

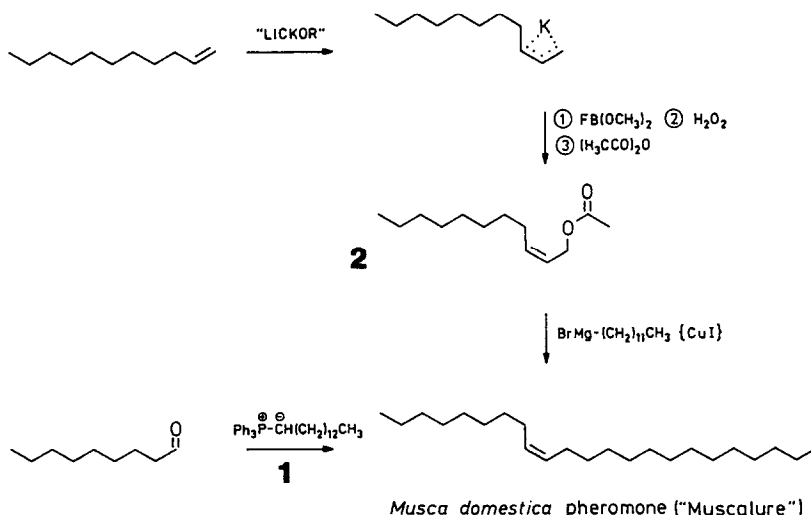
A NEW STEREOSELECTIVE SYNTHESIS OF (Z)-9-TRICOSENE,
THE SEX ATTRACTANT OF THE COMMON HOUSEFLY

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Summary: "Muscalure" (9-tricosene) was prepared very readily by an instant-ylid reaction in a highly cis-selective manner although it was found difficult to assess the (Z/E)-ratio with accuracy.

The instant ylid method [1] allows the preparation of lithium salt-free phosphorus ylids in a particularly convenient manner. When a solution, thus generated, of triphenylphosphonio-tetradecylid (**1**) was combined at -75°C with nonanal (pelargonic aldehyde) and kept 15 min at 25°C, 9-tricosene having a (Z/E)-ratio of approximately 97.5 : 2.5 was formed and isolated in 81% yield (bp 143 - 145°C/10⁻² mmHg). Very similar yields and stereoselectivities were obtained when the acetate **2** (resulting from consecutive treatment of 1-undecene with butyllithium in the presence of potassium *tert*-butoxide ["LICKOR"], fluorodimethoxyborane [2], alkaline hydrogen peroxide and acetic anhydride in the presence of pyridine) was submitted to the copper-catalyzed condensation [3] with dodecylmagnesium bromide.



The *cis*-isomer of 9-tricosene ("muscalure"), the sex attractant of the common housefly (*Musca domestica*), is a pheromone without practical importance. Moreover, many syntheses are already known [4], some of which use oleic acid or erucic acid as a readily available starting material carrying already the required double bond at the proper position and with the proper configuration. The purpose of this communication is just to call attention to two facts :

1. Gas chromatography fails to separate *cis/trans*-isomers of straight-chain alkenes having a molecular weight higher than 150. We have mixed varying amounts of authentic (*Z*)- and (*E*)-9-tricosene (the latter being prepared *via* the betaine-ylid [5]; 84%; bp 149 - 151°C; mp 26 - 27°C) and injected the samples into 9 columns (4 of them belonging to the capillary type) all of them packed or coated with different stationary phases: neither broadening of the peaks nor shoulder formation gave the slightest hint on the presence of stereoisomers. We had to resort to a special nmr technique for determination of (*Z/E*)-ratios. The peak areas of the olefinic hydrogens were measured by high-resolution (360 MHz) nmr spectrometry under selective decoupling of the allylic positions. The signals of the (*Z*)- and (*E*)-isomer appeared at slightly different field (δ_{cis} 5.34; δ_{trans} 5.38) and their intensity could be measured by integration. The analytical accuracy of this method is, of course, a limited one (in general \pm 2%).
2. Ylids generated with sodium amide in liquid ammonia [6] or as "instant ylids" in tetrahydrofuran [1] give the highest possible *cis/trans*-ratios. As pointed out already previously, no other technique is superior nor even competitive with this approach [1]. Thus, a *cis*-selectivity of 97% or, in fortunate cases, 98% must be considered as the best that presently can be achieved by carbonyl olefination of ordinary aldehydes.

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- [1] M. Schlosser & B. Schaub, *Chimia* 1982, 36, 396.
 [2] G. Rauchschwalbe & M. Schlosser, *Helv. Chim. Acta* 1975, 58, 1094.
 [3] G. Fouquet & M. Schlosser, *Angew. Chem.* 1974, 86, 50; *Angew. Chem., Int. Ed. Engl.* 1974, 13, 82.
 [4] K. Eiter, *Naturwiss.* 1972, 59, 468; R.L. Cargill & M.G. Rosenblum, *J. Org. Chem.* 1972, 37, 3571; G.W. Gribble, J.K. Sanstead & J.W. Sullivan, *Chem. Commun.* 1973, 735; H.J. Bestmann, O. Vostrowsky & H. Platz, *Chem. Ztg.* 1974, 98, 161; H.C. Brown & D. Basavaiah, *J. Org. Chem.* 1982, 47, 3806; V.N. Odinkov, G.A. Tolstikov, R.I. Galeyeva & T.A. Kargapolteva, *Tetrahedron Lett.* 1982, 1371.
 [5] M. Schlosser & K.F. Christmann, *Angew. Chem.* 1966, 78, 115; *Angew. Chem., Int. Ed. Engl.* 1966, 5, 126; M. Schlosser, *Topics in Stereochemistry* 1970, 5, 1.
 [6] G. Wittig, H. Eggers & P. Duffner, *Justus Liebigs Ann. Chem.* 1958, 619, 10; M. Schlosser & K.F. Christmann, *Justus Liebigs Ann. Chem.* 1967, 708, 1.

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