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NOVEL SYNTHESIS OF 1,3-DIENES FROM 1-ALKENES VIA "ENE" REACTION WITH PUMMERER REARRANGEMENT PRODUCT: A SHORT SYNTHESIS OF THE SEX PHEROMONE OF THE RED BOLLWORM MOTH

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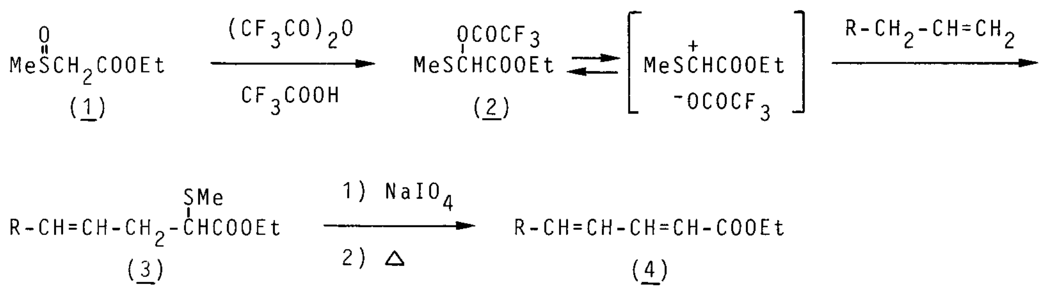
Summary: A Pummerer rearrangement product, 4-chlorophenylthiomethyl trifluoroacetate (6), obtained from 4-chlorophenyl methyl sulfoxide (5) and trifluoroacetic anhydride, reacted with 1-alkenes in trifluoroacetic acid to give the ene products 8, which were readily converted into the terminal 1,3-dienes 10 by oxidation and subsequent pyrolysis. Using this method, 9,11-dodecadien-1-yl acetate (12), a sex pheromone of the red bollworm moth, was synthesized.

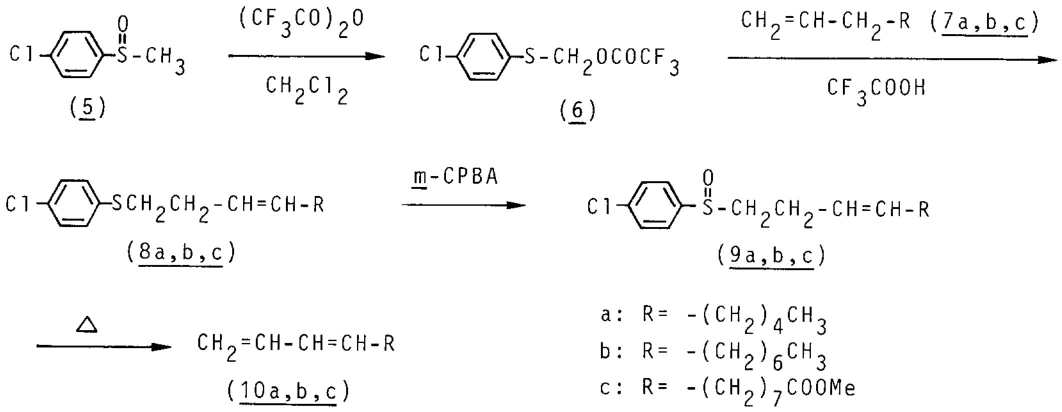
Synthesis of conjugated dienes is one of the major problems in organic and natural product chemistry.[1] In a previous paper,[2] we reported that the Pummerer rearrangement product 2 from ethyl methylsulfinylacetate (1) reacts with 1-alkenes in trifluoroacetic acid to produce the so-called "ene" products 3, which are readily converted into the 2,4-alkadienoic esters 4 through oxidative desulfurization. The present paper describes a further extention of this reaction to the synthesis of terminal conjugated dienes by using 4-chlorophenyl methyl sulfoxide (5) and its application to the synthesis of the sex pheromone of the red bollworm moth.



$$\underset{(1)}{\mathrm{Me\overset{O}{\overset{\|}{S}}CH_2COOEt}} \xrightarrow[\mathrm{CF_3COOH}]{\mathrm{(CF_3CO)_2O}} \underset{(2)}{\mathrm{Me\overset{OCOCF_3}{\overset{|}{S}}CHCOOEt}} \rightleftarrows \left[\begin{array}{c}\mathrm{Me\overset{+}{S}CHCOOEt} \\ {}^{-}\mathrm{OCOCF_3}\end{array}\right] \xrightarrow{\mathrm{R{-}CH_2{-}CH{=}CH_2}}$$

$$\underset{(3)}{\mathrm{R{-}CH{=}CH{-}CH_2{-}\overset{SMe}{\overset{|}{C}}HCOOEt}} \xrightarrow[2)\ \Delta]{1)\ \mathrm{NaIO_4}} \underset{(4)}{\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}COOEt}}$$

In contrast to the sulfoxide 1, which undergoes readily the Pummerer rearrangement by treatment with trifluoroacetic anhydride (TFAA) in trifluo-



a: R= $-(CH_2)_4CH_3$
b: R= $-(CH_2)_6CH_3$
c: R= $-(CH_2)_7COOMe$

roacetic acid, the sulfoxide 5 was found to be stable under similar conditions. Therefore, the following two-step procedure was developed to obtain the desired ene product 8.

A solution of the sulfoxide 5 (349 mg, 2 mmol) in CH_2Cl_2 (5 ml) was treated with TFAA (420 mg, 2 mmol) at room temperature for 3 h to give the trifluoroacetate 6 [δ 5.53 (2H, s) and 7.32 (4H, br s)] in quantitative yield after removal of the solvent. Subsequently, a solution of 1-octene (7a) (112 mg, 1 mmol) in trifluoroacetic acid (2 ml) was added to the acetate 6 at 0°C and the mixture was stirred at the same temperature for 90 min. The reaction mixture was poured into CH_2Cl_2 and washed with a saturated $NaHCO_3$ solution. The solvent was evapoprated off and the residue was chromatographed on silica gel (n-hexane) to give 1-(4-chlorophenyl)-3-nonene (8a)[3] in 83% yield (based on 1-octene)[4]. A similar reaction of 6 with 1-decene (7b) gave the product 8b[3] in 77% yield.

The sulfoxide 5 is the best of several reagents we have examined for the ene reaction. With phenyl methyl sulfoxide the yield of ene product was much lower (~50%) and with 3,4-dichlorophenyl methyl sulfoxide the reactions of its Pummerer rearrangement product with 7a,b were very sluggish.

Oxidation of the ene products 8a,b with m-chloroperbenzoic acid (m-CPBA) (CH_2Cl_2, 0°C) gave the corresponding sulfoxides 9a,b, quantitatively, which were subjected to the pyrolysis without a solvent at 140°C (30 min) and then distilled to afford 1,3-nonadiene[5] (10a) [bp 125°C (bath temp.)/40 mmHg] and 1,3-undecadiene (10b)[6] [bp 135°C (bath temp.)/40 mmHg] in 76 and 65% yields, respectively. The ratios of E and Z isomers of 10a and 10b were estimated to be 80/20 and 79/21, respectively, by the integrated intensities of the peaks in their 300 MHz ^1H NMR spectra (Table 1).

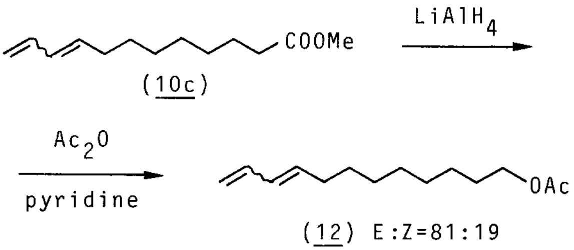
Conjugated dienes are widely encountered in insect sex pheromone.[7] 9,11-Dodecadien-1-yl acetate (12) [E/Z=80/20 (±5%)] is the major component of the

Table 1. 300 MHz ^{1}H NMR Data for $H^1H^2C=CH^3-CH^4=CH^5-R$ in $CDCl_3$[a)] (J in Hz)

Compd.	Geometry	δ: H^1	H^2	H^3	H^4	H^5	$J^{cis}_{1,3}$	$J^{trans}_{2,3}$	$J_{3,4}$	$J^{cis}_{4,5}$	$J^{trans}_{4,5}$
10a	E	4.96	5.10	6.32	6.06	5.72	10.3	17.2	10.3	-	15.1
	Z	5.09	5.19	6.66	6.01	5.47	10.8	16.4	10.8	11.2	-
10c	E	4.95	5.08	6.30	6.04	5.70	10.3	17.2	10.3	-	15.2
	Z	5.08	5.18	6.63	6.00	5.44	10.4	17.2	10.4	10.8	-
12	E	4.94	5.08	6.31	6.04	5.70	10.3	17.3	10.3	-	15.2
	Z	5.08	5.18	6.64	6.00	5.45	10.4	16.8	10.4	10.8	-

a) Diene peaks of 10b were the same as those of 10a (± 0.01 ppm)

sex pheromone of the red bollworm moth,[8] which does substantial damage to the cotton crop in southeastern Africa. Using the present method, we were able to synthesize easily this compound starting from commercially available methyl 10-undecenoate (7c). The reaction of the trifluoroacetate 6 with 7c gave the ene product 8c[3] in 83% yield. Oxidation (*m*-CPBA) of 8c and subsequent pyrolysis [at 150°C, $(MeO)_3P$] of the resultant sulfoxide 9c yielded methyl 9,11-dodecadienoate (10c) [E/Z=81/19 by ^{1}H NMR (Table 1)] in 82% yield (based on 8c) after purification with silica gel chromatography (benzene:*n*-hexane=1:2). The ester 10c was reduced with lithium aluminum hydride (ether, 0°C) to give the alcohol 11, in 87% yield, which was then converted into the acetate 12 [E/Z=81/19 by ^{1}H NMR (Table 1)] with acetic anhydride and pyridine in 98% yield.



Although a number of methods have been reported for the synthesis of the acetate 12 so far,[6,8b,9] the present method is probably the shortest one (five steps) with highest overall yield (58% from 7c). In addition, it should be noted that the E/Z ratio of the compound 12 thus obtained closely resembles that of the natural product.

Further applications of this method to the synthesis of more elaborated molecules are currently underway.

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3) The 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra of 8 show them to be the mixture of E (80-90%) and Z (10-20%) isomers. 300 MHz ^{1}H NMR data: 8a: δ 0.88 (3H, t, J=6.9 Hz), 1.2-1.4 (6H, m), 1.97 (2H, q, J=6.8 Hz), 2.26-2.40 (2H, m), 2.90 [2H, t, J=~7.5 Hz with further splitting (~2 Hz)], 5.33-5.54 (2H, m), and 7.24 (4H, s). 8c: δ 1.29 (10H, br s), 1.61 (2H, q, J=7.3 Hz), 1.97 (2H, q, J=6.4 Hz), 2.30 (2H, t, J=7.3 Hz), 2.26-2.40 (2H, m), 2.91 (2H, br t, J= 7.5 Hz), 5.41 (dt, J=15.2 and 5.5 Hz, one olefinic proton of E isomer), 5.47 (dt, J=15.2 and 5.5 Hz, one olefinic proton of E isomer), 5.33-5.48 (m, olefin protons of Z isomer), and 7.24 (4H, s).

4) Reaction of the trifluoroacetate 6 with 1-octene in CH_2Cl_2 gave no ene product 8a.

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