Photoreaction of a Stable Thioaldehyde 2,4,6-Tri-*tert*-butylthiobenzaldehyde

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The photochemical reaction of the only isolable aromatic thioaldehyde ArCHS (**1**; Ar = 2,4,6-tri-*tert*-butylphenyl) in alkaline medium yields $ArCH_2CH_2Ar$ (**2**), $ArCH_2SCH_2Ar$ (**3**), 6,8-di-*tert*-butyl-3,4-dihydro-4,4-dimethyl-1*H*-2-benzothiine (**4**) and ArMe (**5**). A radical mechanism which accounts for the formation of these compounds is proposed, mainly on the basis of the direct observation (EPR spectroscopy) of a number of radicals such as $ArCHS^{\bullet -}$ (**A**), $Ar\dot{C}HCH_2Ar$ (**B**), and $ArCH_2^{\bullet}$ (**D**). Results of scrambling of deuterium atoms confirmed the structure of these radicals through interpretation of the corresponding EPR spectra.

Although the chemistry of thioketones has been extensively studied in recent years,[1] thioaldehydes have eluded isolation until very recently. Since thioaldehydes are usually very unstable and exist as transient species, their reactions have mostly been restricted to Diels–Alder-type cycloadditions with dienes.[2–6] We have recently reported the synthesis and some reactions of a stable aromatic **1**[7] and of an aliphatic thioaldehyde.[8] We report here the photoreaction of thioaldehyde **1** in alkaline alcoholic solution which has revealed interesting properties of this stable thioaldehyde.

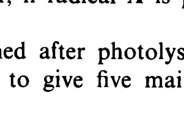
Results and Discussion

Photolysis of ArCH=S (**1**; Ar = 2,4,6-tri-*tert*-butylphenyl) in EtOK/EtOH yields radical anion $ArCHS^{\bullet -}$ (**A**) whose EPR spectrum has been detected and described.[9] The spectrum of radical **A** slowly disappears to be substituted by the spectrum of a different radical, which eventually becomes the only visible spectrum. To this second radical the structure **B** has been assigned.[10]

$Ar\dot{C}HCH_2Ar$

B

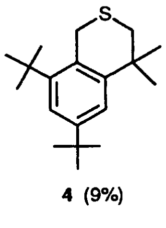
Ar =



It has also to be pointed out that reaction of compound **1** with metallic potassium in the absence of radiation does not yield radical **B** but only radical **A**, which is much more persistent under these conditions. However, if radical **A** is photolysed, then radical **B** appears.

Product analysis was performed after photolysis (7 h) of thioladehyde **1** in EtOK/EtOH to give five main products (compounds **2**–**6**).

$$\mathbf{1}\xrightarrow{\text{EtOH/EtOK}}\underset{\mathbf{2}\ (12\%)}{ArCH_2CH_2Ar}+\underset{\mathbf{3}\ (37\%)}{(ArCH_2)_2S}+$$



4 (9%)

$$+\underset{\mathbf{5}\ (8\%)}{ArMe}+\underset{\mathbf{6}\ (9\%)}{ArCHO}$$

Aldehyde **6** was most likely produced from unchanged substrate **1** during the isolation procedure since compound **1** is known to be readily oxidized to aldehyde **6** in solution[7a] and to be partly converted into aldehyde **6** when subjected to chromatography.

We shall discuss first how compound **2** can be obtained, because its production is clearly related to the presence of intermediary radical **B** which has very interesting properties, as described in a previous paper.[10] The following steps (Scheme 1) are considered to be the most likely mechanism occurring in this reaction: they will be discussed on the basis of several lines of experimental evidence.

$$\underset{\mathbf{1}}{ArCH{=}S}\xrightarrow{\text{i}}\underset{\mathbf{A}}{Ar\dot{C}HS^-}\longleftrightarrow\underset{\mathbf{A}}{Ar\bar{C}H\text{–}S^{\bullet}}\underset{-\,H^+}{\overset{\text{ii}}{\rightleftharpoons}}$$

$$\underset{\mathbf{C}}{ArCH_2S^{\bullet}}\xrightarrow[\text{(SET)}]{+\,e^-}\underset{\mathbf{C'}}{ArCH_2S^-}\xrightarrow{\text{iii}}\underset{\mathbf{D}}{ArCH_2^{\bullet}}+S^{\bullet -}$$

$$\underset{\mathbf{D}}{ArCH_2^{\bullet}}+\underset{\mathbf{A}}{Ar\dot{C}HS^-}\longrightarrow\underset{\mathbf{7a}}{ArCH_2CH(S^-)Ar}\xrightarrow{\text{iii}}$$

$$\underset{\mathbf{B}}{ArCH_2\dot{C}HAr}\xrightarrow{\text{iv}}\underset{\mathbf{2}}{ArCH_2CH_2Ar}$$

Scheme 1 *Reagents and conditions:* i, EtOK–EtOH, *hν*; ii, H^+; iii, *hν*; iv, $H^{\bullet}$

Formation of Radical $Ar\dot{C}HCH_2Ar$ (**B**) and Hydrocarbon $ArCH_2CH_2Ar$ (**2**).—As mentioned above, the formation of radical **A** as the first step of the reaction mechanism is confirmed by the observation of the corresponding EPR spectrum. The subsequent production of radical **D** (Scheme 1) is required at a certain stage in order to explain the EPR observation of radical **B** as well as the presence of hydrocarbon **2** in the final products. The possibility of direct coupling between two molecules of radical **D** to yield compound **2** is considered unlikely since it cannot explain the formation of radical **B**. Furthermore, although the EPR spectrum of radical **D** had been reported,[11] we could not observe it under our conditions. This suggests that, in our system, radical **D** disappears *via* a very fast reaction which does not reach steady-state conditions with a sufficient amount of radical **D** to be spectroscopically detected. Second-order reactions involving a pair of radicals are likely to be relatively slow owing to the relatively low radical concentrations, whereas reaction of radical **D** with radical anion **A**, which is known from its EPR spectrum to exist in a very high concentration, would be much faster. The radical **B** formed in this way will give compound **2** irreversibly *via* H-abstraction from the environment. An alternative, obvious route to radical **B** one might suggest, *i.e.*, H-abstraction from compound **2** by $Bu^tO^{\bullet}$, did not yield any EPR spectrum, probably because of severe congestion at the benzylic position. Supporting evidence for the proposed mechanism comes from the following experiments.

(1) Photolysis (for a short time) of compound **1** in EtOK–EtOH followed by neutralization with HCl allowed us to identify a small amount of $ArCH_2SH$. This is consistent with suggested transformation of species **A** into anion **C′** which is the precursor of radical **D**. Proof that the H^+ required to transform **A** into **C** comes from the solvent is given by the fact that deuterium is incorporated to give ArCHDSH as a final product when this experiment is carried out in EtOD.

(2) Pulse radiolysis studies[12] of thiols in alkaline media have demonstrated that thiolates can react by either eqn. (1) or (2):

$$R_2CHS^- + OH^{\bullet} \longrightarrow R_2\dot{C}S^- + H_2O \qquad (1)$$

$$R_2CHS^- + e^- \longrightarrow R_2CH^{\bullet} + S^{2-} \qquad (2)$$

Alternatively, the loss of sulphur in the second reaction might also occur[13] as depicted in eqn. (3):

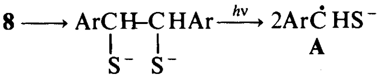
$$R_2CHS^- \longrightarrow R_2CH^{\bullet} + S^{\bullet -} \qquad (3)$$

(3) Proof of the existence of the radical $ArCH_2^{\bullet}$ (**D**) comes also from the detection, in the reaction products, of a certain amount (8%) of ArMe (**5**) which can be obtained by H-abstraction from the medium. The key proof that radical **D** is indeed formed but not directly observed in the EPR spectra because of its rapid consumption under our conditions was obtained in the following experiment. Photolysis of the thiol $ArCH_2SH$ in EtOK–EtOH did not give the radical anion $ArCHS^{\bullet -}$ (**A**) most probably because of sluggishness in hydrogen abstraction due to steric hindrance. This behaviour is at variance with that of unhindered $PhCH_2SH$ which does yield[9] the radical anion $PhCHS^{\bullet -}$ under the same conditions. Although the EPR spectrum of species **A** was not observed when $ArCH_2SH$ was employed, we did observe the spectrum of the radical **D**, $ArCH_2^{\bullet}$, when $ArCH_2S^-$ was photolysed. This result provides supporting evidence for the existence of the following step [eqn. (4)] described in Scheme 1.

$$ArCH_2S^- \longrightarrow \underset{\mathbf{D}}{ArCH_2^{\bullet}} + S^{\bullet -} \qquad (4)$$

In addition this experiment indicates that the absence of the radical anion **A** does prevent fast decay of radical **D** so that the EPR spectrum of radical **D** can be observed. Finally, since radical **B** was not observed under these conditions, we can conclude that the reaction of **D** with **A** is a necessary step for the production of radical **B**.

(4) Photolysis, in an alkaline medium, of dithiol ArCH(SH)CH(SH)Ar (**8**) slowly yields the EPR spectra of both species **A** and **B**. This behaviour is readily explicable if one considers that the dianion **8a** of dithiol **8** can be homolytically cleaved to give species **A** [eqn. (5)].



$$\mathbf{8} \longrightarrow \underset{\mathbf{8a}}{Ar\underset{S^-}{CH}-\underset{S^-}{C}HAr} \xrightarrow{h\nu} 2\underset{\mathbf{A}}{Ar\dot{C}HS^-} \qquad (5)$$

The observation that the radical anion **A** can be obtained even in the absence of the thioaldehyde **1** and nonetheless that the radical **B** can still be observed requires that radical **D** (obtained from radical anion **A**) reacts with the excess of **A** itself (and not with substrate **1**) since compound **1** is now absent. Thus, the above facts provide further evidence that radical **D** reacts with radical anion **A** rather than with the thioladehyde **1**. Although the EPR spectrum of radical **B** could be observed in this way, its intensity was lower than that in the experiment where the thioaldehyde **1** itself was employed. This finding also agrees with the proposed scheme, because photolysis of compound **8** cannot produce as large an amount of radical anion **A** as does photolysis of thioladehyde **1** and hence only a lower concentration of species **A** is now available to produce radical **B**.

(5) It is also worth mentioning that photolysis of $ArCH_2SSCH_2Ar$ (**9**) does not yield the EPR spectrum corresponding to the radical $ArCH_2^{\bullet}$ (**D**). This indicates that cleavage of the S–S bond in disulphide **9**, which would produce the radical $ArCH_2S^{\bullet}$ **C**, cannot be the source of radical **D** *via* loss of a sulphur atom. However, if the photolysis of compound **9** is carried out in alkaline medium, then radical **D** is readily observed by EPR spectroscopy. We must therefore admit that the following sequence (also described in Scheme 1) takes place [eqn. (6)].

$$\underset{\mathbf{9}}{(ACH_2S)_2} \xrightarrow{h\nu} \underset{\mathbf{C}}{ArCH_2S^{\bullet}} \xrightarrow{\text{SET}}$$

$$\underset{\mathbf{C'}}{ArCH_2S^-} \longrightarrow \underset{\mathbf{D}}{ArCH_2^{\bullet}} + S^{\bullet -} \qquad (6)$$

(6) Very conclusive proof that radical **B** is indeed generated, *via* loss of sulphur, from the anion (**7a** in Scheme 1) of the thiol $ArCH_2CH(SH)Ar$ (**7**) has also been obtained. The thiol **7** was synthesized and photolysed (in EtOK/EtOH) in the cavity of the EPR spectrometer: a very intense signal of radical **B** was instantaneously observed. On the other hand, when the thioaldehyde **1** was employed, the detection of the radical **B** required a long interval of time as the radical anion **A** had first to disappear by reaction with radical **D** before yielding a sufficient amount of anion **7a** to afford the radical **B**.

(7) Finally a number of deuterium-labelling experiments were also carried out to confirm the nature of radical **B**. (*a*) Photolysis of ArCD=S in EtOK–EtOH yields an EPR spectrum corresponding to the radical **B′** which incorporates two deuterium atoms, one in position α and one in position β. Since

$$\underset{\mathbf{B'}}{Ar\dot{C}DCHDAr}$$

the two β positions are not equivalent as discussed in ref. 10, the radical **B′** yields two superimposed EPR spectra (Fig. 1) that show the deuterium atoms either as a replacement for the H^{β}-atom with the larger splitting (25.9 G) or as a replacement for the H^{β}-atom with the smaller splitting (7.4 G). In the spectra corresponding to this pair of topomers, the D^{β}-splitting values are reduced, with respect to the corresponding H^{β}-values of radical **B**, by a factor (6.48) determined by the H/D nuclear gyromagnetic values, the two β-splittings of deuterium being 4.0 and 1.15 G. The original H^{α}-splitting of radical **B** (14.25 G) is also reduced by the same factor in both topomers (D^{α}-splitting 2.2 G).

(*b*) Photolysis of ArCH=S (**1**) in EtOK–EtOD yields an EPR spectrum corresponding to the radical $Ar\dot{C}HCHDAr$ (**B″**) which, for the same reasons previously discussed, exists as a pair of topomers. In this case, however, the spectrum of the fully protonated radical **B** (20%), superimposed on the pair of spectra corresponding to the topomers of radical **B″** (40% each), was also observed.

(*c*) The trideuteriated thioaldehyde Ar′CD=S (Ar′ = 2,4,6-tri-*tert*-butyl-3,5-dideuteriophenyl) was photolysed in the presence of C_2D_5OK–C_2D_5OD. The spectrum corresponding to the

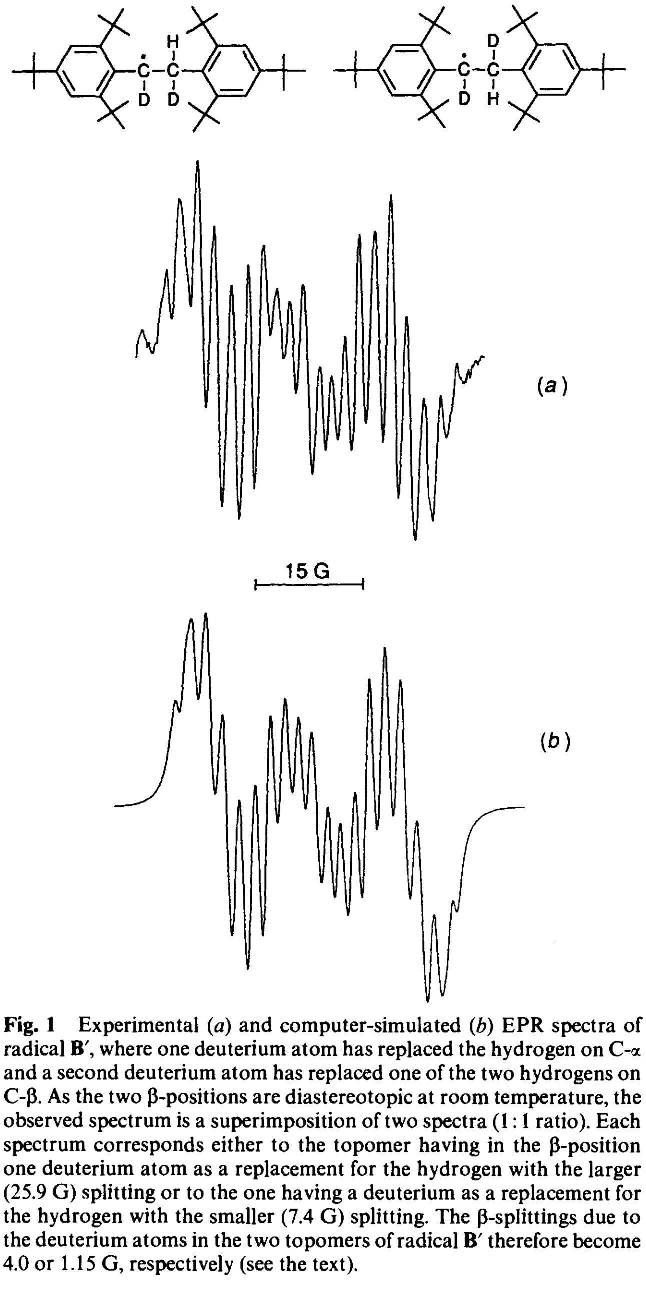


Fig. 1 Experimental (*a*) and computer-simulated (*b*) EPR spectra of radical **B**′, where one deuterium atom has replaced the hydrogen on C-α and a second deuterium atom has replaced one of the two hydrogens on C-β. As the two β-positions are diastereotopic at room temperature, the observed spectrum is a superimposition of two spectra (1 : 1 ratio). Each spectrum corresponds either to the topomer having in the β-position one deuterium atom as a replacement for the hydrogen with the larger (25.9 G) splitting or to the one having a deuterium as a replacement for the hydrogen with the smaller (7.4 G) splitting. The β-splittings due to the deuterium atoms in the two topomers of radical **B**′ therefore become 4.0 or 1.15 G, respectively (see the text).

deuteriated radical **B**‴ (Ar′$\dot{C}$DCD$_2$Ar′) was observed (60%) but the two isotopomers containing a hydrogen atom (20% each) were also detected. They had a **B**′-type structure, *i.e.*, Ar′$\dot{C}$DCHDAr′.

All these results can also be interpreted on the basis of the mechanism proposed in Scheme 1. In experiment 7a, ArCD=S will produce ArCHD$^•$ (**D**′) by picking up H$^+$ from EtOH. The subsequent reaction with ArCDS$^{•-}$ will obviously yield radical **B**′ (Ar$\dot{C}$DCHDAr), where the position α will be always deuteriated, whereas only one of the two β positions bears a deuterium atom. In experiment 7b, ArCH=S will produce the same radical **D**′ (Ar$\dot{C}$HD) by picking up D$^+$ from EtOD, thus accounting for the final formation of the two topomers corresponding to the structure ArCHCHDAr (**B**″). However, the existence of a certain amount of the non-deuteriated radical [*i.e.*, Ar$\dot{C}$HCH$_2$Ar, (**B**)] indicates that the solvent (ethanol in our case) is not the only available source of hydrogen atoms. This is indeed confirmed by the results of experiment 7c where C$_2$D$_5$OD and the trideuteriated thioaldehyde (*i.e.*, deuteriated also in the *meta*-positions) were employed: the only possible sources of hydrogens are, consequently, the **Bu^t** groups of the thioaldehyde itself.

Since it seems unlikely that the Bu^t moiety is a source of H$^+$, we are inclined to suggest that the **Bu^t** groups take part in the reaction *via* a homolytic mechanism. Accordingly, in addition to the process described in Scheme 1 the following mechanism (Scheme 2) is considered to also be operative:

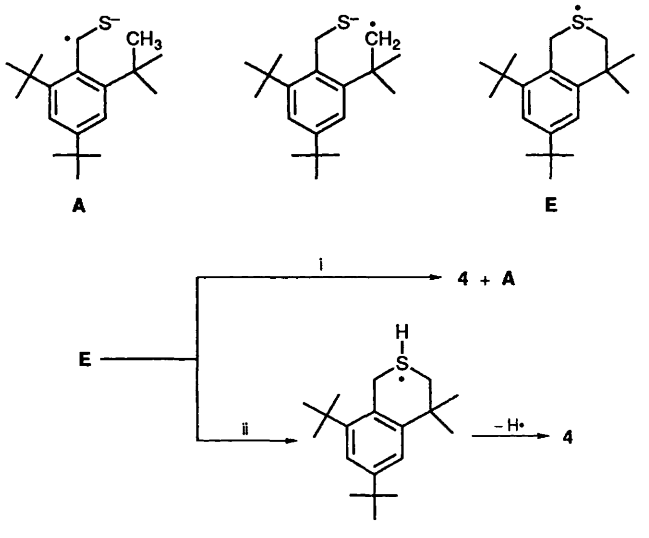
$$\mathrm{Ar'\dot{C}DS^-} \xrightarrow{\mathrm{i}} \mathrm{Ar'CDHS^-} \xrightarrow{\mathrm{ii}} \mathrm{Ar'CDH^\bullet + S^{\bullet -}}$$

Scheme 2 *Reagents and conditions:* i, H$^•$ (from Bu^t); ii, *hν*

In our opinion the latter mechanism is, however, of minor importance, as shown by the fact that the relative amount of the partially undeuteriated radical Ar′$\dot{C}$DCDHAr′ is not constant but decreases when the concentration of Ar′CD=S in C$_2$D$_5$OK–C$_2$D$_5$OD is lowered, with a corresponding increase in the relative amount of Ar′$\dot{C}$DCD$_2$Ar′.

Formation of the Linear **3** *and Cyclic* **4** *Sulphides*.—The mechanism proposed in Scheme 1 can also be used to explain the production of the two major compounds **3** and **4**. Radical **D** (ArCH$_2^•$) can react with radical **C** (ArCH$_2$S$^•$) to give rise to sulphide **3** (ArCH$_2$SCH$_2$Ar).

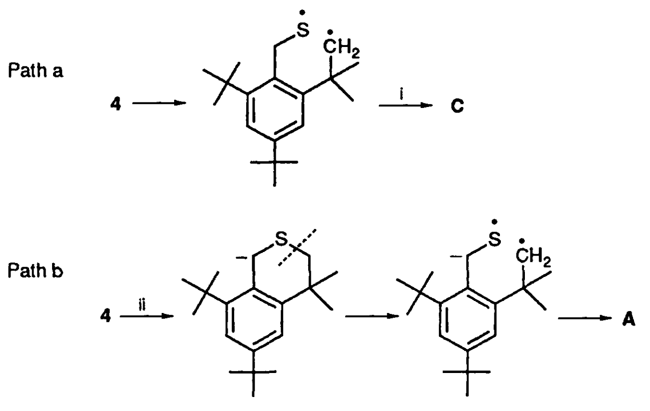
Although radical **C** would be dimerized to give the corresponding dimer (ArCH$_2$S)$_2$, the dimer would eventually end up giving the sulphide **3** either *via* the photodissociation followed by reaction with radical **D** (ArCH$_2^•$) or *via* attack by radical **D** in S$_H$2 fashion. Cyclic sulphide **4** is most likely produced from radical anion **A** as depicted in Scheme 3. A similar mechanism has already been proposed for the reaction of thioaldehyde **1** with organometallics.[7c]



Scheme 3 *Reagents:* i, ArCH=S (**1**); ii, EtOH

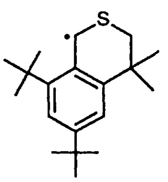
Photolysis of compound **4** in EtOH/EtOK yields the superimposed EPR spectra of both radicals **A** and **B**. This can be explained by path a or path b (Scheme 4) if the reaction **A** $\rightleftharpoons$ **C** (Scheme 1) is a reversible process.

It is also quite important to take into account the possibility that, from analysis of the EPR spectrum, the radical to which we assigned structure **B** might have, instead, a completely different structure, related somehow to that of compound **4** which is one of the main reaction products. Such a possibility derives from the fact that the EPR spectrum[10] of species **B** requires five hyperfine splittings from five different hydrogens and also that a linewidth alternation due to an internal motion has been observed. A radical derived from compound **4**, such as F, also



Scheme 4 *Reagents:* i, H$^•$; ii, EtOH/EtOK

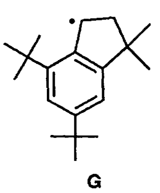
fulfils these requirements, the internal motion possibly being the reversal of the six-membered ring.



F

To check for such a possibility we obtained the EPR spectrum of the authentic radical F by photolysis of compound **4** in the presence of di-*tert*-butyl peroxide: this spectrum turned out to be completely different from the one to which structure **B** was assigned. The hyperfine splittings of radical F were as follows: 1.5 G (2 hydrogens), 12.9 G (1 hydrogen) and 4.6 G (1 hydrogen). They were due, respectively, to the pair of nearly equivalent aromatic hydrogens, to the hydrogen bonded to the sp^2-carbon bearing the unpaired electron (H-α) and to one of the non-equivalent pseudo-axial or pseudo-equatorial SCH_2 hydrogens. One of these hydrogens has a splitting of 4.6 G, whereas the other had a splitting equal to zero, or (at least) lower than the experimental linewidth (1 G). Furthermore the barrier for the ring reversal was too high to be observed in the temperature range of this experiment (−50 – 0 °C) and hence a linewidth alternation could not be detected.

Finally we can also exclude the possibility that the radical under discussion has the structure **G** which might be obtained from compound **4** by loss of sulphur. The EPR spectrum of the authentic radical **G** was obtained by H-abstraction from the corresponding hydrocarbon (4,6-di-*tert*-butyl-1,1-dimethylindane). Although its spectrum shows five hydrogens coupled with the unpaired electron, the values of the corresponding hyperfine splittings are not equal to those of the radical to which we had assigned the structure **B**. The hyperfine splittings of species **G** are as follows: 1.6 G (2 H; *i.e.*, the nearly equal aromatic hydrogens), 15.4 G (1 H; *i.e.*, H-α) and 24.75 G (2 H; *i.e.*, two hydrogens in position β). In a five-membered ring the ring reversal is expected to be very fast, so that the two hydrogens in position β with respect to the radical centre are equivalent, contrary to the case of a six-membered ring.



G

Experimental

Materials.—2,4,6-Tri-*tert*-butylthiobenzaldehyde (**1**; Ar = 2,4,6-tri-*tert*-butylphenyl),[7a,14] its deuteriated analogue (ArCDS),[15] 4,6-di-*tert*-butyl-1,1-dimethylindane[16] and 1,2-bis-(2,4,6-tri-*tert*-butylphenyl)ethane-1,2-dithiol **8**[7c] were prepared by the reported methods. Trideuteriated thioaldehyde Ar′CDS (Ar′ = 2,4,6-tri-*tert*-butyl-3,5-dideuteriophenyl) was synthesized from 1,3,5-tri-*tert*-butyl-2,4,6-trideuteriobenzene[17] in a similar way as for ArCDS[15] except that the trideuteriobenzene was used instead of 1,3,5-tri-*tert*-butylbenzene. 1,2-Bis-(2,4,6-tri-*tert*-butylphenyl)ethanethiol **7** was prepared as follows. To a stirred solution of phenyl 2,4,6-tri-*tert*-butylbenzyl sulphide (0.0612 g, 0.166 mmol) in tetrahydrofuran (THF) (5 cm^3) at − 78 °C was added dropwise lithium naphthalenide (*ca.* 0.32 mol dm^{-3} THF solution; 2 cm^3). To the greenish brown solution at −78 °C was slowly added a solution of the thiolaldehyde **1** (0.0967 g, 0.333 mmol) in THF (3 cm^3) and then the reaction mixture was allowed to warm to room temperature. After being stirred for 1 h the reaction mixture was quenched with aq. NH_4Cl. The usual work-up gave a reaction product (0.1384 g), which was subjected to dry column chromatography on silica gel (hexane) to afford crude compound **7** (80 mg). Purification by preparative high-performance liquid chromatography (HPLC) (column: Japan Analytical Industries, JAIGEL 1H, styrene–divinylbenzene copolymer, pore size 25 Å) gave a pure sample (9.7 mg, 11%) of compound **7** as a viscous oil; δ_H(500 MHz; $CDCl_3$) 0.91 (9 H, br s), 0.93 (9 H, s), 1.24 (9 H, s), 1.25 (9 H, s), 1.66 (9 H, s), 1.78 (9 H, br s), 2.46 (1 H, d, *J* 5.4), 3.96 (1 H, dd, *J* 15.8, 5.4), 4.09 (1 H, dd, *J* 15.8, 1.8), 4.57 (1 H, dt, *J* 5.4, 1.8), 7.04 (1 H, d, *J* 2.2), 7.14 (1 H, br s), 7.43 (1 H, d, *J* 2.2) and 7.60 (1 H, br s); δ_C(125 MHz; $CDCl_3$) 31.19, 31.33, 32.79, 33.01, 33.89, 34.40, 34.68, 36.22, 36.40, 37.47, 38.43, 39.56, 41.67, 43.16, 121.33, 121.83, 124.81, 128.01, 137.35, 141.65, 146.07, 146.88, 147.22, 148.94, 149.55 and 149.80. (Found: M$^+$, 550.4555. Calc. for $C_{38}H_{62}S$: M, 550.4570).

Photolysis of 2,4,6-*Tri*-tert-*butylthiobenzaldehyde* **1** *in* EtOH/EtOK.—The thioaldehyde **1** (149 mg, 0.512 mmol) was dissolved in a degassed ethanolic solution (6 cm^3) of EtOK (2.56 mmol). The reaction tube was sealed under vacuum and the solution was irradiated (400 W high-pressure Hg arc through a Pyrex filter) at 0 °C for 7 h. To the solution was added 2 mol dm^{-3} HCl and the mixture was extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was subjected to dry column chromatography (silica gel; hexane–CH_2Cl_2 20:1) and preparative HPLC (column: Japan Analytical Industries, JAIGEL 1H) to afford compounds **2**[18] (17 mg, 12%), **3**[10] (52 mg, 37%), **4**[7b] (14 mg, 9%), **5**[17] (11 mg, 8%) and **6**[14] (12 mg, 9%), all of which were identified by comparison of their ^1H and ^{13}C NMR spectra with those of authentic samples.

Spectroscopy.—The EPR spectra were taken using quartz tubes, sealed under vacuum, that were then introduced into the cavity of the EPR spectrometer (Varian E3) where they were subjected to photolysis (500 W high-pressure Hg arc). The ^1H and ^{13}C NMR spectra were obtained with a Bruker AM-500 spectrometer. The mass spectra were obtained using a JEOL JMS-D300 instrument.

Acknowledgements

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