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CHARACTERISATION OF THE BISULPHITE ADDUCTS OF α,β-UNSATURATED ALDEHYDES BY NMR SPECTROSCOPY

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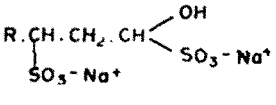
Abstract—The NMR spectra of a series of sodium alkane-1-sulphonates and sodium 1-hydroxyalkane-1-sulphonates show that the two systems may be characterised by the $-CH_2SO_3^-$ and $-CH(OH)SO_3^-$ resonance signals at $\delta = ca.$ 2.85 and *ca.* 4.4 ppm, respectively. Analysis of the NMR spectra of the bisulphite adducts formed by α,β-unsaturated aldehydes confirms the earlier structural assignments of the 1,3-disulphonic acid salts. The NMR spectra of the 1:1, 1:2, and 1:3 citral:bisulphite adducts indicate that the 1:2 adduct is disodium 1-oxo-3,7-dimethyloctane-3,6-disulphonate and not the 3,7-disulphonate as reported by previous workers. The acid-catalysed H/D exchange of 1-hydroxyalkane-1-sulphonates at the C-2 atom has been examined.

In the course of our study of the preservative action of sulphur dioxide (introduced as sodium bisulphite) upon citrus essential oils[2] and, in particular, in its reaction with citral, it was necessary to identify the structures of the initial bisulphite addition products. Previous workers have established that sodium bisulphite only reacts with isolated alkenes in the presence of oxygen or of oxidising agents to yield the anti-Markownikov alkanesulphonate salts via a radical mechanism,[3] whereas the reaction of sodium bisulphite with saturated aldehydes proceeds rapidly by an ionic pathway to form the well known 1-hydroxyalkane-1-sulphonates.[4] The course of the reaction of sodium bisulphite with α,β-unsaturated aldehydes has received less attention and, in the case of the reactions of terpenoid aldehydes evidence for the mode of formation and the structures of the adducts is ambiguous. In general, the structural determinations have been based upon the chemical reactivity of the adducts and, for example, the ability of a bisulphite adduct of an α,β-unsaturated aldehyde to react with semicarbazide or a hydrazine derivative has been taken as confirmatory evidence for the presence of a free aldehyde group. This deduction fails to take into account the facile reversibility of the formation of the aldehyde:bisulphite adducts over a wide range of pH values[5] and therefore throws considerable doubt on the validity of many structural assignments. Infrared spectral analysis of the bisulphite adducts also leads to ambivalent conclusions for, although the alkane-sulphonate salts produced by the addition of the bisulphite group to an alkenic bond, have been characterised[6,7] by the strong IR absorption bands near 1200, 1170 and 1050 cm^{-1}, we have found, not unexpectantly, that the aldehyde:bisulphite adducts also absorb strongly in the same regions; the major difference being a shift to higher frequency (1230 cm^{-1}) of the asymmetric νSO_2 vibrations. Only when these data are taken in conjunction with the absence of the CO stretching frequency from the IR spectra and the appearance of bands characteristic of the OH group is it possible to confirm the formation of the 1-hydroxyalkane-1-sulphonate. Such an analysis fails, however, in any study of the reaction of terpenoid aldehydes with sodium bisulphite, as acid-catalysed rearrangements frequently occur under the conditions prevalent in the formation of the bisulphite adducts with the formation of carbocyclic products and the concomitant loss of the CO function.[8]

It was considered that NMR spectral data could provide more conclusive evidence of the addition of the bisulphite group to both the alkene and aldehyde groups. Examination of the NMR spectra of a series of sodium alkane-1-sulphonates, measured in D_2O, show that the 1-methylene protons resonate at $\delta = 2.85 \pm 0.02$ ppm, whilst the signals for the methine proton of the sodium 1-hydroxyalkane-1-sulphonates resonate at lower field at $\delta = 4.38 \pm 0.1$ ppm. Previous workers have shown that the formation of a disulphonic acid salt from the reaction of α,β-unsaturated aldehydes with sodium bisulphite is not dependent upon the presence of an oxidant and it has been suggested that the reaction proceeds via an ionic Michael addition followed by addition to the CO group.[9] The reaction of acrolein with an excess of sodium bisulphite yields a disulphonic acid salt to which structure 1 (R = H) has been assigned[10] and sodium 1-hydroxyprop-2-ene-1-sulphonate has been shown to be the primary product.[10] As the rate of the 1,2-addition of the bisulphite ion to the CO group is faster than that of the 1,4-Michael addition, the regiospecific addition of the bisulphite ion to the alkenic bond must result from the slow irreversible reaction of the bisulphite ion with an equilibrium concentration of the free aldehyde. The three NMR resonance signals at $\delta = 4.64$ (dd, $-C\underline{H}(OH)SO_3^-$), 3.20 (t, $-CH_2SO_3^-$) and 2.33 ppm (m, $-C\underline{H}_2-$) provide unequivocal evidence for the structure of adduct 1 (R = H). Similarly, the NMR data, obtained for the adduct 1 (R = CH_3) from the reaction of crotonaldehyde with two equivalents of sodium bisulphite[11] and for the monosulphonate (2) formed from mesityl oxide[12] confirm the regiospecificity of the addition of the bisulphite ion to the α,β-alkenic bond.

The sodium salts of the alkane-1-sulphonic acids were converted into the corresponding pyridinium salts, which were soluble in organic solvents, but attempts to obtain the pyridinium salts of the 1-hydroxyalkane-1-sulphonic acids generally resulted in regeneration of the aldehydes.



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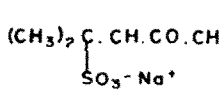

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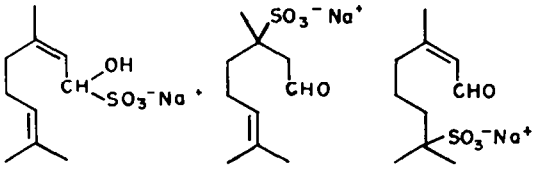
Similarly, although the methyl esters were readily obtained from the alkane-1-sulphonic acids through their reaction with diazomethane, the corresponding reactions on the aldehyde:bisulphite adducts and all attempts to prepare the trimethylsilyl esters via the pyridinium salts[13] failed.



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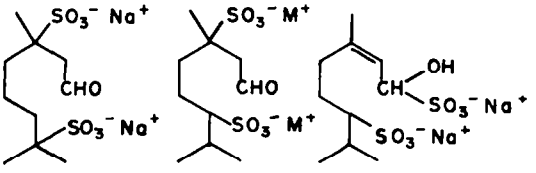

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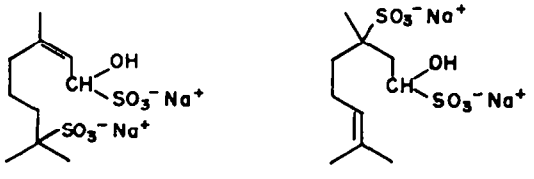
M = Na or C_5H_5NH



9 10

In the reaction of citral with sodium bisulphite there are three sites at which addition could occur, although it would be expected that addition at the isolated double bond would require the presence of an oxidant. Only one 1:1 citral:bisulphite adduct (3) has been isolated.[14] It is readily hydrolysed to the aldehyde and its formation has been used to purify citral.[15] Of the five isomeric disulphonate salts (6–10) it has been claimed, on the basis of the reactivity of the adduct with phenylhydrazine, that the compound normally isolated from the reaction of citral with an excess of sodium bisulphite has structure 6.[15] This report is contrary to the work of Hibbert and Cannon,[16] who claimed that, under similar reaction conditions, a labile disulphonate salt is formed which, by the action of acid, is converted into the stable disulphonate adduct (6). Conflicting evidence has also been presented for the stability of the adduct 6 in basic media[14,16] and it has been claimed that the labile disulphonate salt is converted under mildly basic conditions into a monosulphonate, formulated as 4 or 5. In view of the known stereospecificity of the reaction of isolated alkenes with sodium bisulphite and the relative stabilities of the alkane-1-sulphonates and the 1-hydroxy-alkane-1-sulphonates in alkali, the reported structures and transformations of the citral:bisulphite adducts appear inconsistent.

The NMR spectrum of the simple citral:bisulphite adduct identifies it as the 1-hydroxy-1-sulphonate salt (3; Table 1). Subsequent reaction of 3 with an excess of sodium bisulphite produced the hitherto unreported trisodium trisulphonate salt. Of the four isomeric structures possible for the trisulphonate, (12) would be consistant with previous reports of the reactivity of citral with sodium bisulphite.[15] The NMR spectrum of the compound (Table 1), however, provides unequivocal evidence for structure 11. In particular, the multiplicity of the signals for the 3-Me and the geminal dimethyl groups, together with the 1:1 integration of the signals characteristic of the $\rangle CH\cdot SO_3^-$ and the $-CH(OH)\cdot SO_3^-$ protons confirm the attachment of the $-SO_3^-$ groups to the 1-, 3- and 6-positions. Hydrolysis of the trisulphonate salt produced a 1:2 citral:bisulphite adduct, which is assumed to be identical with that isolated by Tiemann[14] from the reaction of citral with an excess of sodium bisulphite. The adduct was characterised as its bispyridinium salt, the NMR spectrum (Table 1) of which showed the presence of the aldehyde group, an isopropyl group, and the $CH_3C\cdot SO_3$ and $HC\cdot SO_3$ groups, thereby identifying the disulphonate salt as the 3,6-isomer (7) and not the 3,7-isomer (6) as previously reported.

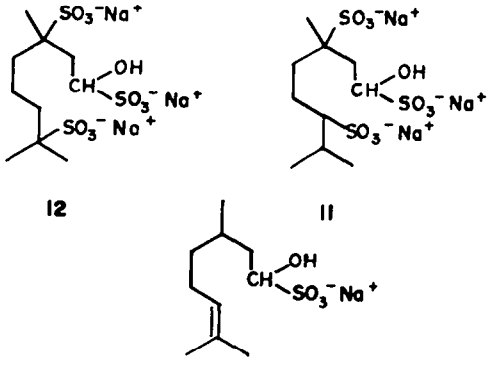


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Table 1. ^1H NMR chemical shift data for the bisulphite adducts of citral and citronellal

	1-CH	2-CH	3-Me	4/5-CH_2	6-CH	7-Me_2
3	4.55 (dd)	5.13 (m)	2.08 (s)	2.3→0.8	5.13 (m)	1.62 (d)
7	9.86 (t)	†	1.50 (s)	2.6→1.3	2.74 (m)	1.04 (dd)
9	3.64 (dd)	†	1.38 (s)	2.5→1.5	2.62 (m)	1.02 (dd)
13	3.93 (dd)	‡	0.83 (d)	2.2→0.7	5.06 (m)	1.60 (d)

†2-CH_2, together with 7-CH signals hidden beneath the 4/5-CH_2 signals.
‡2-CH_2 signals hidden beneath the 4/5-CH_2 signals.

Structures 7 and 11 are both consistent with the observed reactivity of α,β-unsaturated aldehydes and of isolated alkenic bonds. Citronellal reacts with sodium bisulphite to yield only the 1:1 adduct (13). An extended reaction with an excess of sodium bisulphite resulted in molecular rearrangement.[2]

In view of the reports that hydrolysis of the simple 1:1 bisulphite adducts from α,β-unsaturated aldehydes and from citral is not quantitative[15] and that sodium 1-hydroxyalk-2-ene-1-sulphonates may be converted into sodium 1-oxoalkane-1-sulphonates, it was considered of interest to follow the acid-catalysed hydrolysis of the bisulphite adducts of the α,β-unsaturated aldehydes by NMR spectroscopy. Contrary to expectations, disodium 1-hydroxypropane-1,3-disulphonate was stable in 25% (w/w) deuterosulphuric acid at room temperature but H/D exchange occurred rapidly on the C-2 atom (Fig. 1). Similarly, H/D exchange was observed on the C-2 atom of the sodium 1-hydroxyalkane-1-sulphonates without any observable hydrolysis. Predictably, the rate of exchange increased with the concentration of deuterosulphuric acid, indicating general acid-catalysis, and, although no resonance signals were observed for the aldehydes, it is assumed that the H/D exchange occurred on a low equilibrium concentration of the aldehyde. A comparison of the rate of H/D exchange of the Me protons of acetaldehyde and of its bisulphite adduct (Fig. 2) show that, with the exception of measurements in 20 and 25% deuterosulphuric acid in which the rates of exchange are comparable, the rate of the H/D exchange for acetaldehyde is faster that that for the bisulphite adduct. The acid-catalysed hydrolysis of the citral:bisulphite adduct led to the formation of rearrangement products.

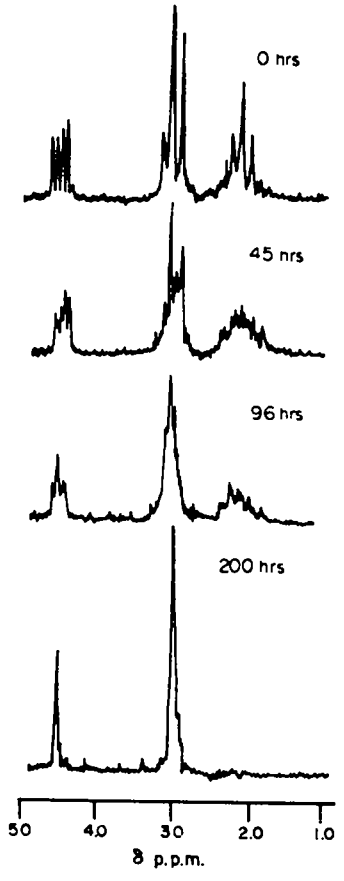

Fig. 1. H/D exchange of the 2-CH_2 group of disodium 1-hydroxypropane-1,3-disulphonate in 20% D_2SO_4.

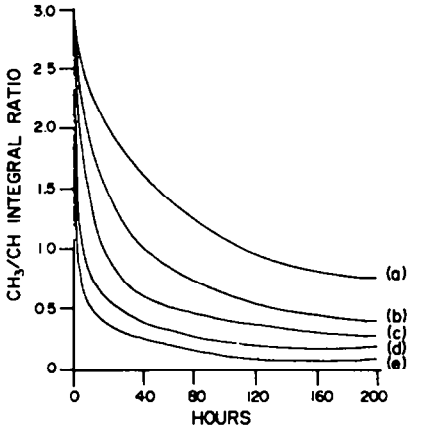

Fig. 2(A).

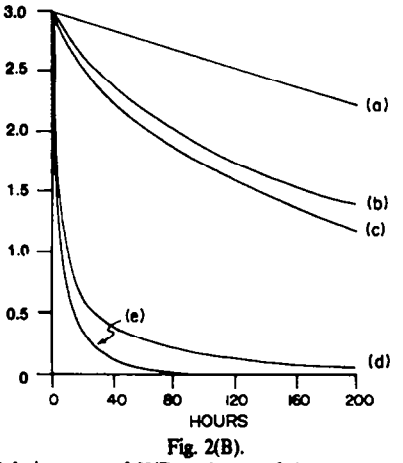

Fig. 2(B).

Fig. 2. Relative rates of H/D exchange of the CH_3 group of (A) acetaldehyde and (B) sodium 1-hydroxy-ethane-1-sulphonate. D_2SO_4 acid strength (a) 5% (b) 10% (c) 15% (d) 20% (e) 25%.

EXPERIMENTAL

IR spectra were obtained for Nujol mulls or liquid films between NaCl plates using a Perkin–Elmer 257 spectrophotometer. NMR spectra of the bisulphite adducts in D_2O or $CDCl_3$ were measured at 60 MHz using a Perkin–Elmer R12 instrument. Chemical shifts (δ) were measured relative to sodium 2,2-dimethyl-2-silapentane-5-sulphonate in D_2O and TMS in $CDCl_3$. The H/D exchange NMR studies on the bisulphite adducts were conducted using *ca.* 10% solns in D_2SO_4 (5–25% w/w).

Sodium alkane-1-sulphonates

(a) The appropriate alk-1-ene (0.08 mole) was heated for 2.5 hr at 110° in a sealed glass tube with $NaHSO_3$ aq (40% w/w, 28.6 g) and 2,2-di(t-butylperoxy)-butane (0.2 g) in MeOH (10 ml). The solid, obtained after removal of the solvent, was extracted with hot EtOH (3 × 50 ml). The cooled extracts yielded the sodium alkane-1-sulphonate (~5%) m.p. >300°.

(b) The appropriate 1-bromoalkane (0.1 mole) was heated under reflux with Na_2SO_3 (0.2 mole) in water (100 ml) for 2 days. The solid, obtained after removal of the water under reduced pressure, was triturated with hot EtOH (150 ml). The cooled ethanolic extracts yielded the sodium alkane-1-sulphonate (30–40%), which were recrystallised from EtOH (Table 2).

Table 2. Sodium alkane-1-sulphonates $CH_3(CH_2)_nSO_3^-Na^+$

n	Sulphur analysis Calc.	Found	NMR¶ (δ) $-CH_2\cdot SO_3^-$	νSO_2 (cm^{-1}) asym.	sym.
4‡	18.4	17.9	2.86	1200 1185	1050
5‡	15.5	15.3	2.85	1200 1180	1045
6‡	15.85	15.6	2.85	1198 1170	1055
7†§	14.8	15.3	2.87	1200 1170	1050
9†‡§	13.1	13.1	2.82	1205 1170	1035

†Prepared by method (a).
‡Prepared by method (b).
§Donated by Procter & Gamble Ltd.
¶Measured in D_2O.

Pyridinium alkane-1-sulphonates

Amberlite resin IR-120(H) was converted into the pyridinium ion form by passing pyridine through a column of the resin. Excess pyridine was removed by washing the resin well with water until the pH remained at *ca.* 8.0. The sodium alkane-1-sulphonate (1.0 g) in water (5 ml) was slowly passed through a 15 cm × 1.5 cm column of the resin and eluted with water (*ca.* 30 ml). Evaporation of the eluate under reduced pressure gave the thermally unstable pyridinium alkane-1-sulphonate (Table 3).

Table 3. Pyridinium alkane-1-sulphonates $CH_3(CH_2)_nSO_3^-C_5H_5NH^+$

n	Sulphur analysis Calc.	Found	NMR† (δ) $-CH_2\cdot SO_3^-$
4	13.9	13.35	2.92
5	13.1	13.0	2.95
6	12.4	12.3	2.93
7	11.7	12.1	2.95
9	10.6	11.1	2.95

†Measured in $CDCl_3$.

Methyl alkane-1-sulphonates

(a) The appropriate sodium alkane-1-sulphonate (1.0 g) in water (5 ml) was passed through a column of Amberlite resin IR-120(H). The effluent (*ca.* 30 ml) was evaporated in a freeze drying apparatus to yield the sulphonic acid. Addition of an etheral soln of diazomethane to the acid in MeOH gave the corresponding methyl ester.

(b) The appropriate sodium alkane-1-sulphonate (1.0 g) in MeOH (20 ml) was passed through a column of Amberlite resin IR-120(H), which had been washed with MeOH. The effluent was allowed to drop directly into an etheral soln of diazomethane. Evaporation of the solvent gave the methyl esters (90–100%). The purity of the products were confirmed by GLC analysis on Apiezon at 200° (Table 4).

Aldehyde : sodium bisulphite adducts

The appropriate aldehyde (0.1 mole) was shaken with sat $NaHSO_3$ aq (10 ml) for 5 min. The ppt was collected, washed with EtOH (10 ml) and with ether (10 ml), recrystallised from MeOH, and dried under high vacuum over silica to yield the sodium 1-hydroxyalkane-1-sulphonates (> 75%) (Table 5).

Table 5. Sodium 1-hydroxyalkane-1-sulphonates $CH_3(CH_2)_nCH(OH)SO_3^-Na^+$

n	Sulphur analysis Calc.	Found	NMR† (δ) $-CH(OH)SO_3^-$	νSO_2 (cm^{-1}) asym.	sym.
0	19.3‡	20.0	4.55	1220 1180	1040
1	19.8	19.6	4.30	1240 1180	1030
2	18.2	18.2	4.40	1230 1180	1040
5	14.7	14.7	4.35	1230 1175	1040
6	13.8	13.75	4.30	1230 1160	1040

†Measured in D_2O.
‡Monohydrate.

Reaction of acrolein with sodium bisulphite

Acrolein (13.8 g) was added over a period of 20 min to $NaHSO_3$ aq (75.5 g in 100 ml H_2O) with constant stirring. The temp of the mixture was maintained at *ca.* 18° and the pH of the medium was kept between 3.6 and 4.0 by the gradual inflow of SO_2. After the complete addition of the acrolein, the mixture was kept at 0° for 12 hr and then diluted with EtOH (100 ml). The ppt was collected, washed with ether (10 ml), and recrystallised from aqueous EtOH to give disodium 1-hydroxypropane-1,3-disulphonate (29.9 g, 36%) as its tetrahydrate. (Found: S, 19.3. Calc. for $C_3H_4Na_2S_2O_7\cdot 4H_2O$: S, 19.1%). NMR ($D_2O$) δ 4.64 (dd, 1H), 3.20 (t, 2H) and 2.33 ppm (m, 2H). IR 3550 (νOH), 1210 and 1180 (asym νSO_2) and 1030 cm^{-1} (sym νSO_2).

Reaction of crotonaldehyde with sodium bisulphite

Crotonaldehyde (10 g) and $NaHSO_3$ aq (40% w/w, 80 ml) were stirred at 20° for 8 hr whilst the pH of the soln was maintained between 3.6 and 4.0 by the gradual inflow of SO_2. The soln was kept at 0° and 12 hr and the volatile compounds removed under high vacuum to give a gum, which was dissolved in water (25 ml) and passed through a column of Amberlite resin IR-120 in its pyridinium ion form. The effluent was evaporated to yield *bispyridinium 1-hydroxybutane-1,3-disulphonate* as a thermally unstable oil (2.4 g, 4%). (Found: S, 11.7. $C_{14}H_{20}N_2O_7S_2$ requires: S, 11.2%). NMR ($CDCl_3$) δ 9.0–8.0 (m, 10H), 4.40 (dd, 1H), 3.10 (m, 1H), 2.24 (m, 2H) and 1.37 ppm (d, 3H). IR 3450 br (νOH), 1200 vbr (asym νSO_2) and 1030 cm^{-1} br (sym νSO_2).

Reaction of mesityl oxide with sodium bisulphite

Mesityl oxide (5.0 g) and $NaHSO_3$ aq (40% w/w, 30 ml) were stirred at 20° for 10 hr, whilst the soln was maintained at pH 3 by the gradual inflow of SO_2. Evaporation of the soln gave an impure solid product, which was passed through a column of

Table 4. Methyl alkane-1-sulphonates† $CH_3(CH_2)_nSO_3CH_3$

n	Sulphur analysis Calc.	Found	B.p.	NMR‡ (δ) $-CH_2\cdot SO_3^-$	νSO_2 (cm^{-1}) asym.	sym.
4	19.3	19.3	80° at 0.3 mm Hg	3.11	1355	1165
5	17.8	17.6	75° at 0.5 mm Hg	3.10	1350	1165
6	16.6	16.4	95° at 0.3 mm Hg	3.10	1350	1160
7	15.4	15.7	103° at 0.3 mm Hg	3.13	1360	1170
9	13.6	13.5	120° at 0.3 mm Hg	3.14	1355	1165

†Prepared by method (b).
‡Measured in $CDCl_3$.

Amberlite resin IR-120 in its pyridinium ion form to yield *pyridinium 2-methyl-4-oxopentane-2-sulphonate* as a pale yellow oil (2.0 g, 19%) which decomposed upon being heated. (Found: S, 11.9. $C_{11}H_{17}NO_4S$ requires: S, 12.4%). NMR ($CDCl_3$) δ 9.15–8.00 (m, 10H), 2.90 (s, 2H), 2.17 (s, 3H) and 1.49 ppm (s, 6H). IR 1700 (νCO), 1220 and 1160 (asym νSO_2) and 1010 cm^{-1} (sym νSO_2).

Reaction of citral with sodium bisulphite

(a) Citral (1 g) was added to $NaHSO_3$ aq (0.83 g in 15 ml H_2O) and AcOH (0.4 g) and the soln stirred at 20° for 20 min. The ppt was collected, washed with ether (2 × 5 ml), and recrystallised from aqueous EtOH to give the thermally unstable sodium 1-hydroxy-3,7-dimethylocta-2,6-diene-1-sulphonate (1.1 g, 72%). (Found: S, 12.4. Calc. for $C_{10}H_{17}NaO_4S$: S, 12.5%). NMR (DMSO-d_6) δ 5.13 (m, 2H), 4.55 (dd, 1H), 2.3–0.8 (m, 4H), 2.08 (s, 3H) and 1.62 ppm (d, 6H). IR 3560 and 3460 (νOH), 1210 and 1180 (asym νSO_2) and 1025 cm^{-1} (sym νSO_2).

(b) The normal citral:bisulphite adduct (7.0 g) was stirred at 20° for 6 hr with $NaHSO_3$ aq (10% w/w, 75 ml) whilst the pH of the soln was maintained below 3.0 by the gradual inflow of SO_2. Removal of the solvent and recrystallisation of the residue from aqueous EtOH gave *trisodium 1-hydroxy-3,7-dimethyloctane-1,3,6-trisulphonate* (8.1 g, 64%), m.p. >300° (dec.). (Found: S, 20.2. $C_{10}H_{19}Na_3O_{10}S_3$ requires: S, 20.7%). NMR (D_2O) δ 3.64 (dd, 1H), 2.62 (m, 1H), 2.5–1.5 (m, 7H), 1.38 (s, 3H) and 1.02 ppm (dd, 6H). IR 3560 and 3460 (νOH), 1205 and 1185 (asym νSO_2) and 1025 cm^{-1} (sym νSO_2).

(c) Conversion of the trisulphonate salt (2.0 g) into the pyridinium salt using Amberlite resin IR-120 in the pyridinium ion form produced *bispyridinium 1-oxo-3,7-dimethyloctane-3,6-disulphonate* (1.5 g, 79%) as a thermally unstable oil. (Found: S, 13.6. $C_{20}H_{30}N_2O_7S_2$ requires: S, 13.5%). NMR (D_2O) δ 9.86 (t, 1H), 9.0–8.0 (m, 10H), 2.74 (m, 1H), 2.6–1.3 (m, 7H), 1.38 (s, 3H) and 1.04 ppm (dd, 6H).

Reaction of citronellal with sodium bisulphite

Citronellal (5.1 g) and Na_2SO_3 (1.0 g) was added to $NaHSO_3$ aq (40% w/w, 10.5 ml) and the soln was stirred at 20° for 1 hr. A further volume of $NaHSO_3$ aq (40% w/w, 30 ml) was added and the soln stirred for a further 2 hr. The aqueous soln was extracted with ether (2 × 20 ml) and evaporated to yield a solid, which was recrystallised from EtOH to give sodium 1-hydroxy-3,7-dimethyloct-6-ene-1-sulphonate (4.0 g, 47%), m.p. >300° (dec.). (Found: S, 12.4. Calc. for $C_{10}H_{19}NaO_4S$: S, 12.4%). NMR (D_2O) δ 5.06 (m, 1H), 3.93 (dd, 1H), 2.2–0.7 (m, 7H), 1.60 (d, 6H), and 0.83 ppm (d, 3H). IR 3540 and 3460 (νOH), 1210 and 1180 (asym νSO_2) and 1045 cm^{-1} (sym νSO_2).

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