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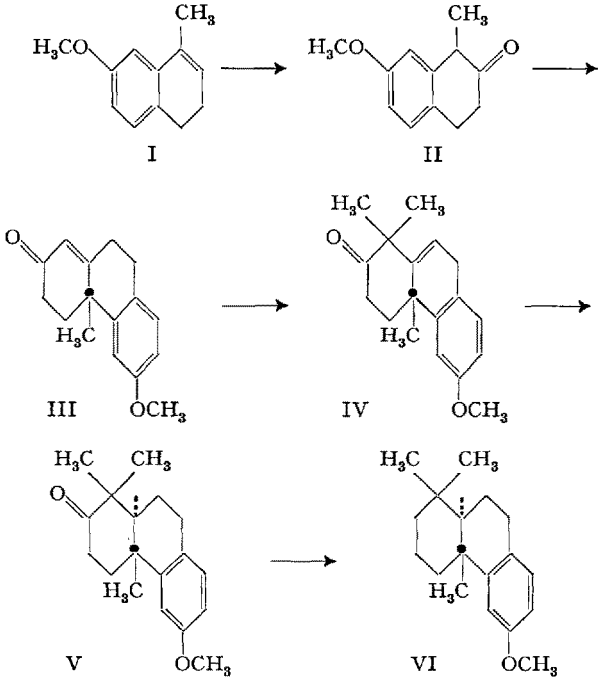
Synthetic Investigations in Diterpenoids

For some time we have been carrying out experiments to develop stereospecific syntheses for the diterpenoids. In view of a recent communication by STORK and SCHWLENBERG[1] on the synthesis of *dl*-dehydroabietic acid, we wish to report the results of our own work on the synthesis of DL-6-methoxypodocarpane (VI).



1-Methyl-7-methoxy-3,4-dihydronaphthalene[2] (I) was oxidized in acetic acid solution with red lead oxide[3] and the crude diacetate rearranged in dilute alcoholic sulphuric acid to 1-methyl-7-methoxytetralone-2 (II), b.p. 125–126°/0·8 mm, n_D^{27} 1·5730 (yield 72%) (calculated for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4; found: C, 76·1; 7·4), semicarbazone m.p. 191–192° (calculated for $C_{13}H_{17}O_2N_3$: N, 17·0; found: N, 17·2). Condensation of the β-tetralone (II) with 4-diethylaminobutanone-2-methiodide[4] afforded 6-methoxy-2-keto-4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene (III), b.p. 115–120° (air-bath)/0·004 mm as a very viscous oil (yield 62%) (calculated for $C_{16}H_{18}O_2$: C, 79·3; H, 7·5; found: C, 78·84; H, 7·5), 2,4-dinitrophenylhydrazone, m.p. 241–242° (dec.) (calculated for $C_{13}H_{17}O_2N_3$: C, 62·6; H, 5·3; found: C, 62·9; H, 5·5). This (III) was then methylated with methyl iodide in the presence of potassium tert-butoxide[5] to give 1,1-dimethyl-2-keto-6-methoxy-4a-methyl-1,2,3,4,4a,9-hexahydrophenanthrene (IV), b.p. 120–125° (air-bath)/0·004 mm as a glass (yield 72%). (Calculated for $C_{18}H_{22}O_2$: C, 79·97; H, 8·2; found: C, 79·9; H, 8·2), the 2,4-dinitrophenylhydrazone m.p. 238–240° (dec.) crystallized from acetic acid and contained one molecule of solvent (calculated for $C_{24}H_{28}O_5N_4$, CH_3COOH: N, 10·97; found N, 11·13). Mixed melting point with the 2,4-dinitrophenylhydrazone of the α,β-unsaturated ketone (III) shows 15° depression. Compound IV on hydrogenation with palladium-charcoal (10%) in acetic acid afforded 1,1-dimethyl-2-keto-6-methoxy-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (V), b.p. 180 to 184°/0·8 mm (calculated for $C_{18}H_{24}O_2$: C, 79·4; H, 8·9; found: C, 79·8; H, 8·9); 2,4-dinitrophenylhydrazone, m.p. 198–199° (calculated for $C_{24}H_{28}O_5N_4$: N, 12·3; found: N, 12·3). The keto group in compound V was reduced by CLEMMENSEN's method to give in good yield 1,1-dimethyl-4a-methyl-6-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (DL-6-methoxy podocarpane[6]) (VI), b.p. 145–147°/0·8 mm as a colourless mobile oil; n_D^{26} 1·5570 (calculated for $C_{18}H_{26}O$: C, 83·68; H, 10·1; found: C, 83·3; H, 10·2).

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Zusammenfassung

Die Synthese von 1,1-Dimethyl-4a-methyl-6-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthren (DL-6-Methoxypodocarpan) aus 1-Methyl-7-methoxytetralon-2 wird beschrieben.

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[2] P. C. MITTER and S. DE, J. Ind. chem. Soc. *16*, 35 (1939).

[3] *Cf.* F. W. NEWHALL, A. S. HARRIS, H. W. FREDERICK, L. E. JOHNSTON, W. J. RICHTER, E. WALTON, N. A. WILSON, and K. FOLKERS, J. Amer. chem. Soc. *77*, 5646 (1955).

[4] J. W. CORNFORTH and R. ROBINSON, J. chem. Soc. *1949*, 1855.

[5] G. COOLEY, B. ELLIS, and V. PETROW, J. chem. Soc. *1955*, 2998.

[6] *Cf.* W. P. CAMPBELL and D. TODD, J. Amer. chem. Soc. *64*, 928 (1942).

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Concentrations of Organic Acids in Animal Tissues *

Insofar as we know there is no summary in the literature of the concentrations of organic acids in animal tissues. Such data are, therefore, presented below.

The references in Table I guide the reader to the appropriate footnote which presents the meaning of the value given. In Table II are shown the sources of the

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