60. *Triterpene Resinols and Related Acids. Part XIII. Note on the Bromination of α-Amyranonyl Benzoate and β-Amyranonyl Acetate.*

By D. E. SEYMOUR and F. S. SPRING.

Treatment of α-amyranonyl benzoate and β-amyranonyl acetate with bromine gives *bromo-α-amyranonyl benzoate* and *bromo-β-amyranonyl acetate*, which on heating with acetic acid containing a trace of hydrobromic acid lose hydrogen bromide and yield *iso*-α-amyrenonyl benzoate and *iso*-β-amyrenonyl acetate respectively.

IN Part VII (Seymour, Sharples, and Spring, J., **1939**, 1075) it was shown that treatment of the saturated keto-ester α-amyranonyl benzoate with bromine led to partial dehydrogenation, giving the αβ-unsaturated keto-ester, *iso*-α-amyrenonyl benzoate. During the bromination we had observed the separation of a crystalline solid which gradually redissolved. We have now shown that this crystalline solid is *bromo-α-amyranonyl benzoate*, m. p. 177—178°. By effecting the bromination under suitable conditions, this bromoketone can be isolated in high yield. When it is heated in acetic acid containing a trace of hydrobromic acid, rapid evolution of hydrogen bromide occurs and the bromo-ketone is converted into *iso*-α-amyrenonyl benzoate (Seymour, Sharples, and Spring, *loc. cit.*).

In the same way the bromination of β-amyranonyl acetate (Picard, Sharples, and Spring, J., **1939**, 1045) has been reinvestigated; under suitable conditions the primary product of the reaction, *bromo-β-amyranonyl acetate*, m. p. 273—274°, is obtained. This bromo-ketone is extremely unstable, profound decomposition occurring when it is heated to 60° in a vacuum. Boiling solutions of the bromo-ketone gradually decompose with evolution of hydrogen bromide, this decomposition being most marked in acetic acid. A solution of the bromo-ketone in this solvent decomposes at room temperature with formation of *iso*-β-amyrenonyl acetate, the reaction being considerably accelerated by warming.

EXPERIMENTAL.

Bromo-α-amyranonyl Benzoate.—A solution of α-amyranonyl benzoate (3 g.) in glacial acetic acid (64 c.c.) was treated with a solution of bromine in acetic acid (8%; 12 c.c.) at 60°. The bromine was rapidly absorbed and the crystalline bromo-ketone separated. The mixture was set aside for 30 minutes at room temperature, and the solid then collected, washed with acetic acid, and recrystallised twice from acetone, from which *bromo-α-amyranonyl benzoate* separated (1·6 g.) in cubes, m. p. 177—178° (decomp.), $[\alpha]_D^{20°} + 22·5°$ ($l = 1, c = 0·6$ in chloroform). The m. p. of the bromo-ketone remained constant at 177—178° on recrystallisation, but after drying in a vacuum at 80° for 5 hours over phosphoric oxide it was 197—198° (Found: C, 70·7; H, 8·6. $C_{37}H_{53}O_3Br$ requires C, 71·0; H, 8·5%).

iso-α-*Amyrenonyl Benzoate.*—A solution of bromo-α-amyranonyl benzoate (1 g.) in acetic acid (30 c.c.) containing 1 drop of a solution of hydrogen bromide in acetic acid (40%) was heated on the steam-bath for 2 hours. The solution was set aside overnight and treated with water, and the precipitated solid collected and washed with water. After three crystallisations from acetone–methyl alcohol (1 : 1) *iso*-α-amyrenonyl benzoate separated in perfectly formed octahedra, m. p. 211—212°. A mixture of this with the specimen previously described (m. p. 205—206°) melted at 209—211° (Found: C, 81·4; H, 9·6. Calc. for $C_{37}H_{52}O_3$: C, 81·6; H, 9·6%).

Bromo-β-amyranonyl Acetate.—A solution of β-amyranonyl acetate (2 g.) in glacial acetic acid (110 c.c.) containing 1 drop of a solution of hydrogen bromide in acetic acid (40%) was treated at 40° with a solution of bromine in acetic acid (23 c.c.; 3%), added as rapidly as the absorption would permit. When the addition was complete, the solution was immediately treated with excess of water, and the precipitated solid collected and crystallised from slightly aqueous acetone, care being taken to avoid prolonged heating of the solution. After four crystallisations *bromo-β-amyranonyl acetate* separated in prismatic needles, m. p. 273—274°, $[\alpha]_D^{27°} \pm 0°$ ($l = 1, c = 0·6$ in chloroform) (Found: C, 68·1; H, 9·1. $C_{32}H_{51}O_3Br$ requires C, 68·2; H, 9·1%).

iso-β-*Amyrenonyl Acetate.*—A solution of bromo-β-amyranonyl acetate (0·7 g.) in glacial acetic acid (17 c.c.) was heated on the water-bath for 2¼ hours, hydrogen bromide being continuously evolved. The solution was set aside overnight and largely diluted with water, and the precipitated solid collected. After five crystallisations from slightly aqueous acetone, *iso*-β-amyrenonyl acetate separated in plates, m. p. 286—287°, undepressed by the specimen described by Picard, Sharples, and Spring (*loc. cit.*) *Light absorption in alcohol :* Maximum at 2480 A.; $\varepsilon_{max.} = 10,000$.

THE UNIVERSITY, MANCHESTER.

[*Received, May 8th,* 1941.]