JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 15
1992

The First Characterisation of a Glyoxal–Hydrogen Sulfide Adduct

Colin T. Bedford,*[a] Asad Fallah,[a] Eric Mentzer[b] and Francis A. Williamson[b]

[a] *School of Biological and Health Sciences, Polytechnic of Central London, 115 New Cavendish Street, London W1M 8JS, UK*
[b] *Production Chemistry Department, Shell UK Exploration and Production, 1 Altens Farm Road, Nigg, Aberdeen AB9 2HY, UK*

Aqueous glyoxal, which is used to scavenge hydrogen sufide in crude oil, reacts with an excess of the gas to yield a white crystalline material, the structure of which is deduced to be one of four isomers of *trans,trans*-4,4′,5,5′-tetrahydroxy-2,2′-bi(1,3-thioxolane) (**8a–d**).

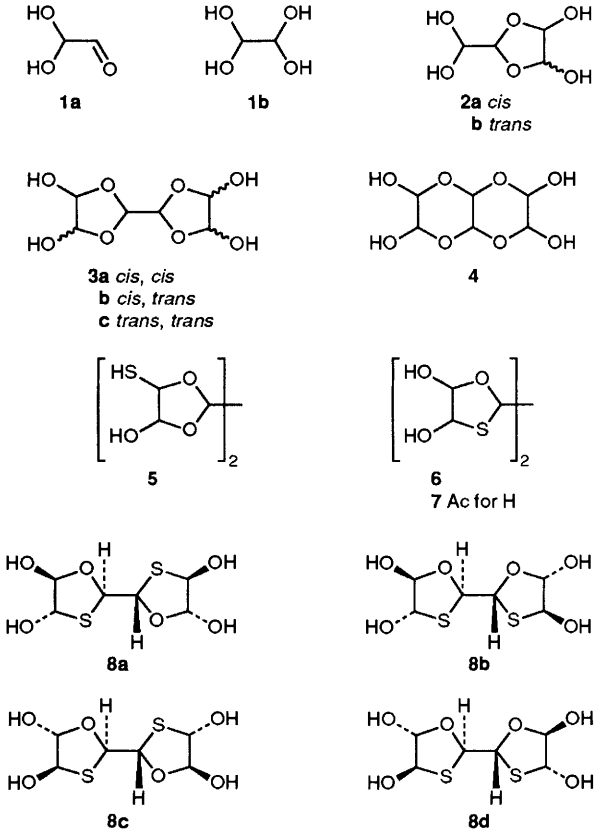
Crude oils produced off-shore are described as 'sour' if they contain dissolved hydrogen sulfide. Removal at the well-head of the hydrogen sulfide, a so-called 'sweetening' operation, may be accomplished by contacting the oil for several hours with aqueous solutions of glyoxal. Although the success of this scavenging procedure attests to the formation of one or more stable adducts of glyoxal and hydrogen sulfide, to our knowledge no report of such a structure has previously been made. Here, we describe the first isolation and characterisation of a crystalline adduct formed from three glyoxal and two hydrogen sulfide molecules: $(C_2H_2O_2)_3(H_2S)_2$.

Aqueous solutions of glyoxal are mainly mixtures of hydrated monomers **1**, dimers **2** and trimers **3**, as has been shown by extensive ^1H and ^{13}C NMR studies.[1–3] A crystalline material, available commercially, is a glyoxal trimer dihydrate depicted as having a fused 1,4-dioxane structure (**4**; stereochemistry unspecified), but it has the *cis,trans*-bi-1,3-dioxolane structure, **3b**, as can be quickly shown from its ^1H and ^{13}C NMR spectra in dry $(CD_3)_2SO$.[4]

When a stream of hydrogen sulfide was passed through a 40% glyoxal solution at room temperature, a single white crystalline compound of >90% purity (^1H NMR) was formed in 80% yield. Dry dioxane was found to be the best solvent for recrystallization, and doubly recrystallized material, m.p. 171–174 °C (decomp.), was assumed to be pure owing to the simplicity of its ^1H and ^{13}C NMR spectra in $(CD_3)_2SO$ (Figs. 1 and 2).

Spectroscopic evidence has allowed us to deduce that the new compound is one of four isomers of *trans,trans*-4,4′,5,5′-tetrahydroxy-2,2′-bi(1,3-thioxolane) **8a–d**. Attempts to obtain crystals suitable for X-ray crystallographic analysis were unsuccessful, although further studies are underway to secure such crystals.

Accurate mass measurement [CI(NH_3); *m/z* 260.0263] gave a molecular formula of $C_6H_{10}O_6S_2$, corresponding to an adduct: $(C_2H_2O_2)_3$ $(H_2S)_2$. The presence in the electron impact (EI) mass spectrum of a major ion (*m/z* 121; $C_3H_5O_3S$) having half the value of the (extremely weak) molecular ion and the simplicity of the ^1H and ^{13}C NMR spectra pointed to a centrosymmetrical compound composed of two C_3 moieties analogous to the starting bi-4,5-dihydroxy-1,3-dioxolane **3**. Replacement of two oxygen by two sulfur atoms in **3** to yield a centrosymmetrical compound can lead to either a bi-4-hydroxy-5-mercapto-1,3-dioxolane **5** or a bi-4,5-dihydroxy-1,3-thioxolane **6**. With near certainty, the mercapto compound was eliminated on consideration of its ^{13}C NMR data. These consisted of three signals due to three pairs of methine groupings, two of which were located at δ 85.3 and 87.5 implying the presence of two pairs of non-identical methine groupings with a sulfur and an oxygen attachment (–S–CH–O–). The other signal was located at δ 104.6 and was assignable to a pair of methine groupings with two oxygen



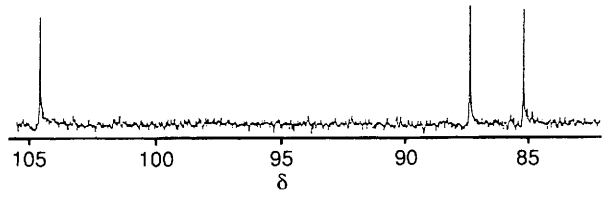


Fig. 1 ^{13}C NMR spectrum (67.8 MHz) of **8** in $(CD_3)_2SO$

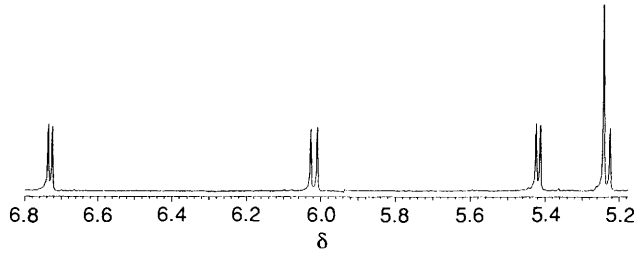


Fig. 2 ^1H NMR spectrum (270.05 MHz) of **8** in $(CD_3)_2SO$

attachments (–O–CH–O–), since it was similar to values seen in the parent 1,3-dioxolane **3** (δ 99.5–104.5).[2,3] These assignments are not compatible with the mercapto compound **5**, but are wholly consistent with the alternative structure, the bi-4,5-dihydroxy-1,3-thioxolane **6**. Other evidence also eliminates the mercapto compound as a possible structure (see below). The ^1H NMR (and COSY) spectral data provided further confirmation of the bis-thioxolane structure **6**, and, in addition, permitted a distinction between the two centrosymmetrical alternatives, a bi-*trans*-diol and a bi-*cis*-diol, to be made. In the ^1H NMR spectrum in the dry solvent (Fig. 2), the hydroxy protons at δ 6.02 and 6.73, each due to 2H, are coupled to two pairs of methine protons at δ 5.23 (*J* 7.32 Hz) and 5.42 (*J* 6.75 Hz), respectively, confirming the presence of two pairs of non-identical CHOH groupings. Since these vicinal protons are not coupled significantly to each other they must be *trans*. The only other signal, a two-proton singlet at δ 5.25, is assigned to the equivalent pair of protons attached to the two carbon atoms linking the two ring systems.

These assignments were further confirmed by the preparation (acetic anhydride–pyridine at 20 °C) of a crystalline tetraacetate derivative **7**, m.p. 231–232 °C, which exhibited spectral properties (IR, NMR, MS) consistent with the assignment.† Notably, no band in the solution IR spectrum was attributable to a thioacetoxy grouping (MeCO·S), confirming the absence of a mercapto group in the parent compound. Nor were there any signals in the ^1H and ^{13}C NMR spectra consistent with its presence.

Disregarding enantiomers, eight structures are possible for *trans,trans*-4,4′,5,5′-tetrahydroxy-2,2′-bi-(1,3-thioxolane). However, applying the constraint that the structure must be centrosymmetrical reduces this number to four. For convenience, the 2-H and the 2′-H have been drawns-*trans* in all four candidate structures **8a–d** and this allows easy recognition of two pairs of structures in which the hydroxy group attached to the carbon-bearing sulfur (C-5, C-5′) in each moiety is *syn* **8a** and **b** or *anti* **8c** and **8d** to the corresponding hydrogen attached to C-2 and C-2′, respectively. Note, **8a** and **c** are *meso* compounds and that **8b** and **d** each exist as a *dl* pair.

We thank Professor T. A. Crabb, Portsmouth Polytechnic for the provision of COSY NMR spectra (270 MHz), Dr J. E. Anderson, University College, London for the provision of 400 MHz ^1H NMR spectra, and Dr J. A. Ballantine, SERC Mass Spectrometry Service Centre, University of Swansea for the accurate mass measurements.

Received, 30th March 1992; Com. 2/01664C

References

1 E. B. Whipple, *J. Am. Chem. Soc.*, 1970, **92**, 7183; J. M. Kliegman, E. B. Whipple, M. Ruta and R. K. Barnes, *J. Org. Chem.*, 1972, **37**, 1276.
2 F. Chastrette, C. Bracoud, M. Chastrette, G. Mattioda and Y. Christidis, *Bull. Soc. Chim. Fr.*, 1983, **11**, 33.
3 C. Rabiller, *New. J. Chem.*, 1987, **11**, 419.
4 C. T. Bedford and A. Fallah, unpublished results.

† *Selected spectroscopic data* for **7**: IR ν/cm^{-1} (CH_2Cl_2) 1754; ^1H NMR (400 MHz) ($CDCl_3$) δ 2.11 (s, 3H, CH_3CO), 2.12 (s, 3H, CH_3CO), 5.42 (s, 2H, C-5, 5′), 6.13 (s, 2H, C-2,2′), 6.61 (s, 2H, C-4,4′); ^{13}C NMR (100.4 MHz) ($CDCl_3$) δ 20.88 (CH_3CO), 20.92 (CH_3CO), 83.3 (C-2,2′), 89.3 (C-5,5′), 101.0 (C-4,4′), 168.8 (CO), 169.3 (CO); MS *m/z* 410.0341 (M^+, $C_{14}H_{18}O_{10}S_2$, calc. 410.0341), 351, 350, 205 (base peak).