A New Bromoallene Alcohol. Its Isolation and Reaction

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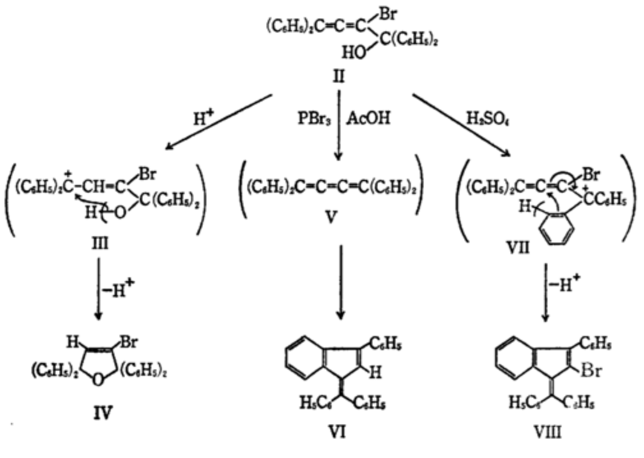
It has been postulated⁽¹⁾ that bromoallene alcohol II is an intermediate in the reaction of 1,1,4,4-tetraphenylbut-2-yne-1,4-diol (I) and phosphorus tribromide in acetic acid to give 2,2,5,5-tetraphenyl-3-bromodihydrofuran (IV) and 1,10,10-triphenylbenzofulvene (VI). We now wish to report the isolation and some reactions of a new bromoallene alcohol II.

The treatment of I with phosphorus tribromide in acetic acid at 0°C, followed by immediate decompostion with water, afforded 1,1,4,4-tetraphenyl-2-bromobuta-2,3-diene-1-ol (II) in a 35% yield, as colorless prisms (from ethyl acetate), mp 118.5—119.5°C. Found: C, 73.87; H, 4.37%; mol wt (Rast), 431. Calcd for $C_{28}H_{21}BrO$: C, 74.17; H, 4.64%; mol wt, 453. NMR: in $CDCl_3$, 2.75 (multiplet, 20 H) and 3.25 τ (singlet, 1H). UV: $\lambda_{max}^{dioxane}$, 290 mμ (ε, 27100). The UV spectrum was comparable to that of 1,1-diphenyl-3-bromopropadiene,⁽²⁾ $\lambda_{max}^{dioxane}$, 280 mμ (ε, 21700). IR: 2.20×10^{-3} mol in 1 *l*. CCl_4, 3566 (νOH) and 1947 cm^{-1} (νC=C=C). The νOH band, at a lower frequencies than that of a usual *t*-alcohol, *ca.* 3620 cm^{-1},⁽³⁾ shows the presence of intramolecular hydrogen-bonding, even though it is not clear whether allene or bromine is the electron-donating site.

The treatment of II in acetone with catalytic amounts of hydrobromic acid at room temperature for a few minutes gave IV⁽¹⁾ in a 53% yield. The reaction can be explained by the protonation of allene, followed by cyclization and deprotonation.

The action of equimolar amounts of phosphorus tribromide on II in acetic acid at room temperature for 30 min afforded IV and VI⁽¹⁾ in 14 and 80% yields respectively. Since the cyclization of tetraphenylbutatriene (V) to VI in acidic media has been well known,⁽⁴⁾ the reaction leading to VI can be explained by assuming the formation of V as an intermediate. The transformation of II into V may be a similar reaction mode to that of I and phosphorus tribromide to give V.⁽⁵⁾

The treatment of II in acetone with catalytic amounts of conc. sulfuric acid at 50°C for a few minutes gave VIII in a quantitative yield, as red prisms, mp 160—161°C. Found: C, 77.20; H, 4.07%; mol wt (Rast), 420. Calcd for $C_{28}H_{19}Br$: C, 77.24; H, 4.37%; mol wt, 435. UV: $\lambda_{max}^{dioxane}$, 252 (24100), 295 (sh) (10600) and 368 mμ (ε, 14500). The UV spectrum was comparable to that of the chloro-analog of VIII.⁽⁶⁾ The formation of VIII may be explained by the intramolecular cyclization of the cation, VII, produced by the dehydroxylation of II.



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