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REACTION OF ALKYL PHENYL KETONES IN SUPER ACID MEDIA. A CONVENIENT SYNTHESIS OF 4,4-DIALKYL-1-TETRALONE DERIVATIVES

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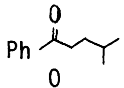
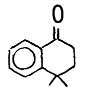
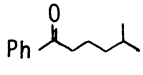
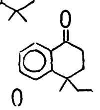
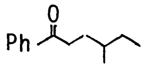
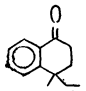
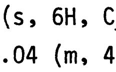
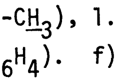
Alkyl phenyl ketones having alkyl group of five or more C atoms are converted into 4,4-dialkyl-1-tetralones in sufficiently good yields via the initial protolysis of C-H bond in alkyl groups giving carbonium ion intermediates which in turn undergo ring closure in the presence of $HF-SbF_5$ super acid media under mild conditions.

The chemistry of alkanes has been greatly extended by using highly acidic solvents such as FSO_3H-SbF_5, $HF-SbF_5$ in recent years[1)]. In connection with such a study, it is of interest to examine the possibility of electrophilic reactions toward single σ bonds (such as C-H and C-C) of various organic compounds in super acidic media[2)]. We now wish to report the reaction of alkyl phenyl ketones in the $HF-SbF_5$ super acid system involving the protolysis at single σ bonds in the starting materials that results in the formation of 4,4-dialkyl-1-tetralones[3)].

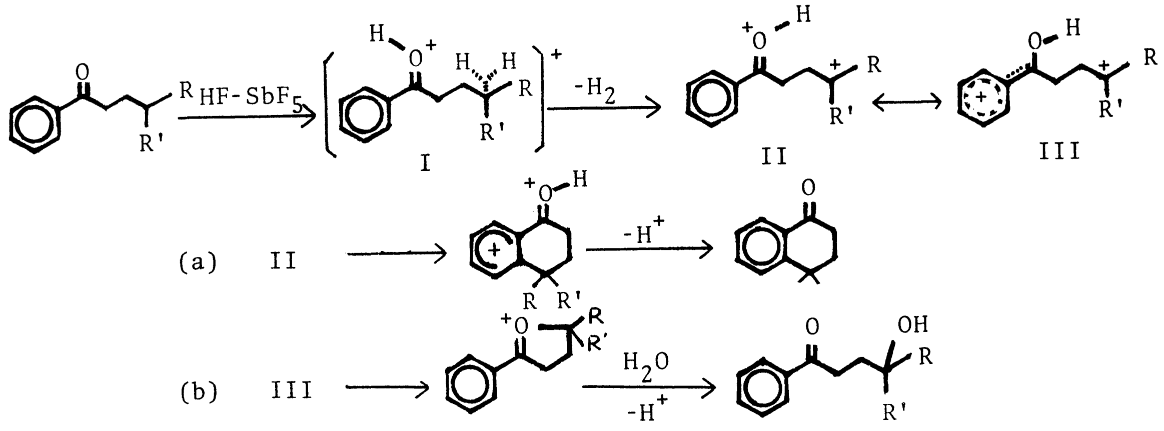
In a typical procedure, a solution of 20 ml of $HF-SbF_5$ having a HF/SbF_5 molar ratio of 5 was placed into a three necked 100 ml Kel-F reaction vessel under sufficient stirring at 0°C. The appropriate alkyl phenyl ketone[4)] was then added dropwise into the acid solution. The reaction mixture was kept under stirring at temperatures and times specified in the Table. Then, the resulting solution was hydrolyzed with ice-water and the products[4)] were obtained by working up in the usual manner. Some of the results are listed in Table.

Table Reaction of Alkyl Phenyl Ketones in $HF-SbF_5$ System[a)]

Substrate[b)]	Reaction		Yield[c)]	Product Distribution	
	Time hr	Temp. °C	%		%
	3	40	68	 e)	100
	1	40	79	 f)	100
	6	40	95		
	3	50	95	 f)	82 others 18[d)]

a) HF/SbF_5 molar ratio 5. b) SbF_5/substrate molar ratio 5-10. c) based on substrate. d) Formation of  and  only was observed. e) MS(m/e): 174 (M^+), 159, 131, 120, 105. IR (neat, cm^{-1}): 1686 (C=0), 1600 (C_6H_4). NMR (CCl_4, ppm, Ho=90MHz): 1.36 (s, 6H, $C\underline{H}_3-C-C\underline{H}_3$), 1.98 (t, 2H, $-C\underline{H}_2-CH_2-C=0$), 2.62 (t, 2H, $-CH_2-C=0$), 7.06-8.04 (m, 4H, C_6H_4). f) MS(m/e): 188 (M^+), 159, 131. IR (neat, cm^{-1}): 1690 (C=0), 1601 (C_6H_4). NMR (CCl_4, ppm, Ho=90MHz): 0.85 (t, 3H, $C\underline{H}_3-CH_2-$), 1.32 (s, 3H, $C\underline{H}_3-C$), 1.69 (q, 2H, $CH_3-C\underline{H}_2-$), 1.80-2.27 (m, 2H, $-C\underline{H}_2-CH_2-C=0$), 2.60 (t, 2H, $-C\underline{H}_2-C=0$), 7.06-8.04 (m, 4H, $C_6\underline{H}_4$).

The results can be best accounted for by an alternate reaction path (a) involving the initial protonation toward the specified single σ bond in the substrate through the pentacoordinated carbonium ion transition state [I]. The pentacoordinated carbonium ion [I] subsequently cleaves to give the carbonium ion [II] intermediately which in turn undergoes a ring closure to produce a formation of 1-tetralone derivative as shown in the following scheme.

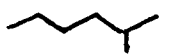


The results also indicate that the tertiary C-H bond in alkyl group located at the third carbon or further away from the carbonyl carbon in the substrates, can undergo the protolysis reaction giving cation [II] rather easily[5]. Thus, the reactivity of alkyl phenyl ketone was greatly affected by the skeletal structure of alkyl group[6]. The ring closure of cation [II] is rather surprising because the protonated acyl group on the aromatic ring is known to have a strongly deactivating effect on the usual electrophilic aromatic substitution. Hence, the resonance structure of cation [II] may be considered to make a stronger contribution than [III] which results in subsequent ring closure.

The reaction of materials having alkyl group with five or more carbons also gives only 1-tetralone derivatives. For example, 5-methylpentyl phenyl ketone [IV] converts into 4-methyl-4-ethyl-1-tetralone, [V] without any formation of the ring closure product with the seven membered ring. The product [V] seems to be obtained by the reaction of 5-benzoyl-3-methyl-3-pentyl cation which should be formed by the subsequent hydride and methyl shifts in 5-benzoyl-2-methyl-2-pentyl cation derived from the preferential protolysis at tertiary C-H bond in [IV].

Scope and limitation of the present reaction together with the electrophilic aromatic substitution in the super acid media are under investigation.

References and Notes

1a) N. Yoneda, and Y. Takahashi, J. Jpn. Petroleum Institutes, 20, 468 (1977). b) G. A. Olah, "Carbocations and Electrophilic Reactions", Verlag Chemie, Wiley (1973).
2) G. A. Olah, N. Yoneda, and R. Ohnishi, J. Am. Chem. Soc., 98, 7341 (1976).
3) Although, 1-tetralone itself can be obtained by the Haworth reaction (J. March, "Advanced Organic Chemistry", 2nd ed., McGraw-Hill, New York (1977), p 492.), synthesis of 4,4-dialkyl-1-tetralone derivatives previously reported was carried out under more complicated reaction steps (R. T. Arnold, J. S. Buckley, Jr., and Richter, J. Am. Chem. Soc., 69, 2322 (1947), R. B. Carlin and K. P. Sivaramakrishnan, J. Org. Chem. 35, 3368 (1970).) or under more severe conditions (G. Baddeley and R. Williamson, J. Chem. Soc., 1956, 4647.).
4) Alkyl phenyl ketones as the starting material were prepared by Friede-Crafts acylation using corresponding acyl chlorides. Products were identified by nmr, ir. and mass spectroscopic data after being obtained by preparative gas chromatography.
5) Alkyl benzenes such as Ph undergo the reaction involving the protolysis at C-H and C-C bonds in alkyl group together with intermolecular transalkylation to give various complicated products under the condition employed.
6) G. A. Olah, Y. Halpern, Y. Shen and Y. K. Mo, J. Am. Chem. Soc., 95, 4960 (1973).

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