THE ALKYLATION OF ALKYLCYCLOPROPANES BY PIVALOYL TETRAFLUOROBORATE*

Yu. V. Tomilov, V. A. Smit, and O. M. Nefedov

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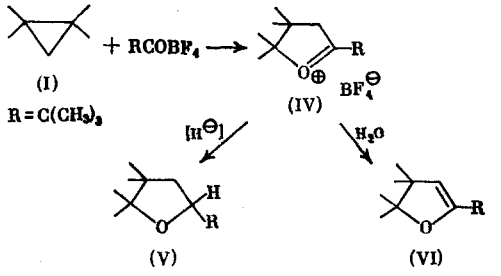
As we have already shown [2, 3], direct opening of the three-membered ring by the action of the acyl cation does not occur in the acylation of derivatives of bicyclo[n.1.0]alkanes by pivaloyl tetrafluoroborate (PTFB). The formation of the final products is most simply explained by an isomerization of the starting hydrocarbons prior to the acylation to yield the corresponding cycloalkenes. In order to determine whether these features of the reaction are general in nature or specific for only bicyclo[n.1.0]alkanes, we studied the PTFB acylation of the simplest alkylcyclopropanes, namely, 1,1,2,2-tetramethylcyclopropane (I), 1,1,2-trimethylcyclopropane (II), and 1,1-dimethyl-2-ethylcyclopropane (III).

The reaction proceeds rather rapidly for all these hydrocarbons even at −60°C. Thus, the introduction of (I) to a suspension of PTFB in methylene chloride leads to the formation of a weakly colored solution, from which after removal of most of the solvent and treatment with dry ether, a colorless crystalline complex, 2-tert-butyl-4,4,5,5-tetramethyltetrahydrofurylium tetrafluoroborate (IV) is isolated. The structure of the compound obtained was proven by ^1H and ^{13}C NMR spectroscopy [1] and also by the results of some chemical transformations. The arrangement and position of the proton signals in the PMR spectrum of (IV) were similar to the data of Rundell and Besserer [4] for 2-tert-butyl-4,4,5,5-tetramethyltetrahydrofurylium perchlorate. In the reaction of (IV) with Bu_4NBH_4 which is a hydride donor, 2,2,3,3-tetramethyl-5-tert-butyltetrahydrofuran (V) is formed with a yield of ~90% and with water, 4,4,5,5-tetramethyl-2-tert-butyl-4,5-dihydrofuran (VI) is formed



The formation of complex (IV) in this reaction formally corresponds to the direct opening of the three-membered ring in (I) by the action of PTFB. In this case, it might be expected that the analogous reaction with 3,3-dideuterotetramethylcyclopropane, d_2-(I) would lead to a carboxonium salt which would have a PMR spectrum lacking the CH_2 group signal for C(3). However, the PMR spectrum shows that the CH_2 group of the dideutero analog of (IV) obtained by the acylation of d_2-(I) by PTFB has primarily protons and not deuterions which are in the CH_3 groups. The integral intensity of the signals of the CH_2 and CH_3 groups at C(5) and the $C(CH_3)_3$ and CH_3 groups at C(4) which appear as well-resolved singlets was ~1.8, 5.1, 9, and 5.1 H, correspondingly. Thus, the carboxonium complex (IV) forms not as a result of the direct opening of the cyclopropane ring (by the Markovnikov rule) but rather by another pathway since it seems unlikely that the redistribution of the label could occur by this reaction mechanism.

The PMR spectrum of d-(V) obtained by the treatment of the deuterated complex of (IV) by Bu_4NBH_4, supported the approximately uniform distribution of deuterium over the CH_3 groups bound to the five-membered ring. The mass spectrum of d-(V) showed the presence not only of a d_2 compound (both deuterium atoms are

*For preceding communication, see [1].

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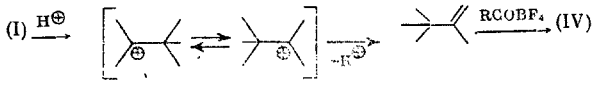
simultaneously in a CH_3 group), but also of d_1 and d_3 compounds in the ratio 7 : 1 : 1, which indicates some intermolecular deuterium disproportionation.

The simplest and most likely explanation is based on the isomerization of the cyclopropane ring of (I) to the olefin, triptene (VII) as the initial step in the reaction mechanism. It is natural to assume that a uniform distribution of the labeled deuterium of the CH_3 group may occur in the intermediate carbonium ion in such an isomerization as well as a partial transfer of a deuterium to d_2-(I), which would lead to some amount of d_1 and d_3 compounds. Under analogous conditions, salt (IV) is readily formed in the acylation of triptene (VII) by PTFB [5]



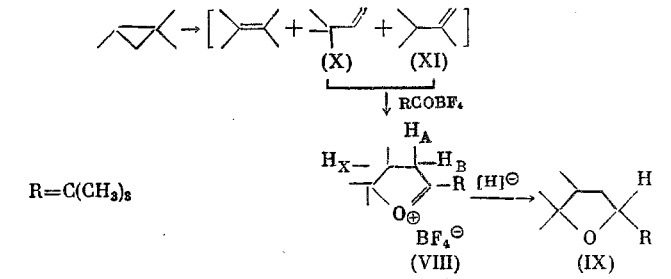
(VII)

The possibility of a prior isomerization of the cyclopropane ring into the corresponding olefins has been considered previously in the Friedel – Crafts acylation of some cyclopropanes. Thus, according to Levina [6], the acylation of tetramethylcyclopropane by Ac_2O in the presence of phosphoric acid is preceded by its isomerization into an olefin, primarily into triptene which is found in the reaction products. According to Hart and Schlosberg [7], the mechanism for the acylation of 1,1-dimethylcyclopropane consists in the initial isomerization of 1,1-dimethylcyclopropane by the action of acid present in the acylating medium into the thermodynamically more favorable 2-methylbutene-2.

In contrast to (I), 1,1,2-trimethylcyclopropane (II) reacts with PTFB in a more complicated manner. Only about 35% 2-tert-butyl-4,5,5-trimethyltetrahydrofuryllium tetrafluoroborate (VIII) is formed, which was identified by comparison with a sample obtained according to our earlier work [5] as well as by its transformation into tetrahydrofuran (IX) by treatment with Bu_4NBH_4.

The PMR spectrum of d-(VIII) obtained by the acylation of 3,3-d_2-(II) has the same arrangement of signals and approximately the same relative intensities as in the spectrum of the undeuterated complex (VIII), which also indicates a redistribution of the deuterium label. The mass spectrum of d-(IX) obtained from the deuterated complex (VIII) showed that, in addition to a d_2 compound, it contained a large amount of undeuterated product, and also d_1 and d_2 compounds, for example, the fragment $(M - C_4H_9)^+$ corresponds to four peaks due to different deuterium contents ($d_3 : d_2 : d_1 : d_0 = 1.2 : 6 : 1 : 4$) with correction for the contribution of ^{13}C.

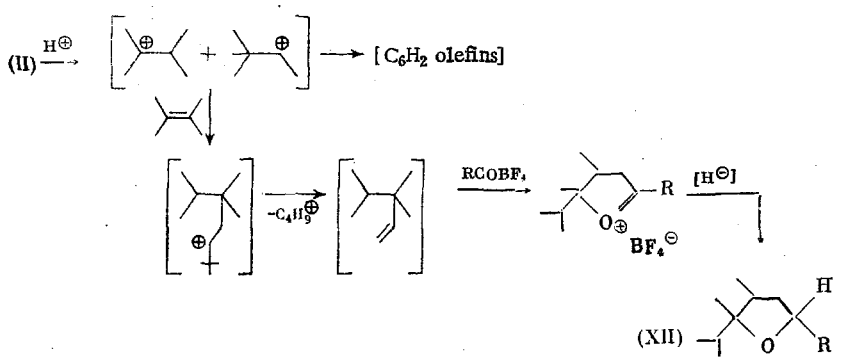
In this case, the first step of the observed transformation is also apparently the isomerization of (II) into olefins which is accompanied by considerable intra- and intermolecular redistribution of the label. The low yield of the carboxonium salt (VIII) (~35%) is apparently related to its formation only from the isomeric olefins (X) and (XI), while significant amounts of 2,3-dimethylbutene-2 are possible during the course of the isomerization; this olefin does not form a salt and does not enter subsequent oligomerization reactions



(VIII) (IX)

This scheme for the transformations also permits an explanation of the formation of the acylation product of the C_8H_{16} hydrocarbon by pivaloyl tetrafluoroborate in the reaction of (II) with PTFB. This compound was isolated as the THF derivative of (XII) after treatment of the reaction mass with Bu_4NBH_4 in 25% yield for two moles of (II). Analysis of the PMR spectrum of the isolated compound taken at 270 MHz showed the presence of CH_3, i-C_3H_7, and $C(CH_3)_3$ groups and one proton on an α-carbon of the ring. The nature of the signal of this proton was a doublet of doublets which indicates the location of a CH_2 group in the adjacent position in the ring. The presence of strong peaks at m/e 155 and 141 in the mass spectrum of (XII) which corresponds to the $(M - C_3H_7)^+$ and $(M - C_4H_9)^+$ fragments indicates the location of C_3H_7 and $C(CH_3)_3$ groups on the α-carbon atoms of the THF ring.

The formation of (XII) from (II) may be represented as the following sequence of transformations which include the cyclopropane – olefin isomerization of (II) which has already been considered with subsequent alkylation – fragmentation and acylation



This scheme is supported by the well-known capacity of the cations obtained from C_7H_{16}-C_9H_{20} hydrocarbons in "superacidic" media towards fragmentation, which is usually accompanied by the loss of a t-$C_4H_9^+$ cation [8] and also the possible formation of olefins as a result of the fragmentation of the carbonium ions [9].

The acylation of 1,1-dimethyl-2-ethylcyclopropane (III) was then studied under analogous conditions. In this case, 2-tert-butyl-3,4,5,5-tetramethyltetrahydrofurylium tetrafluoroborate (XIII) was obtained in 60% yield; the structure of (XIII) was confirmed by the similar nature of its ^1H and ^{13}C NMR spectra when compared to the spectra of similar salts (Tables 1 and 2). The NMR spectra of (XIII) indicate that this compound does not contain an ethyl substituent, but has two methyl groups at C(3) and C(4). The double resonance method (upon irradiation at a frequency corresponding to the center of the doublets of each of the methyl groups) showed that the corresponding methine protons at C(3) and C(4) have vicinal coupling equal to 10.5 Hz. The nature of the signals indicates that (XIII) does not contain structural isomers and largely or entirely consists of one of the possible geometric isomers.

The treatment of complex (XIII) by Bu_4NBH_4 leads to tetrahydrofuran (XIV), which, according to gas chromatographic data, consists of two isomers in ~4 : 1 ratio due to cis – trans isomerization of the $C(CH_3)_3$ and CH_3 groups. The assignment of the signals of the predominant isomer was made on the basis of an analysis of the PMR spectrum obtained at 270 MHz.

Treatment of complex (XIII) by water, in addition to the dihydrofuran derivative (XV) formed in ~50% yield, leads to 3,4,5,5-tetramethyl-2-tert-butyltetrahydrofuranol-2 (XVI). The IR spectrum of (XVI) confirms the presence of an OH group and indicates the absence of C=C and C=O groups; under conditions of the gas

TABLE 1. PMR Spectra of the Carboxonium Complexes (in $CHCl_3$, δ, ppm, and J, Hz)

Complex	R=C(CH3)3	CH3 at			H at	
		C3	C4	C5	C3	C4
(IV)	1,47 s (9H)		1,20 s (6H)	1,75 s (6H)	3,84 s (2H)	
[4] *	1,5 s (9H)		1,25 s (6H)	1,8 s (6H)	3,85 s (2H)	
(XIII)	1,48 s (9H)	1,65 d (3H) J=7	1,15 d (3H) J=6,8	1,56 s (3H) 1,87 s (3H)	3,87 q.d (1H) J=7,0 J=10,5	2,46 q.d. (1H) J=6,8 J=10,5
(VIII)	1,44 s (9H)		1,15 d (3H) J=6,9	1,59 s (3H) 1,83 s (3H)	3,70 d.d (1H) 4,13 d.d (1H) JAB=22,8 JBX=8,2 JAX=9,0	2,85 m (1H)

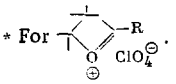
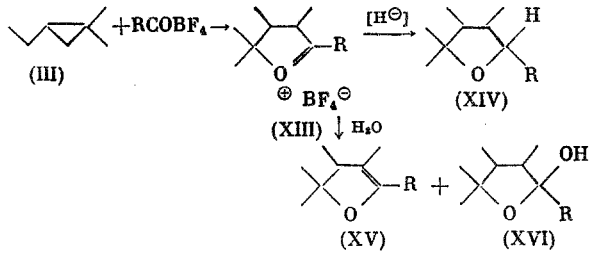
* For 

TABLE 2. ^{13}C NMR Spectra* of the Carboxonium Complexes (in CH_2Cl_2, δ, ppm)

Complex	C^2	C^3	C^5	C^4	$\underline{C}(CH_3)_2$	$C(\underline{C}H_3)_2$	C at		
							C^5	C^4	C^3
(IV)	245,5 s	53,9t	123,2 s	42,0 s (or 42,3)	42,3 s (or 42,0)	24,2 q	20,9 q (or 20,5)	20,5 q (or 20,9)	
(VIII)	245,9 s	48,3t	121,7s	38,0 d	42,7 s	26,2q	20,8 q 26,5 q	12,7 q	
(XIII)	246,3 s	56,9 d	118,3s	46,3 d	44,3 s	26,3q	20,7q 26,8q	11,4 q	14,1 q

*The assignment was carried out considering the intensity and multiplicity of the signals in spectra with incomplete uncoupling from the protons.

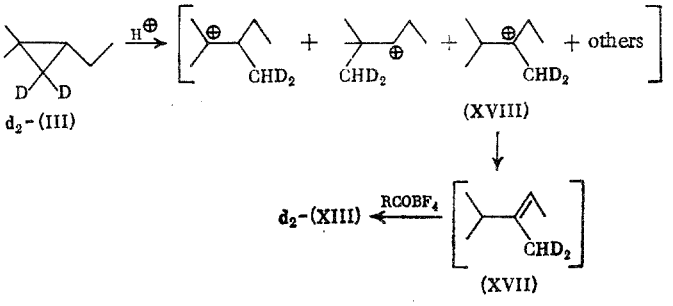
chromatographic analysis (Reoplex 400, 150°C), (XVI) decomposes with the formation of (XV)



The formation of (III) from salt (XIII) which does not contain an ethyl group rather clearly indicates that direct opening of the cyclopropane does not occur in the acylation of (III) by the action of the acyl cation and the process is more complicated, involving the ethyl group.

The study of the acylation of 3,3-d_2-(III) showed that the deuterium in the d_2-(XIII) complex obtained is located in the methyl group at C(4); the PMR signal of this group at 1.15 ppm is a broadened doublet with integral intensity of ~1H. In the ^{13}C NMR spectrum with incomplete decoupling from the protons, the carbon atom of this methyl group (11.4 ppm) is split into a quintet with $J_{C-D} \simeq 23$ Hz. The absence of deuterium in the geminal methyl groups is confirmed by the mass spectral data for the compound d_2-(XIV) obtained from d_2-(XIII) and Bu_4NBH_4 in which the fragment corresponding to the cleavage of the CHD_2 group from the α-carbon of the THF ring is lacking.

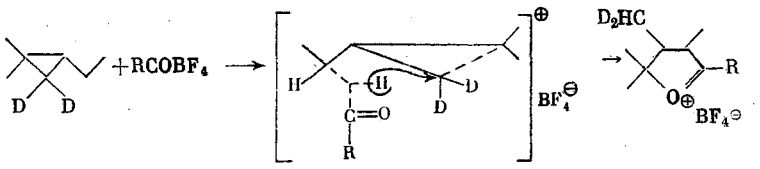
Thus, in the acylation of 3,3-d_2-(III), in contrast to 3,3-d_2-(I) and 3,3-d_2-(II), the formation of the carboxonium salt is not accompanied by the migration of the deuterium label of the methyl group and by some type of intermolecular deuterium transfer. The explanation of the formation of (XIII) through the isomerization of (III) into olefins is not applicable in this case, since we would have to accept the predominant formation of olefin (XVII) (by ≥ 60%) because only this olefin may yield the complex d_2-(XIII) which we isolated in 60% yield



However, such a selective formation of the ion (XVIII) and olefin (XVII) from (III) with complete retention of the deuterium atoms in one methyl group at C(4) is unlikely. Indeed, as side-products of the reaction of (III) with PTFB, a mixture of higher hydrocarbons was isolated in up to 25% yield; the formation of these olefins most likely involves the intermediate formation of carbonium ions. A fraction was isolated from this mixture which largely corresponds to dimers $C_{14}H_{28}$, which is confirmed by the mass spectral data. It was found that the same fraction obtained analogously for 3,3-d_2-(III) corresponds to dimers with varying deuterium content from $C_{14}H_{28}$ to $C_{14}H_{22}D_6$ (for the molecular ion), which indicates an intermolecular deuterium transfer. Thus,

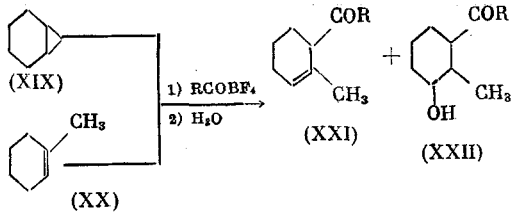
the possible intermediate formation of carbonium ions (and, likely, of some amount of olefins) in the reaction of (III) with PTFB is not related to the formation of salt (XIII) and is a side process.

Since the d_2 label is localized on the methyl group at C(4), we may assume that, in this case, the initial reaction step is electrophilic attack at the C – H bond in the CH_2 fragment of the ethyl group and subsequent or synchronous opening of the cyclopropane ring

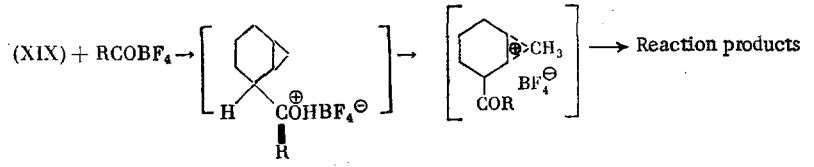


d_2-(III) d_2-(XIII)

Apparently the acylation of norcarane (XIX) previously studied [2] proceeds analogously to the acylation of (III). Both norcarane and 1-methylcyclohexene (XX), which may be formed in the cyclopropane – olefin isomerization of (XIX), upon acylation by PTFB in CH_3NO_2 with subsequent decomposition of the reaction mass by water yield a β, γ-unsaturated ketone (XXI) and secondary ketoalcohol (XXII). To compare the reactivities of (XIX) and (XX), an experiment was run on the concurrent acylation of (XX) and labeled norcarane with ratio of 7,7-d_2-(XIX) : (XX) : PTFB = 1 : 1 : 1.2. As a result, compounds (XXI) and (XXII) were isolated and their deuterium contents were analyzed by mass spectroscopy. Deuterated (XXI) and (XXII) were formed predominantly in the reaction and the ratio of d_2-ketones to nondeuterated ketones was ~1.5 : 1. Thus, not excluding the possibility of the partial prior isomerization of (XIX) to the olefin (XX), we must conclude that a significant portion of norcarane is acylated without isomerization into methylcyclohexene and the rate of this reaction is greater than the rate of the acylation of (XX)



The initial site of the electrophilic attack in norcarane (XIX), similar to dimethylethylcyclopropane (III), is the CH_2 group attached to the cyclopropane ring



Our mechanism for the acylation of the cyclopropane ring, in which electrophilic substitution at the saturated α-carbon atom of the side chain is the first step, has not been considered in the literature. However, rather considerable evidence has been found in recent years [10] which indicates that cationoid electrophiles of various types (protons, alkyl cations, chlorine cations, and nitronium cations) are able to react with various saturated hydrocarbons by electrophilic substitution at a σ bond. Although, according to Olah [11], the reaction of an acyl cation with isoalkanes occurs only in "superacid" media, in the case of alkylcyclopropanes such a reaction apparently may be facilitated significantly due to the electrophilic nature of the three-carbon ring.

EXPERIMENTAL

Samples of 1,1,2,2-tetramethyl- (I), 1,1,2-trimethyl- (II), and 1,1-dimethyl-2-ethylcyclopropane (III) were obtained in 97-99% purity by the cyclopropanation of the corresponding olefins by the Simmons – Smith reaction [12] and had constants: (I), bp 76.2-76.5°C (760 mm), n_D^{20} 1.4004; (II), bp 52.0-52.5°C (750 mm), n_D^{20} 1.3860; (III), bp 77.5-78°C (740 mm), n_D^{20} 1.3958. Samples of the 3,3-dideuterocyclopropanes were obtained analogously from the olefins and CD_2I_2, had ~98% purity, and contained, according to mass spectral data, 91% d_2 and 8% d_1 compounds in accord with the degree of deuteration of the initial CD_2I_2 obtained by the exchange of CH_2I_2 with D_2O in basic medium according to Winstein et al. [13]. Data indicating the absence of redistribution of the label in the course of the Simmons – Smith cyclopropane synthesis from olefins are presented by Simmons et al. [12].

The PMR spectra were obtained using Varian DA-60IL and Brüker H-270 spectrometers and the ^{13}C NMR spectra were taken on a Varian CFT-20 spectrometer under conditions of complete and incomplete noise decoupling from protons; the chemical shifts are given in the δ scale using TMS as the internal standard. The mass spectra were obtained on an MKh-1303 instrument with 70 eV ionizing electron energy. The IR spectra were taken on a UR-20 spectrometer in a liquid film.

The gas–liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with a flow meter. The columns were 300 × 0.25 cm with 5% SKTFT-50Kh on Chromosorb G or 15% Reoplex 400 on Chromaton N-AW-DMCS with helium carrier gas.

Preparation of the Carboxonium Salts of (alkyltetrahydrofurylium tetrafluoroborate). Boron trifluoride (310-320 ml, ~13 mmoles) was slowly added to a stirred solution of 1.36 g (13 mmoles) pivaloyl fluoride in 20 ml CH_2Cl_2 cooled to −60°C in an argon atmosphere. Then 10 mmoles cyclopropane hydrocarbon in 5 ml CH_2Cl_2 was added and stirred for 5-10 min. The solution was removed in vacuum and dry ether was added to the residue and shaken vigorously. Upon the formation of a viscous precipitate, the ethereal solution was decanted; the residue was dissolved in 2-3 ml CH_2Cl_2 and another 40-60 ml dry ether was added. The colorless precipitate formed was filtered off in an argon atmosphere, washed with ether, and dried in a vacuum dessicator.

A yield of 1.9 g (70%) salt (IV) with mp 200-202°C (decomp.) was obtained from 0.98 g (I), 0.9 g (35%) salt (VIII) with mp 168-171°C was obtained from 0.84 g (II), and 1.6 g (60%) salt (XIII) with mp 170-172°C was obtained from 0.98 g (III).

Preparation of Alkyltetrahydrofurans. A solution of 0.78 g (3 mmoles) Bu_4NBH_4 in 5 ml CH_2Cl_2 was slowly added to a stirred solution of 3 mmoles carboxonium salt in 5 ml CH_2Cl_2 at 0°C. Most of the solvent was evaporated at low vacuum and ~20 ml pentane was added to the residue and shaken vigorously. The colorless Bu_4NBF_4 precipitate was filtered off, the solvent was evaporated, and the residue was distilled.

A yield of 0.5 g (90%) 2,2,3,3-tetramethyl-5-tert-butyltetrahydrofuran (V) with mp 186-187°C was obtained from 0.81 g (IV). PMR spectrum: 0.85 s [9H, $C(CH_3)_3$], 0.94 s (3H, CH_3), 1.00 s (3H, CH_3), 1.05 s (3H, CH_3), 1.11 s (3H, CH_3), 1.52 d.d. and 1.65 d.d. (2H, J_{AB} = 12.4, J_{AX} = 9.6, J_{BX} = 7.5 Hz), 3.69 d.d. (1H); compare the work of Rundell and Besserer [4]. Mass spectrum (m/e): 169 $(M - CH_3)^+$, 127 $(M - C_4H_9)^+$. Found: C, 78.11; H, 12.92%. Calculated for $C_{12}H_{24}O$: C, 78.20; H, 13.12%.

Analogously, 0.44 g (86%) 2,2,3-trimethyl-5-tert-butyltetrahydrofuran (IX) with mp 167-169°C was obtained from 0.77 g salt (VIII). PMR spectrum: 0.86 s (9H, $C(CH_3)_3$], 0.96 s (3H) and 1.18 s [3H, $2CH_3$ at C(2)], 0.94 d [3H, CH_3 at C(3), J = 6.5 Hz], 1.3-2.3 m [3H at C(3) and C(4)], and 3.55 d.d. [1H, H at C(5), J_{AX} = 10.5, J_{BX} = 5.0 Hz]. Mass spectrum (m/e): 155 $(M - CH_3)^+$, 113 $(M - C_4H_9)^+$. Found: C, 77.46; H, 12.87%. Calculated for $C_{11}H_{22}O$: C, 77.65; H, 12.93%.

After separation of complex (VIII), the reaction mixture was evaporated in vacuum and the lower colored layer was treated with Bu_4NBH_4; the reagent in CH_2Cl_2 was added until the solution was decolorized. A yield of 0.25 g (25%) 2,3-dimethyl-2-isopropyl-5-tert-butyltetrahydrofuran (XII) with bp 96-98°C (32 mm) was obtained on preparative TLC on silica gel L with 1:1 benzene–hexane (R_f 0.75). PMR spectrum: 0.80 s [9H, $C(CH_3)_3$], 0.90 d (6H, $2CH_3$ in i-Pr, J = 7 Hz), 0.92 s [3H, CH_3 at C(2)], 0.96 d [3H, CH_3 at C(3), J = 7 Hz], 1.74 m [1H at C(3)], 1.1-1.4 m [2H at C(4)], 2.17 septet (1H in i-Pr), 3.44 d.d. [1H at C(5), J_{AX} = 11.5, J_{BX} = 5.0 Hz]. Mass spectrum (m/e): 155 $(M - C_3H_7)^+$, 141 $(M - C_4H_9)^+$. Found: C, 78.12; H, 12.97%. Calculated for $C_{13}H_{26}O$: C, 78.72; H, 13.21%.

A yield of 0.5 g (90%) 2,2,3,4-tetramethyl-5-tert-butyltetrahydrofuran (XIV) with bp 85-86°C (22 m) was obtained by the action of Bu_4NBH_4 from 0.81 g salt (XIII). According to the gas–liquid chromatographic data, the substance consists of two isomers in ~4:1 ratio. The PMR spectrum of the major isomer: 0.91 s [9H, $C(CH_3)_3$], 0.97 s (3H) and 1.20 s [2H, $2CH_3$ at C(2)], 0.88 d [3H, CH_3 at C(3), J = 6.6 Hz], 1.42 m [1H at C(3)], 1.00 d [3H, CH_3 at C(4), J = 6.4 Hz], 1.50 m [1H at C(4)], and 3.21 d [1H at C(5), J = 9.2 Hz]. Mass spectrum (m/e): 169 $(M - CH_3)^+$, 127 $(M - C_4H_9)^+$. Found: C, 77.91; H, 12.89%. Calculated for $C_{12}H_{24}O$: C, 78.20; H, 13.12%.

The Reaction of Carboxonium Salt (IV) with Water. A solution of 0.81 g (3 mmoles) salt (IV) in 5 ml CH_2Cl_2 was poured into ice water containing 0.4 g Na_2CO_3. The organic layer was dried with Na_2SO_4 and after removal of the solvent, distilled in vacuum. A yield of 0.44 g (80%) 4,4,5,5-tetramethyl-2-tert-butyl-4,5-dihydrofuran (VI) with bp 73-74°C (20 mm) was obtained. IR spectrum: 1660, 3100 cm^{-1} (C=CH). PMR spectrum: 0.95 s (6H, $2CH_3$), 1.03 s [9H, $C(CH_3)_3$], 1.17 s (6H, $2CH_3$), and 4.21 s (1H, C=CH); compare the work of

Rundell and Besserer [4]. Mass spectrum (m/e): 182 $(M)^+$, 167 $(M - CH_3)^+$. Found: C, 78.20; H, 11.97%. Calculated for $C_{12}H_{22}O$: C, 79.04; H, 12.27%.

The Reaction of Carboxonium Salt (XIII) with Water. A solution of 0.81 g (3 mmoles) salt (XIII) in 5 ml CH_2Cl_2 was treated with ice water containing 0.4 g Na_2CO_3. The organic layer was subjected to preparative TLC on alumina after drying over Na_2SO_4 and evaporation of the solvent (eluent 3:1 cyclohexane – ether). A yield of 0.1 g (16%) 3,4,5,5-tetramethyl-2-tert-butyl-4,5-dihydrofuran (XV) was obtained. IR spectrum: 1655 cm^{-1} (C=C). PMR spectrum: 0.89 d (3H, CH_3, J = 7 Hz), 1.05 s (3H, CH_3), 1.12 s [9H, $C(CH_3)_3$], 1.20 s (3H, CH_3), 1.65 d (3H, CH_3, J < 1 Hz), 2.05-2.45 m (1H, CH). Mass spectrum (m/e): 182 $(M)^+$, 167 $(M - CH_3)^+$. Also, a yield of 0.31 g (50%) 3,4,5,5-tetramethyl-2-tert-butyltetrahydrofuranol-2 (XVI) was isolated. IR spectrum: 3622 cm^{-1} (OH). Mass spectrum (m/e): 185 $(M - CH_3)^+$, 182 $(M - H_2O)^+$, 167 $(M - H_2O - CH_3)^+$, 143 $(M - C_4H_9)^+$, 125 $(M - H_2O - C_4H_9)^+$.

CONCLUSIONS

1. The acylation of 1,1,2,2-tetramethyl-, 1,1,2-trimethyl-, and 1,1-dimethyl-2-ethylcyclopropanes by pivaloyl tetrafluoroborate leads to the formation of stable carboxonium salts, which react with hydride ion donors to yield derivatives of tetrahydrofuran and undergo hydrolysis in water to yield derivatives of 4,5-dihydrofuran.

2. Direct opening of the cyclopropane ring by the action of the $R\overset{\oplus}{C}O$ electrophile does not occur in the acylation of the gem-dideuterocyclopropanes under the same conditions. For methyl-substituted cyclopropanes, a predominant pathway through an isomerization into olefins accompanied by various carbonium ion rearrangements is likely.

3. For 1,1-dimethyl-2-ethylcyclopropane and norcarane which have a methylene group adjacent to the cyclopropane ring, the most likely direction of the reaction is the initial attack of the pivaloyl cation on the C – H bond of the α-methylene fragment with subsequent opening of the cyclopropane ring and formation of stable carboxonium complexes. This type of mechanism of electrophilic opening of a three-membered ring previously has not been considered.

LITERATURE CITED

1. Yu. V. Tomilov, V. A. Smit, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2620 (1975).
2. Yu. V. Tomilov, V. A. Smit, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1439 (1974); 2512 (1976).
3. Yu. V. Tomilov, V. A. Smit, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2614 (1975).
4. W. Rundell and K. Besserer, Lieb. Ann. Chem., 751, 168 (1971).
5. O. V. Lubinskaya, A. S. Shashkov, V. A. Chertkov, and V. A. Smith (W. A. Smit), Synthesis, 742 (1976).
6. R. Ya. Levina, V. N. Kostin, and P. A. Gembitskii, Zh. Obshch. Khim., 30, 868 (1960).
7. H. Hart and R. H. Schlosberg, J. Am. Chem. Soc., 90, 5189 (1968).
8. G. A. Olah, Y. Halpern, J. Shan, and Y. K. Mo, J. Am. Chem. Soc., 95, 4960 (1973).
9. J. T. Keating and P. S. Skell, in: Carbonium Ions (ed. by G. A. Olah and P. Schleyer), Vol. 2, Wiley-Interscience, New York (1970), p. 573.
10. G. A. Olah, Usp. Khim., 44, 793 (1975).
11. G. A. Olah, A. Germain, H. C. Lin, and D. A. Forsych, J. Am. Chem. Soc., 97, 2928 (1975).
12. H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, Org. React., 20, 1 (1973).
13. C. D. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, J. Am. Chem. Soc., 94, 2291 (1972).