

Synthetic Methods and Reactions; 126¹. Trifluoromethanesulfonic Acid/Triethylsilane: A New Ionic Hydrogenation Reagent for the Reduction of Diaryl and Alkyl Aryl Ketones to Hydrocarbons

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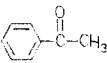
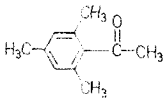



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Benzophenones (except for 4,4'-dialkoxy- and sterically hindered derivatives), certain acetophenones, and 1-indanone can be reduced to the corresponding hydrocarbons in good yields by reaction with trifluoromethanesulfonic acid and triethylsilane.

Extensive studies have been carried out on the use of the main-group hydrides for the reduction of ketones to alcohols. Ionic hydrogenation² is a recently used reducing method for ketones, alcohols, olefins, and others. The most commonly used hydrogenating reagent pair is triethylsilane and trifluoroacetic acid. Sodium borohydride/trifluoroacetic acid³ has also been used.

There are numerous reports on the reduction of aromatic (and in some cases aliphatic ketones) using triethylsilane in the presence of Brønsted³ or Lewis⁷ acids. However, they generally require prolonged reaction times and when crowded aryl ketones or aryl ketones with strongly electron-deficient substituents (such as nitro, etc.) are reduced with trialkylsilanes or sodium borohydride and a Brønsted acid the yields of the corresponding hydrocarbons are either low and alcohols are also obtained or no reduction is achieved.

Table. Reduction of Ketones **1** to Hydrocarbons **2** with Triethylsilane/Trifluoromethanesulfonic Acid

Ketone 1			Yields ^a [%]		b. p. [°C]/torr	
1	(for Benzophenones: R ¹)	R ²	Hydro-carbon 2	Alcohol	found	reported
a	H	H	90	0	60/0.5	60–62/0.35 ^{3a}
b	H	4-CH ₃	92	0	80/0.5	69–71/0.25 ^{3a}
c	4-CH ₃	4-CH ₃	85	0	120/1	165/12 ¹³
d	H	4-OCH ₃	79	0	100/0.5	89–91/0.15 ^{3a}
e	4-OCH ₃	4-OCH ₃	no reaction	"		
f	H	4-Br	72	0	120/2	123/3 ⁸
g	H	4-NO ₂	95	0	160/1	140/0.35 ^{3a}
h	H	4-CF ₃	80	0	120/0.75	75–76/0.05 ¹²
i	H	4-F	76	0	92–95/1	71/0.01 ^{3a}
j	H	2-F	80	0	75/0.2	74/0.2 ⁹
k	H	4-OH	78	0	125/0.25	115–120/0.1 ^{3a}
l			80 ^c	0		
m			84	0	65/2	70/5 ¹¹
m^d	H	2,4,5-tri-CH ₃	80	0	120/0.5	101–113/0.35 ^a
o^e	2,5-di-CH ₃	2,4,5-tri-CH ₃	no reaction	^b		
p	2,4,5-tri-CH ₃	2,4,5-tri-CH ₃	no reaction	^b		
q			96	0	65/10	176/760 ^c
r			22 ^c	75 ^c		
s			20 ^c	79 ^c		

^a Yields of distilled material. Products were identified by FT-IR and ¹³C-NMR spectroscopy, unless otherwise specified.

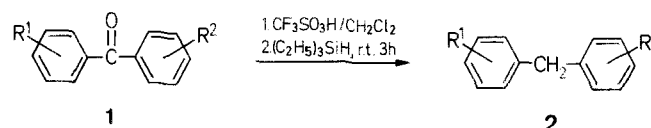
^b Starting material was recovered.

^c Analysis by GLC using comparison with known material.

^d Prepared from 2,5-dimethylphenylmagnesium bromide and mesitoyl chloride⁹.

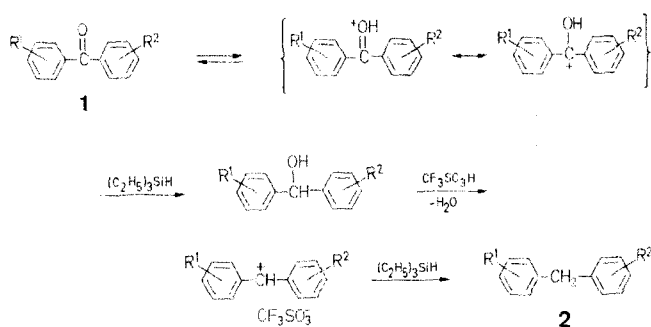
^e Prepared from mesitylmagnesium bromide and mesitoyl chloride (m. p. 138–139°C, from 95% ethanol; Lit.⁹ m. p. 136–137°C).

Since reduction with organosilanes requires activation of the carbonyl carbon center, oxygen complexation with a Lewis or protic acid is needed to allow subsequent hydride transfer to occur. A number of protic acids have been tested in reagent pairs with triethylsilane, the strongest one being trifluoroacetic acid which has $H_o = -3.2$. It was stated² that acids stronger than trifluoroacetic acid cannot be used in conjunction with silanes. Our interest in exploring the synthetic utility of superacid-catalyzed reactions⁵ and need for an improved reducing method for reduction of sterically hindered and electron-deficient diaryl ketones^{3a}, lead to the finding of an efficient new alternative ionic hydrogenating system in trifluoromethanesulfonic (triflic) acid/triethylsilane. Diaryl ketones (**1**) are easily reduced by triethylsilane in the presence of trifluoromethanesulfonic acid in dichloromethane solution, at room temperature within three hours, to give the corresponding diarylmethanes (**2**) in generally high yields.



Aliphatic ketones, however, were reduced in lower yields. The relatively short reaction times are contrasted with the 15–30 h reaction times required in reductions with sodium borohydride/trifluoroacetic acid^{3a}. Our results show that triethylsilane can be effectively used in conjunction with superacidic trifluoromethanesulfonic acid, $H_o = -14.5$, as a new ionic hydrogenating reagent system for the reduction of ketones to the corresponding hydrocarbons.

The reductions with triethylsilane/triflic acid, unlike those with triethylsilane/trifluoroacetic acid², are proposed to proceed through carbocationic intermediates, i. e., protonated ketones which in their hydroxycarbenium ion form abstract hydrogen from the silane



followed by ionization of the intermediate diarylmethanol to diarylmethyl cation which then again undergoes hydrogen transfer to give the corresponding diarylmethane.

We have found that the new reduction system is effective with a variety of substituted diaryl ketones (Table), such as ketones with $-\text{OH}$, $-\text{CH}_3$, $-\text{Br}$, $-\text{F}$, CF_3 , $-\text{CH}_3$, and $-\text{NO}_2$ groups.

The presence of electron-withdrawing substituents on diaryl ketones increases the electrophilic nature of the carbonyl carbon and consequently speeds up the hydride transfer upon protonation by the protic acid. On the other hand, 4,4'-dimethoxybenzophenone (**1e**) is not reduced even when using excess acid and heating the reaction mixture, whereas 4-methoxybenzophenone is reduced under the usual condition. We attribute this to the extreme stability of the intermediate carbocation formed when 4,4'-dimethoxybenzophenone is protonated. The reductions are somewhat retarded by steric effects. For example, whereas mesityl phenyl ketone is smoothly reduced under the usual reaction conditions, dimesityl ketone and mesityl-xylyl ketones gave no reduction product even with 10 equivalents of the acid. The reason probably is a combination of steric and electronic effects.

We have also found the method is applicable to alkyl aryl ketones (**1l**, **m**, **q**). However, cycloalkyl ketones such as 2-adamantanone (**2s**) and cyclohexanone (**2r**) under the usual reaction conditions give mixtures of the corresponding hydrocarbon and alcohol, the latter being the major product.

The triethylsilane/triflic acid system offers a useful alternative to existing methods. It reduces readily diaryl as well as alkyl aryl ketones in good yields, even when substituted with electron-withdrawing or bulky substituents, only mild conditions and short reaction times being required.

Trifluoromethanesulfonic acid (triflic acid) was purchased from 3 M and triethylsilane from Petrarch Systems. All products were characterized by their b.p./m.p. as well as their IR and ^{13}C -NMR data.

Hydrocarbons, in Particular Diarylmethanes (2), from Ketones (1); General Procedure:

A solution of trifluoromethanesulfonic acid (d: 1.6; 0.02 mol, ~ 2 ml) in dichloromethane (20 ml) is added dropwise to a stirred solution of the ketone **1** (0.01 mol) in dichloromethane (20 ml) at 0–5° (ice bath) under nitrogen. The color of the solution usually turns yellow-red. Subsequently, a solution of triethylsilane (0.015 mol, ~ 1.75 g) in dry dichloromethane (20 ml) is added dropwise. An exothermic reaction takes place while the temperature is maintained at 0°C. After 5 min, additional acid (0.02 mol, ~ 2 ml) is added (total amount of acid 0.04 mol), again followed by the addition of triethylsilane (0.015 mol, ~ 1.75 g; total addition time 45 min). When the addition is completed, the ice bath is removed and stirring is continued at room temperature for 2 h. The mixture is then

poured into cold saturated sodium hydrogen carbonate solution (100 ml) and extracted with dichloromethane (3 × 20 ml). The organic layer is dried with magnesium sulfate, and evaporated. The crude product, depending on its purity, is either directly distilled in vacuum or first subjected to column chromatography (silica gel or alumina). Solid products can be purified by crystallization.

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