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Nucleophilic substitution

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$$Cl(CH_2)_4CH \xrightarrow{H_2O} \sqrt{O} + HCl$$

Solvolysis Rates of ω–Chloro Alcohols

ω-Chloro alcohol	Approximate relative rate
Cl(CH ₂) ₂ OH	2000
Cl(CH ₂) ₃ OH	1
Cl(CH ₂) ₄ OH	5700
Cl(CH ₂) ₅ OH	20



Relative Solvolysis Rates of Some ω-Methoxyalkyl *p*-Bromobenzenesulfonates in Acetic Acid

CH ₃ (CH ₂) ₂ OSO ₂ Ar	1.00
CH ₃ O(CH ₂) ₂ OSO ₂ Ar	0.28
CH ₃ O(CH ₂) ₃ OSO ₂ Ar	0.67
CH ₃ O(CH ₂) ₄ OSO ₂ Ar	657
CH ₃ O(CH ₂) ₅ OSO ₂ Ar	123
CH ₃ O(CH ₂) ₆ OSO ₂ Ar	1.16

Relative Rates of Cyclization as a Function of Ring Size

Ring size	Lactonization of ω- bromo carboxylates ^a	ΔH^{\ddagger} (kcal/mol)	ΔS^{\ddagger} (eu)	Cyclization of ω- bromoalkylmalonates ^b
3	8.2×10^{-4}	22.0	-2.5	
4	0.92	17.7	-5.0	0.58
5	108	15.9	-5.5	833
6	1.00	17.2	-4.1	1.00
7	3.7×10^{-3}	17.4	-13.5	8.7×10^{-3}
8	3.8×10^{-5}	21.7	-9.2	1.5×10^{-4}
9	4.3×10^{-5}	20.3	-14.0	1.7×10^{-5}
10	1.3×10^{-4}	17.3	-20.7	1.4×10^{-6}
11	3.3×10^{-4}	16.4	-22.3	2.9×10^{-6}
12	4.1×10^{-4}	17.6	-18.0	4.0×10^{-4}
13	1.2×10^{-3}	15.3	-23.0	7.4×10^{-4}
17				2.9×10^{-3}
18	2.0×10^{-3}	15.2	-21.8	
21				4.3×10^{-3}
23	2.3×10^{-3}	14.5	-22.3	











Extent of Aryl Rearrangement in 2-Phenylethyl Tosylate Solvolysis

	Solvent		
Substituent	80% Ethanol	Acetic acid	Formic acid
NO ₂	0	_	_
CF ₃	0	_	_
Cl	7	_	_
Н	21	38	78
CH ₃	63	71	94
CH ₃ O	93	94	99





Structure and Reactions of Carbocation Intermediates

Structure and Stability of Carbocations

$(CH_3)_3C-CI \longrightarrow (CH_3)_3C^+ + CI^-$

$ROH + H^{+} \longrightarrow R^{+} + H_{2}O$



Values of pK_{R+} for Some Carbocations

Carbocation	pK _R +	Carbocation	pK _R +
A. Triarylmethyl			
Triphenyl	-6.63	4, 4', 4"-Tri(dimethylamino)phenyl	+9.36
4, 4', 4"-Trimethyltriphenyl	-3.56	4, 4', 4"-Trichlorotriphenyl	-7.74
4-Methoxytriphenyl	-3.40	4-Nitrotriphenyl	-9.15
4, 4'-Dimethoxytriphenyl	-1.24	4, 4', 4"-Trinitrotriphenyl	-16.27
4, 4', 4"-Trimethoxytriphenyl	+0.82		
B. Diarylmethyl			
Diphenyl	-13.3	2, 2', 4, 4', 6, 6'-Hexamethyldiphenyl	-6.6
4, 4'-Dimethyldiphenyl	-10.4	4, 4'-Dichlorodiphenyl	-13.96
4, 4'-Dimethoxydiphenyl	-5.71	· · ·	
C. Other Carbocations			
Benzyl ^b	≤ -20	Triphenylcyclopropenyl ^e	+3.1
t-Butyl ^c	-15.5	2,4,6-trimethylbenzyl	-17.4
2-Phenyl-2-propylb	-12.3	Trimethylcyclopropenyl ^f	+7.8
Tropylium (Cycloheptatrienyl)	+4.7	Tricyclopropylcyclopropenyl ^g	+9.7
Tricyclopropylmethyld	-2.3		-



bisected conformation



perpendicular conformation



bisected conformation



perpendicular conformation



R⁺ + H⁻ → R-H

 $R-H \longrightarrow R^+ + H^-$

 $R' + H' \longrightarrow R-H$

∆**G**hom

∆G_HΓ

 $R^{+} + H^{-} \rightarrow R^{+} + H^{-} - F \Delta E^{\circ} [(H^{+}/H^{-}) - (R^{+}/R^{-})]$

$\Delta G_{H^-} = \Delta G_{hom} - F \Delta E^{\circ} [(H^{\circ} / H^{-}) - (R^{+} / R^{\circ})]$

Solution Hydride Affinity of Some Carbocations

Carbocation	ΔH (kcal/mol)	ΔH _{gas} (kcal/mol)
Tropylium ion	83	200
Ph ₃ C ⁺	96	215
Ph₂C⁺H	105	222
PhCH ⁺ ₂	118	238
p-CH ₃ OC ₆ H ₄ CH ⁺ ₂	106	227
p-NCC ₆ H ₄ CH ⁺ ₂	122	247

ΔH for Ionization of Chlorides and Alcohols in SO₂CIF

	ΔH (kcal/mol)		
Reactant	X=CI	X=OH	
(CH ₃) ₂ CH–X	-15		
Ph ₂ C(CH ₃)–X	-16		
(CH ₃) ₃ C–X	-25	-35	
PhC(CH ₃) ₂ –X	-30	-40	
Ph ₂ C(CH ₃)–X		-37.5	
Ph ₃ C–X		-49	
(<mark>)}₃C−X</mark>		-59	



MP2/6-31G^{**} optimized structure of t-butyl cation with three hydrogens aligned with the *p* orbital





Distribution of LUMO orbitals of isomeric 1-methylcyclohexyl cations showing dominant C–C (C) and C–H (D) hyperconjugation.



 θ = Deviation of – CH₃ from the plane of C(1) –C(2) –C(6) of the cyclohexane ring







bridged ethylium carbocation

1-propyl cation rearranges to2-propyl cation by hydride shift



neopentyl cation rearranges to t-pentyl cation by methyl shift



Proton removal leads to alkene formation









$H_3CCH^+-F \longrightarrow H_3CCH=F^+$ $H_3CCH^+-CI \longrightarrow H_3CCH=CI^+$





Destabilization of 2-Substituted i-Propyl Cation by EWG Substituents

Z	Solvolysis rate relative to Z = H	Destabilization HF/4-31G (kcal/mol)
CN	~ 10 ⁻³	9.9
CF ₃	~ 10 ⁻³	37.3
CH=O	_	6.1





1





10⁻³

10⁻¹⁰



Direct Observation of Carbocations

Protonation, Ionization, and Rearrangement in Superacid

A. Alcohols in FSO_3H —SbF₅—SO₂

ALLER

1^a ROH $\xrightarrow{-60^\circ C}$ RO+H₂

R = methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *s*-butyl, *n*-amyl, *i*-amyl, neopentyl, *n*-hexyl, neohexyl

- 2^{b} (CH₃)₂CHCH₂OH $\xrightarrow{-60^{\circ}\text{C}}$ (CH₃)₂CHCH₂O⁺H₂ $\xrightarrow{-30^{\circ}\text{C}}$ (CH₃)₃C⁺
- 3° (CH₃)₃COH $\xrightarrow{-60^{\circ}C}$ (CH₃)₃C⁺



D. Bicyclooctyl systems in $SbF_5 - SO_2CIF$, -78°C



Competing Reactions of Carbocations



Reaction energy profile illustrating competition between elimination and substitution by solvent for a *tert*-cation.



$(H_3C)_3C - C^+(CH_3)_2 \longrightarrow (H_3C)_2C^+ - C(CH_3)_3$





Mechanisms of Rearrangement of Carbocations





























Energy surface for the rearrangement of the 3-methyl-2-butyl cation to the 2-methyl-2butyl cation.







Bridged (Nonclassical) Carbocations













Contrasting energy profiles for stable and unstable bridged norbornyl cation. (A) Bridged ion is a transition structure for rearrangement between classical structures. (B) Bridged ion is an intermediate in rearrangement of one classical structure to the other. (C) Bridged ion is the most stable structure.







π complex

corner-protonated cyclopropane



Computational energy diagram (B3LYP)/6-311+G*) for intermediates and transition states in ionization and rearrangement of protonated 2-norbornanol.





The Role Carbocations and Carbonium Ions in Petroleum Processing

Octane Numbers for Some Hydrocarbons

Heptanes	RON	Octanes	RON
n-Heptane	0.0	n-Octane	-19.0
2-Methylhexane	42.4	2-Methylheptane	21.7
3-Methylhexane	52.0	3-Methylheptane	36.8
3-Ethylpentane	65.0	4-Methylheptane	26.7
2,2-Dimethylpentane	92.8	3-Ethylhexane	33.5
2,3-Dimethylpentane	91.1	2,2-Dimethylhexane	72.5
2,4-Dimethylpentane	83.1	2,3-Dimethylhexane	71.5
3,3-Dimethylpentane	80.8	2,4-Dimethylhexane	65.2
2,2,3-Trimethylpentane	112.1	2,5-Dimethylhexane	55.5
•		3,3-Dimethylhexane	75.5
		3,4-Dimethylhexane	76.3
		2-Methyl-3-ethylpentane	87.3
		3-Methyl-3-ethylpentane	80.8
		2,2,3-Trimethylpentane	109.6
		2,2,4-Trimethylpentane	100.0
		2,3,3-Trimethylpentane	106.1
		2,3,4-Trimethylpentane	102.7

$$\begin{array}{c} H_{8}C \\ C = CH_{2} \xrightarrow{H^{+}} (CH_{8})_{3}C^{+} \\ H_{3}C \\ (CH_{3})_{3}C^{+} \cdots H_{2}C = C \xrightarrow{CH_{8}} (CH_{8})_{3}CCH_{2}C^{+}(CH_{8})_{2} \end{array}$$

$$(CH_{3})_{3}CCH_{2}CH_{1}(CH_{3})_{2} \xrightarrow{H_{2}} (CH_{3})_{3}CCH_{2}C=CH_{2} + (CH_{3})_{3}CCH=C(CH_{3})_{2} \\ CH_{3} \end{array}$$

 $(CH_3)_3CCH_2C^+(CH_3)_2 + H^-C(CH_3)_3 \longrightarrow (CH_3)_3CCH_2CH(CH_3)_2 + {}^+C(CH_3)_3$

$$(CH_3)_3C^{+} \cdots H_2C^{+}C^{+}CH_3 \longrightarrow (CH_3)_3CCH_2C^{+}(CH_3)_2$$

$H \xrightarrow{CH_3C+HCH_3 + H_2}$ $CH_3CH_2CH_3 \longrightarrow CH_3CH_2 \xrightarrow{H} H \xrightarrow{H} H$ $CH_3CH_2^+ + CH_4$

$(CH_3)_2CH^+ + H_2C=CHCH_2CH_3 \longrightarrow (CH_3)_2CHCH_2C^+HCH_2CH_3$

$CH_3CH=CHCH_2CH_2CH_2^+ \longrightarrow H_3C \longrightarrow H_2C^+ ($

$\begin{array}{rcl} CH_3CH_3 &+ H^{\pm} &\longrightarrow & CH_3^{\pm} &+ CH_4 \\ CH_3CH_2CH_3 &+ H^{\pm} &\longrightarrow & CH_3CH_2^{\pm} &+ CH_4 \\ \hline & (CH_3)_3CCH_2CH_3 &+ H^{\pm} &\longrightarrow & (CH_3)C^{\pm} &+ CH_3CH_3 \end{array}$





<mark>СӉСӉ⁺ + СӉСӉ</mark>СӉСӉ — → СӉСӉСӉСӉ + Ҥ СӉ



and $CH_3CH_2^+ + CH_3CH_2CH_3 \longrightarrow CH_3CH_3 + CH_3C^+HCH_3$ $CH_3C^+HCH_3 + :C = O^+ \longrightarrow (CH_3)_2CHC = O^+$

 $CH_3CH_2^+ + :C = O^+ \longrightarrow CH_3CH_2C = O^+$

 $CH_3CH_2CH_3 + H^+ \longrightarrow CH_3CH_2^+ + CH_4$











Representation of C(2)-C(3) and C(1)-C(2) protonation and fragmentation to an alkane and alkene.

