

SYNTHESIS OF BOTH GEOMETRIC ISOMERS OF THE MAJOR
SEX PHEROMONE OF THE RED BOLLWORM MOTH

Brenda F. Nesbitt*, P.S. Beevor, R.A. Cole, R. Lester, and R.G. Poppi
Tropical Products Institute, 56-62, Gray's Inn Road, London, WC1X 8LU

(Received in UK 29 August 1973; accepted for publication 10 October 1973)

We have recently reported that the most potent of the sex pheromones produced by the female red bollworm moth, Diparopsis castanea Hmps. is trans 9,11-dodecadien-1-yl acetate¹, I.



Pure trans and cis isomers of I were required for field testing, both separately and combined in known ratios. Mixed isomers (60:40 trans:cis) were obtained in 70% yield by a Wittig reaction between allyl triphenylphosphonium bromide and 9-oxonon-1-yl acetate² using butyl lithium in ether. Enrichment in one or other isomer within the range 80:20 to 30:70 trans:cis could be effected by alterations in solvent polarity but attempts to obtain greater stereoselectivity were unsuccessful. Separation of the isomers was extremely difficult because of the terminal, conjugated unsaturation. Only partial resolution was achieved by argentation chromatography, (25% AgNO₃ on silica gel with hexane:ethyl acetate 98.4:1.6 as eluent). We found that 99+% trans I could be prepared in high yield by formation and thermal decomposition of the sulphone II³. The Wittig product was treated with liquid sulphur dioxide containing a trace of quinol at -20°C for 2 days and the resultant sulphone separated from unreacted cis I by gradient elution from Florisil with hexane: ether (95:5 to 0:100). The sulphone was decomposed stereospecifically to give trans I either by flash distillation at 120°C/1mm or by refluxing for 30 min. in n-octane⁴.

Pure cis I was isolated in high yield from the Wittig product by

treatment with excess tetracyanoethylene in tetrahydrofuran at room temperature⁵ followed by chromatography on Florisil in hexane:ether, 95:5, to remove the Diels-Alder adduct of the trans isomer. Other less reactive dienophiles (maleic anhydride, p-benzoquinone) gave only poor yields of adduct.

As the isomers of I were not resolved by glc, even using capillary columns, the following methods were used to establish isomeric purity, (i) epoxidation with m-chloroperbenzoic acid in benzene at 6°C and glc analysis of the cis and trans internal mono-epoxides on Carbowax 20M (2¼% on Chromosorb G)⁶, (ii) reduction of the terminal double bond with diimide (from $\text{NH}_2\text{NH}_2/\text{H}_2\text{O}_2/\text{CuSO}_4$)⁷ in ethanol and glc analysis of the 9-dodecen-1-yl acetate isomers on tetracyanoethylated pentaerythritol (9% on Chromosorb W). IR analysis of I (in CS_2) could be used to detect small percentages of trans in predominantly cis material (trans C=C, 947cm^{-1}) but not vice versa. The IR spectrum of the synthetic trans isomer was identical with that of the natural pheromone¹. However, microscale application of assay methods (i) and (ii) to the natural pheromone indicated that it contained 15-25% cis isomer, which would not have been detected by IR analysis. It has recently been suggested that small proportions of the opposite geometric isomer may occur frequently in insect sex pheromones⁸, but no actual instances of this phenomenon have been reported previously.

REFERENCES AND NOTES

1. Brenda F. Nesbitt, P.S. Beevor, R.A. Cole, R. Lester, R.G. Poppi, Nature New Biology, 244, 208 (1973).
2. Obtained by reductive ozonolysis of oleyl acetate in CS_2 using Ph_3P .
3. IR, mass spectra and elementary analyses were in agreement with the assigned structure. Bp of I, 108-110°C/0.5mm. Impurities <1% by glc analysis.
4. William L. Mock, J. Amer. Chem. Soc., 88, 2857 (1966).
5. L.A. Paquette, J. Org. Chem., 29, 3447 (1964).
6. Leslie M. McDonough, and Donald A. George, J. Chromat. Sci., 8, 158 (1970).
7. E.J. Corey, Y. Hisashi, D.K. Herron, K. Achiwa, J. Amer. Chem. Soc., 92, 6635 (1970).
8. Morton Beroza, G.M. Muschik, C.R. Gentry, Nature New Biology, 244, 149 (1973).