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# Dibromocamphor Bromination Product of 1-Hydroxycamphene Skeleton

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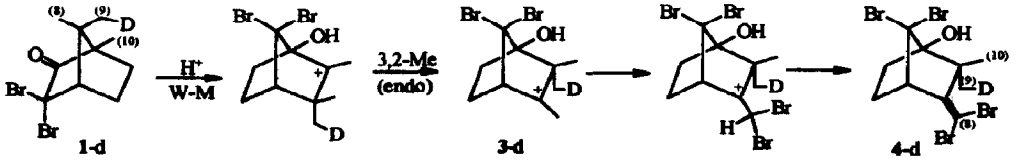
*Abstract:* The formation of 7,7-dibromo-3-dibromomethylene-2,2-dimethyl-1-hydroxynorbornane as a minor-product of the 3,3-dibromocamphor bromination was found. The structure of this compound was established on the basis of spectral data analysis. The occurrence of alcohol in the bromination product mixture can be taken as evidence supporting the assumed mechanism of camphor methyl group bromination.

The bromination of 3,3-dibromocamphor (**1**) in chlorosulfonic acid leading to the formation of 3,3,8-tribromocamphor (**2**) as the main product is the essential step in the stereospecific synthesis of 8-bromo-camphor[1]. The bromination process is believed[2] to proceed by the electrophilic substitution (or addition preceded by proton elimination) at the methyl carbon which is directly bounded to the carbocationic centre of the substituted hydroxynorbornyl cation **3**; this is followed by a reversed sequence of rearrangements. The tertiary alcohol character of the intermediate was never supported experimentally by the isolation of a product of the alcohol structure.

We would like to report that a careful chromatographic examination of the post-reaction mixture of bromination of **1** ($[\alpha]_D$= +38.9°) led us to isolate, beside the main product **2** and the known tetrabromo-campheniloneˡ, a few minor-products of an unknown structure[3]. One of them, **4**, of mp.121-122°C (from $CCl_4$) and $[\alpha]_D$= -41.0° (c=1, $CHCl_3$), recovered from a silica gel column by 20% PhH-hexane with 6% yield, revealed no IR carbonyl absorption. The elemental composition of **4** was found to be $C_{10}H_{12}OBr_4$ on the basis of a combustion analysis and the HRMS of M-1, m/z 467 [from a quintet of m/z: 463/465/467/469/471][4]. The presence of an OH group was demonstrated by an IR absorption (KBr) due to the O-H and C-O stretching vibration at 3540 $cm^{-1}$ and at 1198 $cm^{-1}$ and 1125 $cm^{-1}$, respectively and confirmed by the deuterium exchangeable proton resonance absorption at 2.38 ppm. Both the elemental composition and the IR absorption at 1622$cm^{-1}$ as well as the absence of an ethylene proton signal in the NMR spectrum suggested the presence of a tetrasubstituted polarized double bond in the molecule. The exocyclic character of the double bond and its position in **4** followed from its $^1$H-NMR and $^{13}$C-NMR spectra[5]. The proton resonance absorption at (ppm)1.56, 1.98, 2.11, 2.19 and 3.55, which could be precisely analyzed when recorded at 500 MHz (the results were confirmed by $^1$H-$^1$H-COSY), revealed a coupled system of five protons of the structure unit comprising C(4)H-C(5)$H_2$-C(6)$H_2$. The two three-proton singlets of the geminal methyls appeared at 1.48 ppm and 1.75 ppm; however, when the C-9 methyl of the starting **1** was labelled with deuterium[6] the intensity of the former in **4**-d analogue corresponded to two protons only which immediately made it possible to identify both methyls. The carbon absorption of C-8 was shifted upfield to 81.41 ppm due to the shielding effect exerted by the two bromines, and appeared in the proton-coupled spectrum as a

doublet because of a long-range coupling of the carbon to H-4 ($^3J_{CH}$= 4.0 Hz, COLOC) contrary to the nodule shape of the most deshielded C-3 and the quaternary C-1, C-2 and C-7. The resonance assignments for C-9 and C-10 were based on proton-carbon correlation ( $^1$H-$^{13}$C HETCOR).

The above observations indicate that the obtained product **4** has the structure of 7,7-dibromo-3-dibromomethylene-2,2-dimethyl-1-hydroxynorbornane[7]. Along with the retained optical activity of **4**, the structural assignments supported the assumption of the alcohol character of the carbocationic intermediates which are involved in the electrophilic substitution mechanism and are brominated at the stage of cation **3**. Additionally, since the whole amount of deuterium labelling was found in the C-9 methyl of **4-d**, the 3,2-methyl shift had to occur from the endo face. The supposed mode of the **4** formation, shown for the deuterated analogue, is presented in the scheme.

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**References and Notes**

1. Cachia, P.; Darby, N.; Eck, C.R.; Money, T. *J.Chem.Soc.Perkin I*, **1976**, 359-362
2. Dadson, W.M.; Money, T. *J.Chem.Soc.,Chem.Commun.*, **1982**, 112-113
3. Antkowiak, R.; Antkowiak, W.Z. submitted to publication in *Pol.J.Chem.*
4. HRMS, found (for M-H): m/z 466.75025, calcd. for $C_{10}H_{11}O^{79}Br_2{}^{81}Br_2$:m/z 466.75024. HRMS, found [for (M-H)-$Br_4$]: m/z 147.080163, calcd. for $C_{10}H_{11}O$: 147.080990. Anal.calcd. for $C_{10}H_{12}OBr_4$: C, 25.65; H, 2.58; Br, 68.35; found: C, 25.60; H, 2.75; Br, 68.18.
5. The methyl carbons of **4** bear the same numbers as they used to have in the parent **1**. $^1$H-NMR (500.135 MHz, $CDCl_3$)δ: 1.48 [s, 3H, 9-$CH_3$], 1.56 [ddd, 1H, J:12.5 Hz (gem.), 10.1 Hz (to 6endo), 5.5 Hz (to 6exo), H-5endo], 1.75 [s, 3H, 10-$CH_3$], 1.98 [ddd, 1H, J:12.5 Hz (gem.), 10.1 Hz (to 5endo), 3.1 Hz (to 5 exo), H-6endo], 2.11 [td, 1H, J:12.5 Hz (gem.), 12.4 Hz (to 5exo), 5.5 Hz (to 5endo), H-6exo], 2.19 [dddd, 1H, J:12.5 Hz (gem.), 12.4 Hz (to 6exo), 3.1 Hz (to 6 endo), 5.1 Hz (to 4), H-5exo], 2.38 [s, 1H, OH], 3.55 [d, 1H, J=5.1 Hz (to 5 exo), H-4]. $^{13}$C-NMR (125.759, $CDCl_3$)δ: 22.39 [q, C-10], 25.06 [t, C-5], 26.26 [q, C-9], 28.03 [t, C-6], 46.77 [s, C-7], 60.54 [d, C-4], 73.22 [s, C-2], 81.41 [s, C-8], 88.89 [d, C-1), 151.40 [s, C-3].
6. Dadson, W.M.; Hutchinson, J.H.; Money, T. *Can.J.Chem.* **1990**, *68*, 1821-1828
7. Very recently, the structure was confirmed by an x-ray diffraction currently investigated by Kubicki, M. et al. The results will be published separately in *Acta Cryst.* when they are completed.

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