Electrophilic Reactions of 1-Substituted Camphenes

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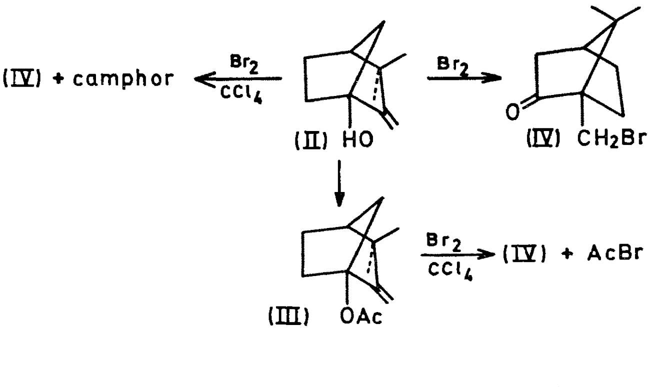
Summary 1-Hydroxy-, 1-acetoxy-, and 1-chloro-camphene in their reaction with bromine or ozone show a remarkable reactivity range in that the 1-hydroxycamphene favours rearrangement while the 1-chlorocamphene disfavours rearrangement.

BECAUSE the bicyclic camphane skeleton rearranges readily, electrophilic addition reactions of camphene and halogens yield a variety of products.[1] The addition of bromine to 1-hydroxycamphene has been reported to yield a single product—10-bromocamphor,[2] suggesting that the ease of rearrangement is sensitive to substituents at the 1-position. To clarify the effect of substituents at the 1-position we have prepared 1-hydroxy-, 1-acetoxy-, and 1-chloro-camphene and have treated them with bromine or ozone in several solvents.[3]

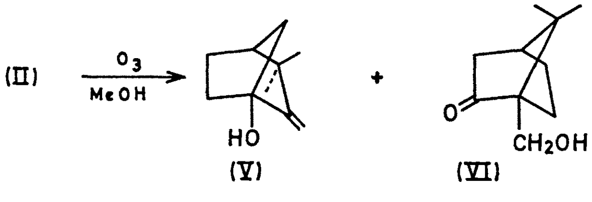
Camphor was converted into 1-chlorocamphene (I) by a slightly modified reaction with PCl_3–PCl_5 in 70% yield.[1c] Reaction of (I) with lithium in refluxing heptane followed by treatment with oxygen[4] gave, in modest yield, 1-hydroxycamphene (II). Acylation of (II) with acetic anhydride gave 1-acetoxycamphene (III) in 90% yield.

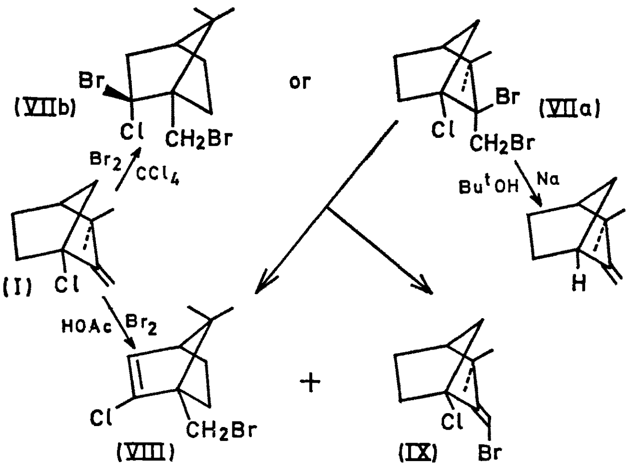
Treatment of (II) in carbon tetrachloride with bromine gave camphor and 10-bromocamphor (IV). The camphor arose from (II) and hydrogen bromide which was formed in the reaction yielding (IV). When the hydrogen bromide was scavenged by pyridine solvent, 10-bromocamphor was obtained in quantitative yield. Reaction of (III) with bromine in carbon tetrachloride followed a similar course to give (IV) and acetyl bromide. Since camphor can be converted into (II) directly by treatment with trichloroacetic anhydride[5] and hydrolysis and 1-trichloroacetoxycamphene[5] yielded (IV) as well, a convenient two-step synthesis of 10-bromocamphor is provided.[6]

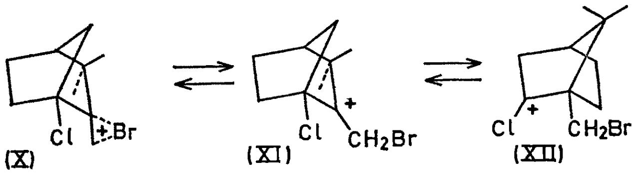


Ozonolysis of (II) gave two major products which were identified as (V) and (VI). The formation of 10-hydroxycamphor[6] was unexpected since ozonolysis does not ordinarily proceed with rearrangement. This provides an example of ozonolysis where sufficient carbonium-ion character must be involved to cause rearrangement in a substrate sufficiently disposed to rearrangement. Ozonolysis of (III) proceeds without rearrangement.

Bromination of 1-chlorocamphene in carbon tetrachloride yielded a dibromide which has been assigned structure (VIIa). The dibromide yields camphene on reduction with sodium in t-butyl alcohol and will not hydrolyse to the ketone (IV).[7,8] Correlation of the chemical shifts of the methyl groups in the camphene and camphor series strongly suggests that the dibromide has a camphene-type skeleton (VIIa) rather than camphor-type skeleton (VIIb). The only tenable structure for the dibromide in light of the observed facts is (VIIa). Since the addition of bromine to camphene yields a mixture of products, [9] the formation of a single dibromide (VIIa) from bromination of 1-chlorocamphene confirms that 1-chlorocamphene has a reduced tendency to rearrangement. Solvolysis of the dibromide in aqueous acetic acid, aqueous ethanol, aqueous methanol, sodium hydroxide–methanol, and silver nitrate–ethanol yielded two products, (VIII) and (IX). No product derived from attack of solvent on a carbonium-ion intermediate was ever detected. Addition of bromine to (I) in aqueous acetic acid yielded (VIII) and less than 5% of (IX).







The lack of any products derived from attack of solvent under solvolytic conditions requires that proton loss from (XII) must be rapid as compared with solvent collapse with (XI) or (XII). The low stability of (XII) [expressed as a low concentration of (XII) with respect to (XI) or as a low contributor to a nonclassical ion receiving contributions from (XI) and (XII)] coupled with the steric hindrance at the positive centre of (XI) combine to reduce the rate of solvent collapse. In the extreme, proton loss from the 7-position can be drawn to occur in a completely concerted manner.

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