Acylation of 1,5-Cyclooctadiene with Pivaloyl Tetrafluoroborate. Stereoselective Synthesis of *endo*-2-Pivaloyl-*endo*-8-hydroxybicyclo[3.3.0]octane. Study of the Reaction Mechanism

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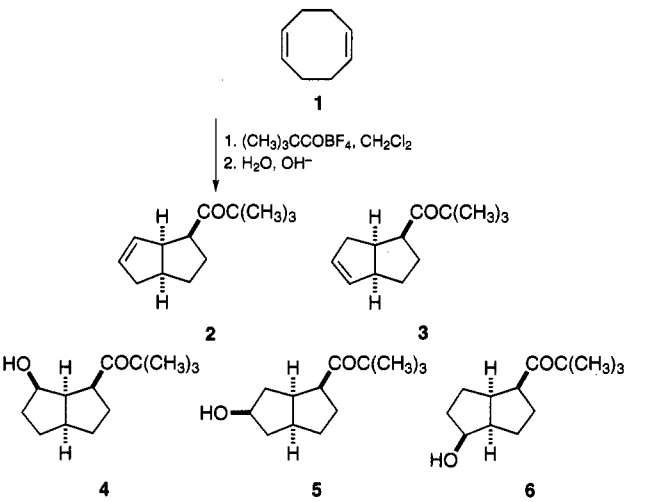
Reaction of (*Z,Z*)-1,5-cyclooctadiene (**1**) with pivaloyl tetrafluoroborate at −78 °C gives *endo*-2-pivaloylbicyclo[3.3.0]oct-7-ene (**2**) and *endo*-2-pivaloylbicyclo[3.3.0]oct-7-ene (**3**) in a 5:1 ratio. If the reaction mixture was stored at room temperature before hydrolysis, a mixture of hydroxy ketones **4**–**6** is obtained. The ratio for compounds **4**–**6** depends on the particular temperature conditions; to give pure *endo*-2-pivaloyl-*endo*-8-hydroxybicyclo[3.3.0]octane **4**, the reaction mixture was refluxed at 42 °C for 36 h before hydrolysis. The NMR study of the reaction mixture showed that the primary product is protonated ketone **8** equilibrating with its isomer **7** *via* protonation–deprotonation. At temperatures higher than −20 °C, **7** and **8** give rise to a mixture of carboxonium salts **9**–**11**, which rearrange into pure **9** after prolonged reflux.

Introduction

(*Z,Z*)-1,5-Cyclooctadiene **1** is a very interesting substrate in the addition reactions both from the theoretical and synthetic points of view. The possibility of 1,2-addition[1] together with easy transanular cyclizations by several acceptable pathways[2] makes this diene a convenient probe for the comparative study of the properties of electrophilic reagents. On the other hand, bicyclo[3.3.0]octanes, which are the most usual products of its electrophilic or radical reactions proved to be frequent structure fragments in various natural products,[3] and an easy access to these compounds by transannular cyclization of 1,5-cyclooctadiene could be of significant synthetic value.

However there are surprisingly few studies of the synthesis of bicyclo[3.3.0]octanes from 1,5-cyclooctadiene.[4] The main reasons for this are the rare selectivity and the serious problem of the structural assignment of the reaction products. Although it is very easy to judge whether the transannular cyclization have occurred, the stereochemistry of both mono- and bicyclic adducts often remains unclear. The purpose of this work was to study the acylation of **1** with pivaloyl tetrafluoroborate, characterize all of the products forming in the reaction, determine their structure and stereochemistry, find out the conditions for increasing selectivity, and study the mechanism of the reaction *via* the analysis of the structure of intermediates.

Scheme 1. Products Observed in the Acylation of 1 with Pivaloyl Tetrafluoroborate



Results

The composition of the products of the acylation of **1** with pivaloyl tetrafluoroborate depends on the temperature conditions of its realization (see Scheme 1 and Table 1). At the temperature −78 °C, two unsaturated ketones **2** and **3** with bicyclo[3.3.0]octane skeleton are the main products of the reaction. Increasing the temperature of the reaction leads to the formation of three hydroxy ketones **4**–**6**. The ratio between the products **2**–**6** changes depending on the particular temperature conditions, giving pure **4** as a single product after a prolonged reflux of the reaction mixture (see Table 1).

Compounds **2** and **4**–**6** were isolated in a pure form by the column chromatography of the reaction mixtures. Unsaturated ketone **3** was only obtained as a 3:2 mixture with **2** due to its low content and close R_f values of **2** and **3**.

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Table 1. Composition of the Products of the Acylation of 1 with Pivaloyl Tetrafluoroborate Depending on the Temperature Conditions of the Reaction[a]

temperature conditions	overall yield, %	2	3	4	5	6
2 h at −78 °C, then pouring the reaction mixture into aqueous Na_2CO_3 at −20 °C	78	80	15	5	trace	trace
2 h at −78 °C, 1 h at −30 °C, and then pouring the reaction mixture into aqueous Na_2CO_3 at −20 °C	85	20	5	45	15	15
2 h at −78 °C, 1 h at 20 °C, and then pouring the reaction mixture into aqueous Na_2CO_3 at 20 °C	85			55	25	20
2 h at −78 °C, 12 h at 20 °C, and then pouring the reaction mixture into aqueous Na_2CO_3 at 20 °C	92			60	35	5
2 h at −78 °C, 36 h reflux at 42 °C, and then pouring the reaction mixture into aqueous Na_2CO_3 at 20 °C	75			100	trace	trace

[a] Compounds **2**–**6** were separated in each experiment by column chromatography on silica gel, eluent hexane–ether, 10:1; the R_f values are as follows: 0.92 (**3**); 0.90 (**2**); 0.75 (**4**); 0.22 (**5**); 0.15 (**6**).

Determination of the Products Structure

Although for all of the compounds **2**–**6** the occurrence of the transannular cyclization during acylation could be easily elucidated from their mass spectra and the numbers of the signals of the double bonds in the NMR spectra, the structure of the bicyclic skeleton and the position of the substituents and stereochemistry were not clear. We made an unambiguous structural assignment for the compounds **2**–**6**.

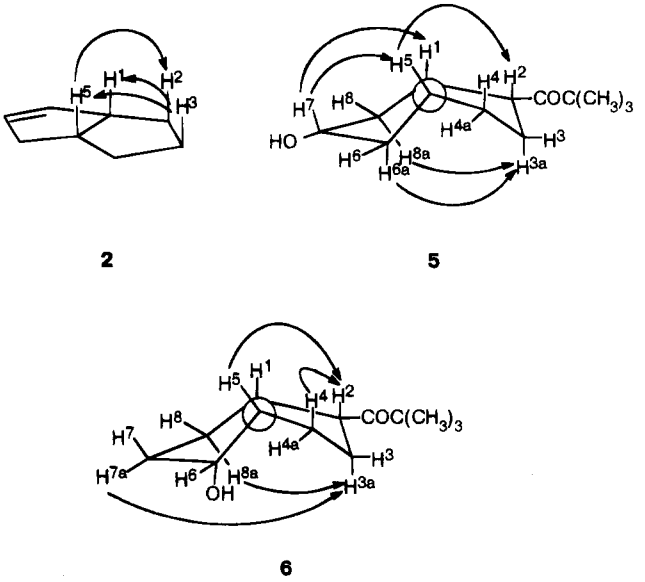
The structures of the carbon skeletons and the positions of double bonds and substituents for compounds **2** and **4**–**6** were determined by their COSY-like 2D INADEQUATE spectra;[5] the structure of unsaturated ketone **3** was elucidated from the $^1H-^1H$ COSY and $^1H-^{13}C$ XHCORR spectra of a sample containing 60% of **3** and 40% of **2**.

Cis-fusion of the five-membered rings in the compounds **2**–**6** follows from the corresponding values of the coupling constants $^3J(H^1,H^5)$, which lay within the limits 6.8–8.3 Hz. For *trans*-fused bicyclo[3.3.0]octanes, the inevitable axial–axial disposition of the protons H^1 and H^5 should lead to much greater values. For example a similar coupling in *trans*-dihydroindenes is known to be 18–20 Hz.[6]

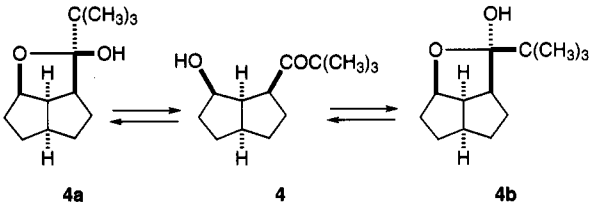
The stereochemistry of compounds **2**, **3**, **5**, and **6** was determined by 2D NOESY experiments (see Scheme 2). The character of the concentration dependence of the IR spectra of the solutions of compounds **5** and **6** in CCl_4 indicated the presence of an intramolecular hydrogen bonds in the molecules of these compounds. This fact independently points out the *syn*-disposition of the hydroxyl and pivaloyl substituents.

Some conclusions about the most stable conformations of compounds **5** and **6** in solution can be made (see Scheme 2). In compound **5** the proton H^{3a} has three large (about 12 Hz) couplings that indicates a significant stability of the conformation with H^{3a} being pseudoaxial,[7] *i.e.* the carbon atom C^3 is located in the most folded part of the cycle $C^1C^2C^3C^4C^5$. This conclusion is confirmed by the NOE's of H^{3a} and H^{6a},H^{8a}. In turn, the NOE's between H^7 and H^1, H^5 clearly indicate the folding of the second cycle on the C^7 carbon atom. In compound **6** the long-range NOE's between H^{3a} and H^{7a}, H^{8a} indicate the relative stability of the conformation similar to that of compound **5**. In the case of **6** this conformation is less stable, because the coupling $^3J(H^2,H^{3a})$ is 9.5 Hz.

Scheme 2. NOE's Observed for 2, 5, and 6 in 2D NOESYTP Experiments



Scheme 3. Equilibria Observed in a Solution of 4



A triple set of signals is observed in the ^1H and ^{13}C NMR spectra of compound **4**. Moreover, in the ^{13}C NMR spectrum of **4** only a small-intensity signal of a carbonyl group can be found, the signals at 112.95 and 111.93 ppm being observed for two major isomers. In the IR spectrum of compound **4** a strong OH group absorption (ν = 3650 cm^{-1}) is present; however no absorption of a carbonyl group can be detected. These facts indicate that compound **4** exists in a solution as a mixture of two cyclic semiketals **4a** and **4b** (in a 4:1 ratio) interconverting reversibly through the open form **4** (Scheme 3). Figure 1 shows a direct detection of the interconversion of the major isomer **4a** and the open form **4** by a 2D phase-sensitive ^1H NOESY spectrum taken at 50 °C. No cross-peaks are observed for the exchange between the open form **4** and the minor isomer **4b** due to comparatively low concentration of the latter. Hence the exchange is slow in the NMR time scale even at 50 °C. The formation of the stable semiketals **4a,b** indicates the *endo,endo*-

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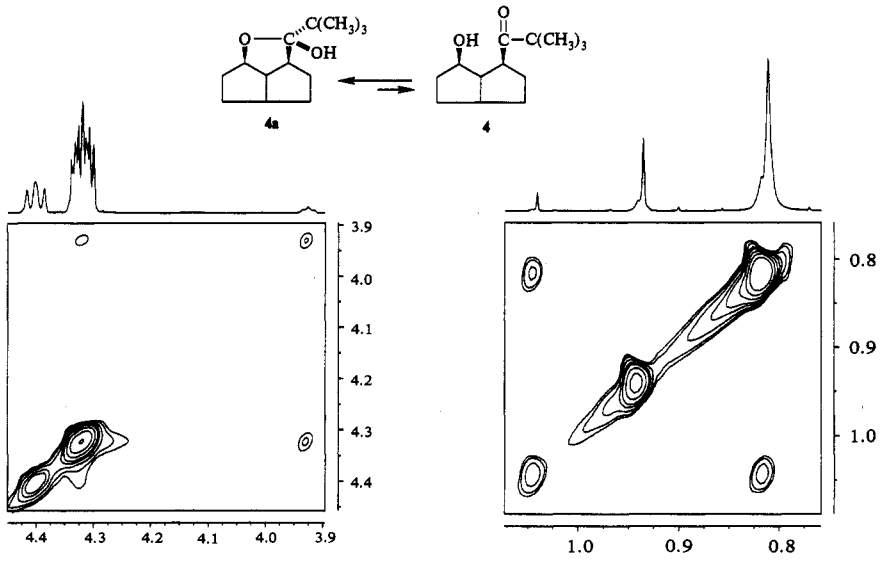


Figure 1. Section plots of the 2D NOESYTP spectrum of compound **4** (400 MHz, $CDCl_3$, 50 °C). Matrix 1024 × 512, initial delay 2 s, number of scans 80, dummy scans 4, mixing time 1 s.

disposition of pivaloyl and hydroxyl groups, because the geometry of the bicyclo[3.3.0]octane skeleton gives no other possibility.

Investigation of the Acylation Mechanism

It should be stressed that the formation of the main products of the acylation of **1** either at −78 °C (unsaturated ketone **2**) or at room temperature (hydroxy ketone **4**) cannot be understood from the point of view of the common mechanism of electrophilic addition to COD proceeding with the transannular cyclization because in that case unsaturated ketone **3** and hydroxy ketone **6** should be the main products. Therefore the mechanism of acylation of COD **1** with pivaloyl tetrafluoroborate deserved a more detailed investigation.

To follow the processes proceeding during the acylation of **1** with pivaloyl tetrafluoroborate, we carried out the reaction in a tube of NMR spectrometer. The results are shown in Figure 2. A solution of COD in CD_2Cl_2 cooled to −78 °C was added to a suspension of $(CH_3)_3COBF_4$ in CD_2Cl_2 at the same temperature, and the resulting solution was inserted into an NMR tube, which was immediately positioned into the spectrometer probe previously cooled to −65 °C. Figure 2a displays the low-field region of ^1H NMR spectra taken immediately after the above described operations. Figure 2b shows the ^1H NMR spectra of the same sample taken at −20 °C, whereas parts e and d of Figure 2 display the changes occurring in the reaction mixture at the positive temperatures. The relative intensities of the signals in the spectra change in the course of the reaction to give only one set of signals after prolonged reflux (Figure 2d). At each reaction stage reflected by Figure 2 the $^1H-^1H$ COSY and $^1H-^{13}C$ correlation experiments were made that enabled us to follow the structures of intermediates, which were found to be protonated ketone **7** and carboxonium salts **9**−**11** (see Scheme 4 and Table 2). Protonated ketone **7** is thermally unstable; the analysis of Figure 2a,b leads to a conclusion that **7** rapidly transforms into **9**−**11** at −20 °C. This is the reason why considerable concentrations of carboxonium salts **9**−**11** are observed even in Figure 2a; they formed during the transfer of the NMR tube from the bath into the probe.

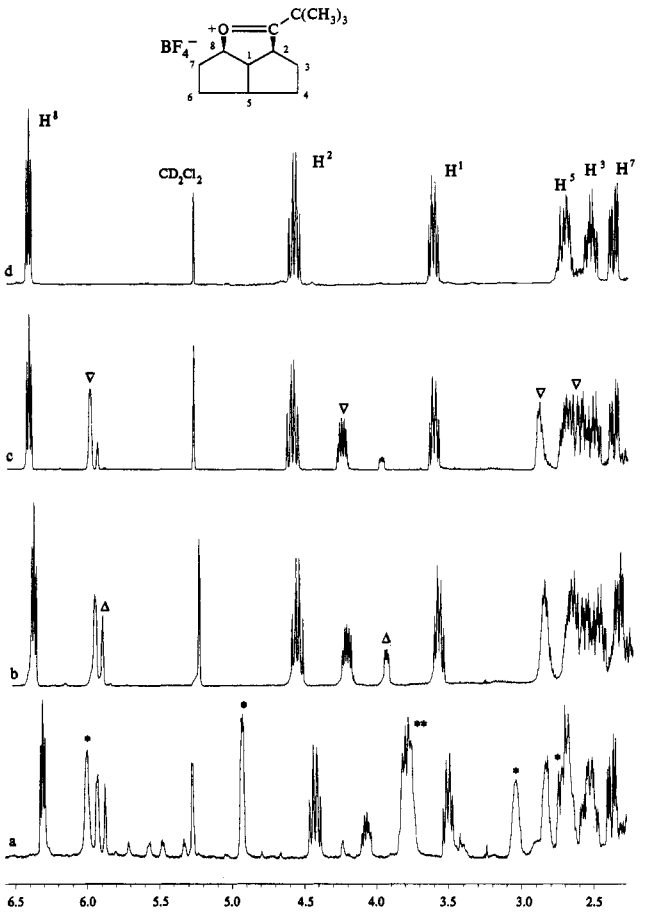


Figure 2. Section plots of the ^1H NMR spectra of the reaction mixture obtained after mixing the suspension of $(CH_3)_3CCOBF_4$ in CD_2Cl_2 and solution of 1,5-cyclooctadiene in CD_2Cl_2 at −78 °C. (a) The spectrum taken immediately after placing the sample into the probe cooled to −70 °C. The signals of protonated ketone **7** are marked by asterisks. (b) The spectrum of the same sample at −20 °C; the signals of **7** have already dissapeared: (△) signals of **11** (found by $^1H-^1H$ COSY spectrum). (c) The spectrum of the same sample at 25 °C after overnight storage at the room temperature: (▽) signals of **10** (found by $^1H-^1H$ COSY spectrum). (d) The spectrum of the same solution after reflux for 36 h; it is the spectrum of a pure carboxonium salt **9**.

Scheme 4. Mechanisms of the Acylation and Acylamidation of 1,5-COD

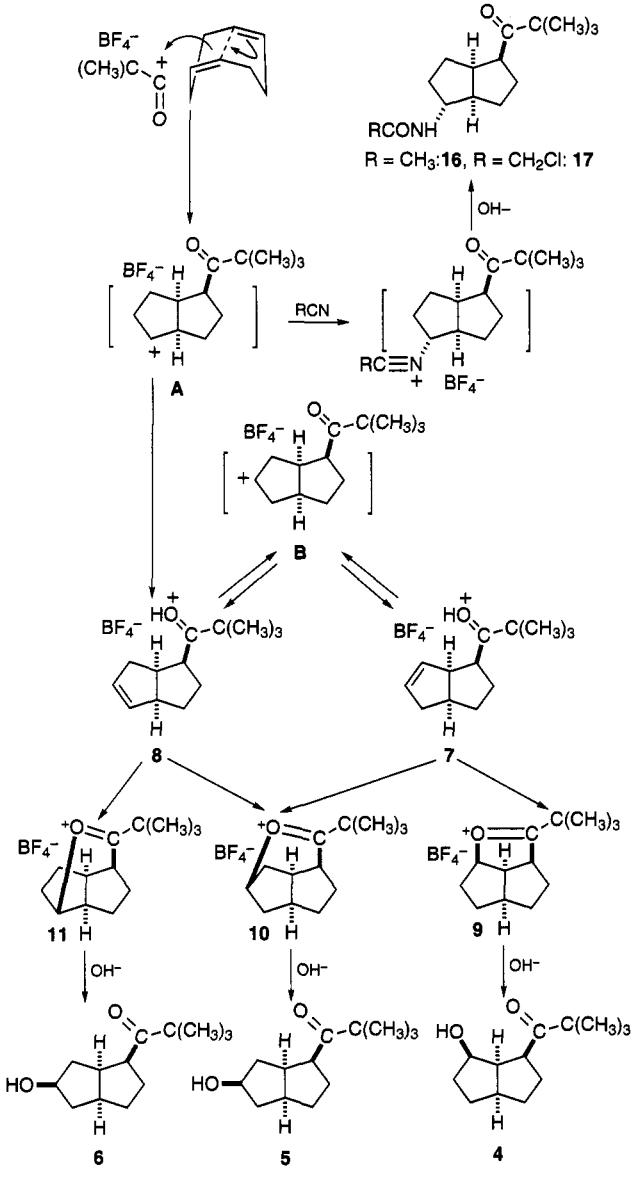


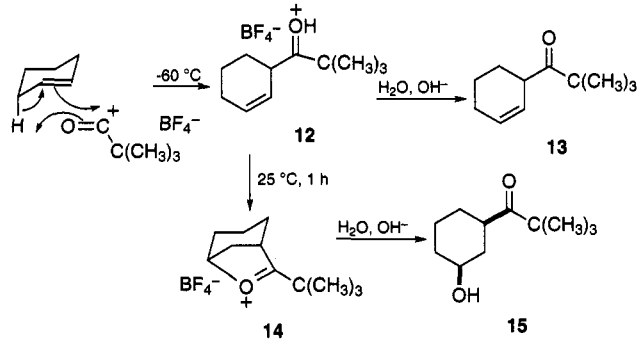
Figure 2b–d shows that **10** and **11** slowly transform to **9**, indicating a relative thermodynamic stability of the latter.

Another interesting fact is the dynamics observed in the ^{13}C NMR spectra of the reaction mixture for the signals of protonated ketone **7** (see Figure 3). Variable-temperature experiments showed that the cooling of the reaction mixture to −90 °C leads to an appearance of the signals of the second protonated ketone equilibrating with **7** (Figure 3a). Since the low-temperature deprotonation of the reaction mixture gives 20% of unsaturated ketone **3**, it was natural to propose that **7** equilibrate with corresponding protonated ketone **8** *via* reversible protonation–deprotonation (see Scheme 4). The recording of six spectra at different temperatures and the line shape analysis[8] (see Figure 4) gave the following activation parameters of the equilibrium between **7** and **8**: $\Delta H^{\ddagger} = 21.5 \pm 0.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -94 \pm 11$ J mol^{-1} K^{-1}.

Discussion

It is known that in many cases a protonated β,γ-unsaturated ketone is the initial product in acylation

Scheme 5. Acylation of Cyclohexene with Pivaloyl Tetrafluoroborate



reactions. For example, acylation of cyclohexene initially gives protonated β,γ-unsaturated ketone **12**. Workup of the reaction mixture at −60 °C affords unsaturated ketone **13**, whereas the raise of the temperature to 20 °C leads to the formation of carboxonium salt **14** and hydroxy ketone **15** becomes the product of the reaction (Scheme 5).[9] Exclusive formation of the unconjugated β,γ-unsaturated ketone **13** is believed to be strong evidence against intermediate formation of a carbocation, because in that case one should expect the appearance of a conjugated α,β-unsaturated ketone.

Apparently, similar processes take place in the reaction of 1,5-COD (**1**) with pivaloyl tetrafluoroborate; however in this case the matter is complicated by the transannular cyclization. Compounds with a cyclooctene structure were neither detected in the reaction mixture nor found among the reaction products. Therefore it can be assumed that the transannular cyclization proceeds concertedly with the attack of the pivaloyl cation on the double bond of cyclooctadiene (Scheme 4). Similar to the acylation of cyclohexene, one might propose a simultaneous and concerted transfer of the proton to the carbonyl group directly, providing protonated ketone **8**, which is enough to produce all other observed products according to the experiments on the NMR monitoring of the reaction. However the results of the acylamidation of **1** give interesting evidence in favor of the intermediate formation of a carbocation.

We have reported that the reaction of 1,5-cyclooctadiene with pivaloyl tetrafluoroborate in the presence of a 5-fold excess of a nitrile gives stereospecifically the high yields of *endo*-2-pivaloyl-*exo*-(acylamino)bicyclo[3.3.0]-octanes **16** and **17** (Scheme 4).[4b]

The special experiment showed that no traces of **16** or any other amido ketone can be obtained by treatment of the solution of the mixture of carboxonium salts **9**–**11** with the large excess of acetonitrile, *i.e.* the carboxonium salts **9**–**11** are not cleaved with nitriles. On the other hand, the conditions of the acylamidation of 1,5-COD (**1**) are the same as those leading to the exclusive formation of the hydroxy ketone **4** with 2-*endo*-8-*endo* disposition of the substituents. Taking into account the same stereochemistry of the pivaloyl group in the products of acylation and acylamidation, one can propose that the first step in both reactions is the same, *viz.* the *endo* attack of a pivaloyl cation on the double bond of cyclooctadiene conjugated with the transannular cyclization,

(8) The line shape analysis was carried out *via* direct iterative search of the activation parameters from the whole set of the experimental spectra; see: Laatikainen, R. *J. Magn. Reson.* **1985**, *64*, 375–383.

(9) Lubinskaya, O. V.; Shashkov, A. S.; Chertkov, V. A. *Synthesis* **1976**, 742–748.

Table 2. Chemical Shifts (ppm) in the ^1H and ^{13}C NMR Spectra of Intermediates 7 and 9–11

atom no.	7 δ ^1H	7 δ ^{13}C	9 δ ^1H	9 δ ^{13}C	10 δ ^1H	10 δ ^{13}C	11 δ ^1H	11 δ ^{13}C
1	3.71	54.60	3.60	51.55	4.18	50.58	3.89	53.73
2	3.80	59.95	4.59	62.20	2.82	44.31	2.88	45.54
3	1.68, 2.51	33.79	2.11, 2.50	31.85	1.78, 2.49	31.70	*a*	33.53
4	1.75, 1.83	34.89	1.78,	32.47	2.66,	32.44	2 × 2.12	22.66
5	3.03	42.19	2.68	46.66	2.89	44.56	2.75	43.29
6	2.05, 2.60	41.19	1.07, 1.63	27.62	2.19, 1.85	35.39	5.86	111.00
7	5.98	124.81	2.37	35.39	5.95	99.72	*a*	33.77
8	4.92	139.55	6.42	116.18	1.70, 2.61	39.55	1.79, 2.20	24.33
C=O		251.78		248.41		242.49		245.81
C quart		46.31		47.18		47.05		*a*
CH_3	1.22	26.99	1.20	28.14	1.14	27.04	1.18	27.68

[a] The chemical shifts were not determined due to overlapping of the cross peaks.

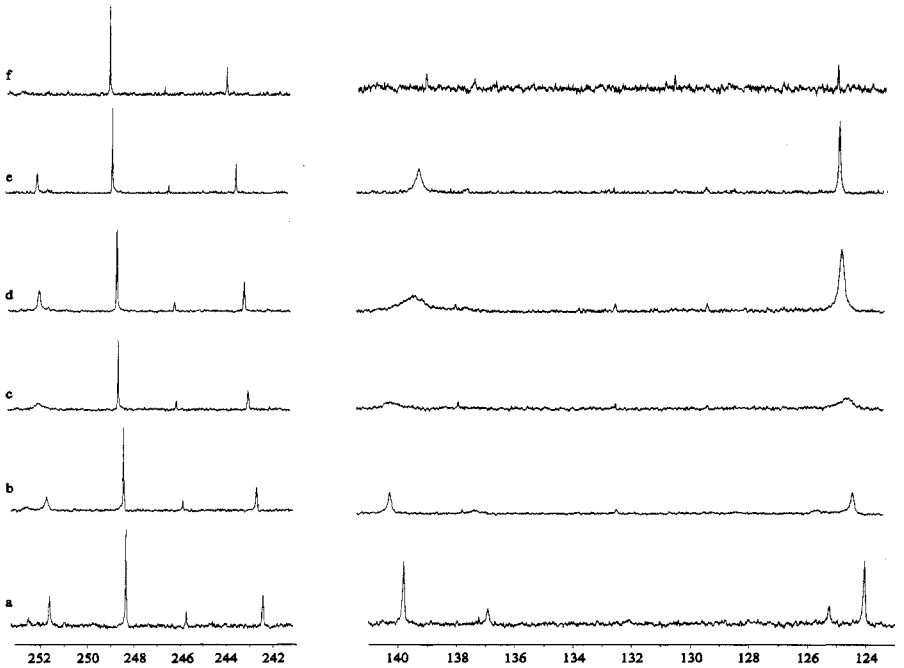


Figure 3. Section plots of the temperature dependent ^{13}C NMR spectra of the reaction mixture obtained after mixing the suspension of $(CH_3)_3CCOBF_4$ in CD_2Cl_2 and solution of 1,5-cyclooctadiene in CD_2Cl_2 at −78 °C: (a) −90 °C; (b) −83 °C; (c) −71 °C; (d) −52 °C; (e) −38 °C; (f) −20 °C. It is evident from the carbonyl region of the latter spectrum that protonated ketones **7** and **8** are rapidly consumed at this temperature, tranforming into carboxonium salts **9**–**11**.

producing a carbocation **A** (Scheme 4). In the case of the acylation it is stabilized *via* proton transfer to the oxygen atom of the carbonyl group giving protonated ketone **8**, which later gives intermediates **7** and **9**–**11** according to the previous discussion. In this case the stereochemistry of the carboxonium salts **9**–**11** and later of the hydroxy ketones **4**–**6** is determined by an intramolecular character of the stabilization of carbocation **A**. In acylamidation, when a large excess of a nitrile is present in the reaction mixture, the cation **A** is trapped by a molecule of a nitrile, which adds from the outer side of the molecule, giving rise to 2-*endo*-6-*exo*-amidoketones **16** and **17** after hydrolysis (Scheme 4).

Conclusions

Acylation of (*Z,Z*)-1,5-cyclooctadiene with pivaloyl tetrafluoroborate proceeds stereoselectively, affording unsaturated ketones **2,3** or hydroxy ketones **4**–**6**, depending on the reaction conditions. Prolonged reflux of the reaction mixture gives **4** as a single product; unsaturated ketone **2** and hydroxy ketones **5** and **6** can be separated in pure form by column chromatography of the appropriate reaction mixtures.

The reaction begins from the *endo* attack of the pivaloyl cation on the double bond of cyclooctadiene. Transannular cyclization proceeds simultaneously, giving a carbocation, which is immediately stabilized by intramolecular deprotonation. Protonated unsaturated ketone **8** equilibrates with its isomer **7** *via* protonation–deprotonation at the temperatures below −20 °C, while at higher temperatures the rapid irreversible protonation of **7** and **8** takes place, giving rise to carboxonium salts **9**–**11**. Thus, the intramolecular character of the stabilization of an initially formed cation is responsible for the strict *endo,endo* disposition of the substituents in the final hydroxy ketones **4**–**6**. This conclusion is in agreement

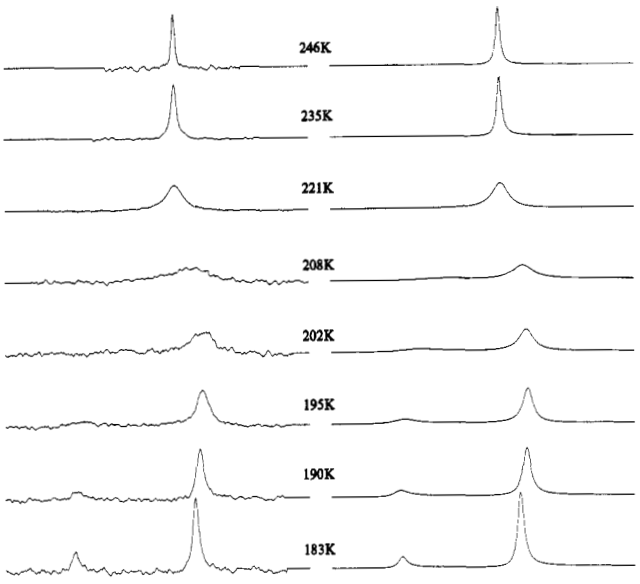


Figure 4. Experimental (left) and best-fit calculated (right) spectra of the C^6 carbon atoms of protonated ketones **7** and **8**.

with the stereochemical result of the acylamidation of **1**, where only *endo,exo* adducts are formed.

Experimental Section

NMR spectra were recorded at 400 MHz for ^1H and at 100 MHz for ^{13}C. IR spectra were obtained in CCl_4. Methylene chloride was distilled over P_2O_5, pivaloyl fluoride was refluxed and distilled over KF, and 1,5-cyclooctadiene was distilled over sodium.

Acylation of (*Z,Z*)-1,5-Cyclooctadiene with Pivaloyl Tetrafluoroborate. BF_3 was passed until saturation through a solution of 2.6 g (0.025 mol) of $(CH_3)_3COF$ in 100 mL of CH_2Cl_2 at −78 °C. Then at the same temperature a solution of 2.6 g (0.024 mol) of (*Z,Z*)-1,5-cyclooctadiene in 10 mL of CH_2Cl_2 cooled to −70 °C was added dropwise. The following treatment of the reaction mixture and the yields of the products are given in Table 1.

***endo*-2-Pivaloylbicyclo[3.3.0]oct-7-ene (2):** bp 87 °C (1 mmHg); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.02 s (9H, $3CH_3$), 1.30−1.45 (m, 2H, H^3, H^4), 1.56−1.77 (m, 2H, H^{3a}, H^{4a}), 1.97 (dm, 1H, H^6, $^2J(H^6,H^{6a})$ = 17.9 Hz), 2.56 (ddq, 1H, H^{6a}, $^3J(H^{6a},H^5)$ = 9.2 Hz), 2.70 (m, 1H, H^5), 3.16 (ddd, 1H, H^2, $^3J(H^2,H^{3a})$ = 11.2 Hz, $^3J(H^1,H^2)$ = 8.1 Hz, $^3J(H^2,H^3)$ = 5.5 Hz), 3.28 (tt, 1H, H^1, $^3J(H^1,H^5)$ = 7.9 Hz, $^3J(H^1,H^8)$ = $^4J(H^1,H^7)$ = 2.3 Hz), 5.01 (dq, 1H, H^7, $^3J(H^7,H^8)$ = 5.7 Hz), 5.59 (dq, 1H, H^8); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 24.55 ($3CH_3$), 27.08 (C^4), 32.58 (C^3), 39.16 (C^5), 40.47 (C^6), 42.95 (C quart), 48.78 (C^2), 53.02 (C^1), 128.85 (C^8), 130.02 (C^7), 204.24 (C=O); HRMS (M^+) 192.150 23, $C_{13}H_{20}O$ calcd 192.151 31.

***endo*-2-Pivaloylbicyclo[3.3.0]oct-6-ene (3):** bp 87 °C (1 mmHg); ^1H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 1.41 (dddd, 1H, H^4), 1.55, 1.65 (m, 2H, H^3, H^{3a}), 1.69 (m, 1H, H^{4a}), 1.96 (ddddd, 1H, H^8, $^2J(H^8,H^{8a})$ = 17.1 Hz, $^3J(H^1,H^8)$ = 3.6 Hz, $^3J(H^8,H^7)$ = $^4J(H^a,H^6)$ = 2.3 Hz, $^4J(H^{8a},H^5)$ = 1.2 Hz), 2.14 (ddddd, 1H, H^{8a}, $^3J(H^1,H^{8a})$ = 9.2 Hz, $^3J(H^{8a},H^7)$ = $^4J(H^{8a},H^6)$ = 2.3 Hz, $^4J(H^{8a},H^5)$ = 1.2 Hz), 2.98 (dddd, 1H, H^1, $^3J(H^1,H^5)$ = 3.8 Hz, $^4J(H^1,H^4)$ = 0.9 Hz), 3.20 (ddd, 1H, H^2, $^3J(H^1,H^2)$ = 8.2 Hz, $^3J(H^2,H^3)$, $^3J(H^2,H^{3a})$ = 5.1, 11.9 Hz), 3.23 (m, 1H, H^5), 5.42 (dq, 1H, H^7, $^3J(H^6,H^7)$ = 5.7 Hz), 5.55 (dq, 1H, H^6); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 26.91 (CH_3), 28.22 (C4), 31.57 (C^3), 35.76 (C^8), 44.04 (C^1), 45.01 (C quart), 51.92 (C^2), 52.06 (C^5), 130.91 (C^7), 133.77 (C^6), 205.15 (C=O); mass spectrum, *m/e* 192 (M^+), 135 ($M^+ - C_4H_9$), 57 (C_4H_9).

***endo*-2-Pivaloyl-*endo*-8-hydroxybicyclo[3.3.0]octane (4):** mp 79 °C (from hexane). Description of the NMR spectra is given only for the major tautomer **4a**: ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.13 (s, 9H, $3CH_3$), 1.40−1.53 (m, 5H, H^{3a}, H^{4a}, H^{6a}, H^{6b}, H^{7a}), 1.55 (dddd, 1H, H^{4b}), 1.78 (m, 1H, H^{7b}), 1.88 (dddd, 1H, H^{3b}), 2.04 (s, 1H, OH), 2.55 (m, 1H, H^5), 2.55 (ddd, 1H, H^2); 2.88 (ddd, 1H, H^1), 4.28 (ddd, 1H, H^8), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 24.51 ($3CH_3$), 28.79 (C^3), 29.87 (C^6), 33.00 (C^4), 34.98 (C^7), 39.45 (C quart), 44.97 (C^5), 47.80 (C^2), 56.66 (C^1), 84.90, (C^8), 112.50 (CO); mass spectrum, *m/e* 192 (M^+), 135 ($M^+ - H_2O - C_4H_9$), 57 (C_4H_9). Anal. ($C_{13}H_{22}O_2$) Found: C, 74.18; H, 10.44. Calcd: C, 74.24; H, 10.54.

***endo*-2-Pivaloyl-*endo*-7-hydroxybicyclo[3.3.0]octane (5):** mp 62 °C (from hexane); ^1H NMR (400 MHz, CD_3OD, 25 °C) δ 1.25 (dt, 1H, H^{6a}, $^2J(H^{6a},H^6)$ = 12.0 Hz, $^3J(H^{6a},H^5)$ = 10.2 Hz, $^3J(H^{6a},H^7)$ = 10.3 Hz), 1.31 (s, 9H, $3CH_3$), 1.40 (dt, 1H, H^{8a}, $^2J(H^{8a},H^8)$ = 12.1 Hz, $^3J(H^{8a},H^7)$ = 10.7 Hz, $^3J(H^{8a},H^1)$ = 8.5 Hz), 1.70 (m, 3H, H^8, H^3, H^{4a}), 1.81 (dddd, 1H, H^4, $^2J(H^{4a},H^4)$ = 12.7 Hz, $^3J(H^{3a},H^4)$ = 12.7 Hz, $^3J(H^3,H^4)$ = 5.2 Hz, $^3J(H^4,H^5)$ = 0.5 Hz), 2.17 (dddd, 1H, H^{3a}, $^2J(H^{3a},H^3)$ = 12.3 Hz, $^3J(H^{3a},H^2)$ = 12.3 Hz, $^3J(H^{3a},H^2)$ = 5.7 Hz), 2.33 (dddd, 1H, H^6, $^3J(H^6,H^5)$ = 5.1 Hz, $^3J(H^6,H^7)$ = 5.2 Hz, $^4J(H^6,H^8)$ = 1.8 Hz), 2.69 (ddddd, 1H, H^5, $^3J(H^1,H^5)$ = 8.5 Hz), 2.88 (dddd, 1H, H^1, $^3J(H^1,H^8)$ = 10.5 Hz, $^3J(H^1,H^2)$ = 8.5 Hz), 3.46 (ddd, 1H, H^2, $^3J(H^2,H^3)$ = 5.3 Hz), 4.10 (tt, 1H, H^7); ^{13}C NMR (100 MHz, C_6D_6, 25 °C) δ 26.31 ($3CH_3$), 27.72 (C^3), 31.70 (C^4), 37.20 (C^8), 40.50 (C^5), 42.83 (C^6), 43.59 (C^1), 44.11 (C quart), 49.60 (C^2), 73.35 (C^7), 215.84 (C=O); mass spectrum, *m/e* 192 ($M^+ - H_2O$), 57 (C_4H_9). Anal. $C_{13}H_{22}O_2$ Found: C, 74.57; H, 10.43. Calcd: C, 74.24; H, 10.54.

***endo*-2-Pivaloyl-*endo*-6-hydroxybicyclo[3.3.0]octane (6):** mp 56 °C (from hexane); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.11 (s, 9H, $3CH_3$), 1.32 (m, 2H, H^8, H^{8a}), 1.49 (m, 1H, H^{4a}), 1.55−1.75 (m, 3H, H^3, H^7, H^{7a}), 1.80−1.98 (m, 2H, H^4, H^{3a}), 2.19 (br s, 1H, OH), 2.58 (dddd, 1H, H^5, J = 9.5, 3.4, 5.3, 5.3 Hz), 2.70 (dddd, 1H, H^1, J = 8.3−8.5 Hz), 3.27 (ddd, H^2, J = 9.5, 8.4, 5.1 Hz), 4.12 (ddd, 1H, H^6, J = 5.1, 4.5, 4.5 Hz); ^{13}C NMR (100 MHz, C_6D_6, 25 °C) δ 24.74 (C^4), 25.23 (C^8), 26.32 ($3CH_3$), 31.12 (C^3), 36.71 (C^7), 47.03 (C^1), 49.28 (C^2), 49.74 (C^5), 74.34 (C^6), 216.40 (C=O); mass spectrum, *m/e* 192 ($M^+ - H_2O$), 57 (C_4H_9). Anal. $C_{13}H_{22}O_2$ Found: C, 74.14; H, 10.50. Calcd: C, 74.24; H, 10.54.

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Supporting Information Available: ^1H NMR spectra of **2**−**6**, COSY-like 2D INADEQUATE spectra of **2** and **4** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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