CYCLIZATION OF ISOPRENE COMPOUNDS

REPORT 20. CYCLIZATION OF THE ESTERS OF GERANIC ACID UNDER THE INFLUENCE OF CATIONIC INITIATORS

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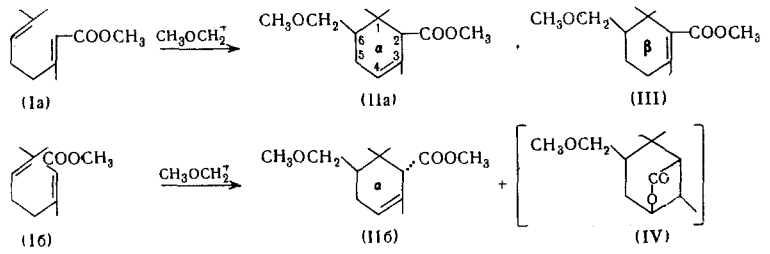
We have already described a new method of aprotonic initiation of cyclization, using the 1,5-dienes of the isoprene series with isolated double bonds as an example [1]. To demonstrate the universal applicability of this method, the possibility of its application in the case of isoprenoids containing double bonds conjugated with the carbonyl group was studied in the work presented here, using the esters of geranic acid as an example.

Cyclization under the Influence of $[CH_3OCH_2]^+ [BF_4]^-$

The cyclization of the methyl ester of trans-geranic acid (Ia) under the influence of $[CH_3OCH_2]^+[BF_4]^-$ under the conditions described earlier [1], yielded a mixture of monocyclic products (IIa) and (III) (in a ratio of 4:3) in a maximum yield of 60%, which could be separated by chromatography on Al_2O_3. Under analogous conditions, the cis-isomer (Ib) gives different products, namely an ester (IIb) and a large quantity (up to 40%) of the γ-lactone (IV).



The structure of the esters (IIa and b) and (III) as monocyclic products with a double bond in the α or β position, respectively, and with CH_3OCH_2- substituent in the ring, follows from the data of the NMR spectra [2] (table 1), and the location of the substituent CH_3OCH_2- at the C_6 is determined in analogy with the previously studied example [1].

The configuration of the steroisomeric esters (IIa) and (IIb) was assumed on the basis of the selectivity of their formation from (Ia) and (Ib), respectively, and on the existing data on the stereochemistry of the proton cyclization of the cis and trans isomers of apogeranic acid [3]. The product (IV) has not been isolated in pure form, and its structure has been derived from the data of the IR-spectra (ν = 1778 cm^{-1}) and by analogy with the structure of the lactone, formed in some cases during proton cyclization of the ester of geranic acid [4].

TABLE 1. Chemical Shifts of the Protons of the Characteristic Groups (ppm)

Compound	1-$(CH_3)_2$	2-CH_3OOC	3-CH_3	6-CH_3OCH_2	4-H
(IIa)	0,95 1,07	3,62	1,57	3,20	5,43 (1-H)
(IIb)	1,95 1,03	3,58	1,60	3,20	5,47 (1-H)
(III)	0,95 1,04	3,58	1,38	3,20	2,37 (2-H, Multiplet

Cyclization under the Influence of $[RCO]^+ [BF_4]^-$

Reactions of the Methyl Esters of Geranic Acid with $[CH_3CO]^+BF_4]^-$. An attempt to effect cyclization of

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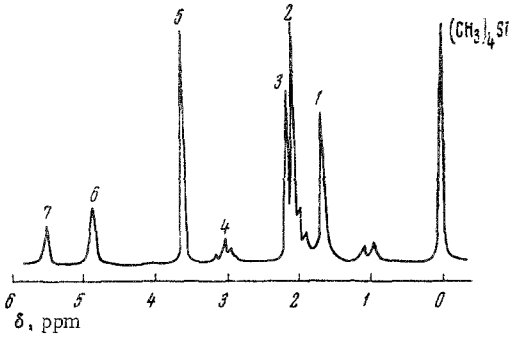
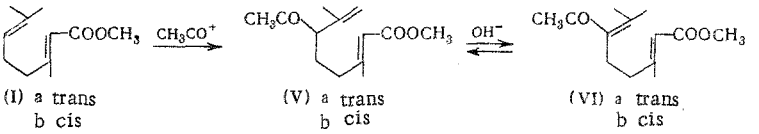


Fig. 1. NMR spectrum of the compound (Va): 1) $CH_3-C=CH_2$ (1.65); 2) $CH_3-C=C-COOR$ (2.03); 3) CH_3CO (2.10); 4) $RCO-C-H$ (3.01); 5) CH_3OCOR (3.57); 6) $R-C=CH_2$ (4.86, two protons); 7) $C=C(COOR)H$ (5.50). δ ppm is given in parentheses.

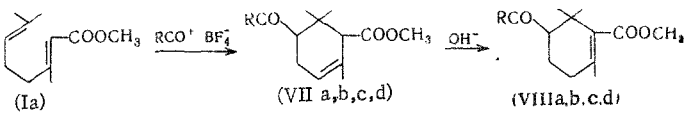
the trans-geranic ester (Ia) under the influence of the other above-described cationic initiators (CH_3CO^+) [1] led to the formation of the acyclic product (Va) with a yield of 80%, whose structure was shown on the basis of the data of the NMR spectrum (Fig. 1), the IR- and UV-spectra.



(I) a trans b cis (V) a trans b cis (VI) a trans b cis

In contrast to the monocyclic products (II) and (III), the acyclic ester (Va) is readily hydrolyzed in alkaline medium. At the same time, a partial isomerization of the terminal double bond into a conjugated position is observed (appearance of an absorption band at 1682 cm^{-1} which is typical for α, β unsaturated ketones [5]). This isomerization is also observed on attempting to isolate the ester (Va) by distillation or chromatography on Al_2O_3; in the pure form (Va) could be obtained only by chromatography on silica gel. The reaction of the cis-geranic ester (Ib) with CH_3CO^+ takes place exactly the same way as in the case of the trans isomer. The acyclic ester (Vb) formed is identical in its properties to the trans isomer (Va).

Cyclization under the Influence of $[CH_3CH_2CO]^+[BF_4]^-$ $[(CH_3)_2CHCO]^+[BF_4]^-$ and $[(CH_3)_3CCO]^+[BF_4]^-$. We have also studied the possibility of effecting the cyclization of (Ia) through the action of complexes obtained from the chlorides of propionic, isobutyric and pivalic acid and silver fluoborate



(Ia) (VII a,b,c,d) (VIIIa,b,c,d)

a R = CH_3CH_2- b R = $(CH_3)_2CH$- c R = $(CH_3)_3C$- d R = CH_3CO

It was found that the substitution of the acetyl chloride by propionyl chloride markedly alters the nature of the reaction of the complex $RCO^+BF_4^-$ with geranic ester (Ia); in addition to the acyclic product, 20-22% of the monyclic product (VIIa) is formed. In the case of the isobutyryl chloride the yield of the analogous product (VIIb) increases to 32%. Upon transition to pivaloyl chloride the monocyclic ester (VIIc) becomes the main reaction product (56%).* The ester of α-cyclogeranic acid is formed as a side product which is obviously the result of proton cyclization of (Ia) under the influence of the HBF_4 evolved during this reaction. The determination of the concentration of cyclic and acyclic products in the mixture was carried out on the basis of analysis by the GLC method as well as of the data as to the degree of hydrolysis of the mixture under standard conditions, which ensure complete hydrolysis of the acyclic esters. The cyclic esters (VII a, b, c), which are derivatives of cyclogeranic acids, are not hydrolyzed under these conditions [7], but are merely isomerized to the β isomers (VIII a, b, c). In some cases the cyclic esters (VII) and (VIII) were subjected to additional treatment with alkali for purposes of verification, but hydrolysis was not observed.

The structure of the esters (VII a, b, c) and of the α monocyclic products with RCO- substituents in the ring was elucidated on the basis of the NMR- † (Table 2) and IR-spectra.

The enhancement of the formation of cyclic ester upon transition from acetyl chloride to pivaloyl chloride can be explained on the basis of the data on the structure of the corresponding complexes. It is

*Of interest is the fact that during the acylation of aromatic compounds with the complex $(CH_3)_3CCO^+BF_4^-$, ketones $ArCOC(CH)_3$ are normally not formed, but that alkylation products of the type $ArC(CH_3)_3$ are mainly formed [6].

†The data of the NMR-spectra (absence of a signal of the 4-H vinyl proton in presence of the signals of the other groups) were also used as indications of the structure of the products (VIII a-d) as derivatives of β cyclogeranic acid.

TABLE 2. Chemical Shifts of the Protons of the Characteristic Groups (ppm)

Compound	1-$(CH_3)_2$	2-CH_3OOC	3-CH_3	4-H	Other H
(VIIa)	0,88 0,90	3,52	1,50	5,38	0,90 (Doublet) $CH_3CH_2C{=}O$ 2,38 (Quadruplet) CH_3CH_2CO
(VIIб)	0,90 0,92	3,52	1,51	5,40	0,96; 1,02 (Two doublets) $(CH_3)_2CH{-}CO$ 2,01 $(CH_3)_2CH{-}CO$
(VIIв)	0,87 1,04	3,50	1,51	5,30	1,04 $(CH_3)_3C{-}CO$
(VIIг)	0,88 1,00	3,54	1,51	5,31	2,06 $CH_3C{=}O$

known that when catalysts of the Friedel-Crafts reaction of the type MX_n (where M is a metal and X a halogen) react with aromatic and aliphatic acid chlorides, salts of the acyl cations $RCO^+MX^-_{n+1}$, as well as donor-acceptor complexes ($R{-}\overset{\delta+}{C}O \rightarrow \overset{\delta-}{M}X_n$). are formed.

X

In some cases it has been shown that in crystalline form the complexes $RCOMX_{n+1}$ have the acyl cation structure $RCO^+[MX_{n+1}]^-$. This applies also to the complex $RCO^+BF_4^-$ [8] used in the present investigation. The problem of the structure of these complexes in solution is much more complex and in many cases the spectral data indicate clearly the presence of a salt-like as well as a donor-acceptor complex, their relative quantities varying with variation of the radical R of the anion $[MX_{n+1}]^-$ and also with the experimental conditions (nature and purity of the solvent, etc.) [8-11]. In particular, it was shown by means of the NMR spectra that the complex CH_3COBF_4 in SO_2 solution exists solely in the form of a donor-acceptor complex $CH_3CO \rightarrow BF_3$ [8]. Under the same conditions, in SO_2 solution, the presence of a considerable

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quantity of salt-like complex has been shown for the complex $CH_3CH_2COBF_4$. It was also found that transition to the anion SBF_6^- greatly increases the concentration of the acyl ketone salt compared with that of the donor-acceptor complex [8].

In the discussion of the Friedel-Crafts reaction [12-14] it was assumed that the complexes $RCOMX_{n+1}$ can react either through electrophilic attack of the acyl cation RCO^+ (path 1) or in accordance with a substitution reaction similar to S_N2 (path 2)

$$ArH + [RCO]^+[MX_{n+1}]^-(A) \rightarrow ArCOR + H[MX_{n+1}]^- \quad (1)$$

ArH + R—C(=O)—X (B) → ArCOR + $H[MX_{n+1}]$ (2)

O MX_n

Obviously, for the case under consideration here, the electrophilic cyclization reaction of the 1,5-diene (I) under the influence of $RCOBF_4$ complexes, analogous mechanisms can also be proposed for the two possible limit cases, namely the reaction with participation of $RCO^+BF_4^-$ and the reaction with participation of $RCO \rightarrow BF_3$

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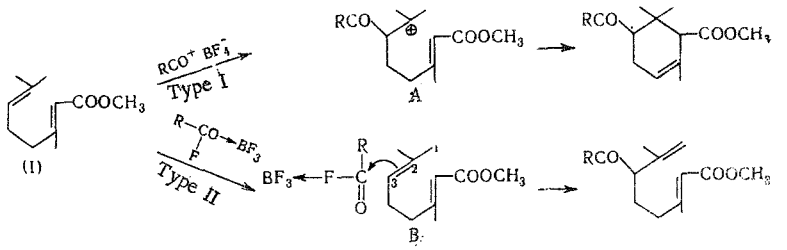

Furthermore, it seems logical to assume that only the intermediate product of the type A is capable of attacking the weakly nucleophilic 6, 7 double bond in (I) with formation of a cyclic product, while for the intermediate product of the type B with weak positive charge at C_2 this reaction should not take place and the stabilization will be achieved exclusively by splitting off of a proton from C_1.* Then it can be assumed that the nearer the structure of the reagent is to that of the salt-like complex $RCO^+BF_4^-$, the higher should be the degree of formation of the cyclic product (path 1); the donor-acceptor structure of the reagent RCO $\rightarrow BF_3$ should favor the reaction by the pathway (2) with formation of an acyclic ester.

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We have pointed out earlier that the spectral data indicate a predominant content of donor-acceptor complex in the CH_3COBF_4 solutions. The transition to $CH_3CH_2COBF_4$ already shows some increase in the proportion of the salt-like complex and, evidently, the further transition to $(CH_3)_2CHCOBF_4$ and $(CH_3)_3 \cdot CCOBF_4$, by virtue of the stabilizing (+J) effect of the CH_3-group, increases the concentration of the salt-like complex $RCO^+BF_4^-$ to an even greater degree. We believe that the observed increase in the yield of the cyclic product in the reaction between (I) and $RCOBF_4$ from 0% for R = CH_3 to 56% for R = $(CH_3)_3C$ can be accounted for precisely by this change in the nature of the complex upon transition from CH_3COBF_4 to $(CH_3)_3CCOBF_4$. Since it follows from the spectral data that replacement of the anion BF_4^- by SbF_6^- greatly increases the concentration of the salt-like complex in the solutions, one could have expected the the proportion of the cyclic product upon transition from $RCOBF_4$ to $RCOSbF_6$ would increase for all R. Indeed, we have shown that the cyclic product (VII) is the main product in the cyclization of (Ia) under the influence of the complexes $RCOSbF_6$ for all R, and only in the case of CH_3COSbF_6 the formation of a certain quantity of the acylic ester (Va) [(VIIId): (Va) = 4: 1] in addition to the cyclic product (VIIId) can be observed; in the case of CH_3COBF_4 the yield of (Va) is ~ 80% (see above).

The correctness of the foregoing reasoning could be confirmed experimentally if it were possible to study the NMR spectra of the complexes used in nitromethane solution at -30°C (cyclization condition), but under these conditions the complex solutions are extremely unstable and cannot be kept for any great length of time. †

It should be pointed out that such a marked change in the reactivity of the above-described complexes with change in the nature of R has not been observed before, although hypotheses to the fact that Friedel-Crafts reagents can react in the form $RCOX \rightarrow MX_n$ as well as in the form $RCO^+MX_{n+}^-$ have been advanced repeatedly, particularly in order to explain the sometimes incomprehensible variations of the rates of reactions such as acylation in the aromatic series upon seemingly slight change in the reagent or the reaction conditions [12-14].

EXPERIMENTAL

The NMR spectra were recorded at 60 MC on the apparatus PC-60 in CCl_4 solution (the chemical shifts δ are given in ppm relative to hexamethyldisiloxane); the IR spectra were recorded on the apparatus UR-10. The purity control of the starting substances and also the analysis of the reaction products was carried out by the GLC method under the following conditions: A) 10% neopentylglycol succinate on Celite 545, 191°, carrier gas He, 35 ml/min, detector: catharometer. B) 10% ApiezonM on Chromosorb W, 212°, carrier gas He, 40 ml/min, detector: catharometer. The conditions (A) were used for the analysis of the

*We have also observed the formation of an acyclic product during the proton cyclization of geranic ester and analogous compounds [15].

†The instability of the solutions of complexes in CH_3NO_2 has been pointed out previously [10].

original geranic esters and their cyclization products (I-V, VIId and VIIId); the conditions (B) for the cyclization products (VIIa-c) and (VIIIa-c).

The individual esters of geranic acid were obtained by the known method [16].

Cyclization of (Ia) under the Influence of $[CH_2OCH_2]^+[BF_4]^-$. To a solution of 1.44 g of CH_3OCH_2Cl in 15 ml CH_3NO_2, cooled to -30°C, we added 1.38 g (Ia) and 3.0 g $AgBF_4$ in 23.5 ml CH_3NO_2 with stirring of the solution. Five minutes later, the reaction mass was decomposed with a mixture of 10% solution of $NaHCO_3$ and methanol (1:1) cooled to -30°. After the usual treatment we obtained 1.7 g of a mixture, containing 40% (IIa) and 30% (III) which was treated with a waver-methanol solution of KOH (4.5%, 60°, 2 hr) to remove the acyclic impurities. The non-saponification fraction (1.0 g) was chromatographed on a column (Al_2O_3, activation state II, hexane-benzene, 1:1). We obtained 0.38 g of the α-ester (IIa), b. p. 112-115°C (0.5 mm); n_D^{20} 1.4730 (elution time 8.3 min) and 0.21 g of the β-ester (III), b. p. 117-120° (0.5 mm); n_D^{20} (elution time 12.5 min). Found (for IIa): C 68.97; 68.98; H 10.05; 10.02%; for (III): C 68.87; 68.76; H 9.81; 9.80%. $C_{13}H_{22}O_3$. Calculated: C 68.99; H 9.80%. The NMR spectrum is given in Table 1.

Cyclization of (Ib) under the Influence of $[CH_3OCH_2]^+[BF_4]^-$. The cyclization was carried out under the same conditions as in the case of (Ia). From 1.38 g (Ib) 1.65 g of a residue was obtained after the usual treatment, containing 24% (IIb) and 40% (IV) (elution time 7.3 and 16.2 min, respectively); IR spectrum (ν, cm^{-1}): 1730 [(CO)COOR] and 1778 (C=O of the γ-lactone). The ester (IIb) was isolated from the non-saponifying fraction of this mixture by redistillation with subsequent chromatography on Al_2O_3. Isolated 0.21 g (IIb), b. p. 108-110° (0.4 mm); n_D^{20} 1.4704. Found: C 68.73; 68.79; H 10.23; 10.14. $C_{13}H_{22}O_3$. Calculated: C 68.99; H 9.80%. The NMR spectrum is given in Table 1. The γ-lactone was not separated.

Reaction of (Ia) with $[CH_3CO]^+[BF_4]^-$. To a solution of 3.0 g CH_3COCl in 12.5 ml CH_3NO_2 cooled to -30°C we added within 45 sec, with stirring, a solution of 1.15 g (Ia) and 3.75 g $AgBF_4$ in 18.2 ml CH_3NO_2. The mixture was stirred for five minutes and decomposed by the usual method. 1.35 g of product was obtained which contained up to 80% of the ester (Va) (elution time 8.3 min). By thin-layer chromatography (TLC) on the lamellar silica gel KSK in the system hexane-benzene (1:1) 0.75 g (53%) (Va) was obtained; n_D^{20} 1.4780. Found: C 69.73; 69.40; H 8.80; 8.86. $C_{13}H_{20}O_3$. Calculated: C 69.61; H 8.99%. The NMR spectrum is shown in Fig. 1; the UV spectrum (λ_{max}, mμ) 219.5, ε 15350; IR spectrum (ν, cm^{-1}): 1720 and 1650 [α, β unsaturated (CO)COOR and C=C−H].

When (Va) is heated for three hours with a 2-5% methanol solution of KOH it is completely hydrolyzed, but the resulting acid (according to the GLC data of the methyl ester) contains up to 37% of an isomer with conjugated 2,3-double bond (elution time of the corresponding ester (VIa) 11.8 min). In the IR spectrum of the mixture of (Va) and (VIa) an absorption band appears at 1682 cm^{-1}. The isomerization (Va) → (VIa) also takes place during alkaline treatment at room temperature, chromatography on Al_2O_3 or redistillation.

The reaction of (Ib) with $[CH_3CO]^+[BF_4]^-$ under the above-described conditions led to the formation of a mixture containing up to 70% (Vb) (elution time 8.1 min), which readily isomerized to (VIb) (elution time 11.4 min). Neither product was isolated in a pure form.

Cyclization of (Ia) under the Influence of $[CH_3CH_2CO]^+[BF_4]^-$. The cyclization was carried out under the conditions of the experiment with $CH_3CO^+BF_4^-$. From 2.84 g CH_3CH_2COCl, 0.92 g (Ia) and 3.0 g $AgBF_4$, a mixture was obtained, consisting (according to the GLC data) of 20-22% (VIIa) (elution time 22 min), 12-13% (Ia), ~20% α-cyclogeranic ester and 45% of high-boiling acyclic esters. (VIIa) was isolated by TLC (Al_2O_3, benzene). Yield (VIIa) 0.11 g (~10%). The NMR spectrum is given in Table 2. When the mixture is treated with alkali, the acyclic fraction is hydrolyzed and (VIIa) is completely transformed into (VIIIa) (elution time 14.5 min): n_D^{18} 1.4775. IR spectrum (ν, cm^{-1}): 1720 (C=O), 1740 [(CO)COOR].

Cyclization of (Ia) under the Influence of $[(CH_3)_2CHCO]^+BF_4]^-$. Cyclization under the same conditions with 4.92 g $(CH_3)_2HCOCl$ of 1.38 g (Ia) and 4.50 g $AgBF_4$ gave a mixture consisting (according to the GLC data) of 32% (VIIb) (elution time 23.0 min), 8% (Ia), 36-37% α-cyclogeranic ester and 23% acyclic esters. (VIIb) was isolated by preparative chromatography on plates (Al_2O_3; benzene-hexane, 2:1). Yield (VIIb) 0.32 g (16.8%), bath temperature 170° (0.05 mm); n_D^{12} 1.4830. Found: C 71.08; 71.19; H 9.34; 9.40%. $C_{15}H_{24}O_3$. Calculated: C 71.39; H 9.59%. IR spectrum (ν, cm^{-1}): 1715 (C=O), 1740 [(CO)COOR], 1650 (C=CH). The NMR spectrum is given in Table 2.

Upon treatment with a 5% methanol solution of KOH the acyclic fraction is saponified, while (VIIb) is completely transformed into (VIIIb) (elution time 15.3 min). IR spectrum (ν, cm^{-1}): 1715 (C=O), 1740 [(CO)COOR].

Cyclization of (Ia) under the Influence of $[(CH_3)_3CCO]^+[BF_4]^-$. Reaction of 4.60 g $(CH_3)_3CCOCl$, 1.15 g (Ia) and 3.75 g $AgBF_4$, under the same conditions, gave a mixture containing (according to the GLC data) 56% (VIIc) (elution time 27.3 min), 2-3% (Ia) and 40-42% α-cyclogeranic ester. The mixtures were redistilled, the fraction with b. p. 107-110° (0.03 mm) was collected, which contained (VIIc), up to 5ω (Ia) and α-cyclogeranic ester. (VIIc) was finally purified by chromatography on plates (Al_2O_3, benzene-hexane 2 : 1). Yield 0.51 g (31%) (VIIc); n_D^{19} 1.4800. Found: C 72.14; 71.96; H 9.44; 9.40%. $C_{16}H_{26}O_3$. Calculated: C 72.14; H 9.84%. IR spectrum (ν, cm^{-1}: 1650 (C=CH), 1738 [(CO)COOR) and 1706 (C=O). The NMR spectrum is given in Table 2.

Alkali treatment of (VIIc) (same hydrolysis conditions as previously) gave a mixture consisting of 79% (VIIc) and 21% (VIIIc) (elution time 17.1 min).

We have modified the well-known method of the synthesis of $AgSbF_6$ [8] as follows: a solution of 12.3 g anhydrous AgF in 150 ml anhydrous HF was placed into a copper flask with four necks, equipped with a stirrer, a cooler (all made of copper) and a thermometer in a copper sheath. 20.7 g SbF_5 was added dropwise at -60° at such a rate that the temperature did not rise above -50°. Then followed five minutes of stirring at -55 to -60°. The temperature was then raised to ambient, the HF removed with a dry nitrogen streatm, 150 ml absolute CH_3NO_2 added and filtered. The resulting $AgSbF_6$ solution contained 30 g $AgSbF_6$ in 150 ml CH_3NO_2.

Cyclization of (Ia) under the Influence of $[CH_3CO]^+[SbF_6]^-$. 3.0 g CH_3COCl, 1.15 g (Ia) and 6.65 g $AgSbF_6$ under the same conditions as above gave a mixture of products consisting (according to the GLC data) of α-cyclogeranic ester, (VIId) and (Va) (ratio of the latter 4 : 1). TLC on silica gal KSK (benzene-ethylacetate 5 : 1) gave 0.44 g (30.9%) (VIId) (elution time 7.7 min), bath temperature 110° (1 mm); n_D^{20} 1.4780. IR spectrum (ν, cm^{-1}): 1654 (C=CH), 1720-1735 [C=O and (CO)COOR]. Found: C 69.48; 69.34; H 8.97; 8.82%. $C_{13}H_{20}O_3$. Calculated: C 69.61; H 8.99%.

Upon alkali treatment (VIId) is completely transformed into (VIIId) (elution time 6.1 min). IR spectrum (ν, cm^{-1}): 1700 (C=O), 1740 [(CO)·COOR].

Cyclization of (Ia) under the Influence of $[CH_3CO]^+[SbF_6]^-$, $[(CH_3)_2CHCO]^+\cdot[SbF_6]^-$ and $[(CH_3)_3CCO]^+\cdot[SbF_6]^-$. Under the conditions of the preceding experiment, monocyclic esters were mainly obtained (according to the data on their stability to alkali treatment) which were identified by GLC as (VIIa), (VIIb), (VIIc), respectively.

CONCLUSIONS

Reaction of geranic ester with cationic initiators of the type $RCOMX_{n+1}$, depending on the nature of the R radical and the anion MX^-_{n+1}, leads to the formation of cyclic or acyclic products containing the radical RCO, or of their mixtures. The factors which determine the trend of the reaction are examined.

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