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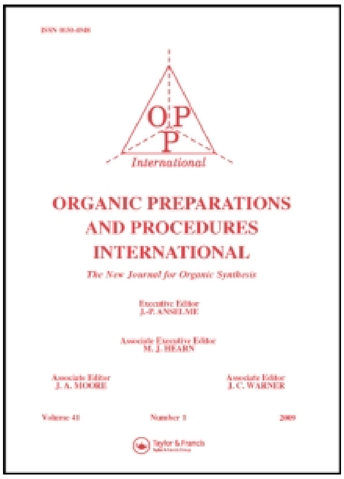

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cis-OLEFINS FROM THE WITTIG REACTION

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cis-OLEFINS FROM THE WITTIG REACTION

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In connection with studies on the isolation and identification of sex pheromones of the face fly, Musca autumnalis, DeGeer, it became necessary to prepare a number of straight chain (Z)-heptacosenes and nonacosenes. These compounds are present in the cuticular hydrocarbons of both male and female flies and several of them are active as male sex excitants.[1] A Wittig olefin synthesis modified to yield predominantly the cis-isomer appeared to be the most direct route to these compounds. Methods for obtaining cis-olefins from the reaction of an unstabliized alkylidene triphenylphosphorane with an alkyl halide include the use of sodium hydride-dimethylformamide (DMF),[2] dimsyl sodium -- dimethyl sulfoxide (DMSO),[3] and potassium -- hexamethylphosphoric triamide (HMPT).[4] We have found that addition of DMSO or HMPT, as cosolvent, to a tetrahydrofuran (THF) solution of a phosphorane yields cis-olefins of 94-96% geometrical purity. Since smaller quantities of the more expensive polar solvents are required in this procedure and n-butylithium (which is in some ways more convenient to use than potassium) serves as the base, the procedure should be particularly attractive for large scale preparations.

The several alkenes synthesized by this method are listed in Table 1. Geometric purity was estimated from the intensity of the 970 cm^{-1} infrared band due to trans olefin, with trans-9-octadecene as the standard.

Our results from the preparation of (Z)-11-nonacosene by several methods and with some variations in solvent composition are summarized in Table 2. The cis content of preparations by Bergelson's procedures [2] (entries 5 and 6 of Table 2) served to corroborate our estimations of geometrical isomer content. Varying solvent composition in Wittig condensations in order to enhance the rate of formation of a desired geometrical isomer is quite common. However, the degree to which the isomer content is affected by a small amount of HMPT or DMSO appears

Table 1

PREPARATION OF cis-OLEFINS BY THE WITTIG REACTION IN HMPT-THF(1:2) [a]

		Elemental		Analysis	
Olefin (Aldehyde used) [b]	n_D^{25}	Calcd C	H	Found C	H
(Z)-10-heptacosene (C_{10})	1.4531	for $C_{27}H_{54}$: C,85.63;H,14.37		85.61	14.21
(Z)-11-heptacosene (C_{11})	1.4541			85.84	14.25
(Z)-12-heptacosene (C_{12})	1.4524			85.60	14.14
(Z)-13-heptacosene (C_{13})	1.4489			85.81	14.43
(Z)-10-nonacosene (C_{10})	1.595	for $C_{29}H_{58}$: C,85.63;H,14.37		85.92	14.26
(Z)-11-nonacosene (C_{11})	1.4490			85.44	14.34
(Z)-12-nonacosene (C_{12})	1.4496			85.71	14.34
(Z)-13-nonacosene (C_{13})	1.4430			85.62	14.43
(Z)-14-nonacosene (C_{14})	1.4514			85.71	14.32

a) Yields were 80-90% and the proportion of cis isomer was 94-96% in each case. b) Aldehydes were obtained commercially and used without further purification or were synthesized as described in the Experimental Section. Satisfactory elemental analyses and spectral data were obtained for all new compounds.

to be noteworthy. This is particularly so since insect sex pheromones are often long chain cis-alkenes, alkenols, and alkenol acetates [5,6], and recent literature emphasizes the use of potassium/HMPT to produce cis-olefins of this same purity [4,7].

EXPERIMENTAL

Alkyl triphenylphosphonium salts were prepared from alkyl halides and triphenylphosphine in refluxing acetonitrile in the usual manner. Tridecanal was prepared (in 72% yield (bp. 78-84°/.5 mm., lit.[8] bp. 156°/23 mm) from tridecanol by oxidation with N-chlorosuccinimide mediated by dimethyl sulfide as described by Corey and Kim.[9] Infrared spectra of CCl_4 solutions of the olefins were obtained with a Perkin-Elmer 457A spectrometer. Commercial solvents were dried over molecular sieves and used without distillation.

Syntheis of cis Olefins.- A slurry of 5.0 mmol of powdered alkyltriphenylphosphonium bromide in 10 ml of THF was prepared under nitrogen. The mixture was cooled in an ice bath, and a 2.0 M solution of n-butyllithium in hexane was injected. The organometallic (5.0 mmol beyond the point of permanent coloration of the reaction mixture) was added at such a rate that the temperature of the mixture was maintained at 10-15°. After 5 min, 5 ml of either DMSO or HMPT was injected. Then 5.0 mmol of the aldehyde was injected, and the resulting mixture was stirred for 30 min at ambient temperature. The mixture was diluted with water and extracted with pet ether.

The dried ($MgSO_4$) extract was concentrated, allowing the crude product to deposit on 5 g of alumina. This material was added to a 10 g column of alumina, and the product was eluted with 50 ml of pet ether. Concentration of the eluate produced the liquid cis olefins. Gas chromatography (5% SE-30 on ABS Gas Chrom Q at 250°) indicated the products were homogeneous. Analytical samples were obtained by distillation in a Hickman apparatus; bath temp 180-220° (0.1 mm). These compounds could also be recrystallized from acetone-pet ether (-20°)

Table 2

cis CONTENT OF 11-NONACOSENE OBTAINED BY VARIOUS MODIFICATIONS OF WITTIG CONDENSATION PROCEDURE [a]

	Solvent	Yield	% cis
1	THF	84	84
2	THF, DMSO(2:1)	87	94
3	THF, HMPT(2:1)	81	96
4	HMPT	81	95
5	DMF(NaOEt)	46	92
6	DMF(NaH)	39	91

a) Unless otherwise stated, n-butyllithium was the base employed.

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