Facile Synthesis of Cyclic Carboxonium Salts by Acylation of Alkenes[1]

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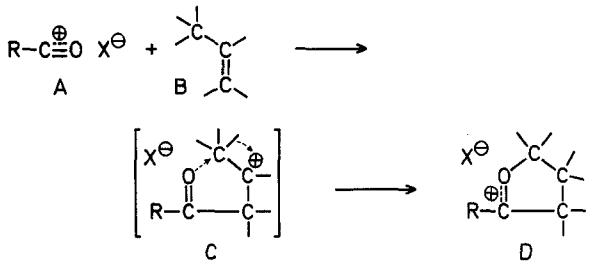
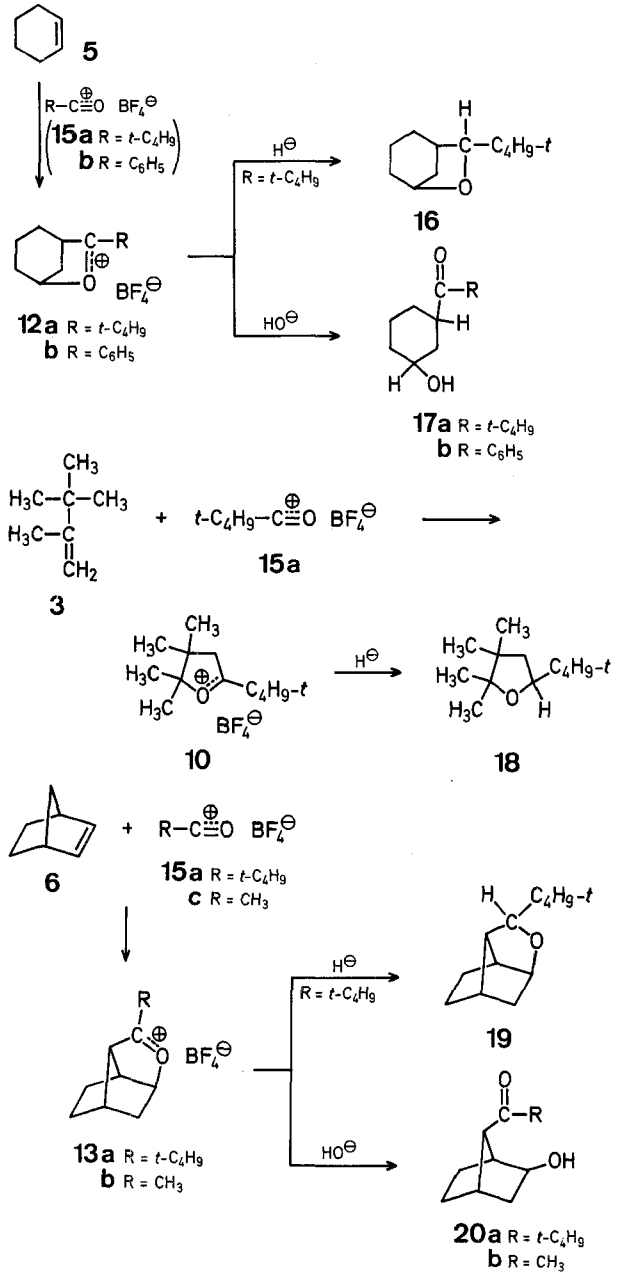
Stable cyclic carboxonium salts (D) can be easily prepared in high yields by the acylation of alkenes (B) with acylium salts (A) according to the following general scheme.



Representative examples of this reaction and synthetic applications are formulated below (see also the Table).



The reaction is carried out in dichloromethane (sulfur dioxide or nitromethane are also suitable solvents) by the addition of the alkene to a slight excess (1.1–1.5 equiv) of the acylium salt. For alkenes such as **1–3**, carboxonium salt formation is complete at −50° within several min (as shown by ^{1}H-N.M.R. of the reaction mixture). For unbranched alkenes (**4, 5**), a reaction temperature of 0° is necessary to ensure complete reaction[2]. The carboxonium salts thus prepared in solution can be directly used in reactions with various nucleophiles. They can also be isolated and purified by removal of volatile material in vacuo and thorough washing with absolute ether.

The structures of the carboxonium salts[4] shown in the Table are supported by ^{1}H-N.M.R.-[3] and ^{13}C-N.M.R. data as well as by conversion into the corresponding tetrahydrofuran derivatives in high yield upon treatment with suitable hydride donors (preferentially tetrabutylammonium borohydride). The formation of the hydroxyketones **17a** and **20a**[5] upon quenching of the carboxonium salts **12a** and **13a**, respectively, with water provides an additional proof of the oxygen-bridged cyclic structure of these salts.

Acylium salts other than **15a** can also be used for the preparation of carboxonium salts. Thus, the formation of carboxonium salts (**12b** and **13b**) was proven by the isolation of the hydroxyketones **17b** and **20b** upon quenching of the reaction mixtures with water[6].

The results obtained allow to regard the present procedure as a fairly general method for the synthesis of substituted five-membered cyclic carboxonium salts. Previously reported methods are:

(a) the protonation of α,β-[7] or γ,δ-unsaturated[8] ketones;
(b) the solvolysis of δ-haloketones[9];
(c) the dehalogenation of δ-haloketones[10];
(d) the acylation of alkanes in superacidic media[11].

All these methods are less versatile and more tedious than the method reported here.

Acylation of Cyclohexene (5):

7-t-Butyl-(6,7)$^{\oplus}$-6-oxabicyclo[3.2.1]octanylium Tetrafluoroborate (**12a**): A solution of cyclohexene (0.6 g, 7.5 mmol) in dichloromethane (5 ml) is added to a stirred slurry of pivaloyl tetrafluoroborate (**15a**; 10 mmol; prepared from pivaloyl fluoride and boron trifluoride) in dichloromethane (50 ml) at −50°. Stirring is continued for 30 min at −50° and for 5 min at 0°. The solvent is removed in vacuo and the crystalline residue washed with dry ether (3 ×); yield: 1.6 g (85%); m.p. 188–191° (dec).

$C_{11}H_{19}BF_4O$	calc.	B 4.34	F 29.90
(254.1)	found	4.70	30.80

t-Butyl 3-Hydroxycyclohexyl Ketone (**17a**): A solution of the carboxonium salt **12a** (0.5 g) in dichloromethane/ether is shaken with aqueous sodium hydrogen carbonate for several minutes. The organic layer is washed with water, dried with sodium sulfate, and the solvent removed in vacuo; yield: 0,33 g (90%); m.p. 88–89° (identical with the product reported in Ref.[5]).

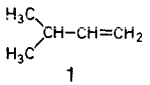
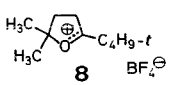
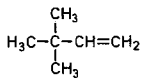
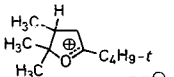
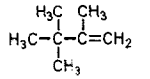
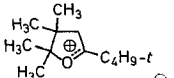
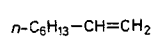
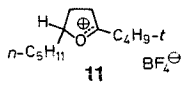
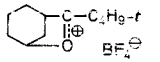
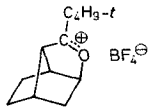
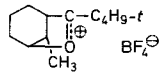
Acylation of 3,3-Dimethyl-1-butene (3):

2-t-Butyl-4,4,5,5-tetramethyl-(1,2)$^{\oplus}$-tetrahydrofuranium Tetrafluoroborate (**10**): A solution of 3,3-dimethyl-1-butene (**3**; 0.74 g, 7.5 mmol) in dichloromethane (5 ml) is added to a stirred slurry of pivaloyl tetrafluoroborate (**15a**; 10 mmol) in dichloromethane (50 ml) at −50°. The solvent is removed in vacuo at −10° to −15°. The residue is washed twice with dry ether, and dried in vacuo; yield: 1.42 g (70%); m.p. 200–202° (dec).

$C_{12}H_{23}BF_4O$	calc.	B 4.09	F 28.10
(270.1)	found	5.37	28.46

2-t-Butyl-4,4,5,5-tetramethyltetrahydrofuran (**18**): A solution of carboxonium salt **10** (0.55 g, 20 mmol) and tetrabutylammonium borohydride (0.52 g, 2.0 mmol) in dichloromethane (10 ml) is kept at 20° for 30 min. Then, 10% aqueous potassium hydroxide (10 ml) is added, the mixture washed with water, and the organic phase dried with sodium sulfate. The solvent is distilled off and the residue is thoroughly extracted with pentane. The pentane is removed from the extract and the residue distilled in vacuo; yield: 0.32 g (86%); b.p. 186–187°/12 torr (identical with the product described in Ref.[7]).

Table. Addition of Pivalolyl Tetrafluoroborate to Alkenes and Reduction of the Resultant Carboxonium Salts to Cyclic Ethers

Alkenes	Carboxonium Salts	Yield[a] [%]	m.p. (dec)	^{1}H- and ^{13}C-N.M.R. (CH_2Cl_2 or $CHCl_3$/TMS)[b] δ [ppm]									Yield of tetrahydrofuran derivative[c] [%]
				Carboxonium ring atoms				Substituents at					
					C-2	C-3	C-4	C-5	C-2	[$C(CH_3)_3$]	C-3	C-4	C-5	
 1	 8 $BF_4^\ominus$	75	164–168°	^{13}C	245.90	42.45	31.58	121.26	42.20	26.07	—	—	26.23	95
				^{1}H	—	3.98	2.42			1.37		—	1.75	
 2	 9 $BF_4^\ominus$	86	168–172°	^{13}C	245.93	48.31	38.04	121.67	42.69	26.22	—	12.69	20.84 26.46	86
				^{1}H	—	3.92	2.85	—		1.44	—	1.15	1.83 1.59	
 3	 10 $BF_4^\ominus$	70	200–202°	^{13}C	245.50	53.86	42.02	123.20	42.26	24.19	—	20.49	20.92	86
				^{1}H	—	3.65	—	—		1.21	—	0.95	1.5	
 4	 11 $BF_4^\ominus$	81	semi-solid	^{13}C	248.21	42.16	34.09	111.24	42.84	26.53	—	—	31.17	83
				^{1}H	—	3.9	1.8–3.0	6.05		1.45	—		1.8–3.0	
 5	 12a $BF_4^\ominus$	85	188–191°	^{13}C	249.98	50.53	37.83	107.04	43.45	25.75	23.0	—	26.33	85
				^{1}H	—	4.13	2.3–3.1	6.4		1.53	2.3–3.1	—	2.3–3.1	
 6	 13a $BF_4^\ominus$	95	110–115°	^{13}C	247.59	61.69	53.30	104.41	43.02	25.20	34.09	32.97	42.40	83
				^{1}H	—	4.21	3.62	6.0		1.43	—	—	—	
 7	 14 $BF_4^\ominus$	[d]	—	^{1}H	—	4.01	2.6–2.9	6.1		1.54	—	0.9	—	50–55

[a] All yields refer to purified products.

[b] The N.M.R. spectra were recorded on Varian DA-60 IL (^{1}H-) and CET-20 (^{13}C-) spectrometers. The intensities and multiplicities of the proton signals correspond to the presence of the shown structural fragments. The assignments in the ^{13}C-N.M.R. spectra are based on the off-resonance decoupling data in conjunction with to the known changes of ^{13}C-shielding caused by α- and/or β-substitution[14].

[c] The tetrahydrofuran derivatives were prepared by reaction of the carboxonium salts with hydride donors such as tetrabutylammonium or sodium borohydride.

[d] We were unable to purify this salts from oligomeric contaminants, thus no yield and ^{13}C-N.M.R. data are given.

Acylation of Norbornene (6):

2-t-Butyl-(2,3)$^{\oplus}$-3-oxatricyclo[4.3.0.0^{4,9}]nonanylium Tetrafluoroborate (**13a**): A solution of norbornene (**6**; 0.71 g, 7.5 mmol) in dichloromethane (5 ml) is added to a stirred slurry of pivaloyl tetrafluoroborate (**15a**; 10 mmol) in dichloromethane (50 ml) at −50°. The solvent is removed in vacuo at −10° to −15°. The residue is washed twice with dry ether, and dried in vacuo; yield: 1.9 g (95%); colorless hygroscopic crystals, m.p. 110–115°.

7-(2,2-Dimethyl-1-oxopropyl)-2-hydroxybicyclo[2.2.1]heptane (**20a**): A solution of carboxonium salt **13a** (0.73 g, 2.74 mmol) in dichloromethane/ether is shaken with aqueous sodium hydrogen carbonate for several minutes. The organic layer is washed with water, dried with sodium sulfate, and the solvent removed in vacuo; yield: 0.37 g (69%); m.p. 68–69°.

$C_{12}H_{20}O_2$	calc.	C 73.40	H 10.27
(196.3)	found	73.52	10.39

^{1}H-N.M.R. ($CDCl_3$): δ = 3.45 (broad t, 1H, CH—OH); 2.75 (broad s, 1H, —CH—CO); 1.02 ppm [s, 9H, $C(CH_3)_3$].

2-t-Butyl-3-oxatricyclo[4.3.0.0^{4,9}]nonane (**19**): A suspension of sodium borohydride (2 g) in dichloromethane (10 ml) is added to a stirred solution of carboxonium salt **13a** (3.1 g, 11.6 mmol) in dichloromethane (50 ml) at −50°. The temperature is allowed to rise to +20°. The mixture is then poured into a mixture of aqueous sodium hydrogen carbonate and ether. The organic product is extracted with ether, the extract washed with water and dried, the solvent evaporated, and the residue distilled in vacuo; yield: 1.7 g (83%); b.p. 75–76°/2 torr; n_D^{19}: 1.4800.

$C_{12}H_{20}O$	calc.	C 79.94	H 11.18
(180.3)	found	79.92	11.16

^{1}H-N.M.R. (CCl_4): δ = 3.87 (m, 1H, H-4); 3.65 (d, 1H, H-2); 2.08–2.48 (m, 2H, H-6 and H-9); 2.0 (1H, m, H-1); 1.18–1.70 (m, 6H, $—CH_2—$); 0.85 ppm [s, 9H, $C(CH_3)_3$].

The acylation of **6** with acylium salt **15c** in the manner described above, followed by quenching with aqueous sodium hydrogen carbonate affords *7-acetyl-2-hydroxybicyclo[2.2.1]heptane* (**20b**); yield: 60%; m.p. 64–65°.

$C_9H_{14}O_2$	calc.	C 70.10	H 9.15
(154.2)	found	69.75	9.35

^{1}H-N.M.R. ($CDCl_3$): δ = 3.83 (1H, CH—OH), 2.33 ppm (3H, CO—CH_3).

Acetylation of **20b** with acetyl chloride/pyridine, followed by Baeyer-Villiger oxidation with trifluoroacetoperoxoic acid and subsequent hydrolysis gives *2-exo-7-syn-dihydroxynorbornane* (70%; identical with a sample prepared according to Ref.[13]).

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[1] For previous reports on the acylation of alkenes with acylium salts, see: V. A. Smit, A. V. Semenovskii, O. V. Lubinskaya, V. F. Kucherov, *Doklady Akad. Nauk SSSR* **203**, 604 (1972); *C. A.* **77**, 87955 (1972).

[2] The mechanism of the reaction will be discussed in a forthcoming publication.

[3] The observed pattern of the chemical shifts in the ^{1}H-N.M.R. spectra is very similar to the data reported for some five-membered cyclic carboxonium salts; see, for example, Ref. 7 and 8.

[4] The sensitivity of these salts to moisture makes microanalyses difficult. Satisfactory data were only obtained for **10** and **12a**. The composition of the carboxonium salts was also substantiated by the quantitative isolation of tetrabutylammonium tetrafluoroborate upon reaction with tetrabutylammonium borohydride.

[5] O. V. Lubinskaya et al., *Doklady Akad. Nauk SSSR* **203**, 829 (1972).

[6] See, for example: V. A. Smit et al., *Otkrytia, Izobret. Tovarni Znaki* **48**, 74 (1971); *C. A.* **76**, 323 (1972).

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M. Charpentier-Morize, *Bull. Soc. Chim. Fr.* **1974**, 343.

[11] D. M. Brouwer, A. A. Kiffen, *Recl. Trav. Chim. Pays-Bas* **92**, 689 (1973).

[12] The spectral (I.R., M.S., and ^{1}H-N.M.R.) and analytical data are consistent with the ascribed structure.

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