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1-(*p*-Substituted)benzyl-1,1-dimethyl-2-(*p*-substituted)benzoyl Hydrazinium Hexafluoroantimonates as Useful Catalysts for the Acetalization of Carbonyl Compounds with Diols

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Carbonyl compounds **1**, alkyl- and arylaldehydes and alkyl, aryl, benzylic, and cyclic ketones were converted to the corresponding 1,3-dioxolanes **2** and 1,3-dioxanes **4** with ethylene glycol and 2,2-dimethyl-1,3-propanediol in the presence of 1-3 mol% of 1-(*p*-substituted)benzyl-1,1-dimethyl-2-(*p*-substituted)-benzoyl hydrazinium hexafluoroantimonates **3** in high yields.

Introduction

The carbonyl function, as present in aldehydes and ketones, is probably one of the most versatile functional groups in organic chemistry; and not surprisingly a great deal of work has been done on the protection and masking of the carbonyl compounds. The formed acetal derivatives are important intermediates or end product in synthetic organic chemistry. One of the most convenient and practical methods for the syntheses of acetals from aldehydes and ketones is to react carbonyl compounds with diols such as ethylene glycol in the presence of an appropriate acidic catalyst with azeotropic removal of water formed by reflux solvent immisible with water.[1]

p-Toluenesulfonic acid (TsOH) is usually used as an acid catalyst,[2,3] while pyridinium *p*-toluenesulfonate is one of the mild catalysts[4] for acid sensitive carbonyl compounds. Generally, the catalysts used for acetalization are not easy to handle due to their hygroscopicity.

We have developed a new class of Lewis acid catalysts, *N*-benzyl group containing pyridinium salts that are characterized by their ease of synthesis and handling due to their reduced hygroscopicity and their chemical stability toward air, water, and organic solvents (e.g., they can be recrystallized from methanol). These salts are conceived to induce benzyl cations by heating to initiate the polymerizations of cyclic ethers[5,6] and a vinyl monomer[7] and to catalyze organic reactions, acetalizations of carbonyl compounds with epoxides[8] or diols.[9]

Recently, we reported a new class of Brønsted acid-inducing catalyst, 1-(*p*-substituted)benzyl-1,1-dimethyl-2-(*p*-substituted)benzoylhydrazinium hexafluoroantimonates **3** of which significances are evaluated as the same as that of *N*-benzyl group containing pyridinium salts in addition to their thermal latency.[10]

In this article, synthesis and the use of **3** as catalysts for the acetalization of carbonyl compounds with ethylene glycol and 2,2-dimethyl-1,3-propandiol are described.

Experimentals

Materials. Commercially available extra pure grade 1,1-dimethylhydrazine, benzoyl chloride, *p*-nitrobenzoyl chloride, benzyl bromide, *p*-methoxybenzyl alcohol, 47% of hydrogen bromide, 98% sulfuric acid, sodium hexafluoroantimonate, benzaldehyde, cyclohexanone, acetophenone, benzophenone,

butyl methyl ketone, ethylene glycol, and 2,2-dimethyl-1,3-propanediol were used without further purification. Solvents were distilled after removal of incorporated water by usual methods and stocked over molecular sieves (4 Å).

Measurements. Melting points of the hydrazinium salts **3** synthesized were determined by Thomas Hoover capillary melting point apparatus and are uncorrected. FT/IR spectra were recorded on a JASCO FT/IR-3. ^{1}H NMR spectra were recorded on a Varian EM 360 A FT/NMR spectrometer, using tetramethylsilane (TMS) as an internal standard. Elemental analyses were carried out with a PERKIN ELMER model 240C CHN analyzer.

Synthesis of Catalysts

1-Benzyl-1,1-dimethyl-2-benzoylhydrazinium hexafluoroantimonate (3a). A solution of 1,1-dimethyl hydrazine (4.50 g, 75 mmol) in benzene (20 mL) is dropped to a solution of benzoyl chloride (10.51 g, 75 mmol) in benzene (50 mL) for 10 min at room temperature. The collected yellow precipitate by filtration is dissolved in small amount of water and titrated with 0.1 N aqueous NaOH solution in the presence of an indicator phenolphthalein, and then the reaction mixture is evaporated and extracted with $CHCl_3$ to give 1,1-dimethyl-2-benzoylhydrazide (10.46 g, 13.7 mmol) in 85% yield. A homogeneous solution of benzyl bromide (20 g, 117 mmol) and the obtained 1,1-dimethyl-2-benzoylhydrazide (1.64 g, 10 mmol) is stirred at room temperature for 2 days. A white precipitate is collected by filtration and dissolved in water (20 mL). $NaSbF_6$ (2.60 g, 10 mmol) is added to the aqueous solution in one portion. White precipitates are collected and recrystallized from methanol. Yield: 4.42 g (9.0 mmol, 90%); mp 127.2-129.3 ℃; IR (KBr) 3518, 1685.4, 652.7 cm $^{-1}$; ^{1}H NMR (acetone-d_6) δ 7.92-7.50 (m, 10H, arom), 5.35 (s, 2H, CH_2), 3.80 (s, 6H, $(CH_3)_2$). Anal. Calcd for $C_{16}H_{19}F_6N_2OSb$: H, 3.87; C, 39.12; N, 5.70; Found: H, 3.96; C, 39.55; N, 5.70.

1-Benzyl-1,1-dimethyl-2-(*p*-nitrobenzoyl)hydrazinium hexafluoroantimonate (3b). To a solution of *p*-nitrobenzoyl chloride (3.70 g, 20 mmol) in ether (40 mL) a solution of 1,1-dimethyl hydrazine (1.20 g, 20 mmol) in ether (20 mL) is dropped for 10 min at room temperature. The collected yellow precipitate (crude 100%), hydrogen chloride salt of 1,1-dimethyl-2-benzoylhydrazid is dissolved in water and neutralized with 0.1 N NaOH solution in the presence of an indicator phenolphthalein and followed by evaporation of almost water and then extraction with $CHCl_3$ to give 1,1-Dimethyl-2-benzoylhydrazid (3.43 g, 16.4 mmol) in 82% yield. A homogeneous solution of benzyl bromide (20.0 g, 117 mmol) and the obtained 1,1-Dimethyl-2-benzoylhydrazide (3.43 g, 16.4 mmol) is stirred at room temperature for 3 days. A yellow precipitate is collected by filtration, washed with acetone (30 mL), and dried under vacuum. $NaSbF_6$ (4.24 g, 16.4 mmol) is added to the methanol solution of the precipitate and the mixture is stirred at room temperature for 4 h. Methanol is evaporated and the residue is extracted with ethylacetate (30 mL×3), and the solvent is evaporated to give a white precipitate, which is collected and recrystallized from methanol. Yield: 8.10 g (15.1 mmol, 92%); mp 203.9-206.1 ℃; IR (KBr) 3320, 1697.7, 636.0 cm $^{-1}$; ^{1}H NMR (acetone-d_6) δ 8.46-7.87 (q, 4H, arom), 7.47 (s, 5H, Ph), 5.20 (s, 2H, CH_2), 3.73 (s, 6H, $(CH_3)_2$). Anal. Calcd for $C_{16}H_{18}F_6N_3O_5Sb$: H, 3.36; C, 35.83; N, 7.84; Found: H, 3.19; C, 36.00; N, 7.42.

1-(*p*-Methoxybenzyl)-1,1-dimethyl-2-(*p*-nitrobenzoyl) hydrazinium hexafluoroantimonate (3c). A homogeneous solution of *p*-methoxybenzyl bromide (20.0 g, 99.5 mmol) and the obtained 1,1-Dimethyl-2-benzoylhydrazide (3.82 g, 18.3 mmol) is stirred at room temperature for 4 days. A white precipitate (6.25 g, 15.2 mmol, 83%) is collected by filtration and the collected is washed with acetone (30 mL), and dried under vacuum. $NaSbF_6$ (1.29 g, 5.0 mmol) is added to the methanol solution of the precipitate (2.05 g, 5.0 mmol) and the mixture is stirred at room temperature for 4 h. Methanol is evaporated and the residue is extracted with ethylacetate (30 mL×3), and the solvent is evaporated to give a white precipitate, which is collected and recrystallized from methanol. Yield: 2.27 g (4.0 mmol, 80%); mp 98.5-102.1 ℃; IR (KBr) 3528, 1689.8, 638.4 cm $^{-1}$; ^{1}H NMR (acetone-d_6) δ 8.37-7.87 (q, 4H, arom) 7.57-6.82 (q, 4H, arom), 5.33 (s, 2H, CH_2), 3.93 (s, 6H, $(CH_3)_2$), 3.77 (s, 3H, CH_3O). Anal. Calcd for $C_{17}H_{20}F_6N_3O_4Sb$: H, 3.54; C, 36.06; N, 7.42; Found: H, 3.87; C, 36.30; N, 7.60.

Acetalization

2-Phenyl-1,3-dioxolane (2a); Typical procedure. A mixture of benzaldehyde (3.20 g, 30 mmol), ethylene glycol (1.86 g, 30 mmol) and 1-benzyl-1,1-dimethyl-2-benzoylhydrazinium hexafluoroantimonate (**3a** : 0.147 g, 0.3 mmol) in benzene (30 mL) is heated to reflux. Water formed during the reaction is removed azeotropically (Dean-Stark trap) until the calculated amount of water is formed (for 1 h). The mixture is cooled to room temperature, poured into 30 mL of 0.1 N NaOH solution and extracted with benzene (3×100 mL). The benzene extract is dried ($MgSO_4$), evaporated, and the residue is distilled under reduced pressure: colorless oil: yield: 4.10 g (91%; GC area 98%; NMR 95%); bp 100-101/10 Torr (lit.[9] 99/8.5 Torr); IR (neat) 3036, 2833, 1459, 1397, 1314, 1220, 1095 cm $^{-1}$; ^{1}H NMR ($CDCl_3$) δ 3.63-3.42 (m, 4H, CH_2CH_2), 5.74 (s, 1H, CH), 7.16 (m, 3H, Ph), 7.52 (dd, 2H Ph).

3,3-Dimethyl-1,5-dioxaspiro[5.5]undecane (4d); Typical procedure. A mixture of cyclohexanone (2.95 g, 30 mmol), 2,2-dimethyl-1,3-propanediol (3.15 g, 30 mmol) and 1-benzyl-1,1-dimethyl-2-benzoylhydrazinium hexafluoroantimonate (**3a** : 0.147 g, 0.3 mmol) in benzene (30 mL) is refluxed. Water formed during the reaction is removed azeotropically (Dean-Stark trap) until the calculated amount of water is formed. The mixture is cooled to room temperature, poured into 0.1 N aq NaOH solution and extracted with benzene (3×100 mL). The benzene extract is dried ($MgSO_4$), evaporated, and the residue is distilled under reduced presure: colorless oil: yield: 4.74 g (94%); bp 79-80/5 Torr (lit.[9] 77/4.5 Torr); ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 6H, 2×CH_3), 1.33-1.75 (br, 10H, 5×CH_2), 3.33 (s, 4H, 2×CH_2).

Results and Discussion

Synthesis of catalysts. Hydrazinium salts **3** were synthesized by exchanging the corresponding halide ions, which were synthesized from 1,1-dimethylhydrazine by the reported

Table 1. Acetalization of Carbonyl Compounds **1** with Equimolar Ethylene Glycol to 1,3-Dioxolanes **2** in the Presence of Hydrazinium Salts **3**

Product 2	Cat.[a]	Temperature	Time (h)	Yield[b] (%)	bp (℃)/Torr or mp (℃) found	reported[g]
a	-	benzene(r. t.)	72	3[c]		
	3a	〃	15	92[c]		
	3b	〃	4	93[c]		
	3c	〃	4	95[c]		
	3a	benzene reflux	1	91	100-101/10	99/8.5
b	〃	〃	1	91	83-84/30	83/30
c	〃	〃	1	89	53-55/20	83/65
d	〃	〃	1	89	65-66/10	91/44
e	〃	〃	1	64	69(MeOH)[d]	68
	3b	〃	1	93		
	3c	〃	1	92		
f	**3a**[e]	toluene reflux	10	71	61(MeOH)[d]	61
	3b[e]	〃	10	91		
	3c[e]	〃	10	91		
g	**3b**[e]	xylene reflux	12	86	124-5/1	123/1
	3b[e]	toluene reflux	20	71		
	TsOH[e]	〃	8.5	82		
h	**3b**	benzene reflux	10	93	89-90/12	89/12
i	〃	〃	10	93	100-1/10	96-97.5/7

[a] 1 mol% of **3** based on the carbonyl compounds was used. [b] Isolated yields by distillation or recrystallization. [c] NMR yields. [d] Solvents for recrystallization. [e] 3 mol% of **3** and 10 equivalents of ethylene glycol to carbonyl compounds were used.

method,[11] with hexafluoroantimonate anion.[12,13] The counter anion exchange reaction was conducted in methanol in cases of **3b** and **3c** because the corresponding halide anion was slightly soluble in water.

$$N(Me)_2NH_2 \xrightarrow[\text{i), iii) in benzene, ii) in } H_2O]{\text{i) } R^1COCl\text{, ii) aq. NaOH (- HCl), iii) } R^2Br} R^2(CH_3)_2N^+NHCOR^1\ Br^- \xrightarrow[\text{in } H_2O \text{ or } CH_3OH]{NaSbF_6} \underset{\mathbf{3}}{R^2(CH_3)_2N^+NHCOR^1\ SbF_6^-} \quad \text{(Eq 1)}$$

3a: $R^1 = C_6H_5$, $R^2 = C_6H_5CH_2$ Yield : 90%

3b: $R^1 = p\text{-}NO_2\text{-}C_6H_4$, $R^2 = C_6H_5CH_2$ Yield : 92%

3c: $R^1 = p\text{-}NO_2\text{-}C_6H_4$, $R^2 = p\text{-}CH_3O\text{-}C_6H_4CH_2$ Yield : 80%

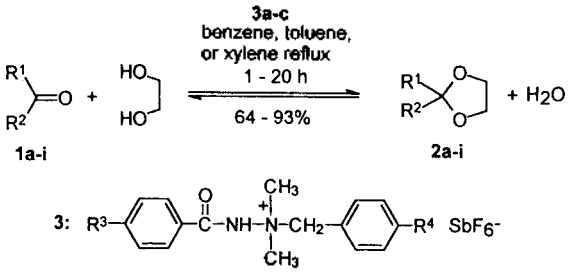
Acetalization. First, catalytic activity of **3** (1 mol%) was examined in the acetalization of benzaldehyde **1a** with equimolar ethylene glycol in benzene at room temperature.

All the hydrazinium salts **3** converted benzaldehyde **1a** to 2-phenyl-1,3-dioxolane **2a** in excellent yield even at room temperature. The reaction was sluggish without catalyst as shown in Table 1. Meanwhile, the acetalization of **1a** was accelerated and the reaction was completed within 1 h with **3a** under the benzene reflux condition. Alkyl aldehyde **1b**, alkyl ketone **1c** and cyclic ketone **1d** were easily converted to the corresponding 1,3-dioxolane **2b-d** in 91, 89, and 89% yield, respectively with 1 mol% of **3a**. In case of dibenzyl ketone, the acetalization was incomplete (64%) with **3a**, however, the acetalization was completed (93, 92%) with **3b** and **3c**. In the cases of the less active alkyl aryl ketone **1f** was also converted to the corresponding 1,3-dioxolane **2f** in 91% yield with 3 mol% of **3b** and **3c** under toluene reflux condition for 10 h, although the acetalization was sluggish and the yield was 71% with 3 mol% of **3a**. The order of the activity was **3c**≅**3b**>**3a** and was in good accordance with that in the cationic polymerization of glycidyl phenyl ether.[10] **3b** was considered as the best catalyst in this system because **3b** is more easily synthesized than **3c**. In case of diaryl ketone **1g** was also converted to 2,2-diphenyl-1,3-dioxolane **2g** under xylene reflux condition in 86% yield. In this case the acetalization activity of **2b** was lower than that of *p*-toluenesufonic acid, however, the selectivities to acid-sensitive car-

Table 2. Acetalization of Carbonyl Compounds **1** with Equimolar 2,2-Dimethyl-1,3-propanediol to 5,5-Dimethyl-1,3-dioxanes **4** in the Presence of Hydrazinium Salts **3**

Product 4	Cat.[a]	Temperature	Time (h)	Yield[b] (%)	bp (℃)/Torr or mp (℃) found	reported[g]
a	**3a**	benzene reflux	1	94	86-88/1	56-58/0.1
	3b	〃	1	94	34-35	34-35
	3c	〃	1	95		
d	**3a**	〃	1	95	79-80/5	77/4.5
f	**3a**[c]	〃	1	66	88-89/3	88-89/3
	3b[c]	toluene reflux	1	93		
	3c[c]	〃	1	92		
g	**3b**[c]	xylene reflux	15	85	79-80	79-80
h	**3b**[c]	benzene reflux	3	94	135-6/1	96/0.06

[a] 1 mol% of **3** based on the carbonyl compounds was used. [b] Isolated yields. [c] 3 mol% of **3** and 10 equivalents of 2,2-dimethyl-1,3-propanediol to carbonyl compounds were used.

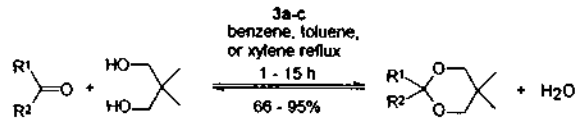


1, 2	R^1	R^2
a	Ph	H
b	n-C_5H_{11}	H
c	n-C_6H_9	Me
d	-$(CH_2)_5$-	
e	CH_2Ph	CH_2Ph
f	Ph	Me
g	Ph	Ph
h	$MeOOCCH_2$	Me
i	$C_2H_5OOC(CH_2)_2$	Me

3	R^3	R^4
a	H-	H-
b	NO_2-	H-
c	NO_2-	MeO-

bonyl group-containing 1,3-dioxolanes **2i** and **2j** were higher (93%) than that of *p*-toluenesulfonic acid.[1]

A few carbonyl compounds were also examined to the corresponding 5,5-dimethyl-1,3-dioxanes **4** with 2,2-dimethyl-1,3-propanediol in the presence of 1-3 mol% of **3**.



1a, d, f, g, h **4a, d, f, g, h**

1, 4	R^1	R^2	1, 4	R^1	R^2
a	Ph	H	g	Ph	Ph
d	-$(CH_2)_5$-		h	$MeOOCCH_2$	Me
f	Ph	Me			

Results shown in Table 2 demonstrate that **3b** effectively catalyzes the acetalization to give high yields of various 1,3-dioxanes **4** under the xylene reflux conditions.

Thus, a new class of acid catalysts for acetalization is developed which have high activities in the acetalization not only of arylketones but also of acid-sensitive carbonyl group-containing ketones. The significances of these catalysts are easy to use owing to their less hygroscopic nature and chemical stability toward air, water, and organic solvents.

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Dynamics and Transport of Molecules Studied by Transient Grating Method: Methyl Red in Solution

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Time profile of the transient grating signal induced by a nanosecond pulsed laser excitation of methyl red is investigated in alcohols and toluene at several solvent temperatures. The signal decays biexponentially with well-separated time constants; the faster decay is identified as due to thermal diffusion of the solvents and the slower one as mainly due to translational diffusion of the solute. The measured translational diffusion constants of methyl red in toluene are close to a hydrodynamic prediction with a slip boundary condition while those in alcohols are larger by 30% and increase slightly with the size of alcohols. We compare the results with modified hydrodynamic models.

Introduction

Transient grating (TG) technique,[1] also known as laser-induced dynamic grating,[2] forced Rayleigh scattering,[3] holographic relaxation spectroscopy,[4] and many other names, is a sensitive method of measuring molecular relaxation and diffusion. The time scale that the TG technique covers is from femtoseconds to minutes. In the ultrashort time scale (shorter than a nanosecond),[4] the depopulation,[5,6] the vibrational dynamics,[7] the overall rotation,[6,8] the local structural relaxation,[9] the ultrasonic wave propagation,[10] the electron transfer,[11] etc in liquid or solid phases have been studied with state-of-the-art instrumentations of ultrafast lasers combined with precise control over optical and electronic timings. In the other extreme (slow) time scale, the TG method employs conventional instrumentations: cw lasers, a mechanical shutter and common detection electronics. The method probes mainly the translational diffusion of a dye in rigid hosts such as polymers,[12~14] liquid crystals,[15~17] or polymeric solutions.[18~20] The time resolution of such experiments is limited

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