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STERESELECTIVE SEPARATION OF SUBSTITUTED ALLYLIC CHLORODERIVATIVES

The relative velocities of formation and thermal decomposition of quaternary ammonium salts, products of the reaction of isomeric allylic chlorides, and *N,N*-dimethylphenylamine have been determined. Methods for separating geranyl and *E,E*-farnesyl chloride from the mixtures of their isomers based on the difference in reaction velocities of the latter have been worked out. These methods have been applied to synthesis of geranyl and *E,E*-farnesyl esters, components of sex pheromones of click beetles, from isoprene telomers.

Earlier, a regiospecific method for separating primary allylic chlorides from the mixture of structural isomers via quaternary ammonium salts with *N,N*-dimethylphenylamine has been developed by one of us [1, 2]. Also, the stereospecificity of formation and decomposition of these quaternary ammonium salts has been established [3].

In the present work the results of elaborating this method for the stereoselective separation of the mixture of *E*-3-methyl-, *Z*-3-methyl-, and *E*-2-methyl-3-alkyl chlorides (structural and stereoisomers of geranyl and farnesyl chlorides obtained according to [4]) have been presented. Kinetic studies of the above reactions of isomeric chlorides gave the relative velocities of formation of quaternary ammonium salts at 30 °C: *E*- and *Z*-3-methyl \gg *E*-2-methyl. For the rate of reversible dissociation at 55—60 °C the following series different from the previous one has been established: *E*-2-methyl, *Z*-3-methyl \gg *E*-3-methyl. These differences in the rates of formation and dissociation of *N,N*-dimethylphenylammonium salts of isomeric allylic chlorides studied allowed us to propose a stereoselective method for their separation. It involves a fractional separation of 3-methyl-substituted allylic isomers from the mixture of chlorides in the form of the quaternary ammonium salts formed at 30—35 °C. These salts are subjected to fractional thermal decomposition at 55—60 °C to separate thermally less stable *Z*-3-methyl and traces of *E*-2-methyl isomers. The remaining quaternary salts contain mainly the salt of *E*-3-methyl isomers, 98—99.5%, and are useful in subsequent syntheses. The *E*-2-methyl isomer is concentrated in the mixture of the remaining chlorides and may be separated from 3-methyl isomers by repeated treatment with *N,N*-dimethylphenylamine. The product obtained contains 85.0% of *E*-2-methyl isomer. In this work, we failed to separate *Z*-3-methyl isomer with the required purity due to its low content (4—5%) in the starting mixture of chlorides. The purified isomeric chloroderivatives and their compounds with *N,N*-dimethylphenylamine were used for synthesis of esters of terpenic alcohols and their structural analogs, the main components of sex pheromones of various harmful click beetle species [4, 5].

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Experimental

The isomeric composition of allylic chloroderivatives was established by GLC on a "Chrom-5" using a capillary glass column (24000×0.27 mm), a flame ionization detector, TCEP as stationary phase, and argon as carrier gas. Conditions: column temperature 60°C, evaporator temperature 170°C, carrier gas flow-rate 1.5 ml/min. The chemical structure of isomeric chloroderivatives and the corresponding relative retention times have been presented in [6].

GLC analysis of N,N-dimethylphenylamine (DMPHA) salts of chlorides was carried out in the same conditions as that of the starting chloroderivatives. At the same time, complete thermal dissociation of quaternary salts into the starting N,N-dimethylphenylamine and the corresponding chlorides takes place. The percentage ratio of the latter corresponds to that of DMPHA salts of these chlorides.

GLC analysis of esters was performed on a "Chrom 5" using a fused silica capillary column (23000×0.22 mm), a flame ionization detector, OV-101 as stationary phase, and argon as carrier gas. Conditions: column temperature 140–170°C, evaporator temperature 270°C, carrier gas flow-rate 1.2 ml/min.

The ¹³C chemical shifts of the esters investigated have been presented in [7, 8].

Investigation of the rate of formation of quaternary ammonium salts

The samples were taken at certain time intervals by mixing at 30°C from the reaction mixture containing 30 g monoadduct of chlorotelomer of isoprene [6] with the following composition: 1-chloro-3,7-dimethyl-2(*E*),6-octadiene (I) 60.0%; 1-chloro-3,7-dimethyl-2(*Z*),6-octadiene (II) 4.0%; 1-chloro-2,7-dimethyl-2(*E*),6-octadiene (III) 3.0%; 1-chloro-3,5,5-trimethyl-2(*E*)-6-heptadiene (IV) 3.0%; and 17.4 g N,N-dimethylphenylamine and 3 g undecane as internal standard. The samples were analysed and the amount of unreacted chlorides (I–IV) was determined.

The results are illustrated in Fig. 1.

Investigation of fractional thermal decomposition of geranyl-N,N-dimethylphenylammonium chlorides

Geranyl-N,N-dimethylphenylammonium (GDMPHA) chloride (20 g), octane (14 g) as extragent, and undecane (1 g) as internal standard were introduced into the thermostated (40°C) three-necked flask equipped with a stirrer, a reflux condenser, and a thermometer and mixed for 3 h. Then the layers were separated and the geranyl chloride content of the extract was determined. Similar experiments were carried out at 60, 70, 80, and 90°C. The results are shown in Fig. 2.

Study of the velocities of fractional thermal decomposition of quaternary ammonium salts

The mixture of alkenyldimethylphenylammonium chlorides (240 g) obtained according to [9, 10] and containing 81.3% of DMPHA salts of chloride (I) and 5.4% of chloride (II), 9.3% of chloride (III), and 4.0% of chloride (IV) was subjected to distillation at 2 mm/Hg. After the temperature had risen to 60°C, distillation of the dissociation products, viz. N,N-dimethylphenylamine and chlorides (I–IV), began. In the distillates the content of chlorides was determined. The results are demonstrated in Fig. 3. The bath temperature was gradually raised to 80°C. Distillation was stopped after the chloride (III) content of the distillate sample had diminished below 1.0%.

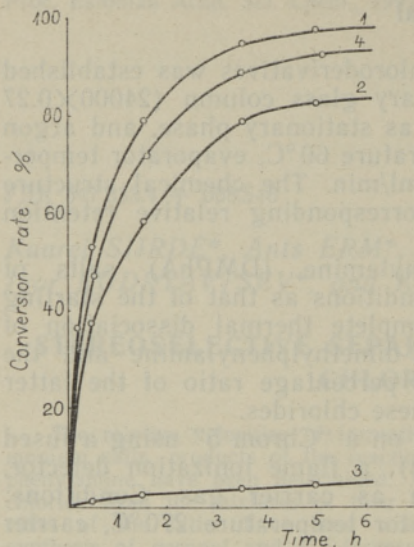


Fig. 1. Kinetics of formation of DMPPhA salts from: 1 — 1-chloro-3,7-dimethyl-2(*E*),6-octadiene (geranylchloride) (I), 2 — 1-chloro-3,7-dimethyl-2(*Z*),6-octadiene (II), 3 — 1-chloro-2,7-dimethyl-2(*E*),6-octadiene (III), 4 — 1-chloro-3,5,5-trimethyl-2(*E*),6-heptadiene (IV).

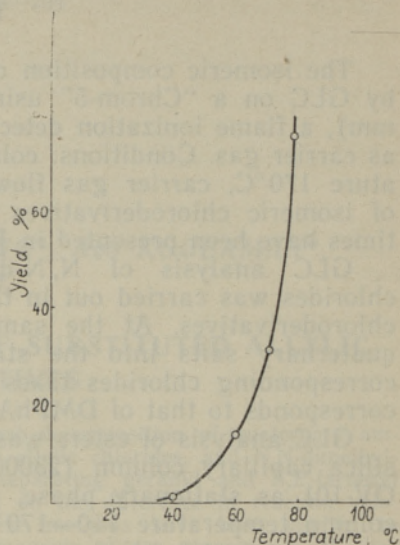


Fig. 2. Yield of geranyl chloride by thermal decomposition of geranyldimethylphenylammonium chloride.

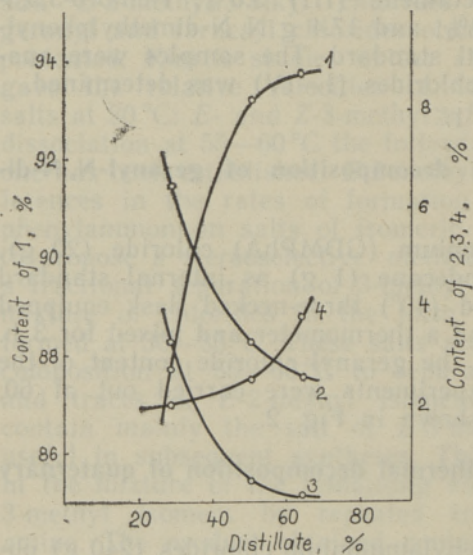


Fig. 3. Content of chlorides in the distillate from fractional thermal decomposition of DMPPhA salts of chlorides (I-IV). Designation as in Fig. 1.

Synthesis of geraniol and *E,E*-farnesol esters

Synthesis of esters was carried out by thermal decomposition of geranyl or farnesyl-*N,N*-dimethylphenylammonium (FDMPPhA) chlorides in toluene solution in the presence of corresponding Na-salts of carboxylic acids [11, 12]. The final products were separated by vacuum distillation.

3,7-Dimethyl-2(E),6-octadienyl-3-methylbutanoate — the main component of the pheromone of *Agriotes tauricus*, purity 95.5%, n_D^{20} 1.4850, d_4^{20} 0.895, b.p. 120—121°C at 4 mm/Hg, obtained in 43% of the yield on the starting chloride (I). The starting GDMPPhA chloride was prepared from the monoadduct of isoprene chlorotelomers [6] by 65% conversion of chloride (I).

3,7-Dimethyl-2(E),6-octadienylhexanoate — the first main component of the pheromone of *A. obscurus*, purity 97%, n_D^{20} 1.4645, b.p. 141—144°C at 2 mm/Hg, and

3,7-dimethyl-2(E),6-octadienyl octanoate — the second main component of the pheromone of *A. obscurus*, purity 96%, n_D^{20} 1.4652, b.p. 152—155°C at 2 mm/Hg were obtained respectively in 44 and 42% yields on the starting chloride (I). The concentration of GDMPPhA chloride was carried out by fractional thermal decomposition of the mixture of the DMPPhA salts of chlorides (I—IV) at 50—55°C and by simultaneous distillation of the decomposition products. The distillate containing N,N-dimethylphenylamine and chlorides (I—IV) was subjected to repeated treatment with N,N-dimethylphenylamine to obtain a mixture of DMPPhA salts followed by concentration to yield an additional amount of GDMPPhA chloride.

2,7-Dimethyl-2(E),6-octadienylbutanoate — an inhibitor of sex communication of *A. gurgistanus*, purity 85%, n_D^{20} 1.4598, b.p. 100—101°C at 2 mm/Hg, obtained in 33% of the yield on the starting chloride (III). The starting DMPPhA salt of chloride (III) was obtained from the distillate by repeated fractional thermal decomposition of the mixture of DMPPhA salts in the synthesis of geranyl hexanoate and geranyl octanoate.

The preconcentration of chloride (III) was performed by separating more reactive chlorides (I) and (II) via their DMPPhA salts.

To accelerate the formation of DMPPhA salt of chloride (III) methanol [10] was used.

3,7,11-Trimethyl-2(E),6(E),10-dodecatrienylethanoate — the main component of the pheromone of *A. ustulatus* — purity 85% (an additional component 3,6,11-trimethyl-2(E),6(E),10-dodecatrienylethanoate 11.0%), n_D^{20} 1.4510 b.p. 136—138°C at 1 mm/Hg obtained in 13% of the yield on the starting 1-chloro-3,7,11-trimethyl-2(E),6(E),10-dodecatriene (V). The starting FDMPPhA chloride was prepared from the diadduct of isoprene chlorotelomer [11] according to [9, 10] by fractional thermal decomposition of isomeric chlorides at 45°C, followed by extraction of the decomposition products with petroleum ether.

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ASENDATUD ALLÜULSETE KLOORIDERIVAATIDE STEREOSELEKTIIVNE LAHUTAMINE

On leitud isomeersetes primaarsetes allüülsete kloriidide ja N,N-dimetüülfenüülamiini vahelise reaktsiooni produktide — kvaternaarseste ammoniumisoolade — suhteline tekke- ja lagunemiskiirus. Isomeeride reaktsioonikiiruse erinevus võimaldas välja töötada meetodid geranüül- ja E,E-farnesüülkloriidi eraldamiseks nende isomeeride segudest. Meetodeid on rakendatud geranüül- ja E,E-farnesüülestrite — naksurmardikate suguferoonide komponentide — sünteesil isopreeni klooriteloomeeridest.

Каарел СИИРДЕ, Антс ЭРМ, Хейно РАНГ, Аво КОГЕРМАН,
Игорь КУДРЯВЦЕВ, Коит ЛЭЭТС

СТЕРЕОСЕЛЕКТИВНОЕ РАЗДЕЛЕНИЕ ЗАМЕЩЕННЫХ АЛЛИЛЬНЫХ ХЛОПРОИЗВОДНЫХ

Установлены относительные скорости образования и термического разложения четвертичных аммониевых солей — продуктов реакции N,N-диметилфениламина с изомерными первичными алильными хлоридами. Разработаны способы выделения геранил- и E,E-фарнезилхлоридов из смесей их изомерных первичных алильных хлоридов и осуществлен синтез сложных эфиров гераниола и E,E-фарнезола — компонентов феромонов жуков шелкунов.