Halogenated Terpenoids. XII*
The Identity of Wallach’s Tetrabromides C_{10}H_{14}Br_{4}

R. M. Carman^A and B. N. Venzke^B

^A Chemistry Department, University of Queensland, St. Lucia, Brisbane, Qld. 4067.
^B Chemistry Department, Queensland Institute of Technology, Brisbane, Qld. 4000.

Abstract
The identity of the two tetrabromides, products from the reaction of r-1,4,8-tribromo-p-menthane (1) with sodium ethoxide followed by bromination, is determined.

Introduction
Wallach\(^1\),\(^2\) treated the 1,4,8-tribromo-p-menthane (1) with base. He reported the product as a hydrocarbon, and since he apparently expected the loss of three moles of hydrogen bromide during the reaction, he formulated the compound as C\(_{10}\)H\(_{14}\). Bromination of the hydrocarbon\(^2\) then gave two crystalline tetrabromides, m.p. 154–155° (as leaves) and 103–104° (as a powder). Both tetrabromides were assigned the molecular formula C\(_{10}\)H\(_{14}\)Br\(_{4}\) although the compounds analysed high in hydrogen and were consistent with a formula C\(_{10}\)H\(_{16}\)Br\(_{4}\).

Discussion and Results
Repetition of Wallach’s dehydrobromination procedure gave a mixture of hydrocarbons with an odour similar to that of terpinolene (2). Bromination of the mixture gave leafy crystals of tetrabromide (3), m.p. 149–150°, identical\(^3\) with authentic (3) and which we believe to be identical with Wallach’s higher melting product. Chromatography of the mother liquor gave stable terpinolene tetrabromide (4) from the first crystalline fractions. Later fractions from the column contained a mixture of (3) and (4) (c. 1 : 5), m.p. 102–103°, which could not be separated or purified further, or raised in melting point by repeated recrystallization. We believe that this eutectic mixture corresponds to the lower melting of Wallach’s tetrabromides. Very little oily product was obtained and the two tetrabromides (3) and (4) comprise >80% of the bromination product.

Compounds (3) and (4) arise\(^3,\(^4\) from the bromination of hydrocarbons (2) and (5). Both these hydrocarbons can be formed from tribromide (1) provided that the base debrominates the vicinal dibromide, presumably by a trans coplanar E2 attack on the

bromine, in preference to bisdehydrobrominating the compound. Evidence from other series suggests that the vicinal debromination reaction is common in strong base.

Treatment of compound (3) with sodium iodide gave a dibromoolefin, m.p. 51.5–52°. The C7 methylene and the C9, C10 methyls resonated as singlets at δ 3.92 and 1.70 and the compound has structure (6). The infrared spectrum did not show a carbon–carbon stretching band, in line with the high symmetry of the molecule. Isomerization of (6) with perchloric acid gave an equilibrium containing (7) (70–80%). Bromination of this mixture gave crystalline (3) as the minor product together with a new oily tetrabromide (8). The p.m.r. spectra of (8) and of unstable terpinolene tetrabromide (9) showed considerable similarity. The C3 proton of (8) resonated as a multiplet, $W_{\text{H}/2} = 8$ Hz, indicating that the C3 bromine is axial, while the axial C2 proton is deshielded sufficiently to resonate uniquely as a quartet at δ 3.38. This compound is then a new tetrabromo derivative of β-terpinene (10).

* Carman, R. M., and Venzke, B. N., unpublished data.
Experimental

P.m.r. spectra were recorded at 60 MHz in carbon tetrachloride solutions with tetramethylsilane ($\delta$ 0·00) as internal reference. Infrared spectra, measured as potassium bromide discs, are given for the pertinent region below 800 cm$^{-1}$ for C-Br bands. Ultraviolet spectra were measured in cyclohexane solutions. Melting points were determined in open capillaries and are uncorrected.

Dehydrobromination of r-1,t-4,8-Tribromo-p-menthane (I)

r-1,t-4,8-Tribromo-p-menthane (I) was prepared* by the hydrobromination and bromination of dipentene (11). The tribromide (1) (10 g) was heated in absolute ethanol (50 g) containing dissolved sodium (4 g) for 0·5 hr. A copious precipitate of sodium bromide formed. The mixture was steam-distilled to give a colourless oil (3·6 g). P.m.r. examination showed the oil to be a mixture with $\delta$ 6·0-5·2 and 4·8-4·45 (C=C-H); 1·68 (C=C-CH$_3$) as significant bands.

The hydrocarbon mixture (3·6 g) in acetic acid (18 ml) and ethanol (3 ml) at $-10^\circ$ was treated with bromine until a pink colour persisted. The precipitated leafy crystals had m.p. 149-150$^\circ$ (from ethanol) (lit.$^2$ 154-155$^\circ$; lit. for compound (3)$^3$ 147·5-149$^\circ$). The p.m.r. spectra of the crystals and of compound (3) were superimposable.

The mother liquor from the bromination was poured into water and extracted into light petroleum. The concentrate partly solidified on cooling. A portion (2·5 g) was chromatographed on neutral alumina (200 g) to give, from the first hexane fraction, stable terpinolene tetrabromide (4), m.p. 114-116$^\circ$ (lit.$^4$ 122$^\circ$), with a p.m.r. spectrum superimposable upon that from authentic compound. Further elution gave fractions of a mixture, m.p. 102-103$^\circ$ (from ethanol, unraised by repeated recrystallization) (lit.$^2$ 103-104$^\circ$), containing (by p.m.r.) compound (4) and compound (3) (c. 5:1). The final fractions afforded the tetrabromide (3), m.p. 150$^\circ$. No other crystalline compound and only a little oil was isolated by chromatography.

Partial De bromination of r-1,t-4,7,8-Tetrabromo-p-menthane (3)

Tetrabromide (3) (1 g) in acetone (50 ml) was treated with sodium iodide (4 g) in acetone (50 ml) at 20$^\circ$. Aliquots (10 ml) were withdrawn 1 hr, 2; 4; 6; 8; 10 hr respectively. The mixture was poured into ice water containing sodium thiosulphate and extracted into light petroleum. The concentrate solidified to give 1,7-dibromo-p-menth-4(8)-ene (6), m.p. 51·5-52$^\circ$ (from methanol) (Found: C, 40·7; H, 5·5. C$_{10}$H$_{16}$Br$_2$ requires C, 40·5; H, 5·4%). P.m.r. spectrum (6): 3·82 (one-proton multiplet, 6 Hz; C$_3$ proton); 3·88 (two-proton singlet; C$_7$ methylene); 2·15 (six-proton doublet, $J$ 6·5 Hz; C$_9$, C$_{10}$ methyls).

The mixture was treated with bromine in ether at $0^\circ$ until a pink colour persisted for 1 hr. Evaporation of the solvent gave a partly crystalline mass. The crystals were identical (p.m.r.) with compound (3). The chief component (60-80%) of the oily residue was consistent with structure (8); p.m.r. spectrum (8): 4·82 (one-proton multiplet, $W_{1/2}$ 8 Hz; eq C$_3$ proton); 3·88 (two-proton singlet, C$_7$ methylene); 3·38 (one-proton quartet; $J_{2,3}$ 18 Hz, $J_{3,4}$ 4·5 Hz; ax C$_2$ proton); 1·12, 1·10 (two three-proton doublets, $J$ 6·5 Hz; C$_9$, C$_{10}$ methyls).

Acid-Catalysed Isomerization of 1,7-Dibromo-p-menth-4(8)-ene (6)

The dibromide (6) (2·1 g) was treated with ethyl acetate (50 ml) containing 72% perchloric acid (5 ml) for 5 days. The mixture was poured into water, extracted into petroleum and concentrated to give an oil. The chief components of the oil were (7) and (6) (c. 4:1). P.m.r. spectrum of compound (7) (6): 5·27 (one-proton multiplet, $W_{1/2}$ 9 Hz; C$_3$ proton); 3·88 (two-proton singlet; C$_7$ methylene); 1·05 (six-proton doublet, $J$ 6·5 Hz; C$_9$, C$_{10}$ methyls).

The mixture was treated with bromine in ether at $0^\circ$ until a pink colour persisted for 1 hr. Evaporation of the solvent gave a partly crystalline mass. The crystals were identical (p.m.r.) with compound (3). The chief component (60-80%) of the oily residue was consistent with structure (8); p.m.r. spectrum (8): 4·82 (one-proton multiplet, $W_{1/2}$ 8 Hz; eq C$_3$ proton); 3·88 (two-proton singlet, C$_7$ methylene); 3·38 (one-proton quartet; $J_{2,3}$ 18 Hz, $J_{3,4}$ 4·5 Hz; ax C$_2$ proton); 1·12, 1·10 (two three-proton doublets, $J$ 6·5 Hz; C$_9$, C$_{10}$ methyls).