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REACTION BEHAVIOR OF CARBON-CARBON AND CARBON-HYDROGEN BONDS IN SUPER ACIDS. CARBOXYLATION OF ALKYL METHYL KETONES WITH CARBON MONOXIDE AND WATER

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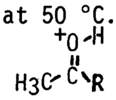
In a HF-SbF_5 solution at -20～30 °C under atmospheric pressure, ketones having alkyl groups with five or more carbon atoms underwent the reaction to give corresponding oxo carboxylic acids without any β -scission processes which occur readily in alkyl cations derived by protolysis of alkanes with seven or more carbon atoms. Tertiary C-H bond located at δ or further away from the oxo group in the substrates could react exclusively to give ($\omega-1$)-oxo-2,2-dimethyl carboxylic acids at -20 °C.

It is becoming increasingly evident that electrophilic attack at a carbon σ-bond is an important reaction despite the low reactivity of saturated compounds.[1)] From this point of view, it is of interest to clarify the reaction behavior of such σ-bonds in the functionalized organic compounds. We wish to report here the reactions initiated by the protolysis of σ-bonds in alkyl methly ketones followed by quenching with carbon monoxide and water to give corresponding carboxylic acids.

The general reaction procedure was carried out in accordance with the method described in the preceding paper.[2)] Some of the results are listed in Table 1. In spite of high reactivity of H^+ towards alkanes in a HF-SbF_5,[2)] ketones having alkyl groups with four or less carbon atoms do not undergo the same type of reaction even at 50 °C. Presumably in such a solution, ketones exist as completely protonated species such as,  $H_3C-\overset{\overset{+}{O}-H}{\overset{\|}{C}}-R$; thus H^+ as an electrophile will not readily react with σ-bonds located in close proximity to the carboxonium center. On the other hand, σ-bonds located at a sufficient distance from the carboxonium center undergo the reaction. Treatment of methyl pentyl ketones in HF-SbF_5 by introducing carbon monoxide results in the formation of oxo carboxylic acids together with a small amount of dicarboxylic acid.[3)] Although the pathway of the formation of the dicarboxylic acid is not yet clear, one may postulate that the path for the formation of oxo carboxylic acids is initiated by the protolysis at σ-bonds of the alkyl group. The resulting dicationic intermediate i.e., carbenium methyl protonated ketone then undergoes the reaction with carbon monoxide and water as shown in the following scheme.

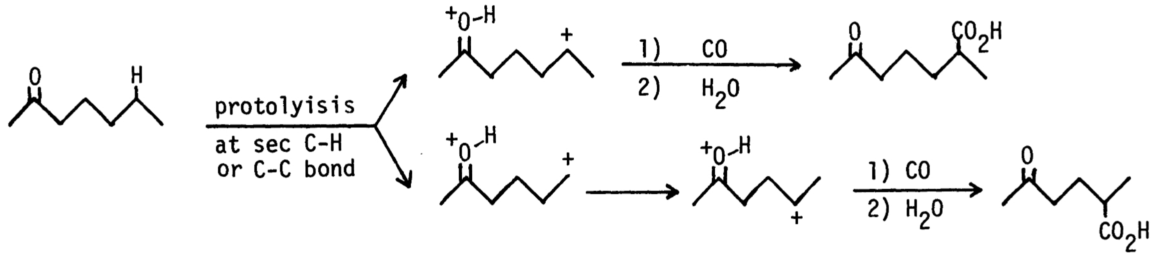
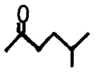
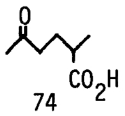
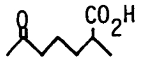
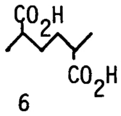
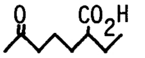
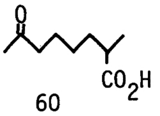
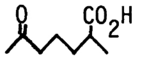
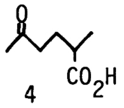
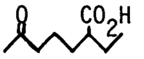
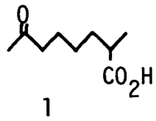
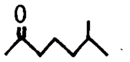
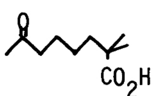
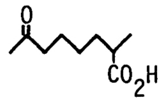
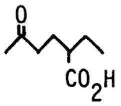
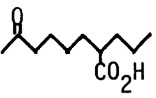
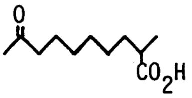
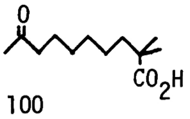


Table Reaction of Alkyl Methyl Ketones with CO[a)]

Substrate	Temp. °C	Yield[b)] %	Product Distribution %				
	50	NR[c)]					
							
	20	62	74	20	6		
							
	20	50	3	60	33	4	
							
	-20	16	83	16	1		
	20	53	6	8	85		
							
	-20	60	100	—	—	—	
	20	73	11	10	56	23	
							others
	-20	65	100	—	—	—	
	20	62	27	14	13	26	6
							
	-20	66	100				

a) Reaction time 3hr, ketone 5 mmol, SbF_5/ketone = 10 mole ratio, HF/SbF_5 = 3.3 mole ratio
b) Total Yield, based on ketone used c) No reaction

Tertiary C-H bonds located at δ or further away from the oxo group in the substrates can react preferentially to give (ω-1)-oxo-2,2-dimethyl carboxylic acid at -20 °C. By increasing the temperature, however, it gives a distribution of products stemming from the skeletal isomerization of initially formed intermediate dications. In contrast to the reaction of alkanes with seven or more carbon atoms,(2) the β-cleavage of the alkyl carbenium ion groups is strongly prevented by the protonated oxo group even in isooctyl methyl ketone. From the products obtained in these reactions, the relative order of reactivity of single bonds in alkyl methyl ketones towards protolysis may be shown as ; tertiary C-H>C-C>secondary C-H>H_2C-H. This order agrees with the chlorolysis and the nitrolysis of alkane.(4)

References
1) a) R.D.Bach, J.W.Holubka, R.C.Badger and S.J.Rajan. J.Am.Chem.Soc., 101, 4416 (1979); b) N.Yoneda, and Y.Takahashi, J.Jpn.Petroleum Institute, 20, 468 (1977); c) G.A.Olah, Science 206, 13 (1979).
2) N.Yoneda, T.Fukuhara, Y.Takahashi and A.Suzuki, Chem.Lett., 1983, 17.
3) No formation of dicarboxylic acids was observed except for the reaction of methyl pentyl ketone.
4) a) G.A.Olah, R.Renner, P.Schilling and Y.K.Mo, J.Am.Chem.Soc., 95, 7686 (1973); b) G.A.Olah, A.Germain, H.C.Lin, and D.A.Frosyth, J.Am.Chem.Soc., 97, 2923 (1975).

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