Synthesis, Structure and Absolute Configuration of a New Bromocamphorsulfonate Isomer

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Treatment of $(+)_{589}$-(1*R*)-3-*endo*-bromobornan-2-one ["$(+)_D$-α-bromocamphor"] in fuming sulfuric acid (34 % SO_3) gave $(-)_{589}$-(1*S*)-6-*endo*-bromo-2-oxobornane-8-sulfonic acid in a facile synthesis. The structure and absolute configuration of the NH_4^+ salt was determined by X-ray diffraction (orthorhombic, $P2_12_12_1$, a = 7.216(5), b = 10.793(3), c = 16.362(4) Å; Z = 4). The results imply that under these conditions sulfonation is accompanied by extensive rearrangement of the carbon skeleton amounting formally to inversion of the camphor segment. The structural changes are rationalized in terms of carbocation rearrangements consistent with results of other work relating to the racemization of camphor in sulfuric acid. The new isomer reported here is suggested as a member in the arsenal of easily-produced chiral resolving agents.

Sulfonic acid derivatives of (+)-camphor[§] and related compounds have been known for almost a century. Several of these acids continue to find widespread use as efficient resolving agents.[1] Characteristically, their syntheses involve direct sulfonation in strong acid media.[2] Thus, at an early stage it was noted that sulfonation of (+)-camphor in concentrated sulfuric acid led to racemization[2,3] of the camphor and its sulfonated product, whereas the (+)-α-halocamphors and their known sulfonic acid derivatives failed to racemize under the same conditions.[2,3,4] Later, these observations, combined with the results of isotopic labelling studies, were rationalized in terms of carbocation rearrangements in the strongly acidic media.[2]

Among the sulfonation products of (+)-(1*R*)-3-*endo*-bromobornan-2-one (**1**), only the 8-(**3**)[3,4,5] and 10-substituted (**2**)[6] sulfonic acid derivatives[#] have been reported so far. In both instances the (+)-(1*R*)-3-*endo*-bromobornan-2-one segment is retained unaltered after reaction. In this report we describe a new sulfonic acid derivative (**4**) whose structure and absolute configuration imply formal inversion of the camphor core and migration of the bromo substituent during synthesis.

Experimental

Specific rotations (in units of deg·dm^{-1}·g^{-1}·ml) and circular dichroism were monitored with a Perkin-Elmer P22 polarimeter (1 dm quartz cell) and a Roussel-Jouan Dicrographe model III, respectively. For ^{13}C NMR spectra, Jeol JNM-FX-200 and Brucker HX-270 spectrometers were used. 1,4-Dioxane was used as internal standard and chemical shifts δ (positive downfield) are given relative to this. Chemicals were reagent grade. Solid (+)-(1*R*)-3-*endo*-bromo-2-oxobornane-8-sulfonic acid was obtained from the corresponding ammonium salt[8] by ion exchange essentially as described by Kauffman.[9] The product

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[§]Unless otherwise stated, the signs of optical rotation given refer to 589 nm.

[#]The literature numbering of the bornane nucleus is not consistent throughout. The numbering adopted here is that recommended by IUPAC.[7]

was thoroughly dried *in vacuo* over P_4O_{10} and solid KOH.

*Ammonium (−)$_{589}$-(1S)-6-*endo*-bromo-2-oxobornane-8-sulfonate* (**4**). To a stirred solution of fuming sulfuric acid [made by mixing 90 ml 65% (w/w) SO_3 (in H_2SO_4) and 60 ml 96% sulfuric acid] was added (+)-(1*R*)-3-*endo*-bromobornan-2-one (**1**) (96 g), in portions at a rate such that the temperature did not exceed 30 °C at any time (ice bath). Stirring was continued for 1/2 h with cooling in ice and subsequently for 1.5 h at room temperature before the amber-coloured reaction mixture was poured onto crushed ice (1 kg). After 20 min a colourless solid had separated and was removed by filtration. Cooled to < 10 °C, the filtrate was neutralized with 12 M NH_3 (0.45 l) and was subsequently concentrated by rotary evaporation. During this process solid $(NH_4)_2SO_4$ crystallized in quantity and was removed, in batches, by filtration at intervals during the evaporation process. Each batch of crystals was extracted successively with portions of EtOH/H_2O (2:3, v/v), EtOH/H_2O (1:1) and absolute EtOH before evaporation of the resulting combined filtrates was resumed. At a low volume (< 100 ml) crystals of crude product deposited from the viscous solution. After cooling in ice the crystals were collected and washed with 60% EtOH and absolute EtOH. Evaporation of filtrate and washings produced an additional batch, and the combined products were recrystallized from boiling water to yield large rectangular blocks. Average yield 20 g. Calc. for $C_{10}H_{18}BrNO_4S$: C, 36.59; H, 5.53; Br, 24.34; N, 4.27; S, 9.77. Found: C, 36.3; H, 5.7; Br, 24.1; N, 4.2; S, 9.7. ^{13}C NMR (D_2O): δ 152.7 (*C*O), −0.5 (quart. *C*), −13.5 (*C*H_2), −15.8 (*C*H), −17.0 (quart. *C*), −24.3 (*C*H_2), −26.7 (*C*H), −27.8 (*C*H_2), −48.8 (*C*H_3), −59.6 (*C*H_3). Specific rot. (0.3% in water): $[\alpha]_{589}$ −63.7; $[\alpha]_{578}$ −66.7; $[\alpha]_{546}$ −81.0; $[\alpha]_{436}$ −208; $[\alpha]_{364}$ −576; $[\alpha]_{313}$ −2400. Circular dichroism (0.1% in water): $\Delta\varepsilon_{292}$(max) −6.3 $M^{-1} \cdot cm^{-1}$. These values for the optical activity did not change on further recrystallization. In a separate experiment the production of (−)-(1*S*)-6-*endo*-bromo-2-oxobornane-8-sulfonate (**4**) from (+)-(1*R*)-3-*endo*-bromo-2-oxobornane-8-sulfonic acid (**3**) was demonstrated. Employing the latter (62 g, 0.20 mol) as starting material *in lieu* of (+)-(1*R*)-3-*endo*-bromobornan-2-one (**1**), the above procedure was repeated at half-scale. A total of 7.5 g of crude product was obtained. Recrystallization of this yielded optically pure ammonium (−)-(1*S*)-6-*endo*-bromo-2-oxobornane-8-sulfonate (0.9 g), as evidenced by the ^{13}C NMR spectrum and specific rotations.

X-Ray structure determination

Relevant crystal data are summarized in Table 1. The crystal density was determined by flotation using 1,2-dibromopropane and 1-bromonaphthalene. A regular colourless crystal of dimensions 0.35×0.15×0.13 mm with faces {012}, {120}, and {133} was mounted with the rotational axis parallel to the longest edge and the *a* axis. Precession and Weissenberg photographs indicated the crystal system to be orthorhombic with systematically absent reflections (*h*00 for $h \neq 2n$, 0*k*0 for $k \neq 2n$, and 00*l* for $l \neq 2n$) uiquely determining the space group as $P2_12_12_1$ (D_2^4, No. 19). For intensity data collection an Enraf-Nonius CAD4 automatic diffractometer with standard low-tem-

Table 1. Crystal data.

Formula	$C_{10}H_{18}BrNO_4S$
Formula weight/g·mol^{-1}	328.26
Space group	Orthorhombic, $P2_12_12_1$ (No. 19)
a/Å	7.216(5)
b/Å	10.793(3)
c/Å	16.362(4)
V/Å^3	1274
D_{obs}/g·cm^{-3} (295±2 K)	1.65(1)
D_{calc}/g·cm^{-3} (105±5 K)	1.711
Z	4
μ/cm^{-1}	33.53
F(000)/electrons	672

perature equipment (providing temperature stability of ± 0.5 K at working temperature) was used. All diffractometer work was done at 105 ± 5 K with graphite-crystal-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). The lattice constants were determined by a least-squares analysis of 2θ, ω, and χ values for 18 carefully centered reflections ($23° > \theta > 17°$). For 6 of these reflections the centering was checked for every 300 reflections measured. The intensity data were collected using the $\omega/2\theta$-scan technique with θ varied between 1 and 32.5°. Data were collected for $-10 \leq h \leq 10$, $0 \leq k \leq 16$, and $0 \leq l \leq 24$. The range of each scan was $(1.0 + 0.35\tan\theta)°$ with the background extending over an angle of 25 % of this range on either side. For each reflection a pre-scan with scan speed 5.6° min^{-1} was performed, and if $\sigma(I)/I < 0.01$ or $\sigma(I)/I > 1.0$ no further scan was carried out. However, if after the pre-scan $0.01 \leq \sigma(I)/I \leq 1.0$, a final scan with adjusted slower scan speed was performed, the maximum scan-time (including background) not exceeding 150 s. The intensities of three reference reflections (200, 022, and 006) monitored for every 10,000 sec of irradiation time displayed no significant intensity loss over the entire period of exposure. All computations were performed with the Enraf-Nonius Structure Determination Package Vax SPD 3.0 and a Microvax II computer. A total of 4581 reflections, all unique, were measured and reduced, including corrections for Lorenz and polarization effects and for absorption to values of $|F_o|$ and $\sigma(F_o)$. 3733 reflections for which $I > 3\sigma(I)$ were included in the final structure analysis.

The Br atom was located from the Patterson map, and all other atoms were located from subsequent Fourier syntheses. Atomic coordinates for all atoms and anisotropic thermal parameters for non-hydrogen atoms were refined by a full-matrix least-squares refinement minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + (p/4)F_o^2$ with $p = 0.04$ (this value chosen on the basis of an optimization procedure so as to allow $\Sigma w \Delta F^2$ to be close to being uniformly distributed in $|F_o|$). In the final refinement cycles, hydrogen-atom isotropic thermal parameters were fixed at B = 1.5. After the final refinement cycle the R values were R = 0.033 and R_w = 0.040, and no parameter was shifted by more than 0.02σ. A final Fourier synthesis was essentially featureless, with 10 largest residuals between 0.4 and 0.7 e Å^{-2}. The absolute configuration of the anion (1*S*) was determined by the Rogers test.[10] Upon a separate refinement of structural parameters with the imaginary term of the anomalous dispersion factors omitted ($f'' = 0$), structure factor amplitudes, with f'' terms now included, were calculated on the basis of the refined model [(1*S*) configuration] giving R = 0.034 and R_w = 0.040. With the signs of all positional coordinates inverted – corresponding to the (1*R*) configuration – a similar calculation gave R = 0.069 and R_w =

Table 2. Atomic fractional coordinates for ammonium $(-)_{589}$-(1*S*)-6-*endo*-bromo-2-oxobornane-8-sulfonate.[a]

Atom	*X*	*Y*	*Z*
Br1	0.11092(4)	0.24114(2)	0.18580(2)
S1	−0.29258(9)	−0.01787(6)	0.47429(4)
O1	−0.2907(3)	0.4011(2)	0.2011(1)
O2	−0.1154(3)	0.0240(2)	0.5076(1)
O3	−0.4521(3)	0.0362(2)	0.5156(1)
O4	−0.3060(4)	−0.1527(2)	0.4692(1)
N1	0.2230(4)	−0.1055(2)	0.4752(2)
C1	−0.2509(4)	0.1945(2)	0.2602(2)
C2	−0.2631(4)	0.3356(3)	0.2601(2)
C3	−0.2287(4)	0.3796(2)	0.3472(2)
C4	−0.1866(3)	0.2571(3)	0.3911(1)
C5	0.0038(4)	0.2131(3)	0.3599(2)
C6	−0.0406(4)	0.1677(3)	0.2724(2)
C7	−0.3237(4)	0.1670(2)	0.3492(2)
C8	−0.2987(4)	0.0284(2)	0.3698(2)
C9	−0.5277(4)	0.2018(3)	0.3594(2)
C10	−0.3396(4)	0.1303(3)	0.1884(2)
H1	0.104(8)	−0.069(5)	0.482(3)
H2	0.237(7)	−0.117(5)	0.422(3)
H3	0.219(8)	−0.179(5)	0.493(3)
H4	0.323(7)	−0.053(5)	0.496(3)
H31	−0.137(7)	0.435(4)	0.352(3)
H32	−0.328(7)	0.423(5)	0.364(3)
H41	−0.198(7)	0.266(5)	0.451(3)
H51	0.050(7)	0.146(5)	0.391(3)
H52	0.092(6)	0.282(4)	0.360(3)
H61	−0.017(7)	0.077(4)	0.264(3)
H81	−0.191(7)	−0.004(4)	0.349(3)
H82	−0.392(8)	−0.013(4)	0.347(3)
H91	−0.597(7)	0.145(4)	0.334(3)
H92	−0.557(7)	0.207(4)	0.419(3)
H93	−0.553(7)	0.283(4)	0.337(3)
H101	−0.291(7)	0.160(5)	0.139(3)
H102	−0.329(7)	0.044(4)	0.193(3)
H103	−0.464(7)	0.149(4)	0.181(3)

[a]Estimated standard deviations in units of the last significant digit are given in parentheses.

0.088, clearly indicating this to be a significantly poorer model.

Table 2 gives atomic fractional coordinates for all atoms. A table of anisotropic thermal parameters for non-hydrogen atoms and a listing of structure factor amplitudes are available from the authors on request.

Results

Treatment of (+)-(1*R*)-3-*endo*-bromobornan-2-one (**1**) in SO_3(34 %)/H_2SO_4 afforded a new bromocamphorsulfonate isomer, isolated in ~ 15 % yield as the optically pure NH_4^+ salt. The same product was also obtained when (+)-(1*R*)-3-*endo*-bromo-2-oxobornane-8-sulfonic acid (**3**) was employed as the starting material, although a poorer yield was observed. The complete structure of the new isomer did not follow unambiguously from spectroscopic evidence alone, and a single-crystal X-ray structure determination of the ammonium salt was undertaken. This identified the product as ammonium (−)-(1*S*)-6-*endo*-bromo-2-oxobornane-8-sulfonate, depicted in Fig. 1.

Despite the fact that both of the individual reagents (**1** and **3**) indisputably have the (1*R*) absolute configuration,[11,12] the resulting product (**4**) displays the inverted, i.e. the (1*S*) configuration. This is in accord with the relative signs of the optical rotations. Furthermore, the bromo substituent, present in the 3-*endo* position of either reagent, is now located at the 6-*endo* site in the common product.

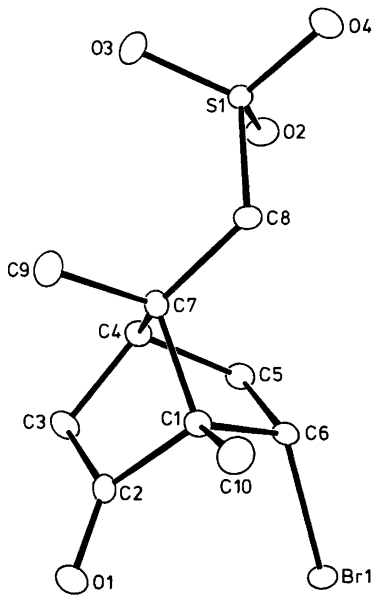


Fig. 1. Molecular geometry and atom numbering in the $(-)_{589}$-(1*S*)-6-*endo*-bromo-2-oxobornane-8-sulfonate anion. Hydrogen atoms are omitted for clarity.

Table 3. Selected interatomic distances (Å).[a]

Br1–C6	1.957(2)
S1–O2	1.461(2)
S1–O3	1.458(2)
S1–O4	1.462(2)
S1–C8	1.781(2)
O1–C2	1.214(3)
C1–C2	1.526(3)
C1–C6	1.558(4)
C1–C7	1.576(3)
C1–C10	1.507(4)
C2–C3	1.523(4)
C3–C4	1.535(4)
C4–C5	1.541(3)
C4–C7	1.548(3)
C5–C6	1.547(4)
C7–C8	1.545(3)
C7–C9	1.528(4)

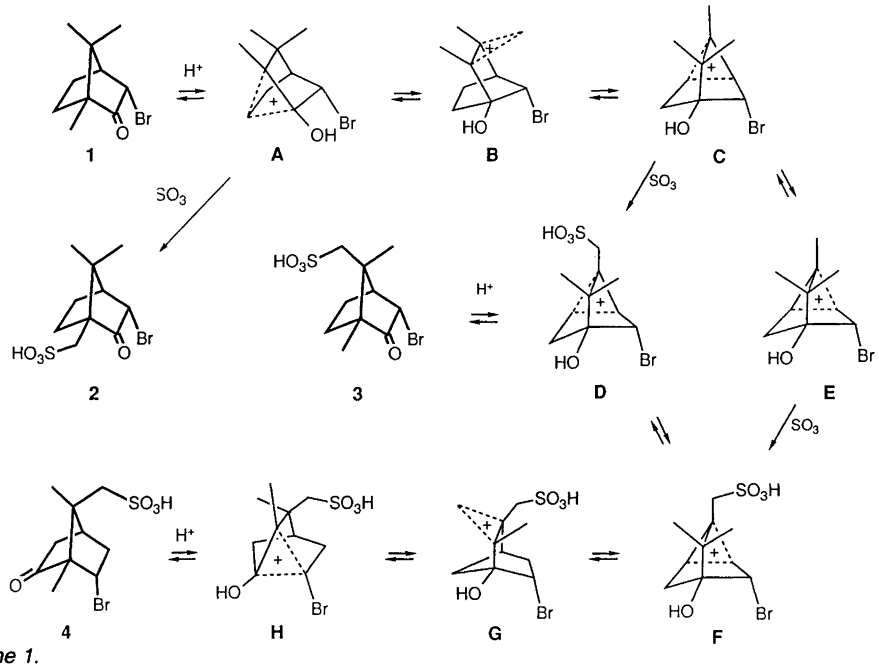
[a]Estimated standard deviations in units of the last significant digit are given in parentheses.

Apart from the inversion aspect, the camphor backbone is preserved and the molecular dimensions are consistent with those of related structures.[11–13] Table 3 lists important bond lengths.

Complete tables of interatomic distances, bond angles and hydrogen-bonding contact distances are available from the authors on request.

Discussion

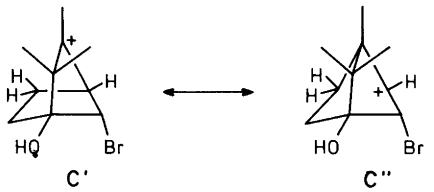
Reported syntheses of (+)-(1*R*)-3-*endo*-bromo-2-oxobornane-8-sulfonic acid (**3**) (Scheme 1) from (+)-(1*R*)-3-*endo*-bromobornan-2-one (**1**) have employed either oleum[3,5,7–9,14,15] or $ClSO_3H$ in $CHCl_3$[4,5] as sulfonating media, whereas (+)-(1*S*)-3-*endo*-bromo-2-oxobornane-10-sulfonic acid (**2**) was produced[6] with sulfuric acid in acetic anhydride. For the sulfonations in oleum yielding **3**, the amount of SO_3 was stoichiometric[14,15] or less,[9] with initial SO_3 concentrations of 7 %[9,14,15] or, in one case, 10 %.[3] Here, employing fuming sulfuric acid (34 % SO_3) in excess, the new



Scheme 1.

isomer, viz. (−)-6-*endo*-bromo-2-oxobornane-8-sulfonic acid (**4**) was obtained as the main product and was isolated as the NH_4^+ salt. Initial experiments, aimed at optimising yields, indicated that for lower initial concentrations, and hence a smaller excess of SO_3 in sulfuric acid, comparable amounts of both **3** and **4** were produced. Thus, for constant reaction time and temperature, specificity is markedly linked to the initial SO_3 concentration, with **4** dominating over **3** in the products at the higher concentrations.

Both isomers **2** and **3** may be viewed, simply, as substitutional derivatives of **1**, obtained by sulfonation at C-10 and C-8, respectively, and with the 3-*endo*-bromobornan-2-one segment otherwise unaltered. In contrast, the new isomer (**4**), also synthesized from (+)-**1**, displays a formally inverted bornan-2-one skeleton with the bromo substituent, originally present at the 3-*endo* position in **1**, now occupying the 6-*endo* site. Similar results have been reported for the parallel chloro systems,[16] where treatment of (+)-3-*endo*-chlorobornan-2-one in $ClSO_3H$ produced the chloro analogue of **4**[17,18] as a by-product (8%) in addition to the main component (+)-3-*endo*-2-oxobornane-8-sulfonic acid. Also, the (+)-3,8-dihalogenobornan-2-ones (halogen substituents: Cl,Cl, Br,Br, Cl,Br or Br,Cl) rearrange to the corresponding (−)-6,8-dihalogenobornan-2-ones, and (+)-8-chlorobornan-2-one racemizes in oleum (10% in SO_3).[18,19] In all these instances the chiral bornan-2-one segment of the precursors appears inverted in the products. Bornan-2-one itself is known to racemize in sulfuric acid,[3] and the steric course of this reaction has been explored by Finch and Vaughan.[2] Employing ^{14}C-labelled (+)-bornane-2-one-9-^{14}C, they established that upon racemization in sulfuric acid the C-9 and C-10 methyl groups had interchanged, producing (−)-bornane-2-one-10-^{14}C, whereas the C-8 group, sulfonated or not, remained in the same position. Based on this and additional evidence, the bornan-2-one racemization was rationalized[2] in terms of a series of carbonium ion rearrangements. Later, in a computer-aided enumeration[19] this rearrangement sequence emerged as the least complex of several likely pathways composed of an array of generally accepted, standard rearrangement steps. Our proposal for the production of the isomers **2**, **3** and **4** is depicted in Scheme 1. Each isomer arises through sulfonation of a methyl group at various stages along the rearrangement sequence starting with **1**. Although, as already discussed, the pro-



Scheme 2.

duct specificity is clearly medium dependent, the mechanistic paths to all three isomers are included here in a single scheme. Species denoted with letters are postulated, and the almost classic question of whether such species represent true intermediates or transition states is left open. The entity **C** derives from **1** through a series of rearrangements including an *exo*-methyl shift. The two canonical structures of which **C** may be a hybrid are the classical cations **C'** (tertiary) and **C''** (secondary) (Scheme 2). The tertiary ion would be expected to contribute the more, not least due to the inductive effect of the bromo substituent which would destabilize **C''**. Overall, sulfonation at the methyl so as to produce **D** would be facile. The sulfonated isomer **3** may result from a rearrangement sequence essentially the reverse of that yielding **C** from **1**. By a similar argument, **2** is obtained from **A**.

The rearrangement step **D** $\rightleftharpoons$ **F** involves a hydride transfer analogous to the norbornyl 6,2-H shift and generally termed a *hominal* shift by Nickon *et al.*[20] In principle, the hydride shift may also precede the sulfonation step, thus providing the alternative path **C** $\rightleftharpoons$ **E** $\rightleftharpoons$ **F**. However, as argued later, the path via **D** is likely to be the preferred one. Finally, the sequence producing **4** from **F** is essentially parallel to that producing **1** from **C**, except for the presence of the sulfonic acid group and the different location of the bromo substituent. It is worth noting that in the case of the non-halogenated ketone camphor, ions **C** (Br = H) and **E** (Br = H) become enantiomers, as do each of the pairs **D** (Br = H)/**F** (Br = H) and **3** (Br = H)/**4** (Br = H). Thus, for Br = H the hominal hydride shifts represent racemization steps. In this way the mechanism depicted in Scheme 1 accords with that proposed by Finch and Vaughan[2] for the camphor system. In the present system, however, no racemization can occur as long as the stereogenic [21] center at the site of the bromo substituent remains unaffected.

In ~ 34 % SO_3, isomer **4** clearly is produced in greater quantity than **3**; however, in 7 % SO_3 this trend is reversed for similar reaction times and temperatures. In a separate experiment, **3** was noted to isomerise to **4** in ~ 34 % SO_3, but the reverse did not apply at either concentration of SO_3. It cannot be ruled out that **3** is thermodynamically preferred in 7 % SO_3 and **4** in 34 % SO_3, with the isomerisation **4** → **3** being slow in the weaker acid. However, a more plausible explanation is that **4** is thermodynamically preferred, overall, and that the preference for **3** seen with 7 % SO_3 is kinetically controlled. This interpretation falls in line with the known facts that the (+)-3,8-dihalogenobornan-2-ones rearrange[17,18] to the corresponding (−)-6,8-dihalogenobornan-2-ones in sulfuric acid (10 % SO_3), and that some (−)-6-chloro-2-oxobornane-8-sulfonic acid is produced when (+)-3-*endo*-chlorobornan-2-one is sulfonated in chlorosulfonic acid. From these examples and that of the present study it would appear that with substituents such as −Cl, −Br and $-SO_3H$, the 6,8-disubstituted bornan-2-one systems are more stable than their 3,8-disubstituted equivalents, at least in the media investigated. This situation may arise from a greater mutual dipole-dipole repulsion between the vicinal carbonyl and C-halogen dipoles in the 3,8-disubstituted systems.[22]

Whereas in sulfuric acid of even moderate SO_3 concentration (+)-bornan-2-one readily iomerizes[2,3] to (−)-bornan-2-one, with or without sulfonation, the equivalent structural change for 3-*endo*-bromobornan-2-one, so far seen only for the sulfonated product, requires more stringent conditions (34 % SO_3). This may be due[2] to differences in the willingness of **C** and **D** to undergo the hominal hydride shift relative to **C** (Br = H) and **D** (Br = H), respectively. The imagined secondary carbocation ion **C''** should be constitutionally better suited to undergo the hydride shift than **C'**. In line with the argument presented earlier (Scheme 2), the Br in cation **C** diminishes its **C''** character and hence would lessen its tendency to undergo the hydride shift. Furthermore, by the same argument the sulfonic acid group in **D** and **D** (Br = H) should enhance the secondary carbonium ion character, and thus favour the hydride shift. Hence, for the isomerisation step, **D** (Br = H) should be the most reactive, **C** the least reactive, and **D** and **C** (Br = H) should be of intermediate reactivity. The paths via **D** or **D** (Br = H) are thus favoured over those via **E** or **E** (Br

= H). This interpretation agrees with the fact that for the (+)-bornan-2-one system in sulfuric acid, the sulfonated product **3** (Br = H) and the enantiomer **4** (Br = H) were found to be fully racemized, whereas recovered bornan-2-one from the same reaction mixture was only partially so.[2] On this basis only very little, if any, (−)-6-*endo*-bromobornan-2-one would be expected to arise during sulfonation of (+)-3-*endo*-bromobornan-2-one.

For almost a century the hitherto known isomers of bromocamphorsulfonate, i.e. **2** and **3**, have found widespread use for optical resolution work.[1] Based on their past merit in this respect and in view of its relatively easy synthesis, the new isomer described above is recommended as another member in the arsenal of easily produced, chiral resolving agents.

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