Synthesis of (±)-Methyl Tetradeca-*trans*-2,4,5-trienoate, the Allenic Sex Pheremone Produced by the Male Dried Bean Beetle

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Summary Dodeca-2,3-dien-1-ol was synthesised by the reductive elimination of the tetrahydropyran-2′-yloxy group from 4-tetrahydropyran-2′-yloxydodec-2-yn-1-ol, and oxidised with active manganese dioxide to the corresponding allenic aldehyde which, on treatment with the anion of trimethyl phosphonoacetate, gave (±)-methyl tetradeca-*trans*-2,4,5-trienoate.

THE first allenic sex attractant, produced by the male Dried Bean Beetle, *Acanthoscelides obtectus* (Say), was recently isolated by Horler,[1] and was shown to be (−)-methyl tetradeca-*trans*-2,4,5-trienoate.

We now report a synthesis of the racemic ester. The key allenic alcohol, dodeca-2,3-dienol (IVa; R = n-octyl) was synthesised by application of our new general method[2] as follows. 3-Tetrahydropyran-2′-yloxyundec-1-yne (IIa) obtained from undec-1-yn-3-ol (Ia) and dihydropyran, was converted into the Grignard derivative (with EtMgBr) which, with gaseous formaldehyde, gave 4-tetrahydropyran-2′-yloxydodec-2-yn-1-ol (IIIa). Reductive elimination of the tetrahydropyran-2′-yloxy group with excess of $LiAlH_4$ gave dodeca-2,3-dien-1-ol (IVa), ν_{max} 3350 (OH), 1960 (C=C=C), 870 cm^{-1} (C=C=CH–), which was oxidised with active manganese dioxide† in hexane to the unstable allenic aldehyde (Va). For optimum yields of aldehyde i.r. monitoring of the reaction mixture is essential. The crude aldehyde was added to the anion of trimethyl phosphonoacetate in dimethoxyethane and the mixture kept at 60° for 2·5 h. Repeated chromatography over Woelm acid alumina (Activity grade II) and elution with hexane–ether (90 : 10) gave (±)-tetradeca-*trans*-2,4,5-trienoate (VIa), ν_{max} 1940 (C=C=C), 1720 (CO_2Me), 1630 (C=C–), 980 cm^{-1} (*trans*-C=C–),λ_{max} 254 nm (ϵ 16,000), τ (CCl_4) 2·87 (1H, dd, *H*C=CHCO, $J_{2,3}$ 15, $J_{3,4}$ 10), 3·77—4·9 (3H, m, C*H*=C=CH and =C*H*–CO), 6·30 (3H, s, CO_2*Me*), 7·9 (2H, m, CH_2–C=), 8·7 (12H, m, $[CH_2]_6$), 9·12 (3H, t, CH_3–), in close agreement with the spectral data obtained by Horler.‡

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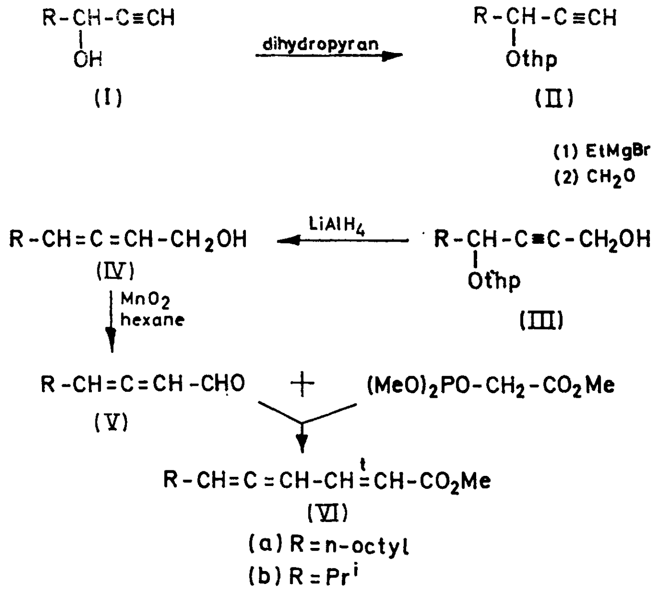
‡ We thank Dr. Horler for making available to us copies of the i.r. and n.m.r. spectra of the natural product.



Before proceeding to the synthesis of the ester from the Dried Bean Beetle we had tested the route with a model compound (R = Pr^i). The allenic alcohol, 5-methylhexa-2,3-dien-1-ol (IVb), ν_{max} 3500 (OH), 1960 cm^{-1} (–C=C=C–), τ ($CDCl_3$) 8·97 (6H, d, Me_2CH), 7·6 (1H, m, Me_2CH), 7·67 (1H, s, *OH*, disappears on deuteriation), 5·93 (2H, dd, –CH_2–OH), 4·62 (2H, m, –C*H*=C=C*H*–), obtained by the method outlined above was oxidised to the conjugated aldehyde (Vb), ν_{max} 1940 (C=C=C) and 1695 (CH=O) which, with the modified Wittig reagent, trimethyl phosphonoacetate, gave the model ester, methyl 7-methylocta-*trans*-2,4,5-trienoate (VIb), ν_{max} 1940 (C=C=C), 1720 (CO_2Me), 1630 (C=C), 980 cm^{-1} (*trans*-CH=CH–), τ (CCl_4) 8·97 (6H, d, Me_2CH, *J* 6·5), 7·67 (1H, m, Me_2CH), 6·23 (3H, s, CO_2Me), 4·83 (1H, m, C=C*H*–C=C), 4·5 (1H, m, CH–C*H*=), 4·12 (1H, d, C*H*–CO, *J* 15), 2·87 (1H, dd, CHC*H*=CHCO, $J_{2,3}$ 15 and $J_{3,4}$ 10).

We are now proceeding with the synthesis of the laevorotatory enantiomer.

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[1] D. F. Horler, *J. Chem. Soc.* (*C*), 1970, 859.

[2] J. S. Cowie, P. D. Landor, and S. R. Landor, *Chem. Comm.*, 1969, 541.