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Dehydrogenation of Polycyclic Ketones using Trichloromethyl Cation in Superacid.

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Abstract : *In HF/SbF$_5$/CCl$_4$ bicyclic cyclohexanones are dehydrogenated to enones and dienones, superelectrophilic trichloromethyl cation CCl$_3^+$ reacting as a strong hydride acceptor. Dehydrogenation is also observed with steroidal enones.*

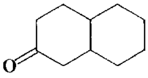
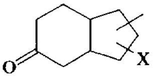
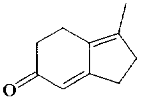
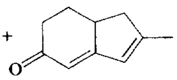
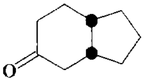
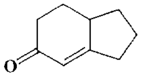
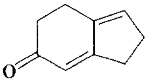
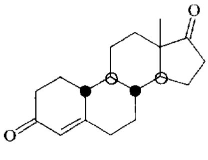
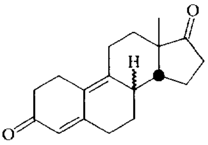
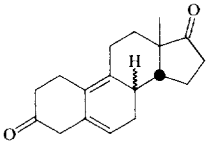
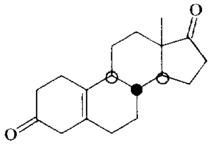
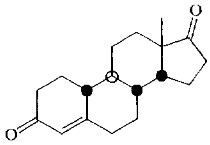
The reactivity of trichloromethyl cation CCl$_3^+$, previously prepared and observed using NMR by Olah[1], has been studied by several groups. It was found that in superacids, cation CCl$_3^+$ is an extremely reactive hydride abstracting reagent with hydrocarbons to yield carbocations [2,3]. Recently we reported ionization of ketones and amides, reaction occurring at a carbon far located from the protonated functional groups, to give hydroxy and / or fluoroderivatives after quenching [4].

This unexpected reactivity of trichloromethyl cation has been explained by protosolvation of the chlorine atoms, enhancing the electrophilic character of carbon in this species [5,6].

We wish to report here our results on the dehydrogenation of various cyclohexan-(cyclohexen-) ones in HF/SbF$_5$ in the presence of carbon tetrachloride. No reaction was observed with these substrates in HF/SbF$_5$ alone in the same experimental conditions, except for ketones **7** and **8** which are isomerizing to ketone **9** [7].

Table 1 shows that at low temperature, decalone **1** leads within a few minutes and after hydrolysis to a complex mixture of ring contracted hydroxy or fluoroderivatives. This is due to hydride abstraction at the more reactive C-H bonds, far from the protonated carbonyl group, in a process similar to what is observed with acyclic ketones, the resulting cyclohexyl cation(s) rearranging to methylcyclopentylcation(s) [4]. At 0°C with a large excess of CCl$_4$, the reaction goes further to yield dienones **2** and **3**. Their formation implies a second hydride abstraction conducting finally, through a mechanism involving hydride shifts and / or deprotonation - protonation processes, to allylic ions **2'** and **3'** precursors of the dienones. These results are rationalized as depicted in Scheme 1.

Table 1 : Reactions of ketones with HF-SbF$_5$-CCl$_4$ [a,b]

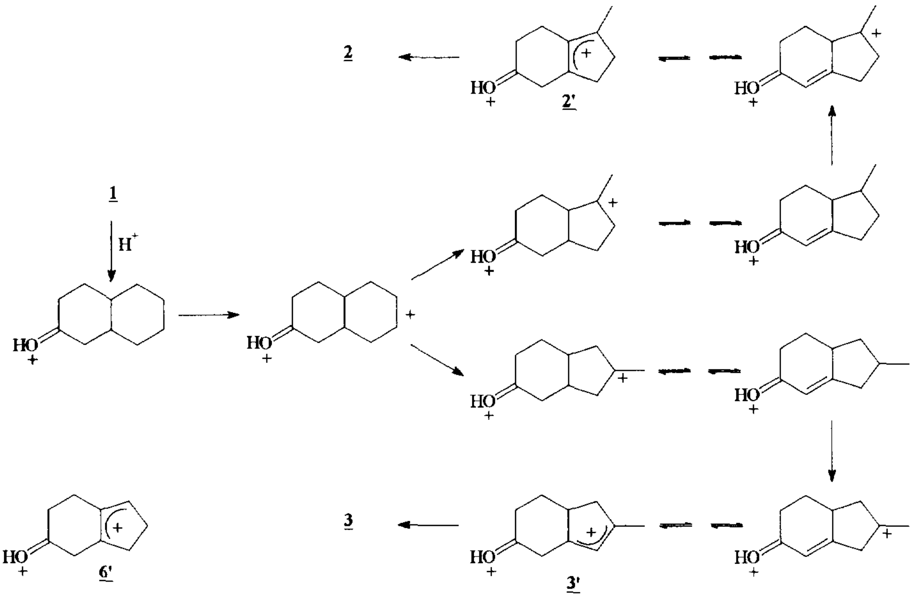
	CCl$_4$ (eq.)	Temp(°C)	Time(min)	Products (Yields %)
 **1**[c]	1.2	-30	10	 (OH, F)
	3.6	0	30	 +  **2**(25) **3**(12)
 **4**	0.5	-30	45	 + **4**(43) **5**(38)
	1.2	-30	45	**5**(31) +  **6**(46)
	3.6	-30	45	**6**(63)
 7	2.4	0	10	 **10a** (8αH) **10b** (8βH) (35) ratio(1/1) +  **11a** (8αH) **11b** (8βH) (34) ratio(1/1)
 8	2.4	0	10	
 9	2.4	0	10	

a) HF/SbF$_5$/Substrate molar ratio : 20/1/0.05

b) Quenching conditions: Na$_2$CO$_3$/Ice/H$_2$O.

c) Mixture of cis/trans isomers molar ratio 5/95.

Scheme 1

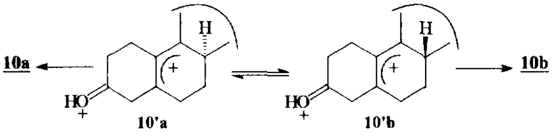


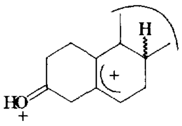
Ions **2'** and **3'** have been previously fully characterized by NMR in studying phenol - dienone isomerization [8]. The more reactive ketone **4** gives at -30°C a mixture of enones **5** and / or **6** and the sole dienone **6** with a large excess of CCl_4. The precursor of this dienone in superacids has been shown to be allylic ion **6'** and its formation can be accounted for as described above in Scheme 1.

Steroidal ketones are less reactive and only enones are dehydrogenated in $HF/SbF_5/CCl_4$ (estrane-3, 17-dione is completely unreactive).

Table 1 shows that ketones **7**, **8**, **9** yield the same dienones **10a** and **10b**, **11a** and **11b** with a cis C/D ring jonction. This implies that isomerization of ketones **7** and **8** to the more stable ketone **9** is faster than hydride abstraction [7].

Ketones **10a** and **10b** have been prepared previously by isomerization of 14-isoestrone in HF/SbF_5. Precursors of these dienones are allylic ions **10'a** and **10'b**, respectively, which are in equilibrium in the medium and exhibit similar stabilities [9].





11' a 8αH
b 8βH

Ketones **11a** and **11b** are new compounds. Their spectral data (UV, IR, ^{1}H and ^{13}C NMR, MS) favor the assigned structures, suggesting ions **11'a** and **11'b** as their precursors [10].

It should be noticed that the **10a** + **10b** / **11a** + **11b** molar ratio does not change during the reaction, ruling out any interconversion between ions **10'** and **11'**.

Furthermore we have found that protonation of **10a** or **11a** yields the same species **10'a,** and protonation of **10b** or **11b** ion **10'b**. This implies that ions **11'**(a or b) do not deprotonate *in situ* to the corresponding ketones **11** (a or b).

Formation of allylic ions results from hydride abstraction by CCl_3^+, probably occurring in the B ring as far as possible from the two protonated carbonyl groups. In both series 8α-H and 8β-H isomers are formed in equal amounts, and this might be due to loss of hydrogen at C-8, followed by 1,2 or 1,3 hydride shifts and / or deprotonation - protonation involving alkenes Δ-8 and Δ-7 to lead finally to ions **10'** and **11'** [7,9,12,13].

Finally we have observed that for dehydrogenation of ketones chloroform is less efficient than carbon tetrachloride, and dichloromethane completely unreactive, conforming that the reactivity of chloromethylcations in hydride abstraction decreases in the order: $CCl_3^+ > CHCl_2^+ >> CH_2Cl^+$ [4,11].

The dehydrogenation of ketones reported in this paper constitutes a novel example of the interest of chloromethyl cations as reagents in synthetic organic chemistry.

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10. Spectral data for mixture of **11a** and **11b**: **UV** in EtOH: λ_{max} nm (ε $mol^{-1}.l.cm^{-1}$): 292(1.2×10^4); **IR** cm^{-1}: 1741 (υC=O 5-membered), 1722 (υC=O 6 membered); **^{1}H NMR** ($CDCl_3$): δ 0.98 and 1.05 (s, 3H, CH_3-18), 2.98 (dl, 1H, J=21Hz, H-4),3.09 (dl, 1H, J=21Hz, H-4), 5.65 (sl, 1H, H-6); **^{13}C NMR** ($CDCl_3$): δ 18.8 and 21.0 (C-18), 114.9 and 115.4 (C-6), 210.3 and 210.4 (C-3), 222.8 (C-17); **EI MS** m/z(%): 270(18), 228(12), 84(100).
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