Synthetic Methods and Reactions; 72[1]. Mild Fragmentative C—C Bond Cleavage of α-Hydroxyketoximes with Trifluoromethanesulfonic Anhydride, Trifluoroacetic Anhydride, or Trifluoromethanesulfonyl Chloride.

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α-Hydroxyketoximes **1** undergo cleavage by reagents such as phosphorus pentachloride[2], benzenesulfonyl chloride[3], phosphoryl chloride[4], polyphosphoric acid[5], thionyl chloride[6], phosphonitrile dichloride[7], and dichlorocarbene[8]. Most of these reagents, however, except the last two, necessitate rather harsh conditions. We now wish to report that trifluoromethanesulfonic anhydride and trifluoroacetic anhydride, known as mild and effective dehydrating agents[9,10,11,12], as well as trifluoromethanesulfonyl chlo-

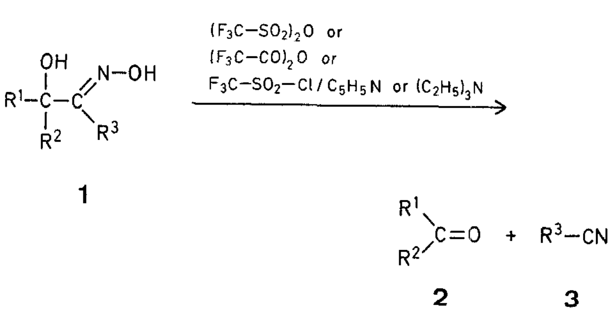

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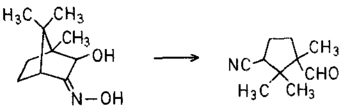
Table. C—C Bond Cleavage of α-Hydroxyketoximes **1**

R^1	R^2	R^3	Product	Yield [%] by Method[a] A	B	C	b.p./torr or m.p.[b] found	reported[15,16]	m.p. of 2,4-DNP found	reported[15,16]
C_6H_5	H	C_6H_5	**2**	77	78	75	177 °C/760	178 °C/760	234 °C	237 °C
			3	74	72	71	65 °C/8	69 °C/10	—	—
C_6H_5	H	4-H_3CO—C_6H_4	**2**	70	76	69	42 °C/2; 177 °C/760	62 °C/10; 178 °C/760	234 °C	237 °C
			3	65	70	62	95 °C/1.5; 58–59 °C	106–108 °C/6; 61–62 °C		
4-H_3CO—C_6H_4	H	4-H_3CO—C_6H_4	**2**	79	81	72	86–87 °C/3	83 °C/2	250.4 °C	253–254 °C
			3	69	72	68	58–59 °C	61–62 °C	—	—
4-Cl—C_6H_4	H	4-Cl—C_6H_4	**2**	66	80	76	70–71 °C/2	72–75 °C/3	251–253 °C	254 °C
			3	62	70	70	91–93 °C	96 °C	—	—
				65[c]	81[c]	79[c]	—	—	195–198 °C	195–196 °C[8]

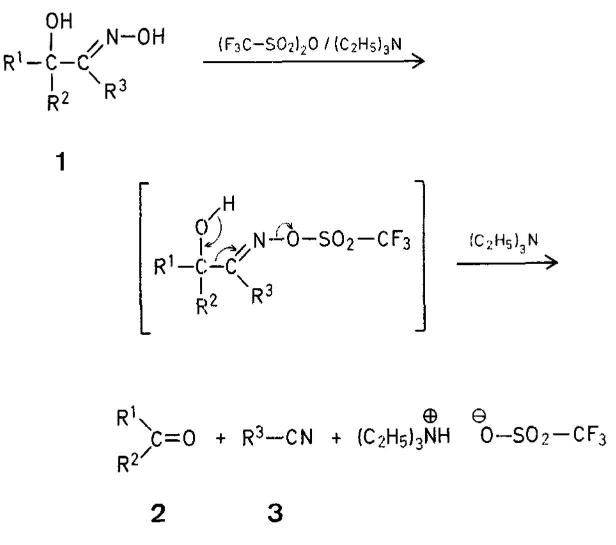
[a] Method A: $F_3C—SO_2—Cl$; B: $(F_3C—SO_2)_2O$; C: $(F_3C—CO)_2O$.

[b] Purity of product: ≥96% as determined by I.R., ^{1}H-N.M.R., and T.L.C. (silica gel; hexane/benzene(10:1) as eluent).

[c] Isolated as 2,4-dinitrophenylhydrazone.

ride, efficiently cleave the carbon-carbon bond of α-hydroxyketoximes **1**, under mild conditions, to yield the corresponding aldehydes or ketones **2** and nitriles **3** in good yields. Results are summarized in the Table.

We consider that our method, described herein, is mild and effective to both aromatic and aliphatic α-hydroxyketoximes. The mechanism of the reaction may be represented as shown below for triflic anhydride. Clearly, the method is related to the well known Beckmann rearrangement[13].



General Procedure for the C—C Cleavage of α-Hydroxyketoximes with Triflic Anhydride, Trifluoroacetic Anhydride, or Trifluoromethanesulfonic Chloride:

To a well stirred solution of the α-hydroxyketoxime **1** (10 mmol) in dry dichloromethane (15 ml; dried over P_2O_5) at 0 °C, is added dry triethylamine[14] (25 mmol) followed by the dehydrating agent (11 mmol) in dichloromethane (10 ml). The stirring is continued for 3 h at room temperature and the reaction mixture is then heated under reflux for 1 h. After cooling, it is poured on ice/water and the organic layer separated. The aqueous layer is twice extracted with dichloromethane (15 ml × 2). The combined organic layers are further washed with 2% aqueous hydrochloric acid (50 ml), followed by water (2 × 25 ml), and brine (15 ml), dried with anhydrous sodium sulfate, and the solvent subsequently evaporated. The products are isolated either by distillation or column chromatography (silica gel/hexane). The spectral characteristics (I.R., ^{1}H-N.M.R.) of the purified products, as well as the melting points of the 2,4-dinitrophenylhydrazones, are identical to those of authentic samples.

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