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FORMATION OF CARBOXONIUM SALTS IN THE ACYLATION OF ALKENES BY ACYLIUM SALTS AND SOME PROBLEMS OF THE MECHANISM OF ACYLATION

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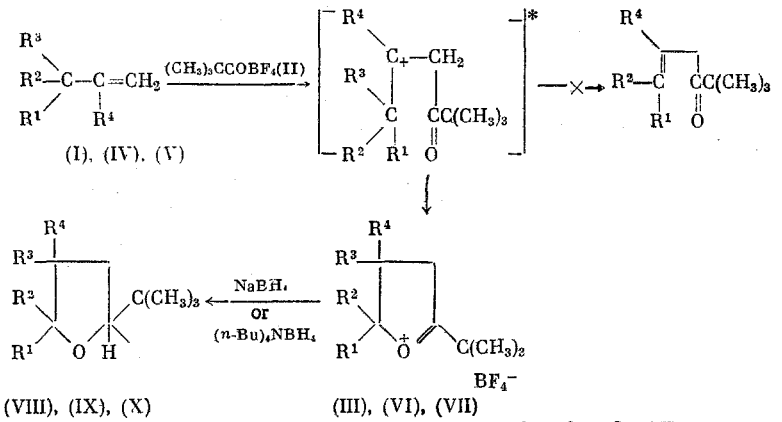
UDC 541.124:542.951.1:547.313

Low-temperature acylation of alkenes by acylium salts leads to β, γ-unsaturated ketones [1]. We have now shown that this reaction can be carried out in a different way and constitutes a general route to five-membered carboxonium salts. The reaction is particularly facile for alkenes with branching at the allylic carbon. Thus, addition of isopropylethylene (I) to a suspension of $(CH_3)_3CCOBF_4$ (II) in CH_2Cl_2 at −50°C results in the rapid formation of a homogeneous solution whose PMR spectrum shows the signals of carboxonium salt (III), while the signals of starting (I) are almost completely absent. Salt (III) is easily isolated by removal of the solvent under vacuum between −10 and −15°C and can be purified by reprecipitation from CH_2Cl_2 solution with absolute ether. The reactions of (II) with tert-butylethylene (IV) and 2, 3, 3-trimethyl-1-butene (V) are similar. The formation of salts (III), (VI), and (VII) can be described formally by scheme 1, which involves 1,2-shift of hydride [(III)] or CH_3

Scheme 1



(VIII), (IX), (X) (III), (VI), (VII)

$R^1 = R^2 = CH_3$; $R^3 = R^4 = H$ (I), (III), (VIII); $R^1 = R^2 = R^3 = CH_3$; $R^4 = H$ (IV), (VI), (IX); $R^1 = R^2 = R^3 = R^4 = CH_3$ (V), (VII), (X)

These salts are reasonably stable and in the absence of moisture can be stored at room temperature for several weeks at least.

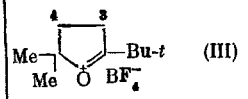
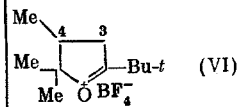
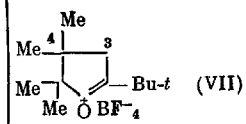
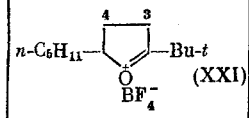
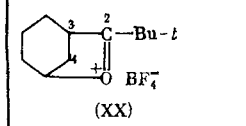
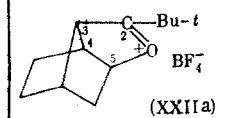
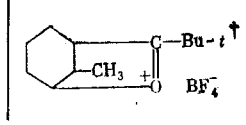
The PMR spectra of (III), (VI), and (VII) (Table 1) are consistent with literature data for several of the simplest cyclic five-membered carboxonium salts [2-4]. However, the ^{13}C NMR spectra are more informative (Table 1). Their most characteristic feature is the presence of two groups of downfield signals at 245-246 and 121-123 ppm, which belong to 2-^{13}C and 5-^{13}C, respectively. The 2-^{13}C signals lie 30-35 ppm downfield from those of the carbonyl carbon in ketones $(CH_3)_3CCOR$ (δ 211-215 ppm [5]), which is close to the value of 40-45 ppm reported for the shift of the carbonyl carbon signal on protonation [6]. The shift of the 5-^{13}C signal

*We write the reaction sequence thus for clarity. A refined version appears in Scheme 6.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 397-408, February, 1978. Original article submitted September 21, 1976.

0568-5230/78/2702-0343 $07.50

TABLE 1

Alkene	Carboxonium salt	Yield, %	mp, °C	NMR parameters, δ, ppm*							
				ring atoms				substituents on			
				2-C	3-C	4-C	5-C	2-C [C(CH3)3]	3-C	4-C	5-C
(I)	 (III)	75	164–168	^{13}C 245,90 ^{1}H –	42,45 3,98	31,58 2,42	121,26 –	42,20 25,07 1,37	– –	– –	26,23 1,75
(IV)	 (VI)	86	168–172	^{13}C 245,93 ^{1}H –	48,31 3,92	38,04 2,85	121,67 –	42,69 26,22 1,44	– –	12,69 1,15	20,84 26,46 1,83 1,59
(V)	 (VII)	85	200–202	^{13}C 245,50 ^{1}H –	53,86 3,65	42,02 –	123,20 –	42,26 24,19 1,21	– –	20,49 0,95	20,92 1,5
(XVIII)	 (XXI)	81	Semicrystalline mass	^{13}C 248,21 ^{1}H –	42,16 3,9	34,09 1,8–3,0	111,24 6,05	42,84 26,53 1,45	– –	– –	31,17 1,8–3,0
(XVII)	 (XX)	90	188–191	^{13}C 249,98 ^{1}H –	50,53 4,18	37,83 2,3–3,1	107,04 6,4	43,45 25,75 1,53	23,0(?) 2,3–3,1	– –	26,33 2,3–3,1
(XI)	 (XXIIa)	95	110–115	^{13}C 247,59 ^{1}H –	61,69 4,21	53,39 3,62	104,41 6,0	43,02 25,20 1,43	34,09 –	32,97 –	42,40 –
(XIX)		–	—	^{1}H –	4,01	2,6–2,9	6,1	1,54	–	0,9	–

*PMR multiplicities and intensities are consistent with the structures.

†Only the PMR parameters are quoted for salt (XXII), since it could not be isolated in the pure state from the mixture with 1-methylcyclohexene oligomers.

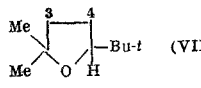
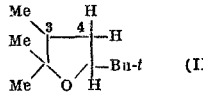
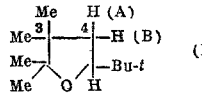
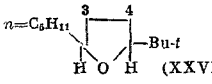
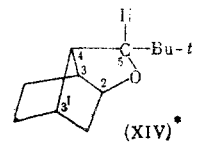
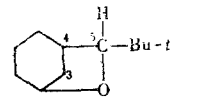
relative to the α-carbon signal of the corresponding tetrahydrofuran derivative is about 30-40 ppm [for (III) and (VIII) $\Delta\delta$ =40 ppm]. These paramagnetic shifts imply partial localization of the positive charge on both 5-C and 2-C, which supports the cyclic structure of the synthetic salts.

We verified the structures of (III), (VI), and VIII) from their reactions with nucleophiles. The most unequivocal evidence comes from their reactions with hydride-ion donors ($NaBH_4$, Et_3SiH, or n-Bu_4NBH_4), which form THF derivatives (VIII), (IX), and (X), respectively, which we characterized by elemental analysis, and PMR (Table 2) and mass spectra.

Acylation of norbornene (XI) (Scheme 2) with (II) [under the conditions of the reaction with (I)] forms carboxonium salt (XIIa), whose structure we deduced from its NMR parameters (Table 1) and verified by the formation of products (XIIIa) and (XIV) on treatment of (XIIa) with water or $NaBH_4$, respectively.

We did not attempt to isolate carboxonium salt (XIIb) from the reaction of (XI) with CH_3COBF_4. However, the products derived from treatment of the reaction complex with water or absolute CH_3OH [preparation of

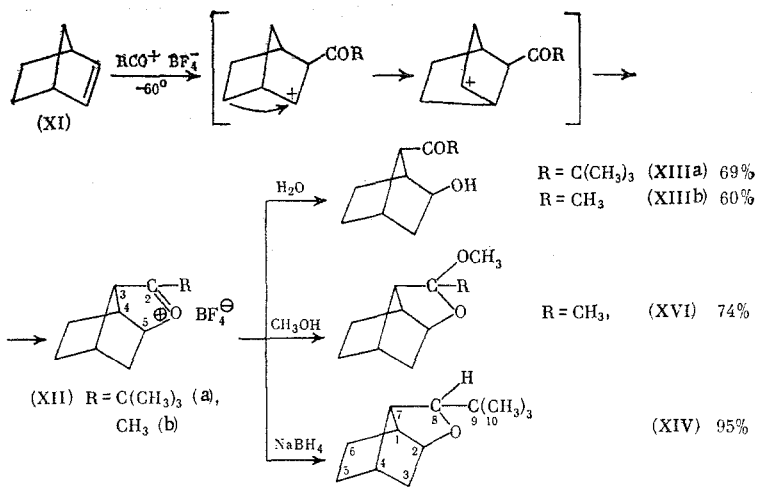
TABLE 2

Compound	bp, °C (p, mm Hg)	Yield, %	PMR parameters, δ, ppm, J, Hz							Empirical formula	Found/Calculated, %	
			ring hydrogen at				hydrogen of the substituent at					
			2-C	3-C	4-C	5-C	2-C	3-C	5-C [C(CH₃)₃]		C	H
 (VIII)	~74—75 (60mm)	95,5	—		1,4—2,02 m (1H)	3,97 m (1H)	1,12 s (6H)	—	0,8 s (9H)	$C_{10}H_{20}O$	76,50 / 76,86	12,86 / 12,90
 (IX)	78—80 (50mm)	85	—		1,3—2,2 m (3H)	3,55 dd (1H) $J = 10,5$ and 5	0,93 s (3H) 1,18 s (3H)	0,94 d (3H) $J = 6,5$	0,86 s (9H)	$C_{11}H_{22}O$	77,54 / 77,65	13,05 / 12,93
 (X)	186—187	86	—	—	1,45 and 1,72 (2H, AB-portion of ABX system) $J = 12$	3,69 dd (1H$_X$) $J_{AX} = 7,5$ $J_{BX} = 9,5$	0,94 s (3H) 1,05 s (3H)	1,00 s (3H) 1,10 s (3H)	0,85 s (9H)	$C_{12}H_{24}O$	78,11 / 78,19	12,92 / 13,13
 (XXVI)	45—50 (2mm)	83	3,6 m (1H)	1,01—2,0 m (4H ring + 8H subst.)		3,42 m(1H)†	—		0,78 s (9H) + m (3H)	$C_{13}H_{25}O$	78,58 / 78,32	13,05 / 13,65
 (XIV)*	75—76 (2mm)	75	3,87 m (1H)	2,08—2,48 (2H at 3-C and 3′-C)	2,0 m (1H)	3,65 d (1H)	1,18—1,70 (ring CH_2)			$C_{12}H_{20}O$	80,02 / 79,94	11,10 / 11,18
	61—65 (2mm)	78	4,17 m (1H)	—	—	3,4 d (1H)†	—	—	0,98 s (9H)	$C_{11}H_{20}O$	77,94 / 78,51	12,01 / 11,98 [7]

*Tentative numbering by analogy with that conventional for (VIII)-(X).
†Signal not given by the 5-d derivative (XXVI).

(XIIIb) or (XVI), respectively] imply that this salt is formed in solution. We verified the structure and stereochemistry of hydroxy ketone (XIIIb) by reduction to the known 2,7-syn-exo-norbornanediol [7, 8]. Since all products derived from acylation of (XI) have the acyl moiety at 7-C, the reaction pathway must obviously involve Wagner — Meerwein rearrangement (Scheme 2)

Scheme 2*



We also found conditions under which carboxonium salts can be prepared from those alkenes whose low-temperature acylation (between —50 and —30°C) gives β, γ-unsaturated ketones [1]. We found that at 0°C the reaction of cyclohexene (XVII), 1-octene (XVIII) (Schemes 3 and 4), or 1-methylcyclohexene (XIX) with (II) forms

* See footnote to Scheme 1.

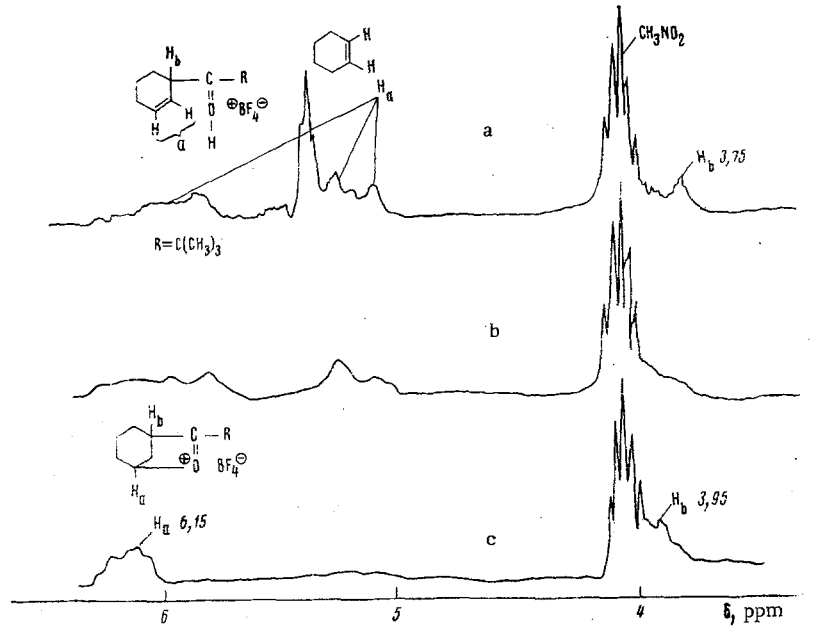
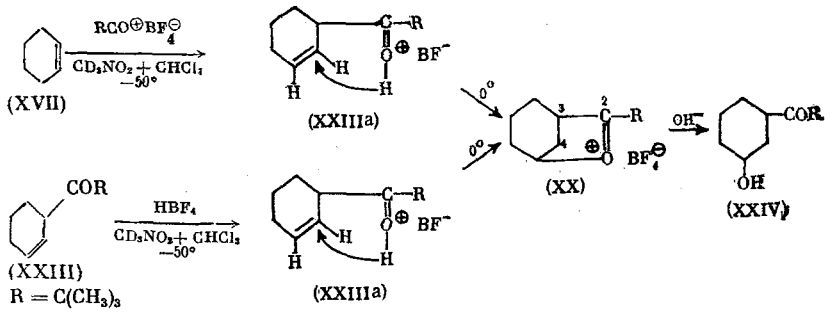


Fig. 1. PMR spectra of the reaction mixture: a) 5 min after mixing of the reactants at −50°C; b) after a further 20 min at −30°C; c) after warming to 0°C and standing for 15 min.

(XX) and (XXI) in good yield; their spectral parameters resemble those of the salts already described (Table 2). We also verified their structures from the products derived by treatment of the salts with nucleophiles such as water or hydride-ion donors.

Since a reaction such as that of (XVII) with (II) can give either β, γ-unsaturated ketone (XXIII) (at −50°C [1]) or salt (XX) (at 0°C), the latter may well originate from the secondary protonation of (XXIII):

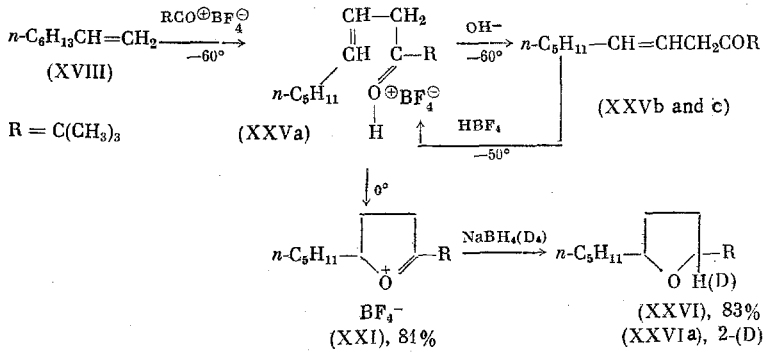
Scheme 3



A study of the acylation of (XVII) in the PMR spectrometer tube (Fig. 1) revealed that ketone (XXIII) is formed first at −50°C [as the protonated species (XXIIIa)] (Fig. 1, spectrum a); shortly after it becomes almost the only detectable product [spectrum b is identical to the spectrum of a solution of (XXIII) containing an equivalent quantity of HBF_4*]. Subsequent increase in temperature to 0°C causes the disappearance of the signals of (XXIIIa) and the appearance of the characteristic signals of salt (XX). This process terminates after about 15 min (Fig. 1, spectrum c): standard workup with aqueous $NaHCO_3$ results in the quantitative formation of hydroxy ketone (XXIV), which we identified by comparison with a sample synthesized earlier [7]. These results suggest that Scheme 3 realistically represents the sequence of steps involved in the reaction of (XVII) with (II). Our investigation of the acylation of (XVIII) in the PMR spectrometer tube also clearly revealed the reaction sequence involved in the preparation of salt (XXI):

* Conversion of (XXIII) to the protonated species (XXIIIa) causes a significant paramagnetic shift of the α proton (0.21 ppm) and of the olefinic protons (Δδ for the center of the multiplet is 0.22 ppm).

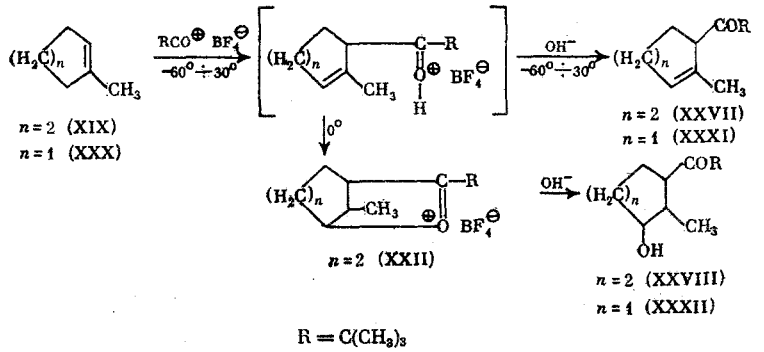
Scheme 4



We were unable to detect such distinct changes in the reaction of 1-methylcyclohexene (XIX), since the PMR spectrum was complicated by the presence of oligomeric products. However, this reaction also exemplifies the dependence of the nature of the products on the reaction conditions: thus β, γ-unsaturated ketone (XXVII) is exclusively formed in the low-temperature reaction of (XIX) with (II) (between −50 and −30°C), whereas salt (XXII) and the corresponding hydroxy ketone (XXVIII) can be obtained if the reaction mixture is warmed to 0°C and then worked up with aqueous $NaHCO_3$.

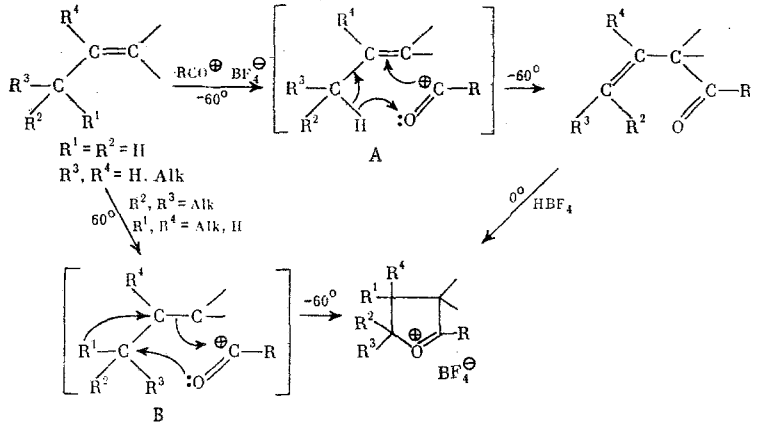
The reaction of 1-methylcyclopentene (XXX) with (II) give equivalent results:

Scheme 5



Our results in their entirety suggest a general scheme for the mechanism of acylation of alkenes by acylium salts (Scheme 6)

Scheme 6



In this scheme we assume that the reaction of alkenes with no branching at the allylic carbon is a concerted process involving the six-membered transition state A, which is also responsible for the formation of β, γ- rather than the more stable α, β-unsaturated ketones [9]. The preferred reaction pathway for alkenes with branching at the allylic carbon is a 1, 2-shift (or skeletal rearrangement) via transition state B, the driving

force for which is reorganization to the stable five-membered cyclic salt system. The β, γ-unsaturated ketones are quite easily converted to the carboxonium salts provided that one of the 2-C substituents is alkyl. We were unable to find conditions for the acylation of cis-trans-2-butenes ($R^1 = R^2 = R^3 = H$) that would give the carboxonium salt, and the reaction at higher temperatures forms conjugate addition products [10].

Thus, as a result of this and earlier work [1, 7], we have elucidated the major patterns in the acylation of alkenes by acylium salts and have demonstrated that this method obviates a whole series of complications accompanying the use of the classical Kondakov — Krapiwin — Darzens acylation of alkenes [11]. Indeed, since this reaction requires rather harsh conditions and involves the presence of reactive nucleophiles in the mixture, its general result is the formation of product mixtures (unsaturated ketones and β-halo, and β-acyloxy ketones) and only in a limited number of cases can it provide a convenient preparative route to α, β-unsaturated ketones. The conditions that we have developed make it possible to carry out the reaction quite unambiguously, thereby preparing either α, β-unsaturated ketones or cyclic carboxonium salts, which in turn can be converted into functionalized ketones or THF derivatives. This route to carboxonium salts seems more general and convenient than those described in the literature, such as protonation of γ, δ-unsaturated ketones in strongly acidic medium [3, 9], dehalogenation of α-bromo ketones [12], solvolysis of γ-substituted ketones [13], and protonation of α,β-unsaturated ketones [2, 4].

EXPERIMENTAL

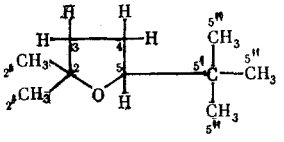
Control of the reactant purity, analysis of reaction mixtures, and in several cases preparative isolation and purification of the products were carried out by GLC on LKhM-5 chromatographic systems: 2-2.5 m × 4-6 mm columns (8-9 mm for preparative separations); detection by katharometer or flame-ionization detector; stationary phases: Apiezon M, neopentyl glycol succinate, SE-30, SKTFT-50 X silicone elastomer (3-10%), on Chromosorb W.

The IR spectra were recorded on a UR-20 instrument in CCl_4; the PMR spectra, on a DA-60-IL instrument; the ^{13}C NMR spectra, on a WP-60 at 15 MHz. Signals were assigned from their multiplicity under off-resonance conditions and from literature data on the dependence of chemical shifts on the degree of branching at neighboring carbon atoms. Chemical shifts were recorded on the δ scale, relative to hexamethyldisiloxane (HMDS) or tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on MKh-5 and CH-6 instruments.

The water content of all solvents did not exceed 0.01%. Acylation of olefins was carried out in an atmosphere of argon.

Acylation of Isopropylethylene. a) Carboxonium Salt (III). After addition of BF_3 (672 ml, 30 mmole) by syringe to a solution of $(CH_3)_3CCOF$ (3.42 g, 33.0 mmole) in absolute CH_2Cl_2 (100 ml) at −50°C, a light precipitate of pivaloyl tetrafluoroborate immediately began to form. After 30 min stirring at −50°C a cold solution of (I) (2.52 g, 30 mmole) in absolute CH_2Cl_2 (10 ml) was added dropwise. The mixture was stirred at −50°C for 10 min, whereupon the solvent was removed under vacuum between 0 and −10°C. The crystalline product (6.7 g) was purified from CH_2Cl_2 solution by reprecipitation with ether and dried under vacuum to give (III) (5.75 g, 74.5%), mp 164-168°C (decomposition) (Table 1). Found: B 4.60; F 31.10%. $C_9H_{19}OBF_4$. Calculated: B 4.30; F 29.60%.

b) 2,2-Dimethyl-5-tert-butyltetrahydrofuran (VIII). To a stirred solution of salt (III) (2.98 g, 11.2 mmole) in absolute CH_2Cl_2 (50 ml) at −50°C was added $NaBH_4$ (2 g) in absolute CH_2Cl_2 (10 ml); the temperature was gradually raised to 20°C (45 min). The reaction mixture was then cautiously poured into a mixture of ether and aqueous $NaHCO_3$. After the usual treatment and removal of the solvent the residue was distilled to give (VIII) (1.67 g, 95.5%)

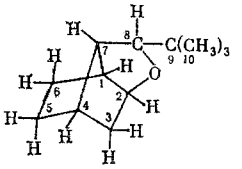


(Table 2). IR spectrum: 1076 cm^{-1} (C — O — C); it lacked the OH, C=C, and C=O absorption bands. ^{13}C NMR spectrum (CH_2Cl_2, δ, ppm from TMS): 86.60 (5-C), 79.95 (2-C), 38.88 (3-C), 26.95 (4-C), 33.42 (5-C), 28.74 and 27.92 (2'-C), 25.89 (3.5"-C). Mass spectrum: 99 $(M - C_4H_9)^+$, 81 $(M - C_4H_9 - H_2O)^+$. Compounds (VI), (VII), and (XIIa) were prepared similarly (Table 1). Because of their hygroscopy, satisfactory elemental analyses could be obtained only for (VII). Found: B 5.32; F 28.22%. $C_{12}H_{23}BF_4$. Calculated: B 4.09; F 28.10%.

2,2,3-Trimethyl-5-tert-butyltetrahydrofuran (IX). To a solution of salt (VI) (0.51 g, 20 mmole) in absolute CH_2Cl_2 (50 ml) was slowly added $(n\text{-}C_4H_9)_4NBH_4$ (0.51 g, 20 mmole) in CH_2Cl_2. The reaction mixture was stirred for 30 min and then washed with 10% NaOH solution and water. After drying over Na_2SO_4 the solvent was evaporated and pentane was added to the residue. The resulting precipitate of $(n\text{-}C_4H_9)_4NBF_4$ was filtered off and pentane was evaporated to give (IX) (0.29 g, 85%) (Table 2).

2,2,3,3-Tetramethyl-5-tert-butyltetrahydrofuran (X) was prepared from salt (VII) under the same conditions as (IX) (Table 2). Mass spectrum: 169 $(M - CH_3)^+$, 127 $(M - C_4H_9)^+$, 109 $(M - C_4H_9 - H_2O)^+$, 57 $(C_4H_9)^+$.

8-tert-Butyl-3-oxabicyclo[2, 2, 1, 2] nonane (XIV) was prepared from salt (XIIa) by the procedure for the preparation of (VIII) (Table 2). Compound (XIV) was a mixture of two isomers (GLC, SE-30, 160°C) in the ratio 1 : 9. Chromato-mass spectrum: (XIVa) 180 (M^+); (XIVb) 180 (M^+). ^{13}C NMR spectrum (δ, ppm, from TMS): 87.94 (8-C), 80.50 (2-C), 50.26 and 48.93 (1-C and 7-C), 35.51 and 35.27 (3-C and 4-C), 33.96 and 33.72 (5-C and 6-C), 27.23 (10-C), 18.27 (9-C).



syn-exo-2-Hydroxy-7-pivaloylnorbornane (XIIIa). Salt (XIIa) (0.73 g, 2.74 mmole) in ether — CH_2Cl_2 was shaken with $NaHCO_3$ solution; the organic layer was washed with water and dried over Na_2SO_4. Removal of the solvent gave hydroxy ketone (XIIIa) (0.37 g, 69%), mp 68-69°C. Found: C 73.52; H 10.39%. $C_{12}H_{20}O_2$. Calculated: C 73.40; H 10.27%. Mass spectrum: 196 (M^+). PMR spectrum: 3.97 br. s (1 H, OH), 3.45 br. t (1 H, CH—OH), 2.75 s (1 H, CH—CO), 2.4 s (1 H, C(OH)—CH—C—CO), 2.18 s (1 H, C—H); 1.02 s [9 H, $C(CH_3)_3$].

Acylation of Norbornene by Acetyl Tetraflurorborate. a) syn-exo-2-Hydroxy-7-acetylnorbornane (XIIIb). To a stirred solution of $AgBF_4$ (4.06 g, 21 mmole) in absolute CH_3NO_2 (10 ml) at —25°C was added a solution of norbornene (1.88 g, 20 mmole) and AcOCl (1.64 g, 21 mmole) in CH_3NO_2 (5 ml). The reaction mixture was stirred for 2 min and treated with a mixture of ether and saturated $NaHCO_3$ solution. The usual treatment and removal of the solvent gave a liquid (3.0 g), which crystallized on treatment with hexane to give (XIIIb) (1.83 g, 60%), mp 64-65.5°C (from hexane). IR spectrum (ν, cm^{-1}): 1700 (C=O), 3620 (free OH), 3470 (intramolecular H bond). PMR spectrum: 2.33 s (3H, CH_3CO), 3.83 m (1 H, CH—OH), 2.63 br. s (1 H; disappeared on shaking with D_2O). Found: C 69.76; H 9.29%. $C_9H_{14}O_2$. Calculated: C 70.10; H 9.15%.

Acetylation of (XIIIb) with AcOCl in pyridine gave in ~100% yield syn-exo-2-acetoxy-7-acetylnorbornane (XIIIc), mp 43-43.5 deg C. IR spectrum: 1715 (C=O), 1742 cm^{-1} (COOR). Found: C 67.65; H 8.29%. $C_{11}H_{16}O_3$. Calculated: C 67.32; H 8.22%.

Oxidation of (XIIIb) with CrO_3 in pyridine gave in ~100% yield 7-acetyl-2-norbornanone, mp 46-46.5°C (from hexane). IR spectrum: 1690 (C=O), 1745 cm^{-1} ($COOCH_3$). Found: C 71.30; 71.14; H 8.06; 7.86%. $C_9H_{12}O_2$. Calculated: C 71.02; H 7.95%.

Oxidation of ketoacetate (XIIIc) (0.4 g, 2.18 mmole) with trifluoroperacetic acid in CH_2Cl_2 and saponification with alkali gave a compound (0.30 g, 88%) with mp 176.5-178°C, identified as 2, 7-syn-exo-norbornanediol by direct comparison with an authentic sample, synthesized by the procedure of [8] (GLC on two stationary phases; mixed melting point; identity of IR spectra).

b) 8-Methoxy-8-methyl-9-oxatricyclo[2.2.1.$2^{7,3}$] nonane (XVI). Acylation of (XI) was carried out under the conditions of the previous reaction, whereupon the reaction mixture was treated with a cold (—70°C) solution of absolute Et_3N (3 g) in absolute CH_3OH (20 ml), extracted with hexane, and separated from the precipitated salts. The residue after removal of hexane was distilled under vacuum to give (XVI) (2.9 g, 74%), bp 30-35°C (2 mm), n_D^{16} 1.4750. Found: C 71.13; H 9.57; CH_3O 18.55%. $C_{10}H_{16}O_2$. Calculated: C 71.39; H 9.59; CH_3O, 18.44%. The IR spectrum lacked the C=O, OH, and C=C absorption bands. PMR spectrum 3.9 (1 H, CH—OCH_3), 3.12 (3 H, CH_3O), 1.2 (3H, CH_3—C—OH). Standing in air or shaking with dilute acid solution quantitatively converted into (XVI) was hydroxyketone (XIIIb), mp 64-65°C.

Acylation of Cyclohexene. a) Carboxonium Salt (XX). After addition of BF_3 (204 ml, 9.1 mmole) by syringe to a solution of pivaloyl fluoride (1.16 g, 11.2 mmole) in absolute CH_2Cl_2 (50 ml) at —50°C, a light precipitate of pivaloyl tetrafluoroborate immediately began to form. After 30 min stirring at —50°C a cold solution of cyclohexene (0.6 g, 7.5 mmole) in absolute CH_2Cl_2 (5 ml) was added dropwise. After 5 min stirring at —50°C the temperature was rapidly raised to 0°C; the mixture was stirred for a further 5 min and then cooled to —10°C. The solvent was removed (between —10 and 0°C, under vacuum) and the residue crystallized.

The usual treatment gave (XX) (1.6 g, 85%), mp 188-191°C (decomposition) (Table 1). Found: B 4.60; F 30.70. $C_{11}H_{19}OBF_4$. Calculated: B 4.34; F 29.90%.

b) 3-Hydroxy-1-pivaloylcyclohexane (XXIV). Hydroxyketone (XXIV) was prepared from (XX) under the conditions of the preparation of (XIIIa), yield 72%, mp 88-89°C, identical to a sample synthesized earlier [8].

Acylation of 1-Methylcyclohexene (XIX). a) 2-Methyl-3-pivaloylcyclohexene (XXVII). To a solution of $AgBF_4$ (1.62 g, 8.33 mmole) in absolute CH_2Cl_2 and $C_2H_4Cl_2$ (1:1) at −60°C was added a cold solution of (XIX) (0.43 g, 5.0 mmole) and pivaloyl chloride (0.92 g, 7.5 mmole) in CH_2Cl_2 (5 ml). The mixture was kept at this temperature for 30 min and treated in the usual way to give (XXVII) (0.58 g, 66%), bp 65-66°C (1 mm), n_D^{20} 1.4720. IR spectrum: 1710 (C=O), 1670, 3040 cm^{-1} (C=CH). PMR spectrum: 5.5 m (1 H, C=CH), 3.5 m (1 H, CH−C=O), 1.41 s (3 H, CH_3C=C), 1.11 s (9 H, C $(CH_3)_3$). Mass spectrum: 180 (M^+), 165 $(M - CH_3)^+$, 123 $(M - C_4H_9)^+$, 95 $(C_7H_{11}^+)$, 95 $(C_7H_{11}^+)$, 85 $(COC_4H_9^+)$, 57 $(C_4H_9^+)$. Found: C 79.95; H 10.92%. $C_{12}H_{22}O$. Calculated: C 79.91; H 11.11%.

b) 2-Methyl-3-hydroxypivaloylcyclohexane (XXVIII). The acylation of (XIX) was carried out like that described above. After mixing of the reactants, the mixture was warmed to 0°C and left at this temperature for 15 min, whereupon it was cooled to −25°C and a mixture of ether and aqueous $NaHCO_3$ was added. After removal of the solvent the residue contained (GLC) mainly (XXVIII), which was isolated in ~50% yield by TLC [silica gel, ether − benzene − hexane (1:1:1.5), R_f 0.22], mp 57.5-58°C, identical to a sample synthesized earlier [14, 15].

c) Carboxonium Salt (XXII) was prepared from (XIX) under the conditions of the preparation of salt (XX). Crystalline (XXII) (1.65 g) could not be separated from the contaminating oligomeric product (PMR parameters in Table 1). Treatment of (XXII) with water gave (XXVIII) in ~40% yield.

Acylation of 1-Methylcyclopentene (XXX). a) 2-Methyl-3-pivaloylcyclopentene (XXXI). The reaction under the conditions of the preparation of ketone (XXVII) from (XIX) gave a mixture of products. The major component was ketone (XXXI), yield ~30% [preparative TLC, silica gel, ether − hexane (1:1), R_f 0.7], bp 81-82°C (9 mm). IR spectrum: 1703 (C=O), 1655, 3048 cm^{-1} (CH=C). PMR spectrum: 5.4-5.55 m (1 H, C=CH), 3.7-4.05 m (4 H, ring $-CH_2-$). Mass spectrum: 166 (M^+), 109 $(M - C_4H_9)^+$, 81 $(C_5H_9^+)$, 85 $(COC_4H_3^+)$, 57 $(C_4H_9^+)$.

b) 2-Methyl-3-hydroxypivaloylcyclopentane (XXXII) was prepared under the conditions of the synthesis of hydroxy ketone (XXVIII) from (XIX). The yield was 28%, purification by TLC [silica gel, ether − hexane (1:1), R_f 0.25], mp 40-41°C; it was identified by comparison with a sample synthesized earlier [16].

Acylation of 1-Octene. a) 2, 2-Dimethyl-5-undecen-3-one (XXV). The reaction was carried out under the conditions of the preparation of (XXVII) but in SO_2 solution. 1-Octene (0.55 g, 4.9 mmole) gave a substance (0.77 g), which contained (XXV) (60-70%, GLC). Distillation gave the pure ketone, bp 70-80°C (2 mm), n_D^{20} 1.4425. IR spectrum: 1710 (C=O), 3030, 1630, 980, 1310 cm^{-1} (CH=CH). Mass spectrum: 196 (M^+), 139 $(M - C_4H_9)^+$, 85 $[(CH_3)_3CCO^+]$, 57 $(C_4H_9^+)$.

Ketone (XXV) was a mixture of cis and trans isomers (XXVb) and (XXVc) in the ratio 18:82 (capillary chromatography l =15 m, polypropylene glycol sebacate 100°C). This mixture (300 mg) was separated by TLC on silica gel impregnated with $AgNO_3$ to give (XXVb) (70-80 mg) (R_f 0.29) and (XXVc) (80-100 mg) (R_f 0.55). PMR spectrum of (XXVb): 1.02 s (9 H, $(CH_3)_3C$), 1.25 m (6 H, $-CH_2$), 1.83 (2 H, $\underline{CH_2}CH$=), 3.08 comp. t (2H, =$CHCH_2C$=O), 5.35 (2 H, CH=CH, J =11 Hz cis isomer). PMR spectrum of (XXVc): the same type of spectrum as for (XXVb); for the signal 5.35 (CH=CH) J =15.5 Hz (trans isomer).

b) Carboxonium Salt (XXI). Compound (XVIII) under the conditions of the preparation of salt (XX) gave salt (XXI), as an oily substance (Table 1).

c) 2-tert-Butyl-5-n-pentyltetrahydrofuran-2-d (XXVIa). The preparation of (XXVIa) from (XXI) was carried out like the preparation of (VIII) using $NaBD_4$ (Table 2). IR spectrum: 1080 cm^{-1} (C−O−C); it lacked the C=O, OH, and C=C absorption bands. Mass spectrum: 142 $(M - C_4H_9)^+$, 124 $(M - C_4H_9 - H_2O)^+$. The PMR spectrum of the hydrogen analog [prepared from (XXI) and $NaBH_4$] contained a signal 3.42 m (1 H, OCHC-$(CH_3)_3$). Mass spectrum: 141 $(M - C_4H_9)^+$, 123 $(M - C_4H_9 - H_2O)^+$.

Acylation in the PMR Spectrometer Tube. To a tube containing a solution of $(CH_3)_3CCOF$ (0.15 g, 1.44 mmole) in CD_3NO_2 (0.5 ml) was added BF_3 (23 ml, 1.02 mmole). The solution was cooled to −50°C and the olefin (1 mmole) was added, whereupon the PMR spectrum was recorded. Our results for the acylation of cyclohexene are shown in Fig. 1. A comparison was provided by the protonation under the same conditions of

β, γ-unsaturated ketones by HBF_4 (1.5 equiv., prepared from anhydrous HF and BF_3 in CD_3NO_2). PMR spectra: (XXIII) 5.60, 5.45, 5.15, and 4.97 (CH = CH), 3.47 (CH − CO); (XXIIIa) 5.90, 5.74, 5.25, and 5.07 (CH = CH), 3.75 (CH − C^+OH).

CONCLUSIONS

Acylation of alkenes with branching at the allylic carbon provides a preparative route to cyclic carboxonium salts. Such salts can be prepared by protonation of β, γ-unsaturated ketones — the products of acylation of unbranched alkenes. We have examined the mechanism of acylation of acylium salts.

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