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The Solvomercuration, Bromination, and Related Reactions of 1,5-Dimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one and Its Related Compounds

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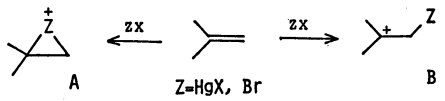
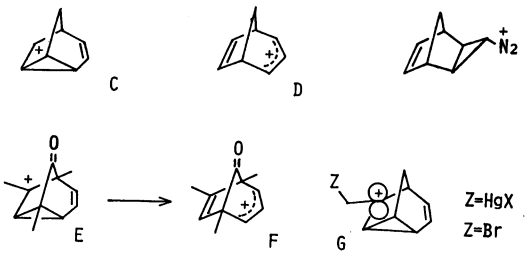
The solvomercuration-demercuration reactions of 1,5-dimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one (**1**), its corresponding alcohol, and 5,8-dimethyl-9-methylenetricyclo[3.3.1.0^{2,8}]non-3-en-7-one (**2**) were investigated. In all cases, the solvent was stereospecifically incorporated on the exomethylene group, and the original tricyclic skeleton did not undergo rearrangement. Similarly, **1** and **2** underwent a stereospecific bromination on the exomethylene group by means of the reaction with pyridinium tribromide. These results suggest the stabilization of the formal cyclopropylcarbinyl cation intermediates by the adjacent acetoxymercury moiety or the bromine atom. On the other hand, the reaction of NBS–MeOH or NBS–H_2O with **1** afforded an addition product on the exomethylene group, and 1,4-addition originated from the cleavage of the cyclopropane ring, while with **2** the reaction afforded only an addition product on the exomethylene group. The difference in this reaction mode is discussed on the basis of the solvent effect and the ring strain of **1**.

The solvomercuration reaction of olefins has been widely studied and has been the subject of frequent reviews.[1-3] Mercurinium ions of Type (**A**) have been postulated as the intermediates in the electrophilic addition of mercury(II) acetate to olefins.[4-7] However, there is an oposing mechanistic interpretation that oxymercuration occurs to give an unsymmetrical open carbocation of Type (**B**).[8-10] The bromination of olefins seems also to be an atypical systems, for its cationic intermediates are not in all cases cyclic, but can also be opened carbocations.[11] Recently, Tidwell *et al.* concluded, in comparison with the rate of the acid-catalyzed hydration and addition reaction of arenesulfenyl chloride to various olefins, that the bromination of various olefins proceeds *via* bridged ion-like intermediates.[12] The high rate of the bromination of cyclopropylethylene is explained by a mechanism involving an open-ion-like rate-determining transition state. This change in mechanism is due to the great ability of the cyclopropyl group to stabilize an adjacent carbocation by resonance electron donation.



It has been elucidated that the tricyclo[3.2.1.0^{2,7}]-oct-3-en-6-yl cation (**C**) rearranges to bicyclo[3.2.1]-oct-3,6-dienyl cation (**D**) at a rate competing with solvent (MeOH) attack, as is shown by the generation of the latter cation from the *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-en-3-anti diazonium ion.[13] Furthermore, the acid-catalyzed rearrangement of 1,5-dimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one (**1**) has been investigated, and it has been elucidated that the tricyclic cation (**E**) rearranges to the bicyclic cation (**F**).[14] A consideration of the formal cation (**G**), which has a skeleton similar to those of the (**C**) and (**E**) cations, suggests that the solvomercuration or bromination reaction of compounds possessing a 6-methylenetricyclo[3.2.1.0^{2,7}]-oct-3-en-8-one or its related skeleton would seem to be of interest for several reasons. The formal cation (**G**) has an adjacent mercury moiety or bromine atom,

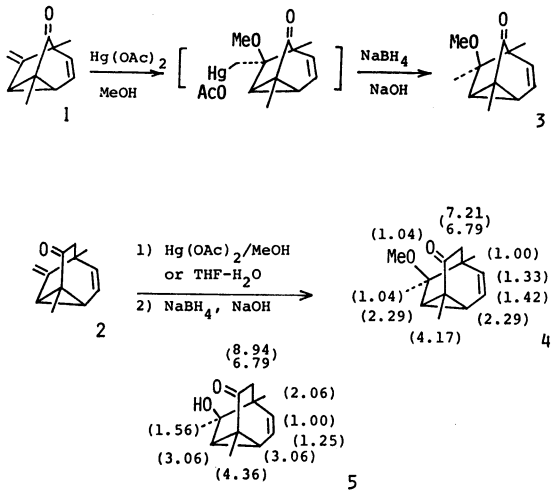


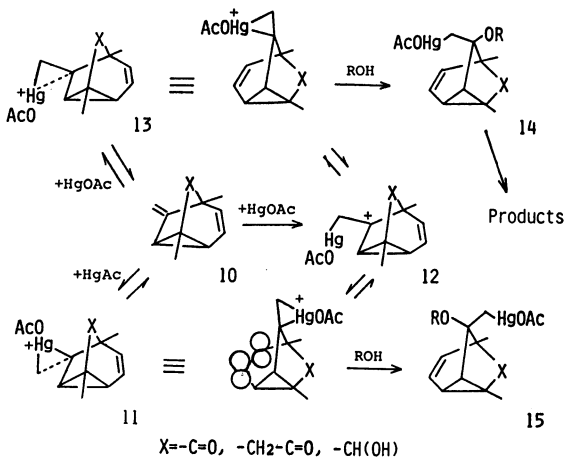
both of which can stabilize the cationic center by making mercurinium ions or bromonium ions similar to Type (**A**), and a cyclopropane ring which also can stabilize the cationic center by resonance electron donation in a bisected conformation.[15] Therefore, if the stabilizing effect of a cyclopropane to the cationic center by electron donation overcomes the formation of mercurinium ions[16] or bromonium ions, the rearrangement of (**G**) to the bicyclo[3.2.1]heptadienyl cation may compete with the solvent attack, as in the case of the behavior of the cation (**C**) or (**E**). From this point of view, the solvomercuration-demercuration, bromination, and related reactions of **1**[17] and 5,8-dimethyl-9-methylenetricyclo[3.3.1.0^{2,8}]non-3-en-7-one (**2**)[18] and their related compounds were investigated. The results will be presented in this paper.

Solvomercuration-demercuration Reaction

A solution of **1** in anhydrous methanol was treated with an equivalent amount of mercury(II) acetate. After the reaction mixture has been stirred for 30 min, it was treated with 3 mol dm^{-3} aqueous sodium hydroxide and then with sodium borohydride in 3 mol dm^{-3} aqueous sodium hydroxide, according to the reported procedure.[19] The usual workup afforded, in a 98% yield, *exo*-6-methoxy-1,5,6-trimethyltricyclo-[3.2.1.0^{2,7}]oct-3-en-8-one (**3**), the structure of which was identified by a comparison of the spectral data.[14] No *endo*-methoxy isomer was detected at all.

In order to examine the ring-size effect on the solvomercuration reaction, the reaction of **2** was carried out in a way similar to the case of **1**, and *exo*-9-methoxy-



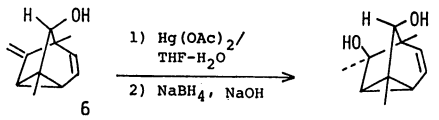


Scheme 1.

5,8,9-trimethyltricyclo[3.3.1.$0^{2,8}$]non-3-en-7-one (**4**) was thus obtained in a 93% yield. Similarly, the reaction of **2** with mercury(II) acetate in tetrahydrofuran (THF)–H_2O and a subsequent demercuration reaction afforded *exo*-9-hydroxy-5,8,9-trimethyltricyclo[3.3.1.$0^{2,8}$]non-3-en-7-one (**5**) in a 94% yield. The spectral data of **4** and **5** were consistent with the proposed structures (see Experimental). The stereochemistry of the methoxyl or the hydroxyl group of **4** or **5** was determined clearly by means of the pseudo-contact NMR spectra obtained by using $Eu(fod)_3$. The relative downfield shifts of δ's are given in parentheses in the structural formulae **4** and **5**.[21] The relatively small shifts of methoxyl and methyl at the 9-position of **4** suggest that the coordination of $Eu(fod)_3$ does not occur on methoxyl oxygen, but on the carbonyl oxygen, and that the methyl group on the 9-position is located anti to the carbonyl group. In the case of **5**, the coordination of $Eu(fod)_3$ seems to occur on the hydroxyl oxygen as well as the carbonyl oxygen. However, the relatively small shifts of the methyl group on the 9-position compared to that of the methyl group on the 8-position suggest that methyl group on the 9-position is *anti* to the carbonyl group.

Compounds **1** and **2** have an electron-withdrawing carbonyl function adjacent to the cyclopropane ring. This carbonyl group may possibly reduce the electron-donating character of the cyclopropane ring to the cationic center. Therefore, the solvomercuration-demercuration reaction of 1,5-dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-*endo*-ol (**6**)[20] was investigated. When **6** was allowed to react with an equivalent amount of mercury(II) acetate in THF–H_2O (4/1) in a manner similar to that in the case of **1** or **2**, 1,5,6-trimethyltricyclo[3.2.1.$0^{2,7}$]oct-3-en-6-*exo*-,8-*endo*-diol (**7**) was obtained in a 95% yield. The spectral data of **7** are in good agreement with those of the known compounds, obtained by the sulfuric acid-catalyzed hydration of **6**.[22]

In all of the presented reactions, the solvent was



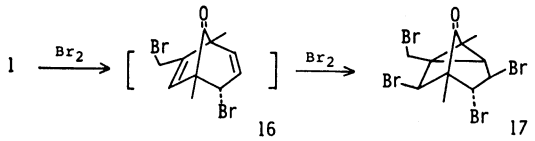
stereospecifically incorporated on the exomethylene group, and the original tricyclic skeleton did not undergo rearrangement. The ring size and the absence of the electron-withdrawing carbonyl group adjacent to the cyclopropane ring did not affect the reaction pathway. These experimental results suggest the formation of mercurinium ions such as **13**, as is shown in Scheme 1. The cationic center of a tricyclic skeleton such as that of **12** is stabilized by the formation of **13**. This fact seems to indicate that the stabilization of the cationic center of the cyclopropylcarbinyl cation by the mercury moiety adjacent to the cationic center is preferable over the resonance-electron donation of the cyclopropane ring in the present case. The initial addition of $^+$Hg(OAc)[23] to the exocyclic double bond seems to favor the formation of **11** over the formation of **13** because of the steric hindrance (*vide infra*). In the supposition of a *trans* addition mechanism, however, the *endo*-attack of the solvent molecule on **11** seems to be unfavorable because of the electronic repulsion of the π-electron lobe of the endocyclic double bond with the solvent molecule, as is shown in the structural formula, **11**.[22] Therefore, the mercuration-demercuration (equilibration) step or the possible short-lived intermediate of the opened cation, **12**, should participate in the present reactions, thereby causing the formation of **13**. In the mercurinium cation **13**, some stabilization by the coordination of the endocyclic double bond to the mercury atom would be expected,[24] the *trans* additions of the solvent molecule from the less hindered site then afford the products.[25]

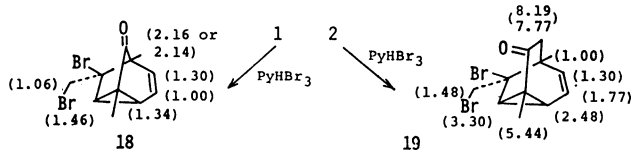
Bromination and Related Reaction

It has been reported that the bromination of **1** with an equivalent amount of bromine in dichloromethane at −78 °C gives an unstable dibromide, **16**, which then affords tricyclic tetrabromide, **17**, by further bromination.[26] In relation to this reaction and the solvomercuration-demercuration reaction described above, the addition reactions of pyridinium tribromide (PyH-Br_3), *N*-bromosuccinimide (NBS)–H_2O, and NBS–MeOH with **1** and **2** were also investigated.

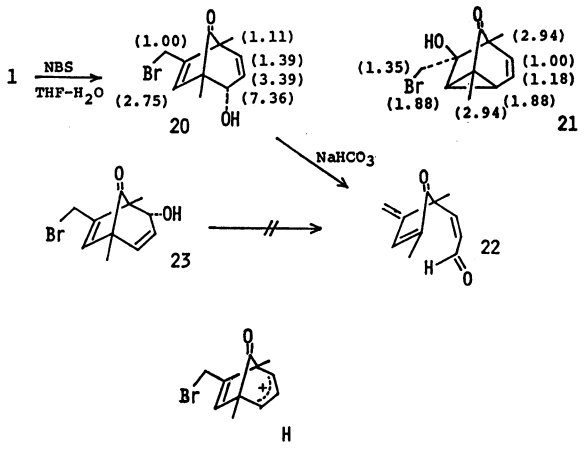
The reaction of **1** with an equivalent amount of $PyHBr_3$ in dichloromethane–carbon tetrachloride (1/1)

at 0 °C for 2 h, and the subsequent column chromatography on alumina afforded a dibromide, **18** (mp 92.9—93.5 °C) in a 77% yield. Similarly, the reaction of $PyHBr_3$ with a one-carbon-ring enlarged ketone, **2**, afforded **19** in a 55% yield. The NMR spectrum of the crude product of the reaction did not exhibit the presence of any other addition product. The dibromide **19** is an unstable oil and turns black even in the refrigerator. Therefore, a correct elemental analysis has not been obtained. However, the mass-spectral data of **18** and **19** clearly indicate that **18** and **19** are dibromides of **1** and **2** respectively. The spectral data of **18** and **19** clearly indicate that these bromides have skeletons similar to those of their starting ketones, **1** and **2** respectively, and that the bromination proceeds on the exomethylene group. The stereochemistry of the bromomethyl group of **18** and **19** was deduced from the pseudo-contact NMR spectra obtained by using $Eu(fod)_3$.[21] These results are completely different from that of **1** and molecular bromine, but are similar to the solvomercuration- demercuration reaction of **1** and **2** described above.





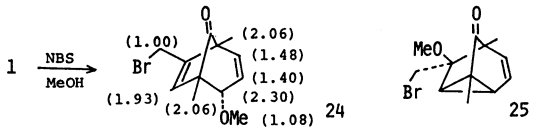
On the other hand, when **1** was allowed to react with NBS in THF–H_2O (4/1) at 25 °C for 30 min, a mixture of two products was obtained. This mixture was separated by TLC on silica gel to afford **20** and **21** in 34% and 17% yields respectively. The partial decomposition of **20** and **21** on the TLC plates causes the low yields of the products. The mass spectral data and the other spectral data indicates that **21** has a tricyclic skeleton and a bromine atom and that a hydroxyl group was incorporated on the exomethylene group. The stereochemistry of the hydroxyl group of **21** was assigned on the basis of the pseudo-contact NMR spectra.[21] Compound **20** is an unstable oil, and so a correct elemental analysis has not been made. However, satisfactory mass-spectral data were obtained. The NMR spectrum of **20** exhibited three protons of vinyl groups at δ 5.72 (dxd, J=10.2, 3.0 Hz), δ 6.26 (dxd, J=10.2, 1.8 Hz), δ 6.14 (s), in addition to two methyl groups at δ 1.25, δ 1.35, an allylic hydrogen at δ 4.07—4.21. The proton of the hydroxyl group has not been assigned distinctly. These NMR data are in accord with the proposed structure of **20**. Another structural possibility for **20** is **23**, however, **23** was discarded on the basis of the following chemical transformation. When **20** was treated with an aqueous sodium hydrogencarbonate solution in THF, **22** was obtained in a 90%



yield. The formation of **22** was considered to be the base induced Grob-type fragmentation of **20**.[7] Therefore, the structure of **20** was determined. The formation of **20** also indicates the absence of a bicyclic intermediate such as (H), from which both of **20** and **23** could be expected to be derived.

The pseudo-contact NMR spectra of **20** were obtained by using $Eu(fod)_3$.[21] The large value (7.36) of the allylic hydrogen indicates that the coordination of $Eu(fod)_3$ occurs on hydroxyl oxygen. The stereochemistry of the hydroxyl group is not elucidates here however, it must be *endo*, judging from the following experimental results.

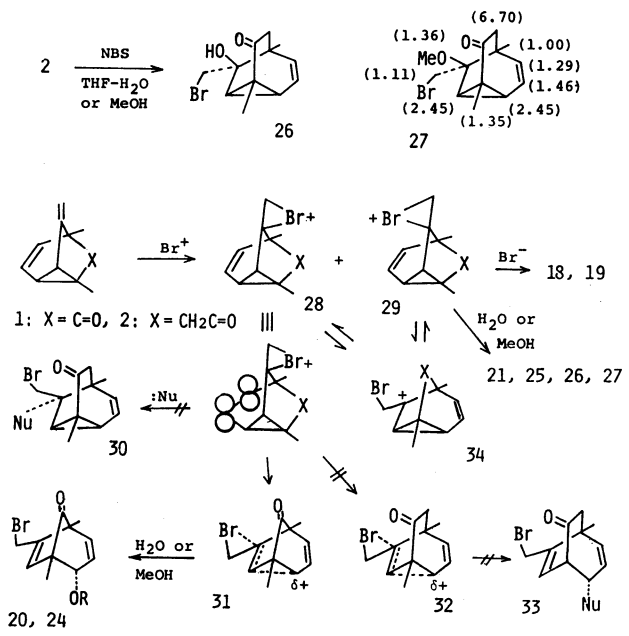
The reaction of **1** with NBS in anhydrous methanol afforded two products, **24** and **25**, in a ratio of 9/5 and in a 90% yield. This mixture was separated by TLC on silica gel. The two compounds, **24** and **25** gradually decomposed and turns black, therefore, satisfactory elemental analyses have not been obtained. However, satisfactory mass-spectral data were obtained. The other spectral data were consistent with the proposed



structures, **24** and **25**. The pseudo-contact NMR spectra of **24** was obtained by using $Eu(fod)_3$.[21] The small value of 1.08 for the methoxyl group suggest that coordination of $Eu(fod)_3$ occurs not on the methoxyl oxygen, but on the carbonyl oxygen. The large value of 2.30 for the allylic hydrogen suggests that the methoxyl group of **24** is located in the *endo* position. Therefore, the stereochemistry of the hydroxyl group of **20** must also be *endo* in this analogy. The orientation of the methoxyl group of **25** has not been determined directly because of the instability of **25**. However, it is probably *exo*, by analogy with the hydroxyl group of **21**.

In these reactions induced by NBS, 1,2-addition on the exomethylene group and 1,4-addition accompanying cyclopropane-ring opening took place with a stereospecific solvent incorporation. The 1,4-addition in the present case is very similar to the case of **1** with molecular bromine.[26]

On the other hand, the reaction of **2** with NBS–H_2O



Scheme 2.

or NBS–MeOH in a similar manner to that in the case of **1** afforded only a 1,2-addition product, **26** (mp 115—117 °C) or **27**, in a 47 or 83% yield respectively, after separation by TLC on silica gel. The structures of **26** and **27** were deduced by a comparison of the spectral data (see Experimental) with those of the related compounds which had been obtained by the solvomercuration-demercuration reaction described in this paper. The stereochemistry of the hydroxyl group or the methoxyl group was assigned on the basis of the pseudo-contact NMR spectra of **27**.[21]

The plausible reaction sequences are summarized in Scheme 2. It has been indicated that the tricyclo-[3.2.1.$0^{2,7}$]oct-3-en-6-yl cation (**C**) rearranges to the bicyclo[3.2.1]octa-3,6-dienyl cation (**D**) at a rate competing with the solvent (MeOH) attack.[13] Furthermore, in the acid-catalyzed reaction of **1**, it was indicated that the cation (**E**) was rearranged to bicyclic cation (**F**).[14] In the case of the reaction of **1**, the cyclopropane-ring opening took place to afford **20**, but not **23**. Therefore, the present experimental results seem to suggest that an initial attack of $^{+}$Br on the *exo*-methylene group affords a bromonium ion, such as **28** or **29**. From the product composition of **20**/**21** or **24**/**25**, the formation of **28** seems more likely than that of **29** because of the steric effect. The *exo*-attack of the nucleophile on **29** (X=–C=O) should afford **18** and **19** or **21**, **25**, **26**, and **27**. On the other hand, the attack of the nucleophile on a bromonium ion such as **28** to afford **30** must be hindered by the π-electron lobe of the endocyclic double bond presented in the structural formula **28**. In the case of **1**, however, a transition state such as **31** may be stabilized in a polar media, such as methanol or THF–H_2O.[28] The nucleophile may then be incorporated in the cyclopropane ring from the *endo* site to afford **20** and **24**. On the other hand, the one-carbon ring-enlarged **32** should be less strained than **31**, therefore, **33** should not be obtained. This fact seems to suggest that an equilibrium between such substances as **28** and **29** may be made possible by bromination-debromination *via* **1** and **2** or by possible short-lived, opened cation, **34**. The difference between the reactions of **1** with molecular bromine and with $PyHBr_3$ is not clear at the present stage.

Consequently, the present results suggest that bromine atoms adjacent to cyclopropylcarbinyl cation centers stabilize these cationic centers, as in the case of the solvomercuration reaction described above, and that the nucleophilic attacks on them are probably affected by the stereoelectronic factor existing in the molecular framework.

Experimental

The IR spectra were recorded with a Shimadzu IR-400 spectrometer. The mass spectra were obtained with a Hitachi RMU-60 mass spectrometer. The NMR spectra were recorded on a JEOL PS-100 high resolution spectrometer. The abbreviations "s, d, dxd, t, m, and br" in the NMR spectra denote "singlet, doublet, doublets of doublet, triplet, multiplet, and broad" respectively. All of the melting points are uncorrected.

Methoxymercuration-demercuration of ***1***. To a well stirred solution of **1** (320 mg, 2 mmol) in 2 cm^3 of anhydrous methanol, was added 689 mg (2 mmol) of mercury(II) acetate. After the reaction mixture had then been stirred for 30 min, 2 cm^3 of 3 mol dm^{-3} sodium hydroxide solution was added, followed by 34 mg (2 mmol) of sodium borohydride in 2 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide. To this mixture, was added 10 cm^3 of brine and 10 cm^3 of ether. It was then filtered. The filtrate was extracted with ether, and the ether extract was dried over sodium sulfate. After the removal of the solvent *in vacuo*, 376 mg (98%) of **3** was obtained: bp 107 °C/582.8 Pa.

Methoxymercuration-demercuration of ***2***. The reaction was carried out as has been described above using 174 mg (1 mmol) of **2**, 319 mg (1 mmol) of mercury(II) acetate, and 19 mg (0.5 mmol) of sodium borohydride. The product, **4**, was obtained in a 93% yield (191 mg): IR (CCl_4), 3027—2848, 1681, 1119, 1058 cm^{-1}; NMR (CCl_4), δ 0.98 (3H, s), 1.13 (3H, s), 1.19 (3H, s), 1.68 (1H, d, J=20.7 Hz), 1.85 (2H, m), 2.58 (1H, d, J=20.7 Hz), 3.26 (3H, s), 5.43 (1H, dxd, J=9.6, 1.5 Hz), 5.76 (1H, dxd, J=9.6, 4.8 Hz).

Oxime of ***4***. A solution of **4** (35 mg, 0.17 mmol), hydroxylamine hydrochloride (24 mg, 0.3 mmol), and sodium acetate (55 mg, 0.67 mmol) in 1 cm^3 of ethanol was refluxed overnight. The reaction mixture was poured into 5 cm^3 of water and then extracted with ether. The combined organic portion was dried over sodium sulfate, filtered, and evaporated *in vacuo*. The residue was crystallized from ethanol to give 24 mg (72%) of an oxime, **8**: mp 134—135 °C; IR (CCl_4), 3516—3064, 2947, 1688, 1114, 947 cm^{-1}; NMR ($CDCl_3$), δ 1.00 (3H, s), 1.12 (3H, s), 1.30 (3H, s), 1.60—1.82 (1H, m), 1.70 (1H, d, J=6.4 Hz), 2.41 (1H, d, J=18.0 Hz), 2.56 (1H, d, J=18.0 Hz), 3.32 (3H, s), 5.42 (1H, dxd, J=9.2, 1.0 Hz), 5.79 (1H, dxd, J=9.2, 3.2 Hz), 9.36 (1H, br s); MS, *m/e* (rel intensity), 221 (M^+, 12), 115 (100). Found: C, 70.69; H, 8.69; N, 6.25%. Calcd for $C_{13}H_{19}O_2N$: C, 70.56; H, 8.65, N, 6.33%.

Hydroxymercuration-demercuration of ***2***. The reaction was carried out as has been described above using 174 mg (1 mmol) of **2**, 319 mg (1 mmol) of mercury(II) acetate, and 19 mg (0.5 mmol) of sodium borohydride. The product, **5**, was obtained in 94% (194 mg) yield: IR (CCl_4), 3450, 1678, 1098, 1045

cm^{-1}; NMR ($CDCl_3$), δ 1.03 (3H, s), 1.25 (6H, s), 1.72 (1H, d, J=8.0 Hz), 1.75—2.00 (1H, m), 2.02 (1H, d, J=18.7 Hz), 2.60 (1H, d, J=18.7 Hz), 3.10 (1H, br s), 5.47 (1H, dxd, J=9.5, 2.0 Hz), 5.75 (1H, dxd, J=9.5, 6.0 Hz). An oxime of **5** was prepared in a manner similar to that used in the case of **4**. The oxime, **9**, exhibited the following physical data: mp 213—215 °C; MS, *m/e* (rel intensity), 207 (M^+, 26), 101 (100). Found: C, 69.95; H, 8.38; N, 6.81%. Calcd for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76%.

Hydroxymercuration-demercuration of ***6***. To a stirred solution of **1** (162 mg, 1 mmol) in 5 cm^3 of THF–H_2O (4/1), was added 345 mg (1 mmol) of mercury(II) acetate. After the reaction mixture had then been stirred for 30 min, 2 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide was added, followed by 17 mg (0.5 mmol) of sodium borohydride in 1 cm^3 of 3 mol dm^{-3} sodium hydroxide. To this reaction mixture, was subsequently added 10 cm^3 of brine and 10 cm^3 of ether. It was then filtered. The filtrate was extracted with ether, and the extract was dried over sodium sulfate. After the removal of the solvent *in vacuo*, 160 mg (94%) of **7** was obtained.

Reaction of ***1*** *with Pyridinium Tribromide.* To a stirred solution of pyridinium tribromide ($PyHBr_3$) (320 mg, 1 mmol) in carbon tetrachloride (3 cm^3), was added **1** (160 mg, 1 mmol) in dichloromethane (3 cm^3) at 0 °C. After this reaction mixture had then been stirred for 2 h, the precipitated pyridinium bromide was filtered off. The filtrate was concentrated under reduced pressure, and the resulting residue was chromatographed on alumina (10 g), using benzene–hexane (1/1) as the eluent, to give 246 mg (77%) of **18**: mp 92.5—93.5 °C (from CCl_4); IR (CCl_4), 1735 cm^{-1}; NMR (CCl_4), δ 1.25 (3H, s), 1.30 (3H, s), 2.10 (1H, m), 2.52 (1H, d, J=7.0 Hz), 3.57 (1H, d, J=11.0 Hz), 3.73 (1H, d, J=11.0 Hz), 5.27 (1H, dxd, J=8.0, 2.0 Hz), 6.06 (1H, dxd, J=8.0, 5.0 Hz); MS, *m/e* (rel intensity), 322 (M^+, 2), 320 (M^+, 2), 119 (100), 117 (95). Found: C, 41.14; H, 3.58%. Calcd for $C_{11}H_{12}OBr_2$: C, 41.29; H, 3.78%.

Reaction of ***2*** *with Pyridinium Tribromide.* The reaction was carried out as has been described above using 320 mg (1 mmol) of $PyHBr_3$ and 174 mg (1 mmol) of **2**. After the reaction mixture had been stirred for 2.5 h, it was worked up as described above to give 183 mg (55%) of **19**: oil, IR (film), 1690 cm^{-1}; NMR (CCl_4), δ 1.24 (3H, s), 1.27 (3H, s), 1.90—2.10 (1H, m), 2.12 (1H, d, J=18.0 Hz), 2.58 (1H, d, J=8.0 Hz), 2.74 (1H, d, J=18.0 Hz), 5.65 (1H, dxd, J=9.0, 2.0 Hz), 5.93 (1H, dxd, J=9.0, 5.0 Hz); MS, *m/e* (rel intensity), 336 (M^+, 3), 334 (M^+, 8), 332 (M^+, 4), 199 (97), 197 (100). Found: C, 44.35; H, 4.23%. Calcd for $C_{12}H_{14}OBr_2$: C, 43.15; H, 4.22%.

Reaction of ***1*** *with NBS in THF–H_2O.* To a stirred solution of **1** (160 mg, 1 mmol) in 2.5 cm^3 of THF–H_2O (4/1). was added NBS (178 mg, 1 mmol). After the reaction mixture has been stirred for 30 min, it was extracted with ether. The ether extract was dried over sodium sulfate and evaporated under reduced pressure to give 205 mg (80%) of a mixture of **20** and **21** in a ratio of 9/5, as determined by means of the NMR spectrum. This mixture was separated by TLC on silica gel, using benzene–dichloromethane (1/1) as the eluent. The first band from the TLC plates afforded 44 mg (17%) of **21**: mp 120—121 °C (from benzene); IR ($CHCl_3$), 3573, 1739 cm^{-1}; NMR ($CDCl_3$), δ 1.17 (3H, s), 1.34 (3H, s), 2.08—2.25 (2H, m), 2.25—2.60 (1H, br s), 3.61 (1H, d, J=10.8 Hz), 3.81 (1H, d, J=10.8 Hz), 5.50 (1H, dxd, J=7.8, 3.0 Hz), 6.21 (1H, dxd, J=7.8, 4.5 Hz); MS, *m/e* (rel intensity), 258 (M^+, 5), 256 (M^+, 2), 177 (100). Found: C, 51.21; H, 4.97%. Calcd for $C_{11}H_{13}O_2Br$: C, 51.38; H, 5.10%.

The second band from the TLC plates gave 88 mg (34%) of **20**: oil; NMR (CCl_4), δ 1.25 (3H, s), 1.35 (3H, s), 3.02—3.35 (1H, br s), 4.07—4.21 (2H, br s), 5.72 (1H, dxd, J=10.2, 3.0 Hz), 6.14 (1H, s), 6.26 (1H, dxd, J=10.2, 1.8 Hz).

Reaction of ***20*** *with Sodium Hydrogencarbonate.* A solution of **20** (129 mg, 0.5 mmol) in 3 cm^3 of methanol and 3 cm^3 of saturated aqueous sodium hydrogencarbonate was stirred for 5 h. The reaction mixture was then extracted with ether, and the combined ether extract was dried over sodium sulfate. After the removal of the solvent, 158 mg (90%) of **22** was obtained as an oil; IR (film), 1710, 1679 cm^{-1}; NMR (CCl_4), δ 1.47 (3H, s), 1.92 (3H, br s), 5.13 (2H, s), 5.73 (1H, dxd, J=12.0, 8.0 Hz), 6.32 (1H, d, J=12.0 Hz), 7.40 (1H, br s), 9.66 (1H, d, J=8.0 Hz); MS, *m/e* (rel intensity), 176 (M^+, 100). Found: C, 74.58; H, 6.81%. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86%.

Reaction of ***1*** *with NBS in Methanol.* To a stirred solution of **1** (160 mg, 1 mmol) in 4 cm^3 of methanol, was added 214 mg (1.2 mmol) of NBS. After this mixture had been stirred for 2 h at the ambient temperature, it was extracted with ether. The ether extract was dried over sodium sulfate, the subsequent evaporation of the ether afforded 244 mg (90%) of a mixture of **24** and **25** in a ratio of 9/5, as determined by the study of the NMR spectrum. This mixture was separated by TLC on silica gel, using benzene–dichloromethane (1/1) as the eluent. The first band from the TLC plates gave **24**: IR (CCl_4), 1765 cm^{-1}, NMR (CCl_4), δ 1.22 (3H, s), 1.29 (3H, s), 3.50 (3H, s), 3.84 (1H, m), 4.22 (2H, br s), 6.17 (1H, s), 5.92 (1H, dxd, J=10.8, 2.7 Hz), 6.37 (1H, dxd, J=10.8, 2.7 Hz); MS, *m/e* (rel intensity), 272 (M^+, 1), 270 (M^+, 1), 191 (100), 159 (99). Found: C, 52.14; H, 5.71%. Calcd for $C_{12}H_{15}O_2Br$: C, 53.16; H, 5.58%.

The second band from the TLC plates contained **25** and decomposed material. This portion could not be purified because of its instability: NMR (CCl_4), δ 1.10 (3H, s), 1.19 (3H, s), 2.03—2.23 (2H, m), 3.45 (1H, d, J=10.5 Hz), 3.68 (1H, d, J=10.5 Hz), 5.54 (1H, dxd, J=8.4, 2.7 Hz), 6.18 (1H, dxd, J=8.4, 4.5 Hz).

Reaction of ***2*** *with NBS in THF–H_2O.* To a solution of **2** (174 mg, 1 mmol) in 2.5 cm^3 of THF–H_2O (4/1), was added NBS (214 mg, 1.2 mmol). After the mixture had been stirred for 1 h, it was extracted with ether. The ether extract was dried over sodium sulfate and evaporated under reduced pressure to give 190 mg, (70%) of a solid, which was then recrystallized from CCl_4 to give colorless crystals of **26**: mp 115—117 °C; IR (CCl_4), 3612—3210, 1693 cm^{-1}; NMR (CCl_4), δ 1.14 (3H, s), 1.31 (3H, s), 1.99 (1H, d, J=18.6 Hz), 1.79—1.99 (1H, m), 2.19 (1H, d, J=7.5 Hz), 2.80 (1H, d, J=18.6 Hz), 2.63—3.12 (1H, br s), 3.60 (1H, d, J=9.9 Hz), 3.83 (1H, d, J=9.9 Hz), 5.69 (1H, dxd, J=9.6, 1.5 Hz), 6.12 (1H, dxd, J=9.6, 6.0 Hz); MS, *m/e* (rel intensity), 272 (M^+, 17), 270 (M^+, 18), 149 (100), 105 (98). Found: C, 53.65; H, 5.61%. Calcd for $C_{12}H_{15}O_2Br$: C, 53.16; H, 5.58%.

Reaction of ***2*** *with NBS–Methanol.* To a stirred solution of **2** (174 mg, 1 mmol) in 4 cm^3 of methanol, was added 214 mg (1.2 mmol) of NBS. After this mixture had been stirred for 1 h at the ambient temperature, it was extracted with ether. The ether extract was dried over sodium sulfate and the subsequent evaporation of the ether afforded 240 mg (83%) of **27**: oil; IR (CCl_4), 1688 cm^{-1}; NMR (CCl_4), δ 1.10 (3H, s), 1.36 (3H, s), 1.92 (1H, d, J=18.6 Hz), 2.67 (1H, d, J=18.6 Hz), 2.42 (1H, d, J=8.4 Hz), 1.91—2.14 (1H, m), 3.60 (1H, d, J=10.5 Hz), 3.72 (3H, s), 3.86 (1H, d, J=10.5 Hz), 5.79 (1H, dxd, J=9.4, 1.5 Hz), 6.25 (1H, dxd, J=9.3, 6.6 Hz); MS, *m/e* (rel intensity), 286 (M^+, 4), 284 (M^+, 4), 205 (100), 177 (99). Found: C, 51.02; H, 5.64%. Calcd for $C_{13}H_{17}O_2Br$: C, 54.75; H, 6.01%.

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