
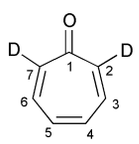


2

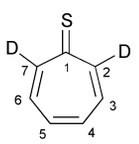
Mass spectra of tropone (**1**) have already been reported and indicated a simple fragmentation pattern of a single transition as Scheme 1 shows.[10–12] The first fragmentation step is the loss of C=O to yield a benzene cation radical.[12] The first fragment ion ($C_6H_6^{+\bullet}$) induces the decomposition of the benzene structure. The CO extrusion (*i.e.*, rupture of the ketone moiety) is an interesting reaction, because the seven-membered ring of **1** is rigid and is hardly subject to its opening reaction. Exceptionally, in basic conditions, the tosylate of troponimine undergoes a ring opening reaction and affords a triene.[13] The mechanism of the CO extrusion in Scheme 1 is still unclear and will be examined by *ab initio* calculations. The mass spectrum of **1** has been measured here for comparison with that of **2**. In order to get a deeper insight into the fragmentation of **1**, an isotope (H ⟶ D) substituted tropone (2,7-$^2H_2$ **1**, simply **1**-d_2) and **2**-d_2 have been synthesized and their mass spectra have also been measured. Mass spectra of **1**-d_2, **2** and **2**-d_2 have not been reported so far.



Scheme 1 Suggested MS fragmentation pathway of tropone (**1**).



1-d_2



2-d_2

It will be shown that the cation radical of **2** has a peculiar ($M^+ - 1$) fragmentation as well as a CS extrusion. The peculiarity will be solved by *ab initio* calculations.

† Electronic supplementary information (ESI) available: reaction paths supporting Figs. 3–6. See http://www.rsc.org/suppdata/p2/b1/b102127n/

 DOI: 10.1039/b102127n

Results and discussion

Synthesis of ^{2}H-labeled tropone and tropothione and computational method

In order to decipher the mass spectra of tropone and tropothione, we need to synthesize [2,7-$^2H_2$]tropone (**1**-d_2) and [2,7-$^2H_2$]tropothione (**2**-d_2) with high isotopic purity. Scheme 2 shows the synthetic route to **2**-d_2 *via* **1**-d_2, which was prepared starting from 2,5-dimethoxy-2,5-dihydrofuran.[14] The obtained 6-hydroxytropinone[15] (**3**) in the first step was deuteriated repeatedly with D_2O (isotopic purity: 99.8%) under basic conditions to give 6-hydroxy[2,2,4,4-$^2H_4$]tropinone (**3**-d_4) with high isotopic purity in high yield. The resulting ^{2}H-labeled product **3**-d_4 was reacted with methyl iodide in methanol leading to a methiodide (**4**-d_4) quantitatively. Hoffmann degradation of **4**-d_4 at 70 °C gave the desired **1**-d_2 in high yield. The ^{2}H-labeled tropone **1**-d_2 was treated with P_4S_{10} in the same way as in the preparation of the unlabeled analogue[2] **2** to yield the desired **2**-d_2 (isotopic purity: 98.3% $^2H_2$, 0.7% $^2H_1$, measured by mass spectrometry) in high yield under the conditions. Thus, we have succeeded in the synthesis of the desired [2,7-$^2H_2$]tropone (**1**-d_2) and [2,7-$^2H_2$]tropothione (**2**-d_2) with high isotopic purity.

The positions of deuteriation in tropone and tropothione have been verified by ^{1}H and ^{13}C NMR spectroscopy. We have performed not only one-dimensional ^{1}H NMR with resolution enhancement[16,17] but also two-dimensional ^{1}H–^{1}H shift correlation spectroscopy[18] as a detailed analysis for **1**-d_2 and **2**-d_2. Detailed experimental procedures are described in the Experimental section.

Ab initio calculations have been performed using the GAUSSIAN 94 program package[19] installed both on a CONVEX SPP 1200/XA computer in the Information Processing Center of Nara University of Education and on a CONVEX SPP 1600/XA computer in the Computer Center of Nara University.

Geometries of cation radicals of **1** and **2**, their fragment ions and neutral species were optimized by the (U)B3LYP/6-31G* method.[20] Vibrational analyses were carried out to confirm that the species obtained by "opt=ts" were correctly at saddle points. Spin contaminations were safely small. The largest $\langle S^2 \rangle$ expectation value was 0.785, where it should be 0.75 for doublet radicals.

MS Fragmentations of tropone (1) and tropothione (2)

Fig. 1 shows the mass spectra of tropone (**1**) and **1**-d_2. Both spectra exhibit simple fragmentations. Fragment peaks *m*/*z* = 78 (for **1**) and 80 (for **1**-d_2) appear almost exclusively. The CO extrusion is the sole fragmentation, and a stable benzene cation radical is formed. The elimination of α hydrogen was not found.

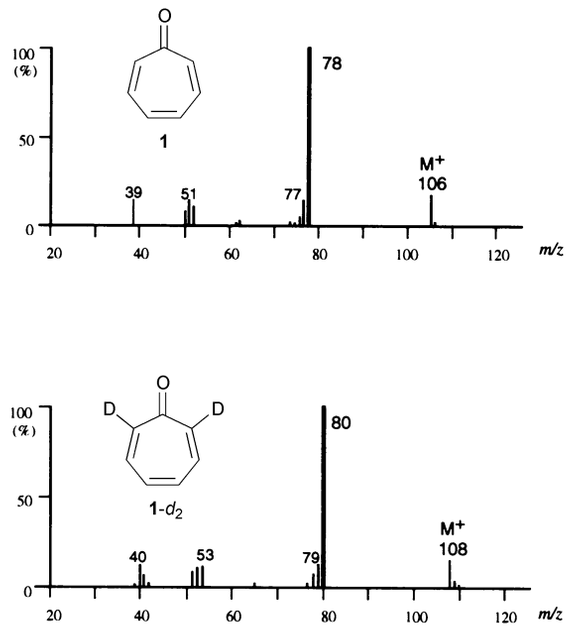
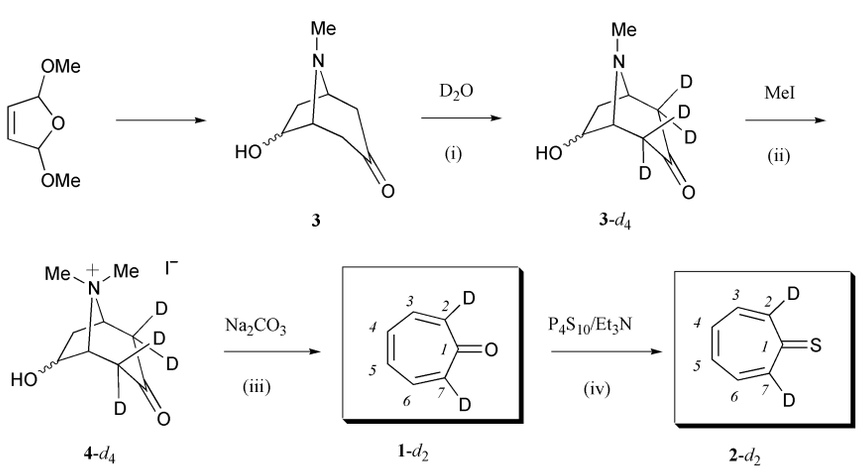


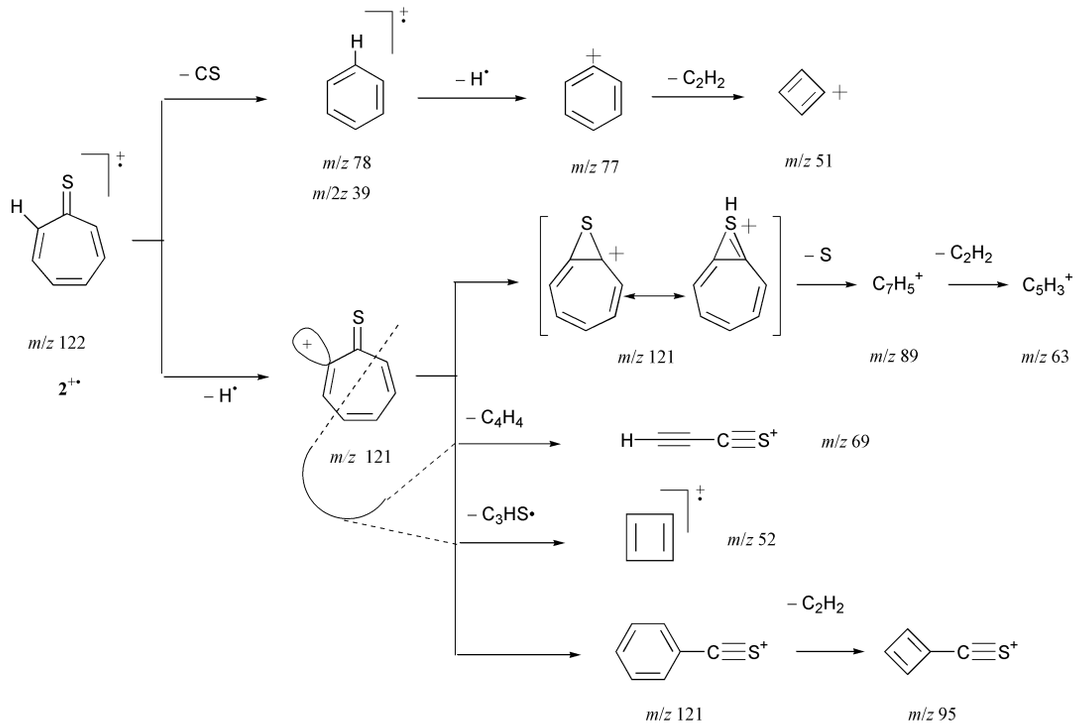
Fig. 1 EI-MS spectra of tropone (**1**) (top) and [2,7-$^2H_2$]tropone (**1**-d_2) (bottom).

We have used a deuteriated compound, [2,7-$^2H_2$]tropothione (**2**-d_2) (isotopic purity: 98.3% $^2H_2$, 0.7% $^2H_1$) for their mass spectra. Fig. 2 shows the result of the mass spectroscopy of **2** and **2**-d_2. Each fragment peak is assignable specifically by high resolution mass spectroscopy.

In the spectrum of **2** [Fig. 2 (top)], the parent peak (*m*/*z* 122) indicates a considerably abundant species, which is in contrast to the poor parent peak (*m*/*z* 106) of $\mathbf{1}^{+\bullet}$ (Fig. 1). The small ($M^+ + 1$) and ($M^+ + 2$) peaks show close correspondence with the calculated intensity based on natural isotopic abundances for the empirical formula C_7H_6S. Prominent peaks in Fig. 2 (top) at decreasing *m*/*z* values indicate extrusion of $H^\bullet$, C_2H_2, S, and CS. The extrusion has produced species $C_7H_5S^+$, $C_5H_3S^+$, $C_7H_5^+$, $C_6H_6^{+\bullet}$, $C_6H_5^+$, C_3HS^+, $C_5H_3^+$, $C_4H_4^{+\bullet}$, and $C_4H_3^+$, respectively, which are derived from high resolution mass spectrometry. In Fig. 2 (bottom), the spectrum of [2,7-$^2H_2$]tropothione (**2**-d_2) is consistent with the formation of species such as $C_7H_4D_2S^{+\bullet}$, $C_7H_4DS^+$, $C_5H_2DS^+$, $C_5H_3S^+$, $C_7H_4D^+$, $C_6H_4D_2^{+\bullet}$, $C_6H_3D_2^+$, $C_6H_4D^+$, $C_6H_5^+$, C_3DS^+, C_3HS^+, $C_5H_2D^+$, $C_5H_3^+$, $C_4H_2D_2^{+\bullet}$, $C_4H_3D^{+\bullet}$ and $C_4HD_2^+$, $C_4H_3D^{+\bullet}$ and $C_4H_2D^+$, and $C_4H_3^+$. The fragment peaks at *m*/*z* 39 in tropothione and at *m*/*z* 40 in [2,7-$^2H_2$]tropothione can be assigned to double cations of benzene and that of dideuteriobenzene, respectively, as well as $C_3H_3^+$ and $C_3H_2D^+$. The spectra indicate two main fragmentation routes (Scheme 3). One



Scheme 2 Synthesis of [2,7-$^2H_2$]tropone (**1**-d_2) and [2,7-$^2H_2$]tropothione (**2**-d_2). Synthetic conditions: (i) **3** ⟶ **3**-d_4: D_2O, 100 °C, 96%; (ii) **3**-d_4 ⟶ **4**-d_4: MeI, MeOH, 0 °C, 100%; (iii) **4**-d_4 ⟶ **1**-d_2: Na_2CO_3, 70 °C, 84%; (iv) **1**-d_2 ⟶ **2**-d_2: P_4S_{10}, 0 °C, 96%.



Scheme 3 MS Fragmentation pathway of tropothione (**2**). The mass spectrum reveals two main fragmentation pathways, a $M^{+\bullet} - 44$ or $M^{+} - 1$ by the initial loss of CS and $H^{\bullet}$ in the ring, respectively, from the molecular ion, $M^{+\bullet}$.

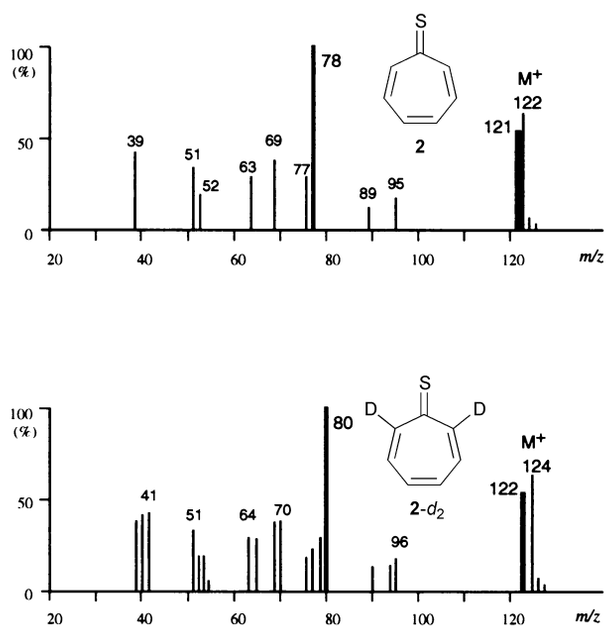


Fig. 2 EI-MS spectra of tropothione (**2**) (top) and [2,7-$^2H_2$]tropothione (**2**-d_2) (bottom).

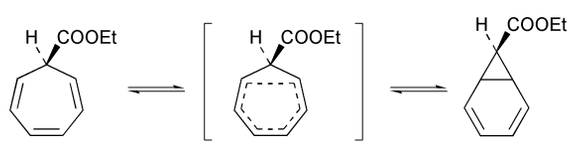
is the elimination of carbon monosulfide with formation of an m/z = 78 species (benzene), which is similar to that of tropone.[11–13] The other is the novel loss of the hydrogen atom from the seven-membered ring (α-proton) with the formation of an m/z = 121 species. This is followed either by the elimination of acetylene or that of a sulfur atom which were responsible for an m/z = 95 and an m/z = 89 species, respectively. Proposed fragmentation pathways are supported by measurements of each metastable ion peak.

Those two principal fragmentation processes in tropothione are in sharp contrast to the single fragmentation process of tropone.[10–12] The elimination of hydrogen from the ring is novel and is the first example in troponoid compounds. Table 1 displays MS fragmentations of **1**, **1**-d_2, **2**, and **2**-d_2. Prominent shifts of some fragments are indicated.

Theoretical interpretation of fragmentations of cation radicals of tropone (1) and tropothione (2)

The mechanism of fragmentation of $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ was examined by UB3LYP/6-31G* calculations. Fig. 3 shows a decarbonylation path from the tropone π radical which is yielded by an electron loss from **1**. The π radical has the lowest frequency, ν_1 = 109.6 cm^{-1}, of the out-of-plane puckering vibration. This vibration is mixed with the 12th vibrational mode, ν_{12}, and the mixed vibration becomes the origin of the norcaradiene formation.

Along the path, the seven-membered ring of the radical is isomerized to a norcaradiene structure (**3**-O) *via* TS1-O.‡ Norcaradiene has a long history, since Buchner suggested it first in 1901 for one component of Buchner's ester (Scheme 4).[21]



7-ethoxycarbonyl-cyclohepta-1,3,5-triene — norcaradiene

Scheme 4 Rapid valence tautomerism of 7-ethoxycarbonylcyclohepta-1,3,5-triene.

Various norcaradiene derivatives were synthesized in the 1960s,[22] and Rubin succeeded in generating the parent norcaradiene.[23] *Ab initio* calculations were performed to examine the structure and reactivity of norcaradienes.[24] However, the norcaradiene cation-radical **3**-O found here seems to be a new species.

In **3**-O, the cation character is located at the cyclohexadiene moiety. The highly strained cyclopropane ring of **3**-O is cleaved to bring about TS2-O. Prior to performing the calculations, a Meisenheimer like complex was anticipated after TS2-O.

‡ The $\mathbf{1}^{+\bullet} \longrightarrow$ **3**-O isomerization is an electrocyclic reaction according to the Woodward–Hoffmann rule. See: R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 395. A disrotatory path with C_S symmetry conserved was expected, but the geometry of TS1-O deviates slightly from the C_S one.

Table 1 Element map for the mass spectra of tropone (**1**), [2,7-$^2H_2$]tropone (**1**-d_2), tropothione (**2**), and [2,7-$^2H_2$]tropothione (**2**-d_2)

1-d_2		**1**		**2**-d_2		**2**	
m/*z*		*m*/*z*		*m*/*z*		*m*/*z*	
				124	$C_7H_4D_2S^{+\bullet}$	122	$C_7H_6S^{+\bullet}$
				122	$C_7H_4DS^+$	121	$C_7H_5S^+$
108	$C_7H_4D_2O^{+\bullet}$	106	$C_7H_6O^{+\bullet}$				
				96	$C_5H_2DS^+$	95	$C_5H_3S^+$
				95	$C_5H_3S^+$		
				90	$C_7H_4D^+$	89	$C_7H_5^+$
80	$C_6H_4D_2^{+\bullet}$	78	$C_6H_6^{+\bullet}$	80	$C_6H_4D_2^{+\bullet}$	78	$C_6H_6^{+\bullet}$
79	$C_6H_3D_2^+$	77	$C_6H_5^+$	79	$C_6H_3D_2^+$	77	$C_6H_5^+$
78	$C_6H_4D^+$			78	$C_6H_4D^+$		
				77	$C_6H_5^+$		
				70	C_3DS^+	69	C_3HS^+
				69	C_3HS^+		
				64	$C_5H_2D^+$	63	$C_5H_3^+$
				63	$C_5H_3^+$		
				54	$C_4H_2D_2^{+\bullet}$	52	$C_4H_4^{+\bullet}$
53	$C_4H_3D^{+\bullet}$	51	$C_4H_3^+$	53	$C_4H_3D^{+\bullet}$		
53	$C_4HD_2^+$			53	$C_4HD_2^+$	51	$C_4H_3^+$
52	$C_4H_2D^+$	51	$C_4H_3^+$	52	$C_4H_2D^+$		
				51	$C_4H_3^+$		
41	$C_6H_4D_2^{++}$	39	$C_6H_6^{++}$	41	$C_6H_4D_2^{++}$	39	$C_6H_6^{++}$
		39	$C_3H_3^+$			39	$C_3H_3^+$
40	$C_6H_5D^{++}$			40	$C_6H_5D^{++}$		
40	$C_3H_2D^+$			40	$C_3H_2D^+$		
39	$C_6H_6^{++}$			39	$C_6H_6^{++}$		
39	$C_3H_3^+$			39	$C_3H_3^+$		

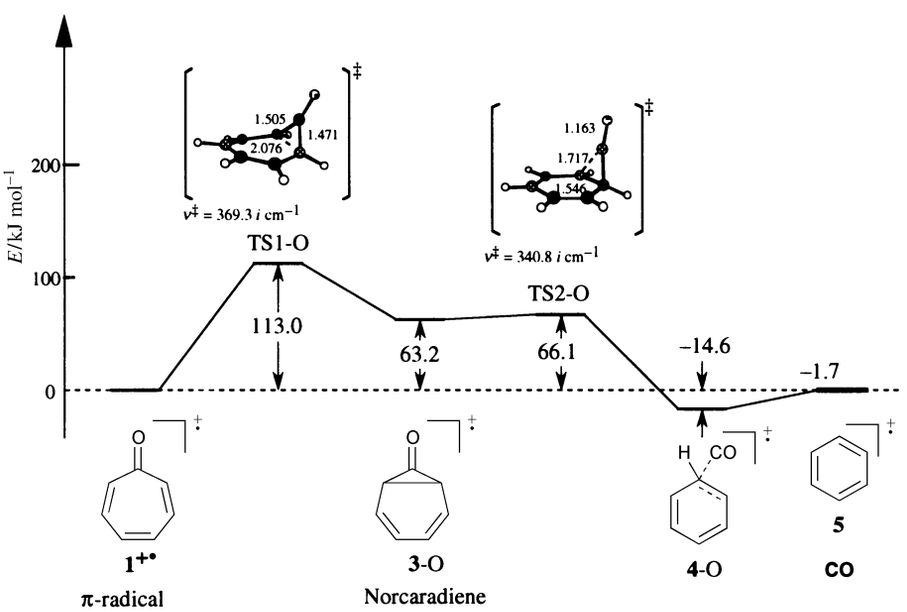
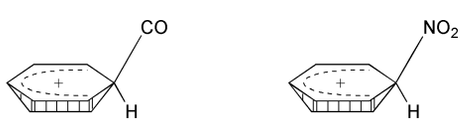


Fig. 3 Relative energies of (U)B3LYP/6-31G* calculations of the π cation-radical of **1**, transition states (TSs), two intermediates (**3**-O and **4**-O) and the benzene cation radical (**5**). Distances are in ångström. Geometries of all species and sole imaginary frequence-vectors of two TSs are in the Supplementary Data.



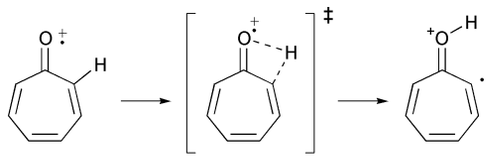
Meisenheimer like complex absent

cf. Intermediate for nitration of benzene

However, a stable species after TS2-O is **4**-O, where the C–C covalent bond is cleaved. That is, the scission of one C–C bond of the cyclopropanone part induces that of the other one. The intermediate **4**-O is regarded as a weak association complex between a benzene cation radical and carbon monoxide. Their dissociation leads to the *m*/*z* = 78 peak of the cation radical. The tropone π radical has been transformed to a norcaradiene intermediate. Its decomposition leads readily to the benzene cation radical and carbon monoxide.

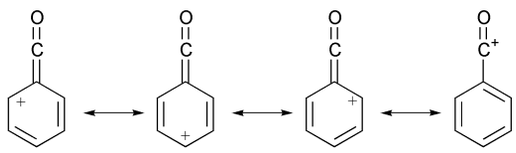
Next, a fragmentation from the tropone σ radical is considered (Fig. 4). In the σ radical, the spin density of an odd electron is localized at the in-plane carbonyl oxygen. A channel of the α hydrogen migration is the route of $\mathbf{1}^{+\bullet}$ ⟶ TS3-O ⟶ **6**-O.

In **6**-O, the distance between the two α-carbon atoms is 2.460 Å, which is smaller than that (= 2.587 Å) of $\mathbf{1}^{+\bullet}$ (π radical, Fig. 3). Ring closure may take place, leading to another norcaradiene intermediate, **7**-O, *via* TS4-O. In **7**-O, the three-membered ring is a cyclopropene cation radical. The very



$1^{+\bullet}$ (σ radical) TS3-O 6-O

strained ring is cleaved readily to give **8**-O *via* TS5-O. The hydrogen loss from **8**-O leads to a ketene like cation **9**-O with the following canonical resonance structures.



9-O

The hydrogen atom can be pushed out only when the residual closed-shell cation species can attain such a large thermochemical stability.

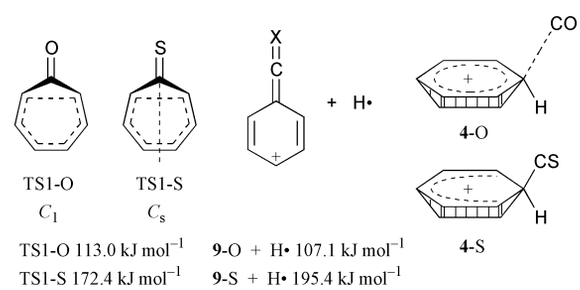
Potential energies of π (Fig. 3) and σ (Fig. 4) radical fragmentations are compared. The pathway of (tropone π radical ⟶ benzene cation radical and CO) has a very small activation energy (113.0 kJ mol^{-1}, TS1-O in Fig. 3) at the rate-determining step under the MS excessive energy condition (the 70 eV energy impact). The CO extrusion is confirmed to be an overwhelmingly probable path. The σ radical of $\mathbf{1}^{+\bullet}$ is by only 16.7 kJ mol^{-1} less stable than the π radical. But, its isomerization path (hydrogen migration, TS3-O) has a much larger activation energy than TS1-O. Comparing the two energy diagrams of the tropone series, one may understand the almost exclusive appearance of the *m*/*z* = 78 peak in Fig. 1. The very small base peak of $\mathbf{1}^{+\bullet}$ is also explainable by low potential energies of the π radical and its derivatives. The CO extrusion is the sole fragmentation from $\mathbf{1}^{+\bullet}$.

Fig. 5 shows a fragmentation pathway of the tropothione π radical. This path is completely different from that of the tropone π radical fragmentation shown in Fig. 3. The π radical is first excited to the σ radical and then it is isomerized *via* TS1-S with C_s symmetry to a norcaradiene intermediate, **3**-S. The second isomerization (TS2-S) leads, interestingly, to a Meisenheimer complex, **4**-S. This complex, **4**-S, dissociates to the benzene cation radical (**5**) and CS.

Fig. 6 exhibits the second fragmentation pathway of the tropothione σ cation radical, which is similar to Fig. 4. The route consists of hydrogen migration (TS3-S), norcaradiene formation (TS4-S), its decomposition (TS5-S) and hydrogen elimination.

The energy diagrams of the two pathways in Fig. 5 and Fig. 6 are compared. The highest energy point of the first fragmentation is (**5** + CS) with 245.6 kJ mol^{-1} in Fig. 5. The point of the second fragmentation is TS4-S with 227.6 kJ mol^{-1} in Fig. 6. The two energies are similar, which corresponds correctly to the two major peaks, *m*/*z* = 78 and *m*/*z* = 121 in Fig. 2. The large parent peak of $\mathbf{2}^{+\bullet}$ arises from the high potential energies of the two fragmentations. The energy levels of the second fragmentation of tropothione do not differ very significantly from those of the σ radical fragmentation of tropone. On the contrary, those of the first fragmentation are decisively different. The difference is reflected in the mass spectra of **1** and **2**.

The effect of exocyclic heteroatoms, X = O and S, on those energies and geometries is examined. Three typical cases of contrast are taken up in Scheme 5.



Scheme 5 Three significant differences between tropone and tropothione fragmentations.

The first difference is the norcaradiene formation path (TS1). For tropone, the π radical isomerizes to the norcaradiene without C_s symmetry. In tropothione, on the other hand, the excited σ radical isomerizes to the norcaradiene with C_s symmetry. Fig.

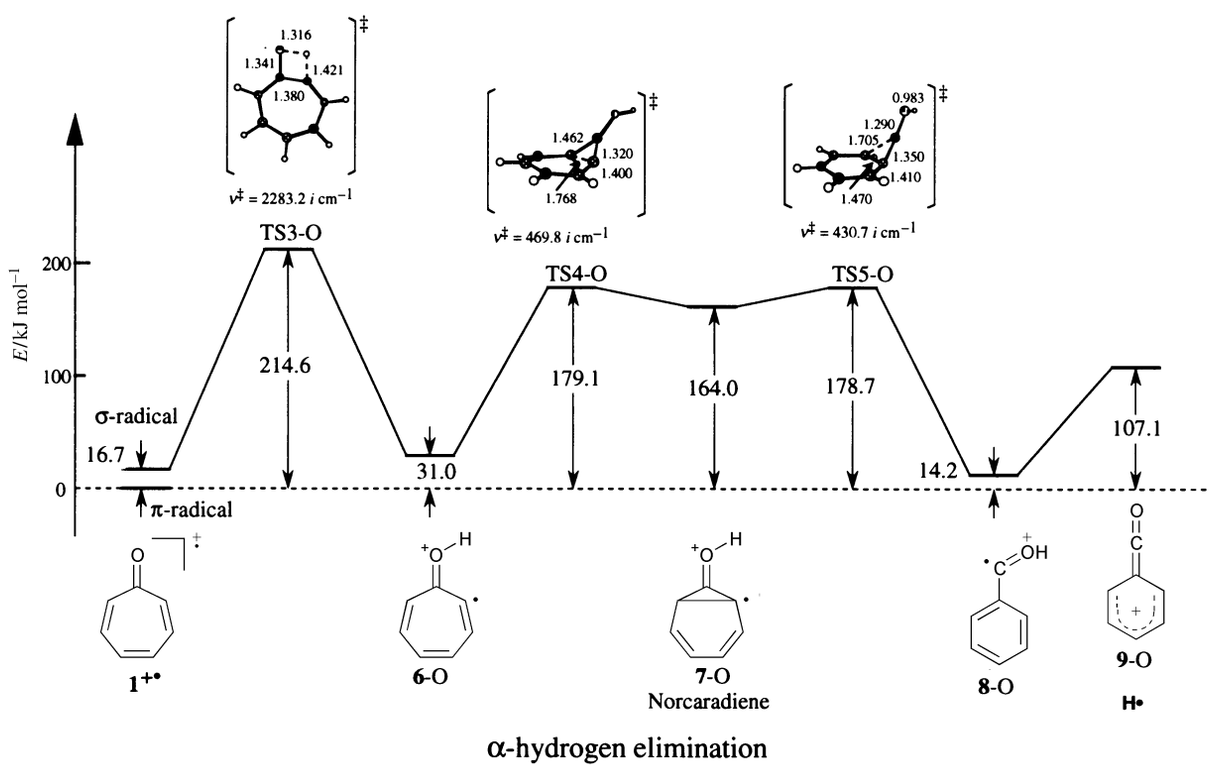
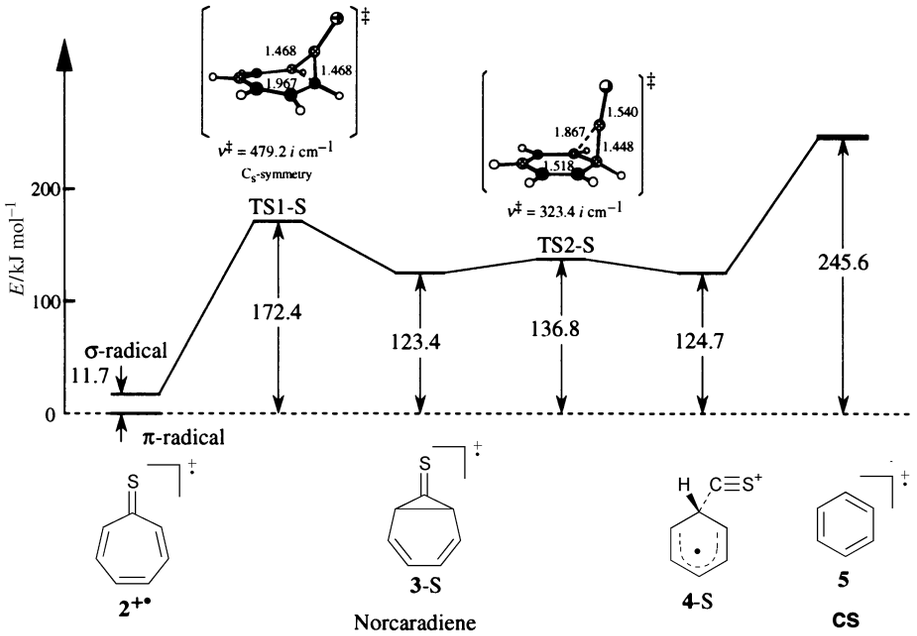
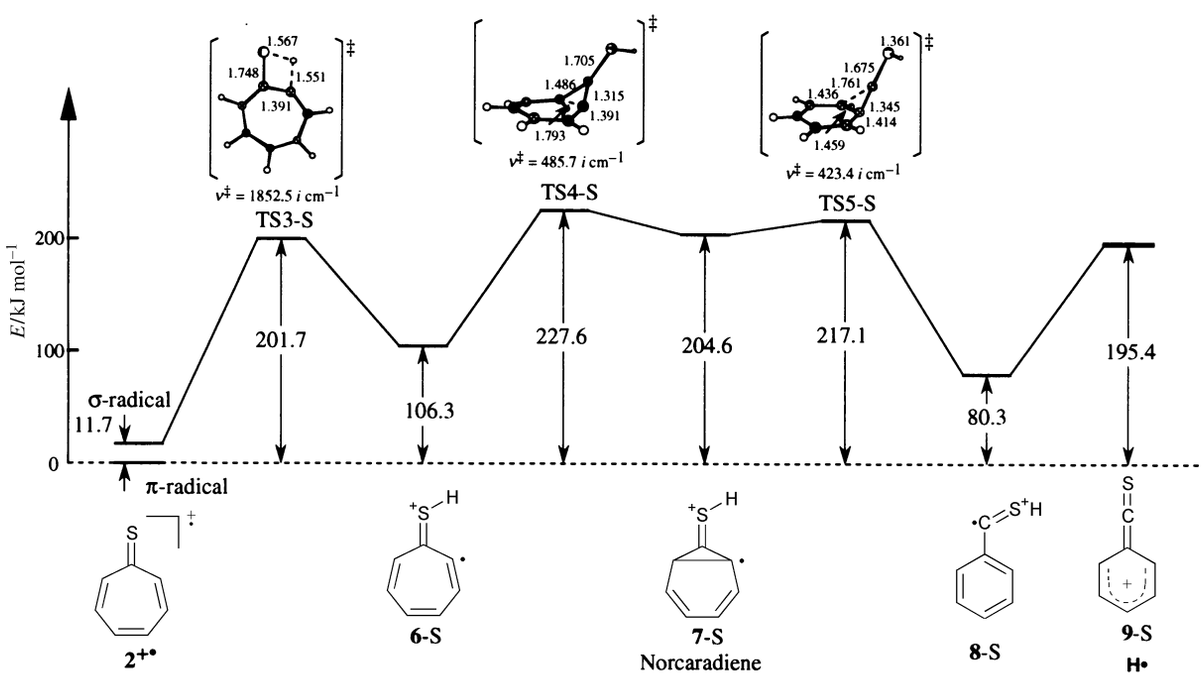


Fig. 4 Relative energies of the σ cation-radical of **1** and its isomers (**6**-O, **7**-O and **8**-O), TSs and a ketene like species (**9**-O).



benzene cation radical formation

Fig. 5 Relative energies of the π cation-radical of **2** and related species.



α-hydrogen elimination

Fig. 6 Relative energies of the σ cation-radical of **2** and related species.

7 shows the origin of this difference. The radical orbitals of the π cation radicals are symmetric orbitals (s) as to the mirror plane, *m*, whereas those of the norcaradienes are antisymmetric orbitals (a). This means that the norcaradiene formation initiated by the π radical requires a symmetry reduction or an excited-state reaction according to the symmetry-conservation rule of Woodward and Hoffmann.[25]

Fig. 8 shows the frontier orbitals of tropone and tropothione π radicals. For tropone, the radical and lone pair orbitals are delocalized over the oxygen, C_2 and C_7 atoms. For tropothione, those orbitals are localized at the sulfur atom and the energy gap between them is small. The deformation of $\mathbf{1}^{+\bullet}$ (π radical) from C_S symmetry mixes the radical orbital (s) with the lone pair orbital (a) using the C_2 and C_7 lobes. The radical orbital contributes to the new C_2–C_7 bond formation by the C_2 and C_7 lobes. The resultant new radical orbital at TS1-O has the oxygen lone pair character. This orbital interacts with the π-type orbitals of the hexadiene moiety (HOMO and LUMO) as the radical orbital of norcaradiene in Fig. 7 shows. This interaction and the original radical orbital (s) stabilize the transition state and this gives the small activation energy (113.0 kJ mol^{-1}). For tropothione, the ($C_S \longrightarrow C_1$) deformation cannot mix the radical orbital (s) and the lone pair orbital (a) because they are localized at the sulfur atom (very small components on C_2 and C_7). However, the energy difference between them is so small in tropothione that the π radical is easily excited to the σ radical. The σ radical isomerizes to the norcaradiene with C_S symmetry (a symmetry allowed reaction).

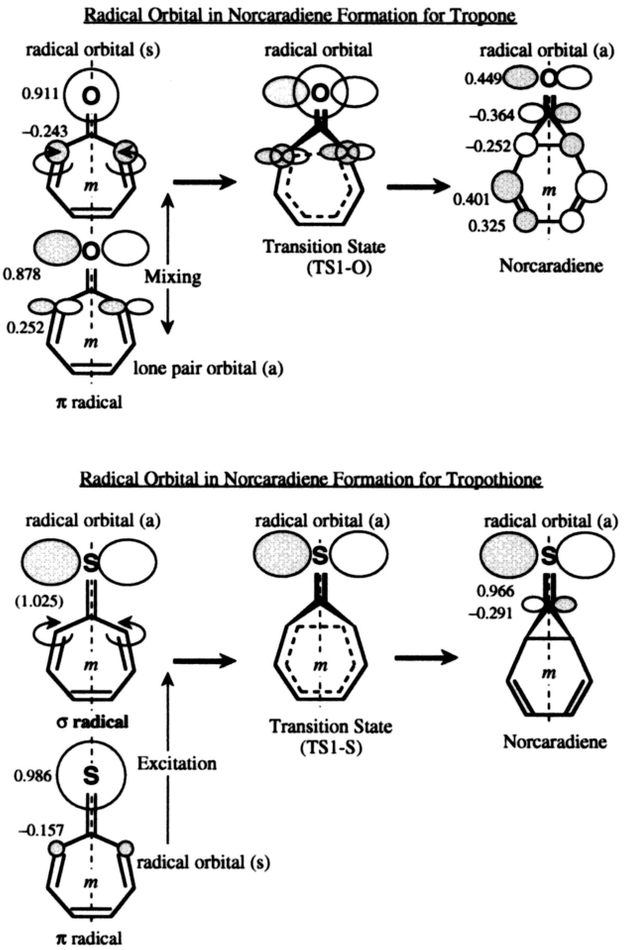


Fig. 7 Norcaradiene formation from tropone and tropothione cation radicals. Circles denote out-of-plane p atomic orbitals. The in-plane radical orbital (a) of tropothione in this figure corresponds to the HOMO of the π radical in Fig. 8, where (s) and (a) stand for the symmetric and antisymmetric orbitals with respect to the mirror plane, *m*, respectively. (1.025) is the coefficient of the sulfur atomic orbital in the HOMO.

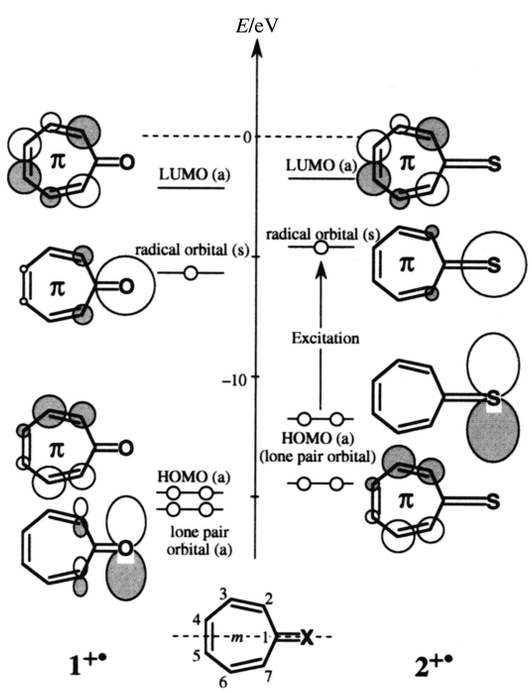


Fig. 8 Frontier orbitals of tropone and tropothione cation radicals calculated by the ROHF/STO-3G//UB3LYP/6-31G* method in C_{2v} symmetry. Circles denote out-of-plane p (p_π) orbitals.

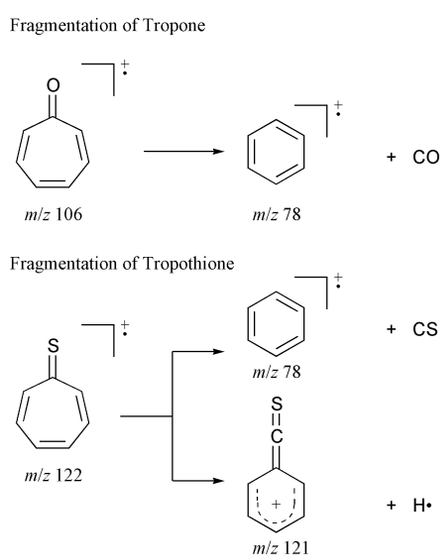
The above discussion may be pictorially described in Fig. 7. For tropone, the norcaradiene forming TS is initiated from the π cation radical. Through the symmetry lowering ($C_S \longrightarrow C_1$), the radical orbital (s) can mix effectively with the lone pair orbital (a) to produce the radical orbital (a) of the norcaradiene. On the other hand, tropothione has very small components of the radical orbital (s) and the lone pair orbital (a) at the C_2 and C_7 atoms. Therefore, the former cannot mix effectively with the latter and the formation of the radical orbital (a) of the norcaradiene is very difficult. That is, the π cation radical cannot initiate the norcaradiene formation. After the switch (π radical ⟶ σ radical), the antisymmetric radical orbital is formed, then the norcaradiene ring closure takes place, conserving the C_S symmetry.

The second difference in Scheme 5 is the stabilization of ketene like cations (**9**-O and **9**-S). The cation **9**-O is much more stable than **9**-S (107.1 *vs.* 195.4 kJ mol^{-1}). This is because the localization of the π orbital at the sulfur atom cannot stabilize the canonical resonance structures of **9**-S effectively.

The last difference in Scheme 5 is the presence or absence of the Meisenheimer like complex (**4**-S or **4**-O). This difference comes from the HOMO energy levels. The orbital energies of the HOMOs of fragments CO and CS are calculated by the RHF/STO-3G//B3LYP/6-31G* method to be −12.1 and −9.3 eV, respectively. According to the extent of the charge transfer (CT) interaction, the CS molecule may be coordinated more strongly than the CO one to the benzene cation radical. The larger CS ⟶ $C_6H_6^{+\bullet}$ CT interaction leads to the Meisenheimer like complex, **4**-S.

Concluding remarks

In this work, D-labeled **1** and **2** (**1**-d_2 and **2**-d_2) have been synthesized carefully. Mass spectra of **1**, **2**, **1**-d_2 and **2**-d_2 have been measured. Base peaks of those spectra correspond to the benzene cation radical (*m*/*z* = 78 and 80). For tropone, the peak is almost exclusive. The CO extrusion from $\mathbf{1}^{+\bullet}$ corresponds correctly to the potential energy surface with remarkably small activation energies in Fig. 3. The formation of the norcaradiene intermediate **3**-O is the rate-determining step. The small activation energy of TS1-O comes from the mixing of the radical orbital and the lone pair orbital through the ($C_S \longrightarrow C_1$) symmetry lowering. For tropothione, a novel ($M^+ - 1$) peak has been found and has been ascribed to a thioketene species, **9**-S, formed *via* the second norcaradiene intermediate, **7**-S. Two MS major peaks of tropothione correspond to two channels starting from the σ cation radical with similar energy barrier heights in Figs. 5 and 6. Scheme 6 summarises the present work.



Scheme 6 Summary of the present work.

The norcaradiene intermediates are needed to transform the seven-membered rings of **1** and **2** into the six-membered rings of the benzene cation radical and the ketene like species **9**.

Experimental

Reagents and materials

Tropone (**1**) was prepared from ditropyl ether using trifluoroacetic acid according to our previously reported method.[26] Tropothione (**2**) was prepared by a direct sulfurization of tropone using phosphorus decasulfide§ and triethylamine¶ according to a previously reported method.[7] Isolation experiments for tropothione were performed in a low-temperature-thermostatted room and the material was recrystallized from cold ether to give deep red needles (mp 20–21 °C). [2,7-$^2H_2$]Tropothione (**2**-d_2) was prepared starting from **1**-d_2 in the same way as in the preparation of the undeuteriated **2**. All the solvents used for the preparation and isolation of **2** were freshly distilled under nitrogen from appropriate drying agents and were degassed. Tropone was prepared under anhydrous conditions to prevent contamination of the hemihydrate according to our previously reported procedure[2] and purified by repeated distillation. The material purities were confirmed by UV–visible spectroscopy as well as by ^{1}H NMR (400 MHz, $CDCl_3$). All the solvents used for the preparation and isolation of tropothione were freshly distilled under nitrogen from appropriate drying agents and were degassed. For deuteriation, deuterium oxide (isotopic purity, 99.75%) (Merck) was employed. To prevent the decomposition of tropothione in various solvents the spectra were recorded immediately after the isolation of the compounds **2** and **2**-d_2.

Instrumentation/analytical procedures

Melting points were measured on a Büchi 511 apparatus in open capillary tubes and are uncorrected. Mass spectra were obtained with a JEOL DX-303 double focusing spectrometer and *m*/*z* values for significant ions are reported with relative intensities in parentheses (% for the base peak) for low resolution analyses. To prevent the decomposition of tropothione the spectrum was taken by a direct inlet system at an ionizing potential of 70 eV. Besides the parent ion, the most abundant *m*/*z* values are given with the appropriate relative abundances in parentheses.

6-Hydroxy[2,2,4,4-$^2H_4$]tropinone (3-d_4)

A solution of 6-hydroxytropinone[27] (**3**) (1.05 g, 6.77 mmol) and anhydrous potassium carbonate (539 mg, 3.90 mmol) in 0.9 mL of deuterium oxide was heated at 90 °C for 4 h. The resulting brownish red solution was cooled to room temperature to precipitate crystalline solid which was extracted with anhydrous ether (50 mL) followed by dichloromethane. The combined extracts were dried over magnesium sulfate. Evaporation gave pale brownish crystalline solid (0.997 g, 6.31 mmol, 95%). This process was repeated three times. The obtained solid was finally shaken with wet ether and then dried over magnesium sulfate. Solvent removal yielded 1.02 g (94.6%) of 6-hydroxy[2,2,4,4-$^2H_4$]tropinone (**3**-d_4) (d_4, 99.2; d_3, 0.7; d_2, 0.1% by mass spectrometry).

3-d_4: colorless prisms, mp 120–121 °C; ^{1}H NMR δ 4.06 (dd, 1 H, J = 5.3, 4.0 Hz, H-6), 3.78 (m, 1 H, H-1), 3.59 (m, 1 H, H-5), 2.95 (br s, 1 H, OH), 2.65 (s, 3 H, NMe), 2.01 (ddd, 2 H, J = 4.5, 4.0, 1.9 Hz, H-7); ^{13}C NMR δ 207.83 (s, C-3), 75.30 (d, C-6), 68.48 (d, C-5), 59.31 (d, C-1), 44.83 (small abundant quintet, C-2 or C-4), 41.81 (small abundant quintet, C-2 or C-4), 41.36 (t, C-7), 35.12 (q, NMe); EI-MS (30 eV) *m*/*z* 159 (M^+, 100) (d_4, 99.2; d_3, 0.7; d_2, 0.1%), 142 (12), 141 (9), 113 (51), 112 (30), 95 (44), 84 (91), 80 (13), 55 (36), 54 (14), 40 (30).

[2,7-$^2H_2$]Tropone (1-d_2)

A mixture of **3**-d_4 (3.55 g, 22.3 mmol) in 40 mL of ethanol and methyl iodide (7.07 g, 49.8 mmol) was stirred at 5 °C for 10 h. Filtration gave 6-hydroxy[2,2,4,4-$^2H_4$]tropinone methiodide (**4**-d_4) (6.62 g, 22.0 mmol, 99%) as a colorless solid. The solid and anhydrous sodium carbonate (2.38 g) were dissolved in 3.5 mL of deuterium oxide and the solution was heated at 60 °C for 3 h. Extraction with ether followed by sublimative distillation gave [2,7-$^2H_2$]tropone (**1**-d_2) (1.81 g, 76%).

1-d_2: Pale yellow liquid, bp 70–71 °C (0.4 Torr); ^{1}H NMR δ 7.34–6.66 (m, 4 H, AA′BB′ pattern); ^{13}C NMR δ 187.99 (s, C-1), 141.67 (small abundant t, C-2,7), 136.09 (d, C-3,6), 134.79 (d, C-4,5); EI-MS (30 eV) *m*/*z* 108 (M^+, 69) (d_2, 97.8; d_1, 2.2%), 80 (100).

[2,7-$^2H_2$]Tropothione (2-d_2)

In the presence of triethylamine (4.5 mL) as a catalyst, a solution of 1.28 g (11.9 mmol) of [2,7-$^2H_2$]tropone (**1**-d_2) in 5 mL of chloroform was added to a solution of tetraphosphorus decasulfide (6.36 g, 14.3 mmol) in 80 mL of anhydrous chloroform at 0 °C. The reaction mixture was stirred for 30 min and extracted with ether. The extract was washed with aqueous 1 mol dm^{-3} hydrochloric acid to remove the catalyst. Solvent removal followed by short column chromatography (silica gel, −20 °C) and recrystallization from cold ether gave 1.40 g (95%) of the product **2**-d_2.

2-d_2: Red needles, mp 19–20 °C (cold ether); ^{1}H NMR δ 7.17–6.93 (m, 2 H, H-4,5), 6.93–6.55 (m, 2 H, H-3,6); ^{13}C NMR δ 213.25 (s, C-1), 153.53 (small abundant t, C-2,7), 138.69 (d, C-4,5), 131.86 (d, C-3,6); EI-MS (30 eV) *m*/*z* 124 (M^+, 59) (d_2, 97.3; d_1, 2.7%), 80 (100).

§ Tetraphosphorus decasulfide was recrystallized from carbon disulfide after an extraction with a Soxhlet extractor from a commercially available reagent.

¶ Triethylamine, used as a catalyst, was freshly distilled and degassed.

Acknowledgements

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References

1 T. Asao and M. Oda, in *Carbocyclische π-Electronen-Systeme: Houben-Weyl, Methoden der organischen Chemie*, E. Müller, O. Bayer, Eds., Georg Thieme, Stuttgart, Germany, 1986, Band 5, Teil 2c, pp. 49–85, 710–780.

2 T. Machiguchi, *Tetrahedron*, 1995, **51**, 1133.

3 (*a*) D. Lloyd, *The Chemistry of Conjugated Cyclic Compounds*, Wiley, New York, NY, 1990, pp. 1–185; (*b*) A. T. Balaban, M. Banciu and V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-Derivatives, and Their Valence Isomers*, CRC, Florida, 1987, 3 volumes; (*c*) P. J. Garratt, *Aromaticity*, Wiley, New York, 1986; (*d*) D. Lloyd, *Non-benzenoid Conjugated Carbocyclic Compounds*, Elsevier, Amsterdam, 1984, pp. 1–431; (*e*) T. Nozoe, in *Nonbenzenoid Aromatic Compounds*, M. Kotake, Ed., *Comprehensive Organic Chemistry*, Asakura-Shoten, Tokyo, 1973, Vol. 13.

4 T. Machiguchi, T. Hasegawa, Y. Ishii, S. Yamabe and T. Minato, *J. Am. Chem. Soc.*, 1993, **115**, 11536 and references therein.

5 T. Minato, S. Yamabe, A. Ishiwata, T. Hasegawa and T. Machiguchi, *J. Mol. Struct. (THEOCHEM)*, 1998, **461–462**, 359.

6 T. Minato, S. Yamabe, T. Hasegawa and T. Machiguchi, *Tetrahedron*, 1995, **51**, 2507.

7 T. Hasegawa, T. Machiguchi, S. Yamabe and T. Minato, *J. Mol. Struct. (THEOCHEM)*, 1997, **418**, 221.

8 T. Machiguchi, T. Hasegawa, H. Otani, S. Yamabe and H. Mizuno, *J. Am. Chem. Soc.*, 1994, **116**, 407.

9 For tropothione derivatives, which are thermally stable and can be handled at room temperature, see: T. Machiguchi, T. Hasegawa and Y. Kano, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 3699.

10 J. D. McCollium and S. Meyerson, *J. Am. Chem. Soc.*, 1963, **85**, 1739.
11 J. M. Wilson, M. Ohashi, H. Budzikiewicz, C. Djerassi, S. Itô and T. Nozoe, *Tetrahedron*, 1963, **19**, 2247.
12 H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Hold-Day, San Francisco, USA, 1967, pp. 539–551.
13 T. Machiguchi, Y. Wada, T. Hasegawa, S. Yamabe, T. Minato and T. Nozoe, *J. Am. Chem. Soc.*, 1995, **117**, 1258.
14 P. Nedenskov and N. Clauson-Kaas, *Acta Chem. Scand.*, 1954, **8**, 1295.
15 E. E. Van Tamelen, P. Barth and F. Lornitzo, *J. Am. Chem. Soc.*, 1956, **78**, 5442.
16 W. P. Aue, E. Bartholdi and R. R. Ernst, *J. Chem. Phys.*, 1976, **64**, 2229.
17 K. Nagayama, A. Kumar, K. Wuethrich and K. Ernst, *J. Magn. Reson.*, 1980, **40**, 321.
18 J. C. Steffens, J. L. Roark, D. G. Lynn and J. L. Riopel, *J. Am. Chem. Soc.*, 1983, **105**, 1669.
19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN 94, revision D, Gaussian, Inc., Pittsburgh, PA, 1995.
20 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
21 W. Braren and E. Buchner, *Chem. Ber.*, 1901, **34**, 982.
22 (*a*) E. Vogel, W. Wiedemann, H. Kiefer and V. F. Harrison, *Tetrahedron Lett.*, 1963, 673; (*b*) E. Ciganek, *J. Am. Chem. Soc.*, 1965, **87**, 652, 1149; (*c*) T. Mukai, H. Kubota and T. Toda, *Tetrahedron Lett.*, 1967, 3581; (*d*) H. Prinzbach, U. Fischer and R. Cruse, *Angew. Chem.*, 1966, **78**, 268; (*e*) H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, 1967, **50**, 1692.
23 M. B. Rubin, *J. Am. Chem. Soc.*, 1981, **103**, 7791.
24 (*a*) N. Hartz, G. K. S. Prakash and G. A. Olah, *J. Am. Chem. Soc.*, 1993, **115**, 901; (*b*) T.-H. Tang, C. S. Q. Lew, Y.-P. Cui, B. Capon and I. G. Csizmadia, *J. Mol. Struct. (THEOCHEM)*, 1994, **305**, 149; (*c*) A. A. Jarzecki, J. Gajewski and E. R. Davidson, *J. Am. Chem. Soc.*, 1999, **121**, 6928.
25 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970.
26 T. Machiguchi, *Synth. Commun.*, 1982, **12**, 1021.
27 E. E. Van Tamelen, P. Barth and F. Lornitzo, *J. Am. Chem. Soc.*, 1956, **78**, 5442.