

A SIMPLE METHOD OF ISOMERIZATION OF THE TERMINAL DOUBLE BOND IN A TERPENE CHAIN

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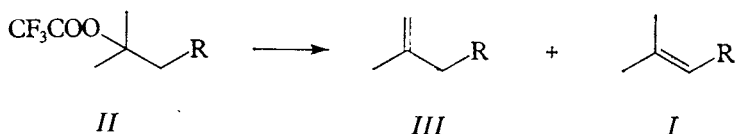
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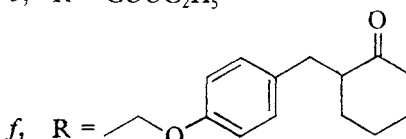
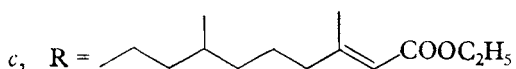
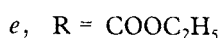
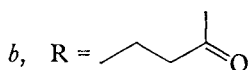
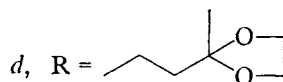
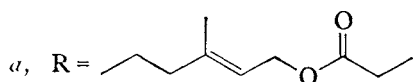
The utilisability of the isomerization of the terminal double bond in terpenic compounds with trifluoroacetic acid was investigated. The results obtained were used in the synthesis of the main part of the pheromone of *Quadraspidiotus perniciosus* COMSTOCK, *i.e.* (2*E*)-3,7-dimethyl-2,7-octadien-1-yl propionate.

Quadraspidiotus perniciosus COMSTOCK is one of the world-wide most serious pests of fruit trees and shrubs, and also in Czechoslovakia it is a quarantine pest. The main components of its sexual pheromone were isolated, identified and synthesized gradually over the last 6 years¹. In our laboratories we prepared one of the components, (2*E*)-3,7-dimethyl-2,7-octadien-1-yl propionate, by pyrolysis of the corresponding trifluoroacetate. This compound is used for the signalization of the occurrence of the pest. Nowadays this route represents one of the simplest methods of preparation of this active substance².

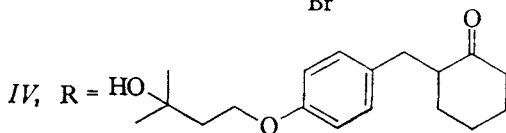
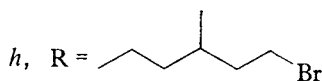
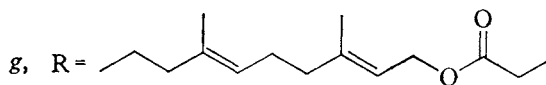


The pyrolysis of the acetates takes place under splitting off of the β -hydrogen atom³⁻⁸. The position of the double bond in the product is usually determined by the statistical factor, *i.e.* by the number and location of the β -protons in the starting acetate. The terminal system of the two methyl groups in the terpene chains is thus very favourable for our purpose, because the ratio of the β -hydrogen atoms is 3 : 1 in favour of the isomer III, and therefore the yield of this isomer may reach more than 70%.

We prepared the esters of trifluoroacetic acid *Ila-h* by mixing solutions of trifluoroacetic acid and the appropriate compound in dichloromethane (under stirring and cooling) and isolation by chromatography on silica gel. In the case of acetal *Id* we isolated compound *Iib* in addition to the product, because a splitting off of the acetal ring took place simultaneously. Similarly, when compound *Iif* was chromatographed on silica gel, hydrolysis of the ester groups took place, so that only derivative *IV* was obtained. Trifluoroacetic acid does not add to the double bond of the α,β -unsaturated ester *Ie* at all.



The pyrolyses were carried out at 220°C; argon was used as carrier gas and the pyrolysis products were collected into a cooled solution of diethylamine in ether. After isolation the products were submitted to analysis. A HPLC analysis of the product showed that the content of isomers *IIIa-h* is mostly in the 30–60% range while the isomers *Ia-h* represent the rest. However, in the case of ketone *Iib* only isomer *Ib* was detected. Evidently in this case a participation of the keto group takes place, which results in a splitting off of the methylene group protons, under formation of isomer *Ib*. This view is supported by the pyrolysis course of acetal *Iid*, where the keto group is blocked by the acetal ring. Under the conditions of the pyrolysis, a splitting off of the acetal group (90%) does take place, but in the final product only a mixture of *Ib* and *IIIb* in a 70 : 30 ratio could be identified.



On summarizing the results presented in Tables I and II, it follows that the isomerization is utilizable for the preparation of isomers *IIIa-h* from which the corresponding relatively stable trifluoroacetyl ester *IIa-h* can then be prepared. The required isomers *IIIa-h* can be separated from the isomers *Ia-h* using the method described in the Experimental.

EXPERIMENTAL

The majority of the products was isolated by column chromatography on silica gel containing 25% of water (Herrmann, Köln-Ehrenfeld). The course of the reactions was monitored by thin-layer chromatography on silica gel G (Merck). The IR spectra were measured in CCl_4 on a UR-20 spectrophotometer (Carl Zeiss, Jena). The mass spectra were measured on an AEI MS 902 spectrometer and the ^1H NMR spectra on an XL-200 (Varian) or BS 467 (60 MHz, Tesla) instrument in C^2HCl_3 , using tetramethylsilane as internal reference. The chemical shift values

TABLE I
Properties of trifluoroacetates *IIa-h*

Compound	Formula m.w.	Mass sp. ^a M^\ddagger	IR sp. ^b cm^{-1}
<i>IIa</i>	$\text{C}_{15}\text{H}_{23}\text{F}_3\text{O}_4$ (324.3)	210	1 780, 1 739, 1 670, 1 170, 1 128
<i>IIb</i>	$\text{C}_{10}\text{H}_{15}\text{F}_3\text{O}_3$ (240.2)	126	1 783, 1 724, 1 369, 1 271, 1 224, 1 123
<i>IIc</i>	$\text{C}_{19}\text{H}_{31}\text{F}_3\text{O}_4$ (380.4)	266	1 779, 1 718, 1 650, 1 224, 1 171, 1 151
<i>IIc</i> ^c	$\text{C}_{12}\text{H}_{19}\text{F}_3\text{O}_4$ (284.3)	170	1 780, 1 225, 1 170, 1 145, 1 125, 1 067
<i>IIe</i> ^d	$\text{C}_7\text{H}_{12}\text{O}_2$ (128.0)	128	1 719, 1 656, 1 230, 1 150
<i>IIe</i> ^c	$\text{C}_{18}\text{H}_{26}\text{O}_3$ (290.4)	272	3 610, 1 712, 1 613, 1 596, 1 526, 1 263
<i>IIg</i>	$\text{C}_{20}\text{H}_{31}\text{F}_3\text{O}_4$ (392.5)	278	1 780, 1 740, 1 672, 1 224, 1 172
<i>IIh</i>	$\text{C}_{12}\text{H}_{20}\text{BrF}_3\text{O}_2$ (333.2)	219	1 781, 1 225, 1 173, 573

^a M^\ddagger — CF_3COOH ; compound *IIe*: M^\ddagger — H_2O ; ^b for details see the introductory section of Experimental; ^c IR recorded for a mixture of compounds *IIb* and *IIc* in a 1 : 1 ratio; ^d the reaction did not take place; ^e only compound *IV* was obtained.

(ppm, δ -scale) were in agreement with the assumed structure, while the trifluoroacetic acid esters *IIa-h* may be characterized on the basis of the signals of methyl group protons (1.55 ppm, 6 H, s) and the products of pyrolysis according to the signals of the exomethylene group protons (4.67 ppm, 2 H, br m). On the basis of the characteristic bands of the pyrolysis products *Ia-h* and *IIIa-h* in the IR spectra (about 890 and 3 075 cm^{-1}), the products could be distinguished from the trifluoroacetates *IIa-h*. At the same time the absence of the bands in the spectra of esters *IIa-h* proved the absence of the starting compounds *Ia-h*. Dichloromethane was filtered through alumina (Woelm neutral, I) before use. The HPLC analysis carried out on a 250×4 (i.d.) mm column packed with Separon VISK-Si C_{18} 5 μ (Laboratorní přístroje, Prague), using methanol with 20% or 8% of water and 50 mmol dissolved AgNO_3 as mobile phase. The flow rate was 1 ml/min and detection was carried out using a differential refractometer RIDK 101 (Laboratory Apparatus, Prague).

Preparation of Trifluoroacetates *IIa-h*

A solution of trifluoroacetic acid in dichloromethane (1 mol l^{-1} , 10 ml) was added dropwise into a cooled (-20°C) and stirred solution of compound *Ia-h* in dichloromethane (0.5 mol l^{-1} , 10 ml) over 30 min. The stirred mixture was allowed to warm to room temperature, while the reaction course was followed by TLC analyses at five minute intervals. As soon as the reaction was over, neutralization with a diethylamine solution in dichloromethane was carried out (to $\text{pH} \approx$

TABLE II
Properties of the pyrolysis products

Compound ^a	Formula m.w.	Calculated/Found		Mass spectrum M^{\ddagger}	IR spectrum ^b cm^{-1}
		% C	% H		
<i>IIIa/Ia</i> (60/40)	$\text{C}_{13}\text{H}_{22}\text{O}_2$ (210.3)	77.24 73.91	10.54 10.50	210	3 075, 1 739, 1 670, 1 649, 1 180, 890
<i>IIIb/Ib</i> (0/100)	$\text{C}_8\text{H}_{14}\text{O}$ (126.2)	76.14 76.28	11.18 11.05	126	3 050, 1 721, 1 681, 1 359, 853
<i>IIIc/Ic</i> (65/35)	$\text{C}_{17}\text{H}_{30}\text{O}_2$ (266.4)	76.64 76.12	11.35 11.18	266	3 075, 1 719, 1 651, 1 223, 1 151, 890
<i>IIId/Id</i> ^c (30/70)	$\text{C}_{10}\text{H}_{18}\text{O}_2$ (170.3)	—	—	170	1 725, 1 678, 1 222, 1 207, 1 140, 1 061
<i>IIIg/Ig</i> (60/40)	$\text{C}_{18}\text{H}_{30}\text{O}_2$ (278.4)	77.65 77.11	10.86 10.80	278	3 075, 1 740, 1 670, 1 650, 1 185, 890
<i>IIIh/Ih</i> (40/60)	$\text{C}_{10}\text{H}_{19}\text{Br}$ (219.2)	—	—	219	3 080, 1 651, 891, 572

^a Approximate ratio *III/I* was determined by HPLC; ^b for details see the introductory section of Experimental; ^c IR recorded for a mixture of compounds *IIIb/Ib* and *IIId/Id* in a 9 : 1 ratio which were obtained by pyrolysis. The amount of isomer *III* refers to compound *IIIb*, not *IIId*.

= 7). The mixture was evaporated on a rotatory evaporator at a temperature as low as possible, and the residue was chromatographed on silica gel with 25% of water. The combined chromatographic fractions were dried at 40°C and 1.6 kPa for 60 min. The yields were in the 30–40% range. The data on the characteristic signals of pure compounds *Ila–h* in the ¹H NMR spectra are given in the introductory section of Experimental.

Pyrolysis of Trifluoroacetates *Ila–h*

Compounds *Ila–h* were pyrolysed in a continuous reactor made of a glass tube (200 × 15 mm, filled with glass beads of 1 mm diameter, heated at 220°C). Compounds *Ila–h* were injected through a septum injection port at a 20 μl/h rate. In this way it was possible to process about 150 μl of esters *Ila–h* during 6–8 h. Argon was used as carrier gas, flowing at an approximately 2 ml/min rate. The pyrolysis products were collected in a trap cooled at –40°C and filled with a diethylamine solution in ether. When pyrolysis was over and the apparatus cooled it was rinsed with 15 ml of ether and the combined ether fractions were evaporated on a vacuum rotatory evaporator. The residue was then percolated through a five-fold amount of silica gel and dried at 40°C and 1.6 kPa for 60 min. The yield of pyrolysis was between 70 and 80%.

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