Vinyl Bromides from Reaction of *N*-Bromosuccinimide with Chromans and Other Benzyl Derivatives: a New Interpretation

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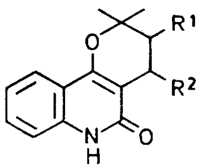
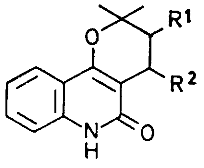
Summary New structures are assigned to vinyl bromides obtained by treatment of *N*-bromosuccinimide with 2,2-dimethylchromans, and the mechanism is shown to involve addition of the reagent to an intermediate chromene; the abnormal reaction also occurs with a dihydrofuranoquinoline.

A GENERAL synthesis of chromenes, benzofurans, and similar systems involves reaction of dihydro-derivatives with *N*-bromosuccinimide followed by dehydrobromination,[1] but the reaction sometimes takes a different course. For example, treatment of the reagent with dihydroflindersine (**1a**) and with the chroman (**4**) affords vinylic bromides.[2,3] We now suggest alternative structures for these products and describe a further example of the reaction.

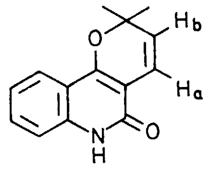
The vinylic bromide from dihydroflindersine was assigned structure (**2a**).[2] The n.m.r. spectrum, however, shows a singlet at τ 2·87, and this appears to be more consistent with the isomeric structure (**2b**) in which the olefinic proton is adjacent to the aromatic system and deshielded by the carbonyl group [compare the spectra of flindersine (**3**), τ 3·23 (H_a) and 4·44 (H_b)[4] of *trans*-1-bromo-2-phenylethene, τ 3·02 (PhC*H*=)[5] and of styrene, τ 3·35 (PhC*H*=)]. To explain the reaction, we suggest that benzylic bromination of dihydroflindersine (**1a**) is followed by spontaneous loss of hydrogen bromide to give flindersine (**3**), which after addition of *N*-bromosuccinimide, (**3**) → (**1b**),[6,7] yields the vinylic bromide (**2b**) by elimination of succinimide from intermediate (**1b**). In support of this mechanism, we find that treatment of flindersine (**3**) with *N*-bromosuccinimide in carbon tetrachloride does not result in precipitation of succinimide, but affords the vinylic bromide (**2b**) only after



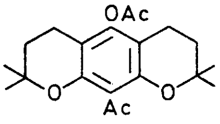
(1a) $R^1 = R^2 = H$
(1b) $R^1 = Br, R^2 = -N(CO)_2C_2H_4$
(1c) $R^1 = Br, R^2 = OEt$



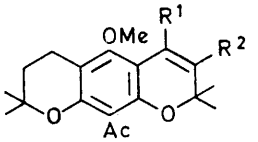
(2a) $R^1 = H, R^2 = Br$
(2b) $R^1 = Br, R^2 = H$



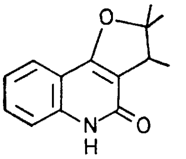
(3)



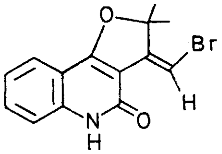
(4)



(5a) $R^1 = Br, R^2 = H$
(5b) $R^1 = H, R^2 = Br$



(6)



(7)

chromatography. The n.m.r. spectrum of the reaction mixture before chromatography indicated the presence of adduct (**1b**) which was confirmed by treatment of the initial bromination product with ethanol to give the bromo-ether (**1c**). Ready substitution of a succinimide group was observed previously with a dihydropyran derivative.[6] The bromo-ether (**1c**) was obtained directly from flindersine in 82% yield by reaction with *N*-bromosuccinimide in the presence of ethanol.

Bromoflindersine obtained by treatment of the alkaloid with bromine and assigned structure (**2a**),[8] is clearly the isomeric compound (**2b**), since, as observed by Piozzi *et al.*,[2] it is apparently identical with the product from dihydroflindersine.

Treatment of the chroman (**4**) with *N*-bromosuccinimide and subsequent hydrolysis and methylation afforded a vinylic bromide that was assigned structure (**5a**; $R^1 = Br$, $R^2 = H$). It was suggested that dibromination at the benzylic position was followed by loss of hydrogen bromide.[3] The reported n.m.r. spectrum (olefinic proton at τ 3·25) again indicates an alternative structure (**5b**; $R^1 = H$, $R^2 = Br$), and the mechanism suggested above for dihydroflindersine is likely to apply in this case.

We have also observed an example of the reaction in a dihydrofuran system. Treatment of the furanoquinoline derivative (**6**)[9] with *N*-bromosuccinimide in carbon tetrachloride afforded the vinylic bromide (**7**) (76%), the n.m.r. signal at τ 2·6 indicating that the olefinic proton is deshielded by the carbonyl group as in the stereoisomer shown.

It appears that the abnormal reaction of benzyl derivatives with *N*-bromosuccinimide leading to vinylic bromides is likely to occur when an initial benzylic bromination product undergoes rapid elimination.

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