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MOLECULAR STRUCTURE AND TAUTOMERISM OF THE 1,3,2-BENZODIOXAARSOLE ETHER OF TROPOLONE

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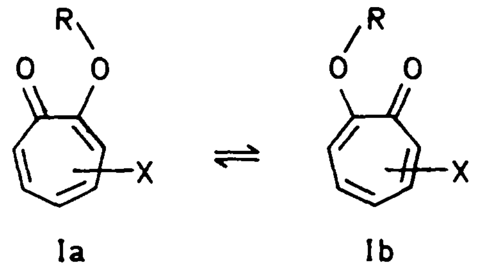
Abstract —The molecular structure of 2'-tropolonyl-1,3,2-benzodioxaarsole (A) was determined by X-ray analysis substantiating the previous structure assignment as II, and refining it. The molecular structure evidences three short O–As bonds and a longer fourth O–As bond, which however is much shorter than the sum of Van der Waals radii. The incipient intramolecular coordination between the CO oxygen and the As atom requires an unusual configuration (distorted trigonal bipyramid) around the As atom, leading to a conformation which is similar to the structure of the transition state for Berry pseudorotations. This explains the ^{13}C NMR spectra of II which indicates a rapid reversible migration of the 1,3,2-benzodioxaarsole moiety from one tropolone oxygen to another. Since the ^{13}C NMR spectra show no broadening at −70°, the upper limit for the free energy of activation is $\Delta G^{\ddagger}_{-70} < 6.5$ kcal/mole.

Several examples of rapid reversible O,O'-migration were found involving acyl,[1-4] polynitrophenyl[4] and trialkylsilyl groups[5] bonded to tropolone, Ia ⇌ Ib. In the present paper we bring evidence that the previously obtained[6,7] analogous derivative (A) of tropolone involving a benzodioxaarsole moiety with trivalent arsenic I,R = $\mathrm{As}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{C_6H_4}$, X = H, also undergoes an extremely rapid degenerate rearrangement of type Ia ⇌ Ib and we discuss the mechanism of this rearrangement on the basis of spectral and molecular structure data. On the basis of IR and ^{1}H NMR spectra, as well as of electronic absorption spectra in various solvents, a non-chelated structure II had been proposed[6] for this compound A. On the contrary, the analogous derivative with boron instead of arsenic was shown to be fully chelated with pairwise equivalent O atoms.[7]



Ia Ib

R = COR' ; p-$C_6H_4NO_2$; $C_6H_3(NO_2)_2$; SiR'_3
X = H ; 3,5,7-Me_3; 3,7-$(PhCH_2)_2$

RESULTS AND DISCUSSION

The proton noise-decoupled ^{13}C NMR spectrum of 2'-tropolonyl-1,3,2-benzodioxaarsole, A, in the

Table 1. ^{13}C NMR spectra of compounds, I, II, V (ppm relative to TMS, in CH_2Cl_2). Only the tropolone carbon resonances are shown

Compound	$C^{(1)}$	$C^{(2)}$	$C^{(3)}$	$C^{(4)}$	$C^{(5)}$	$C^{(6)}$	$C^{(7)}$	Ref.
IIa ⇌ IIb[a]	172.3	172.3	126.4	138.2	130.0	138.2	126.4	[b]
V	175.1	175.1	126.9	146.8	135.4	146.8	126.9	[b]
I,R = OCH_3	180.1	165.0	112.2	132.4	127.6	136.3	136.3	25
I,R = $COCH_3$[a]	178.3	157.5	128.1	132.3	134.1	137.5	139.5	2, 25
I,R = COOMe[a]	177.5	155.2	126.4	130.5	133.1	136.2	136.3	[b]

[a] At −70 °C.
[b] Present work.

temperature range from +100° (in N-methylpyrrolidone) to −70° (in CH_2Cl_2) consists of only seven lines (Fig. 1), indicating that this compound contains a real, or an effective (on the ^{13}C NMR time scale), symmetry plane of the molecule. This deceptively simple ^{13}C NMR spectrum can be explained by one of the following four structural possibilities.

(1) Compound A has a chelate structure with tetracoordinated arsenic and with pairwise equivalent As–O bonds. There are again two possibilities, depicted by structures III and IV for the coordinating centre, namely (i) tetragonal pyramid (III) or (ii) tetrahedral arrangement of oxygen (IV) as found[7,8] for the corresponding 1,3,2-benzodioxaborole derivative of tropolone (V) whose ^{13}C NMR spectrum (Fig. 1 and Table 1) also is temperature independent and consists of seven peaks. However, neither of these two possibilities agrees with the theoretical requirements of

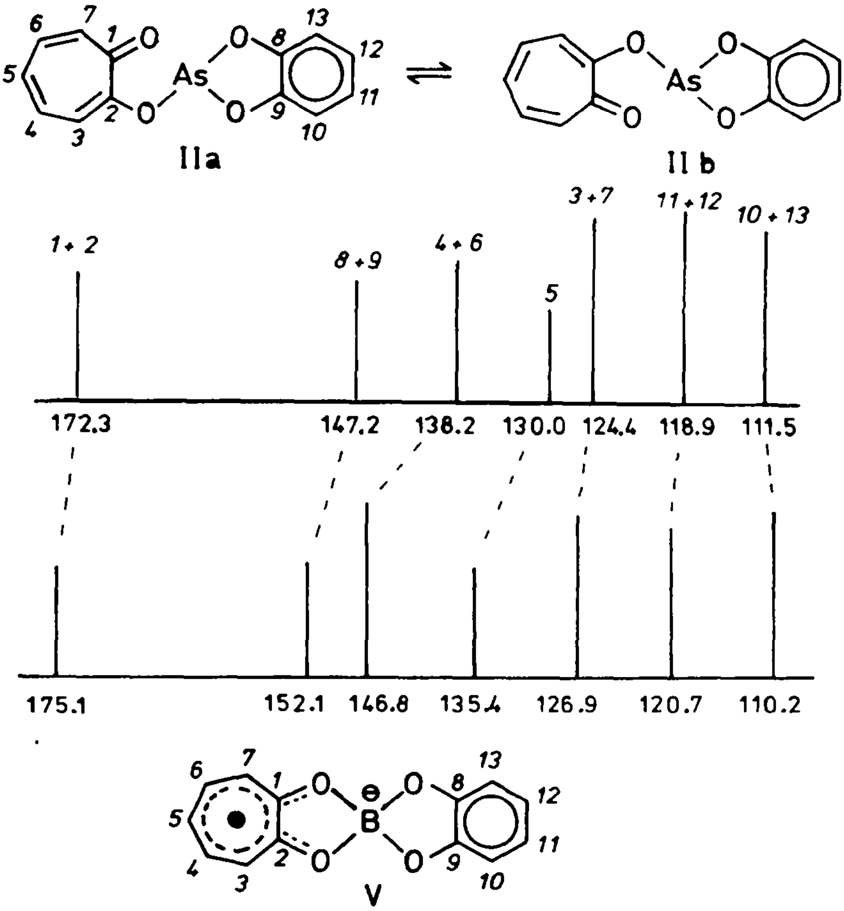
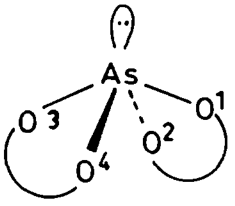
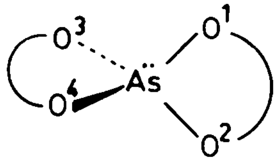


Fig. 1. Proton noise-decoupled ^{13}C NMR spectra of compounds A (II) and V in CH_2Cl_2 at −70°. Chemical shifts are in ppm, referenced to internal TMS.

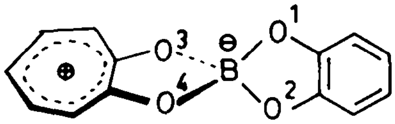
the Valence Shell Electron Pair Repulsion (VSEPR) theory.



III



IV



V

(2) Compound A has a tetracoordinated chelate trigonal–bipyramidal structure VI in agreement with the VSEPR theory. Such a structure is only possible when in each of the two chelate 5-membered rings one As–O bond is axial and the other one equatorial, owing to steric reasons (valence angle O–As–O close to 90°, leading to negligible ring strain). In such a structure there is no symmetry plane.

The two As–O bonds in the benzodioxaarsole moiety may differ slightly because one is equatorial and the other is axial; the other two As–O bonds may also be of slightly different lengths since again one of them is axial, the other is equatorial. However, owing to rapid intramolecular rearrangements VIa $\rightleftharpoons$ VIb all bonds become equalized; as indicated by theoretical calculations[9,10] and by analysis of NMR spectra of conformationally non-rigid trigonal bipyramidal structures,[11,12] such polytopal rearrangements occur preferentially through a Berry pseudorotation mechanism[13] involving tetragonal-pyramidal transition states similar to structure III.

(3) Compound A has a tricoordinated As atom in a non-chelate structure II. The observed time averaging of the ^{13}C NMR spectra is explained by rapid direct O,O′-migration of the benzodioxaarsole moiety IIa $\rightleftharpoons$ IIb through a bond breaking (ion pair) mechanism, resulting in intermolecular processes.

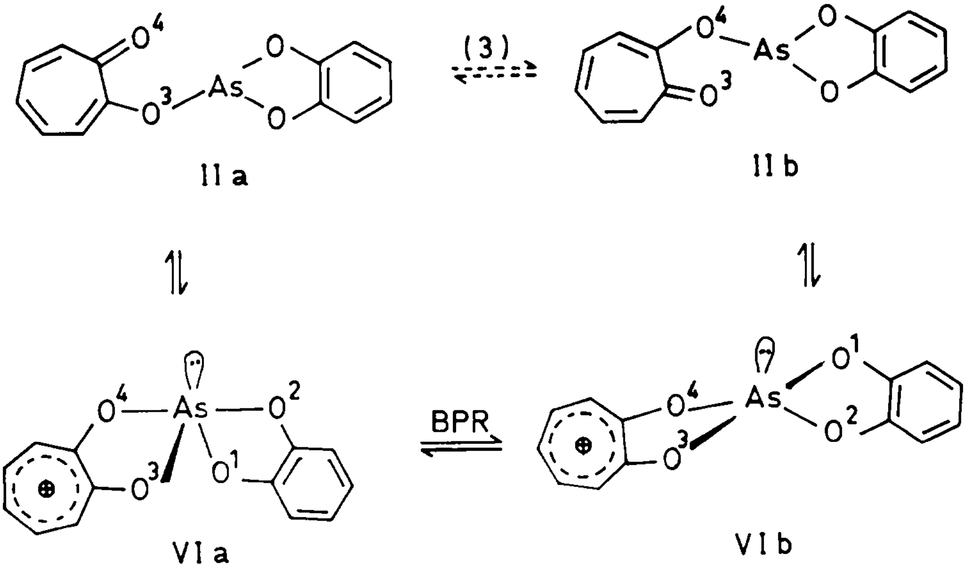
(4) Compound A has a tricoordinated arsenic in a practically non-chelate structure II. The O,O′-migration takes place intramolecularly through an associative internal nucleophilic displacement at the tricoordinated arsenic, involving as intermediate or transition state trigonal-bipyramidal structure VI.

The formation and rapid polytopal rearrangement of such intermediate structures are necessary conditions for the axial attack and axial bond breaking of the entering and leaving groups in the AdE mechanism of nucleophilic substitutions involving elements of the fifth and sixth groups in the periodic system.[14,15] Quantum-chemical calculations of the reaction path for this mechanism in nucleophilic substitutions involving P atoms were reported.[16]

Scheme 1 illustrates the last two possibilities, with dotted arrows for (3) and full arrows for (4).

In order to discriminate between these possibilities for compound A, its IR spectrum and the X-ray analysis of molecular structure were investigated for ascertaining whether the As–O bonds have pairwise equal lengths as requested by (1) or (2) on the basis of structures III, IV or VI, or whether on the contrary they have a non-chelated structure (II) proposed earlier.[6,7] as required by (3) or (4). The IR spectrum of A, either as a solid or in solution (with $CHCl_3$ or CH_2Cl_2 as solvents), differs from the spectrum of the corresponding tetrahedral boron chelate V, since A evidences a tropone CO stretching band at 1580 cm^{-1}. Such a band exists in all IR spectra of non-chelated compounds I.[4]

X-ray crystallographic analysis of A brings decisive data concerning its molecular structure. Figure 2 presents the bond lengths, while Figs. 3 and 4 depict the bond angles. Three As–O bonds are normal covalent bonds which are only slightly longer (1.819–1.879 Å) than ordinary As–O bonds in known tricoordinated arsenic compounds (1.79–1.83 Å)[17] or in spiroarsoranes with pentacoordinated arsenic (1.741–1.817 Å).[18] The fourth As–$O^{(4)}$ bond, however, is appreciably longer, 2.161 Å, indicating that this compound A possesses structure II with a strong intramolecular coordination. The high degree of this intramolecular As–$O^{(4)}$ coordination results from the fact that the indicated bond length is shorter by 1.2 Å relative to the sum of Van der Waals radii for As and O atoms. A consideration of bond angles (Fig. 3) supports this view: the three short As–O bonds are part of a distorted trigonal bipyramid with the arsenic at the centre (two bonds being equatorial, and the third axial with the longest As–$O^{(1)}$ distance, 1.879 Å, from these



Scheme

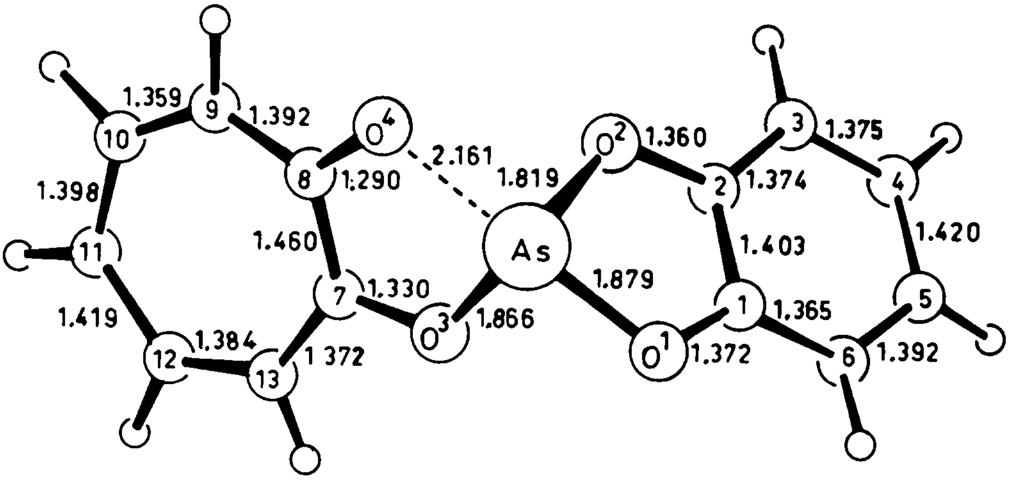


Fig. 2 Projection of the molecule II on the *ab* plane of the unit cell and bond lengths (in Å). Standard deviations of bond lengths: As–O, 0.004, C–O and C–C, 0.008–0.013 Å. Bond lengths for C–H bonds: 0.88–1.22 Å with σ(C–H) = 0.07–0.08 Å.

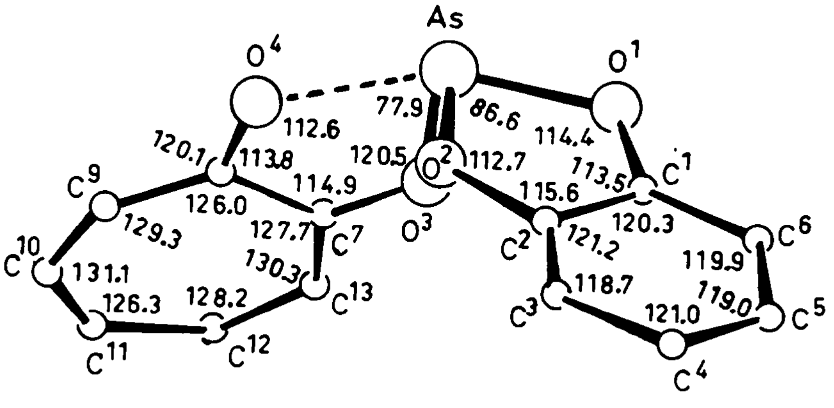


Fig. 3. Projection of the molecule II on the plane O(1)–As–O(4) and valence angles (only two O–As–O angles are shown here, the other ones are presented in Fig. 4). Standard deviations of angles: O–As–O, 0.2°; As–O–C, 0.4°; O–C–C and C–C–C, 0.6–0.8°.

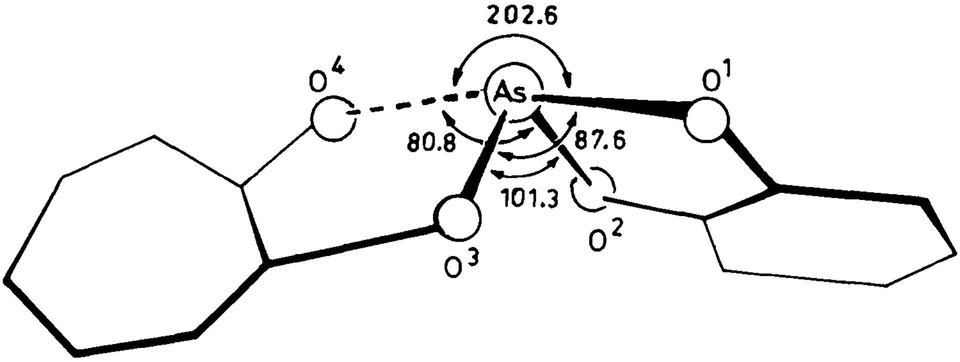


Fig. 4. Another view of molecule II along the plane of the benzenoid ring showing the remaining four angles around the arsenic atom. The chirality of the frozen molecule is clearly apparent

three bonds). The long As–O$^{(4)}$ bond constitutes the second axial bond. The whole assembly around the arsenic atom is a trigonal bipyramid VI (where one equatorial ligand, invisible on Figs. 2–4, is the unshared electron pair) distorted towards a tetragonal pyramid III.

In the tropolone moiety the C–O vonds are also non-equivalent, in that the carbonyl bond C$^{(8)}$=O$^{(4)}$ has a length of 1.290 Å (it coordinates intramolecularly by nucleophilic attack, to a certain extent, the tricoordinated As atom), while the C$^{(7)}$–O$^{(3)}$ bond length is 1.330 Å. As a whole, the molecular structure of this tropolone fragment is close to that of tropolone derivatives with intramolecular H-bonds, in which there is a substantial contribution of a tropolonic structure with localized double bonds and delocalized 10 π-electron system.[19] There is a remarkably close similarity between structure II and the tautomeric tropolone ethers I, e.g. the 2,6-dinitrophenyl ether of 3,5,7-trimethyltropolone,[20] although in the latter compound the delocalized structure has a smaller contribution.

The above particular aspects of the molecular structure reveal a very close similarity to the structure of the transition state in the rearrangement VIa $\rightleftharpoons$ VIb, explaining the extremely rapid migration of the benzodioxaarsole fragment between the two O atoms of the tropolone moiety. These aspects also suggest a preferential AdE-mechanism of the rearrangement which includes a supplementary polytopal rearrangement of the intermediate, i.e. IIa $\rightleftharpoons$ VIa $\rightleftharpoons$ VIb $\rightleftharpoons$ IIb. Indeed, as shown by several analyses,[21,22] molecular deformations in crystalline phase mirror exactly the lowest energy pathways for intramolecular rearrangements; thus the unusually large difference found between the sum of Van der Waals radii for As and O atoms (3.4 Å with Pauling's values) and the length of the As–O$^{(4)}$ bond in IIa indicates that in the stable conformation presented in Figs. 2–4, the intramolecular reaction is already strongly displaced along the reaction coordinate towards the end product IIb.

Analogously, it may be remarked that the 2,6-dinitrophenyl ether of 3,5,7-trimethyltropolone (which rearranges between structures Ia $\rightleftharpoons$ Ib with R = 2.6 $(O_2N)_2C_6H_3$ and X = Me_3) has a strong attractive interaction between the CO oxygen and the *ipso*-C atom, manifested in a shortening of this C ... O distance with 0.55 Å relative to the sum of Van der Waals radii; the O,O′-migration of the dinitrophenyl group in this compound also proceeds with such a high frequency that the reaction rate can no longer be determined by dynamic NMR spectroscopy.[4]

Thus the data we obtained for the 2′-tropolonyl-1,3,2-benzodioxaarsole (A) agree with mechanism (4) for the migration of the arsinyl group. Though mechanism (3) cannot be completely ruled out, this is an unlikely pathway since, on adding to a solution of II a solution of the 2,4-dinitrophenyl ether of 3,5,7-trimethyltropolone (for this compound, dynamic NMR spectroscopy allows[4] the determination of $\Delta G^{\ddagger}_{25}$ = 11.7 kcal/mol), NMR spectroscopy indicates the presence of two independent processes; intermolecular or dissociative pathways would have resulted in interactions between the two reactions. On the other hand, an intermolecular mechanism was advocated[24] for the O,C-transfer of AsR_2 groups in elementotropic ketoenolic equilibration of O- and C-arsenylated ketones, since the rate of these equilibrations increases on adding R_2AsCl.

One may estimate the upper limit of the energy barrier and the frequency of the arsinyl migration of II by comparing its time-averaged ^{13}C NMR spectrum (Fig. 1) with NMR spectra of compounds I whose tautomerization is either absent (R = CH_3), or can be "frozen" at low temperatures (R = COOMe, $COCH_3$), as presented in Table 1.

In the absence of a degenerate rearrangement IIa $\rightleftharpoons$ IIb, the difference between the chemical shifts of $C^{(1)}$ and $C^{(2)}$, by analogy with compounds I, ought to be at least 20–25 ppm (500–600 Hz at the working frequency, 25.2 MHz, of the NMR spectrometer). Since even at −70° in the ^{13}C NMR spectra of II one cannot observe any line broadening of the peaks corresponding to isochronous nuclei (Fig. 1), the frequency of arsinyl migration at this temperature must be higher than 10^5–10^6 sec^{-1}, and therefore $\Delta G^{\ddagger}_{-70} < 6.5$ kcal/mole. This value is lower than the energy barrier of trialkylsilyl O,O′-migration in tropolone derivatives (I, R = $SiAlk_3$), which was estimated by line broadening of the averaged $C^{(1)}$ and $C^{(2)}$ peaks at low temepratures to be approximately 8 kcal/mole.[5] The frequency for II is

Table 2. Atomic coordinates (× 10^4 for non-hydrogen atoms, and × 10^3 for hydrogens).

Atom	x	y	z	Atom	x	y	z
As	4343 (0)	3723 (1)	4559 (1)	$C^{(10)}$	6243 (3)	2762 (6)	1325 (10)
$O^{(1)}$	3723 (2)	4711 (4)	4258 (6)	$C^{(11)}$	6364 (3)	3838 (7)	657 (9)
$O^{(2)}$	3970 (2)	2692 (4)	3319 (6)	$C^{(12)}$	6023 (3)	4844 (6)	754 (9)
$O^{(3)}$	4726 (2)	4596 (4)	3045 (6)	$C^{(13)}$	5511 (3)	4981 (6)	1517 (8)
$O^{(4)}$	5040 (2)	2603 (4)	3950 (6)	$H^{(3)}$*	329 (3)	167 (7)	144 (9)
$C^{(1)}$	3340 (3)	4245 (6)	3222 (8)	$H^{(4)}$	233 (3)	253 (8)	60 (9)
$C^{(2)}$	3478 (3)	3121 (5)	2734 (7)	$H^{(5)}$	208 (3)	462 (7)	114 (10)
$C^{(3)}$	3130 (3)	2511 (7)	1738 (8)	$H^{(6)}$	280 (3)	567 (7)	300 (9)
$C^{(4)}$	2642 (4)	3026 (8)	1210 (10)	$H^{(9)}$	581 (3)	152 (7)	272 (10)
$C^{(5)}$	2501 (3)	4171 (8)	1667 (10)	$H^{(10)}$	658 (3)	222 (7)	111 (9)
$C^{(6)}$	2859 (3)	4763 (6)	2689 (10)	$H^{(11)}$	681 (3)	396 (7)	23 (10)
$C^{(7)}$	5213 (3)	4227 (6)	2449 (8)	$H^{(12)}$	621 (3)	551 (7)	33 (9)
$C^{(8)}$	5373 (3)	3058 (5)	2916 (8)	$H^{(13)}$	529 (3)	558 (6)	136 (9)
$C^{(9)}$	5819 (3)	2418 (6)	2299 (9)				

* The numbering of hydrogens is identical to the numbering of the carbons bonded to them.

similar to that calculated on the basis of ESR spectroscopy for the interligand exchange of the odd electron in a stable radical derived from 2′-(*o*-phenoxyloxy)-1,3,2-benzodioxaarsole,[26] in which the arsinyl migration involves an intramolecular homolytic substitution at the tricoordinated As atom.

Thus II, the 1,3,2-benzodioxaarsole ether of tropolone, more than other tropolone derivatives of type I,[1–5,20] illustrates the possibility of modelling extremely rapid rearrangements based on the idea of matching the structure of starting materials with the structure of the transition state in the rearrangement.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded with a Varian XL-100 spectrometer using TMS as internal standard. IR spectra were recorded on a Specord IR-71 instrument. Compounds II[6] and V[7] were prepared as described previously, and were purified by repeated recrystallizations from benzene and n-hexane. O-Carboxymethyltropolone (I, R = COOMe), m.p. 78° from n-hexane, was obtained in 60% yield from the sodium salt of tropolone and methyl chloroformate in benzene.

X-Ray crystallography. Single crystals of II were grown from the analytically pure compound using n-hexane as solvent. The crystals of $C_{13}H_9AsO_4$ are rhombic with $a = 23.693(5)$, $b = 11.577(12)$, $c = 8.456(2)$ Å, calculated density 1.75 g/cm^3, $z = 8$. Space group P_{bca}. The parameters of the unit cell were determined on an automatic diffractometer CAD-4F, using Mo-K_α X-rays and a graphite monochromator. The intensities of 1359 reflexions were measured with $I > 2\sigma\ (I)$ ($\theta/2\theta$ scanning, $1° < \theta < 25°$).

The molecular structure was determined by the heavy atom method and was refined by the full matrix least square method in the anisotropic approximation till R = 0.069. All calculations were effected using a computer program.[27] At this stage of the difference synthesis the H atoms appeared. Further structure refinement, including the coordinates and the isotropic temperature factors for the H atoms, led to the final value R = 0.063. The atomic coordinates are presented in Table 2. The bond lengths and bond angles may be seen on Figs 2–4. The table of the temperature factors is available on request.

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