

though, that the acylation potential is higher for sulfonic-carboxylic than for carboxylic anhydrides^[4, 5]. So, further increased reactivity may be expected with trifluoromethanesulfonic-carboxylic anhydrides (3).

We have prepared the mixed anhydrides (3) by treating the silver salt (1) with acyl chlorides (2) (method A, Table 1); they are also formed, although in lower yields, by reaction of free trifluoromethanesulfonic acid with (2) (method B, Table 1).

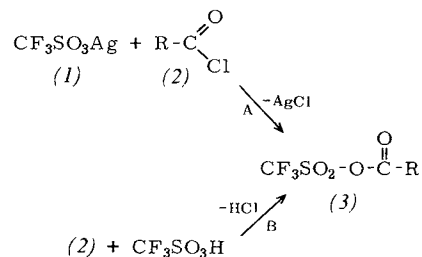
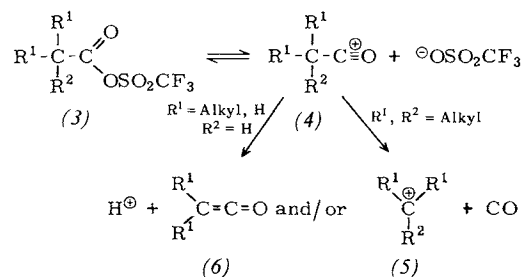


Table 1. Anhydrides (3) from (2) and (1) (method A) or from (2) and $\text{CF}_3\text{SO}_3\text{H}$ (method B).

R	Method	B. p. (°C/torr)	Yield (%) [a]
C_6H_5	A	98-101/11	90
$p\text{-NO}_2\text{-C}_6\text{H}_4$	A	M. p. = 40-53°C	80
$p\text{-CH}_3\text{-C}_6\text{H}_4$	A	62/0.3	94
$p\text{-Cl-C}_6\text{H}_4$	A	78/0.2	100
$(\text{CH}_3)_3\text{C}$	A	[b]	66
$(\text{C}_2\text{H}_5)_2\text{CH}$	A	54-58/0.1	36
C_6H_5	B	96-101/11	35
$p\text{-CH}_3\text{-C}_6\text{H}_4$	B	57-60/0.1	39
$p\text{-Cl-C}_6\text{H}_4$	B	73-75/0.1	63

[a] Crude yields are given in each case. Due to extreme sensitivity to water, elemental analyses of the anhydrides (3) often gives slightly inexact values. [b] Decomposes on distillation.

In the case of aromatic carboxylic acids [(3), R = aryl], the anhydrides may be distilled without decomposition; the aliphatic members (R = alkyl) are thermolabile, and only a few do not decompose upon distillation. This instability can be rationalized in terms of a dissociation equilibrium of the anhydrides (3): if R is an aliphatic group ($\text{R} = \text{CR}_2^1\text{R}^2$), the acylium cations (4) thus formed may either lose CO yielding carbonium ions (5) and/or be deprotonated to give ketenes (6).



Trifluoromethanesulfonic-Carboxylic Anhydrides, Highly Active Acylating Agents^[1]

By Franz Effenberger and Gerhard Epple^[*]

The trifluoromethanesulfonate anion has proved the best leaving group so far in solvolytic displacement reactions^[2]. For acylation with carboxylic acid derivatives, however, a straightforward estimate of the influence of the leaving group on the reaction rate is impossible; depending on substrate and reaction conditions, there are several mechanistic pathways with a varying dependance on the nature of the leaving group^[3]. Recent investigations have shown,

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We have established that carbon monoxide is formed quantitatively in the decomposition of several aliphatic anhydrides; but ketenes have not been observed so far. When R = aryl, ketene formation is impossible, and decarbonylation appears rather unlikely because of the instability of the phenyl cations formed.

The anhydrides (3) are the most powerful acylating agents known so far. Whereas xylenes do not react with other

sulfonic-carboxylic anhydrides even if heated for 24 h at 100°C^[5], non-activated arenes such as benzene are acylated smoothly by the mixed anhydrides (3), without addition of Friedel-Crafts catalysts (Table 2). The trifluoromethanesulfonic acid can be recovered almost quantitatively as its barium salt.

Table 2. Acylation of aromatic compounds by anhydrides (3).

(3), R	Reactants		Conditions		Product [b]	Yield (%)
	Arene		T (°C)	t (h)		
C ₆ H ₅	Benzene		-20	5	Benzophenone	5
C ₆ H ₅	Benzene		+20	5	Benzophenone	52
C ₆ H ₅	Benzene		+60	5	Benzophenone	90
C ₆ H ₅	Anisole		+20	0.5	4-Methoxybenzophenone	77
C ₆ H ₅	Chlorobenzene		+60	5	4-Chlorobenzophenone	67
<i>p</i> -NO ₂ -C ₆ H ₄	Benzene		+80	1	4-Nitrobenzophenone	53
<i>p</i> -NO ₂ -C ₆ H ₄	Anisole		+40	0.1	4-Methoxy-4'-nitrobenzophenone	84
CH ₃	Anisole		-70	2 [a]	Acetophenone	66
(CH ₃) ₂ CH	Anisole		+40	3.5 [a]	Isopropyl phenyl ketone	69

[a] The anhydride (3) was prepared in CH₂Cl₂ and allowed to react directly in this solution with the aromatic compound.

[b] The acylation products obtained were compared with authentic material.

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[2] a) R. L. Hansen, *J. Org. Chem.* 30, 4322 (1965); b) A. Streitwieser jr., C. L. Wilkins, and E. Kielmann, *J. Amer. Chem. Soc.* 90, 1598 (1968); c) Tah Mun Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.* 91, 5386 (1969).

[3] J. March: *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure.* McGraw-Hill, New York 1968, p. 413 ff.

[4] a) A. Baroni, *Atti Accad. Naz. Lincei, Mem., Cl. Sci. Fis., Mat. Natur.* 17, 1081 (1933); b) C. G. Overberger and E. Sarlo, *J. Amer. Chem. Soc.* 85, 2446 (1963); c) G. A. Olah and S. J. Kuhn, *J. Org. Chem.* 27, 2667 (1962); d) H. Böhme and K.-H. Meyer-Dulhever, *Liebigs Ann. Chem.* 688, 78 (1965); e) E. Sarlo and T. Lanigan, *Org. Prepar. and Proced.* 1, 157 (1969).

[5] M. H. Karger and Y. Mazur, *J. Org. Chem.* 36, 528, 532, 540 (1971).