

- (15) The transient species formed during the decomposition of other benzene 1,4-diazooxides have also been viewed as possible oxidophenyl cations. See, for example, (a) M. J. S. Dewar and K. Narayanaswami, *J. Am. Chem. Soc.*, **86**, 2422 (1964); (b) J. K. Stille, P. Cassidy, and L. Plummer, *ibid.*, **85**, 1318 (1963); (c) T. Kunitake and C. C. Price, *ibid.*, **85**, 761 (1963).
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Hypervalent Organoiodine. Reactions of Silver Arylsulfonates with Iodobenzene Dichloride

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The synthesis of iodobenzene diacetate (1) from iodobenzene dichloride (2) and silver acetate, reported by Alcock and Waddington in 1963,¹ suggests that a similar synthesis of iodobenzene ditosylate (3) should be possible. However, when we allowed 1 equiv of 2 to react with 2 equiv of silver tosylate in acetonitrile, compound 3 was not obtained. Instead, phenylhydroxytosyloxyiodine (4a, 46%) and *p*-toluenesulfonic acid (39%) were isolated, and silver chloride was obtained in only 62% yield. Compound 4a was identified by its spectral (IR, NMR) comparison with authentic material prepared by the action of toluenesulfonic acid on 1, a reaction described by Neiland and Karele in 1970.² That phenylhydroxytosyloxyiodine exhibits structure 4a and not the tautomeric structure 5 has recently been established by x-ray analysis.³ The simplest explanation for the formation of 4a and toluenesulfonic acid in comparable yields rests on the assumption that ditosylate 3 enjoys intermediate existence. Hydrolysis of 3, either by atmospheric moisture or by adventitious moisture in the reaction solvent, would lead to the observed products.

Indeed, when the reaction between 2 and silver tosylate was conducted under extremely dry conditions, compound 4a was not obtained. However, all attempts to isolate 3 failed. The crude product, a waxy, yellow solid, was resolved by trituration with ether into silver tosylate and a nearly colorless semisolid which rapidly changed to a black oil upon solvent removal. That the oil is an iodine-containing (not molecular I₂) compound was verified by elemental analysis, but a definitive structural assignment could not be made. When the oil was allowed to stand in air, it crystallized to a brown solid which was shown to consist *partially* of toluenesulfonic acid.

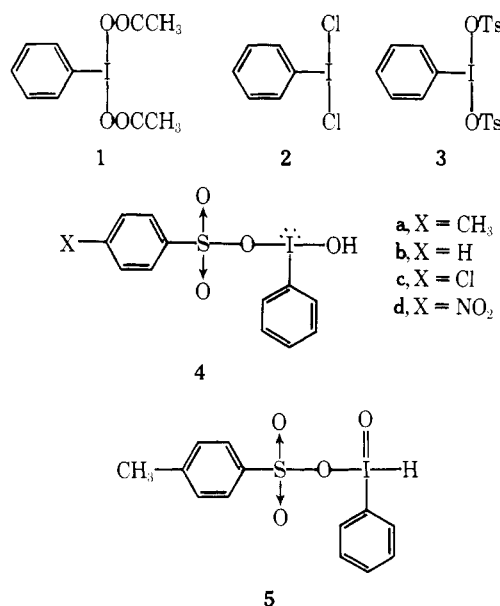
When 2 was allowed to react, in turn, with silver benzenesulfonate, silver *p*-chlorobenzenesulfonate, and silver *p*-nitrobenzenesulfonate, the hydroxysulfonates 4b and 4c and, presumably, the hydroxysulfonate 4d were obtained (yields are given in Table I). Note that the yield of silver chloride failed to exceed 65% in all of those reactions. Compounds 4a-d are insoluble in acetonitrile (the reaction solvent) and crystallize from solution subsequent to the removal of silver chloride. Crystallization may occur shortly after filtration or hours may pass before crystals appear. In the latter instance, addition of a small quantity (ca. 0.1 g) of water to the filtrate has been observed to facilitate product formation.

Authentic samples of 4b, 4c, and 4d were prepared by treatment of 1 with the appropriate sulfonic acid in acetonitrile and were characterized by elemental (C, H, I) and spectral analysis. The structures assigned to the materials derived from

Table I

X	PhICl ₂ + Ag ⁺ -O ₃ SC ₆ H ₄ X		PhI(OAc) ₂ + HO ₃ SC ₆ H ₄ X	
	Yield of 4, %	Yield of AgCl, %	X	Yield of 4, %
CH ₃	46	62	CH ₃	93
H	64	61	H	72
Cl	39	60	Cl	51
NO ₂	32	47	NO ₂	91

iodobenzene dichloride (2) were then confirmed by spectral (IR, NMR) comparisons.



Compound 4d exhibited erratic behavior. For example, for three different PhICl₂/AgO₃SC₆H₄NO₂ runs, product melting points of 126–129, 141–143, and 153–156 °C were recorded. Similarly, for two different PhI(OAc)₂/HO₃SC₆H₄NO₂ runs, product melting points of 126–128.5 and 142–144.5 °C were observed, although most products derived from 1 melted in the 140–150 °C range. Melting points as high as 166–167.5 and 169–171.5 °C have been noted for “purified” 4d. The NMR spectrum of 4d in Me₂SO-*d*₆ has been difficult to reproduce. Two types of NMR spectra have been observed, and they exhibit significantly different aromatic patterns. One of these is nearly identical with the spectrum of a 1:1 mixture of iodobenzene and *p*-nitrobenzenesulfonic acid, and it seems that 4d may undergo reductive decomposition in Me₂SO-*d*₆. We have been unable to isolate dimethylsulfone-*d*₆, the likely oxidation product, but if it is formed, it would be present in very small quantities. The NMR spectra of 4a, 4b, and 4c are clearly distinct from those of 1:1 mixtures of iodobenzene and the corresponding benzenesulfonic acids.

Finally, we have found that 4a can be synthesized directly from iodobenzene. When a solution of iodobenzene (5 mmol) and silver tosylate (10 mmol) in acetonitrile was subjected to a stream of chlorine gas, 4a was formed and was isolated in 48% yield.

Experimental Section

General. NMR spectra were recorded on a Varian Model A-60 NMR spectrometer, Me₄Si being used as an internal reference. IR spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. However, reported band positions in the 8–24 μ range should be regarded as approximate

($\pm 0.05 \mu$). Melting points are uncorrected. Elemental analyses were performed at Galbraith Laboratories, Knoxville, Tenn.

The silver salts employed in this study were prepared by treatment of the corresponding benzenesulfonic acids in acetonitrile with silver(I) oxide. The sulfonic acids were purchased from Eastman Organic Chemicals, both toluenesulfonic and benzenesulfonic acids as their monohydrates. Some silver tosylate was purchased from Eastman Organic Chemicals. Iodosobenzene diacetate (98%) was purchased from the Aldrich Chemical Co., and silver(I) oxide was purchased from MCB. Iodosobenzene dichloride was synthesized from iodobenzene and chlorine and was recrystallized from nitromethane just prior to use.

Compounds **4a-d**, derived from iodosobenzene dichloride, were identified by IR and ^1H NMR spectral comparisons with authentic materials derived from iodosobenzene diacetate (as described herein). Spectra are *nearly* identical in such comparisons but there are occasional minor differences, sometimes due, we believe, to instrument fluctuations.

Reaction of 1 with *p*-Toluenesulfonic Acid in CH_3CN . *p*-Toluenesulfonic acid monohydrate (7.61 g, 40 mmol), dissolved in a minimum quantity of CH_3CN , was added to a solution/suspension of **1** (6.44 g, 20 mmol) in CH_3CN (45 mL) at room temperature. The reaction mixture immediately cleared and turned yellow and, upon standing at room temperature, gave phenylhydroxytosyloxyiodine (**4a**) as fine white needles with a yellowish hue. Two crops were isolated, yield 7.62 g (93%). The crude product was washed with acetone (removes *p*-toluenesulfonic acid) and ether (removes acetic acid) and dried: mp 135–138 °C; the NMR spectrum of this material has been thoroughly described elsewhere;³ IR (KBr) bands at 6.18, 6.25, 6.37, 6.68, 6.80, 6.96, 7.15, 8.01 (sh), 8.5, 8.9, 9.6, 9.9, 10.02, 12.33, 12.82, 13.21, 13.68, 14.35, 15.22, 17.38, 17.65, 21.8, 22.3 μ .

Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{ISO}_4$: C, 39.81; H, 3.34; I, 32.36. Found: C, 39.53; H, 3.09; I, 32.89.

Reaction of 2 with Silver *p*-Toluenesulfonate in Acetonitrile. A solution of **2** (1.00 g, 3.64 mmol) in CH_3CN (20 mL) was added dropwise to a solution of silver *p*-toluenesulfonate (2.03 g, 7.28 mmol) in CH_3CN (20 mL) over a period of ca. 15 min at room temperature. The reaction mixture was then allowed to stir for 45 min at room temperature after which time the AgCl which had precipitated was isolated and dried, yield 0.647 g (62%). Upon refrigeration, the filtrate yielded phenylhydroxytosyloxyiodine (**4a**) as white needles which have a yellowish hue in light: yield 0.580 g (46.1%); mp 135–137 °C.

The final filtrate was concentrated at reduced pressure and 0 °C to a mushy, yellow-white solid. The solid was treated with ether, and 0.205 g of silver *p*-toluenesulfonate was recovered. The resulting ether phase was then concentrated at reduced pressure to a pungent, waxy solid, tan to gray in color. The solid was triturated with acetone and dried in vacuo and had an ^1H NMR spectrum identical with that of *p*-toluenesulfonic acid: yield 0.55 g; mp 89–91 °C.

Reaction of Iodobenzene with Cl_2 in the Presence of $\text{AgO}^+ \cdot \text{O}_3\text{SC}_6\text{H}_4\text{CH}_3$. Iodobenzene (1.08 g, 5 mmol) and silver *p*-toluenesulfonate (2.79 g, 10 mmol) were dissolved in CH_3CN (20 mL). The resulting solution was stirred vigorously while Cl_2 gas was blown across the surface. The precipitation of AgCl began immediately, and the solution yellowed. After the AgCl (1.23 g, 64.1%) was removed, phenylhydroxytosyloxyiodine (**4a**) crystallized from the filtrate as fine white needles with a pale yellow hue: yield, 0.92 g, (48%); mp 132–134 °C.

Reaction of 1 with Benzenesulfonic Acid. A solution of benzenesulfonic acid monohydrate (0.88 g, 5.0 mmol) in a minimum quantity of CH_3CN was added at once to a solution of **1** (1.6 g, 5 mmol) in CH_3CH (35 mL). After ca. 2 min, fine crystals formed throughout the solution, and, after 1 h, the product, **4b**, was isolated by filtration, washed with acetone and ether, and dried: yield 1.58 g (71.5%); mp 127–128 °C; ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 7.15–7.85 (complex multiplet, aromatic hydrogens), 8.05–8.35 (complex multiplet, aromatic hydrogens), 8.90 (s, OH), integration 8:1.8:1.3 (theoretical 8:2:1); IR (KBr) bands at 6.15, 6.36, 6.80, 6.92, 6.96, 7.15, 8.44, 8.85, 9.6, 9.8, 10.05, 13.2, 13.6, 14.45, 14.9, 15.25, 15.95, and 17.6 μ .

Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{SO}_4$: C, 38.11; H, 2.93; I, 33.56. Found: C, 38.11; H, 2.95; I, 33.71.

Reaction of 2 with Silver Benzenesulfonate in CH_3CN . A solution of silver benzenesulfonate (3.26 g, 12.3 mmol) in CH_3CN (20 mL) was added dropwise to a solution of **2** (1.56 g, 5.7 mmol) in CH_3CN (40 mL) with *immediate* precipitation of AgCl which was subsequently isolated and dried (1.00 g, 61.2%). Upon refrigeration, the yellow filtrate yielded phenylhydroxybenzenesulfonoyiodine (**4b**) as well-crystallized needles which were isolated, washed with acetone, and dried: yield 1.36 g (63.5%); mp 123–125 °C.

Reaction of 1 with *p*-Chlorobenzenesulfonic Acid. A solution

of *p*-chlorobenzenesulfonic acid (2.05 g, 10.6 mmol) in CH_3CN (~10 mL) was added at once to a cloudy solution of **1** (3.22 g, 10 mmol) in CH_3CN (50 mL). The reaction mixture cleared to a yellow solution and was allowed to stand for several hours at room temperature (after a small amount of insoluble matter had been removed by filtration) during which time **4c** crystallized from solution. The product was isolated as fine, pale yellow needles, washed with ether, and dried: yield 2.10 g (50.9%); mp 119–120 °C; ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 7.2–7.8 (complex multiplet, aromatic hydrogens), 8.0–8.4 (complex multiplet, aromatic hydrogens), 9.01 (broad singlet, O–H), integration 7:1.76:0.84 (theoretical 7:2:1); IR (KBr) bands at 6.37, 6.75, 6.80, 6.95, 7.18, 8.13, 8.45, 8.9, 9.1, 9.2, 9.45, 9.65, 9.95, 10.05, 11.9, 12.1, 13.2, 13.4, 13.65, 14.05, 14.6, 15.35, 17.6, 17.95, 20.4, 22.3 μ .

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{SO}_4\text{Cl}$: C, 34.93; H, 2.44; I, 30.71. Found: C, 34.71; H, 2.73; I, 30.62.

Reaction of 2 with Silver *p*-Chlorobenzenesulfonate in CH_3CN . A solution of **2** (0.93 g, 3.3 mmol) in CH_3CN (30 mL) was added dropwise to a solution of silver *p*-chlorobenzenesulfonate (2.03 g, 6.7 mmol) in CH_3CN (15 mL) over a period of 15 min with *immediate* precipitation of AgCl. After an additional 1 h, the AgCl was isolated (0.58 g, 59.7%) by filtration. The filtrate, upon standing, yielded phenylhydroxy-*p*-chlorobenzenesulfonoyiodine (**4c**) as fine, white needles: yield 0.55 g (39.2%); mp 119–121 °C.

Reaction of 1 with *p*-Nitrobenzenesulfonic Acid. A solution of *p*-nitrobenzenesulfonic acid (2.03 g, 10 mmol) in a minimum quantity of CH_3CN was added at once to a translucent solution of **1** (1.61 g, 5 mmol) in CH_3CN (25 mL). The reaction mixture immediately cleared to a yellow solution, and, after 1 min, dense, pale yellow plates began to crystallize from solution. After 1 h, the solution was chilled in ice, and the product, **4d**, was isolated, yield 1.92 g (90.8%). The product, after recrystallization from methanol-ether, melted at 145–147 °C; NMR ($\text{Me}_2\text{SO}-d_6$, presumably nondecomposed **4d**) δ 7.5–8.4 (complex multiplet, aromatic hydrogens), this multiplet exhibits lines at δ 7.58, 7.62, 7.68, 7.71, 7.85, 8.17, 8.20, 8.30, and 8.35; 8.75 (very broad singlet, OH), integration 9:1:1 (theoretical 9:1); IR (KBr) bands at 6.19, 6.24, 6.38, 6.59, 6.81, 6.96, 7.13, 7.39, 7.75, 8.05, 8.20, 8.9, 9.6, 9.85, 11.40, 11.65, 13.42, 13.62, 14.4, 15.55, 17.6, 18.0, 21.1 μ .

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{INSO}_6$: C, 34.06; H, 2.38; I, 29.99. Found: C, 33.90; H, 2.48; I, 29.86.

Reaction of 2 with Silver *p*-Nitrobenzenesulfonate. A solution of silver *p*-nitrobenzenesulfonate (3.22 g, 10.4 mmol) in CH_3CN (40 mL) was added dropwise at room temperature to a solution of **2** (1.43 g, 5.2 mmol) in CH_3CN (40 mL). After an additional 0.5 h the AgCl which had precipitated was isolated and dried, yield 0.70 g (47.3%). The filtrate was placed under refrigeration and yielded 0.71 g (32.1%) of **4d** as dense plaques of fine, pale yellow crystals, mp 143–145 °C.

Reaction of 2 with Silver *p*-Toluenesulfonate in CH_3CN under Anhydrous Conditions. The following experiment was conducted under dry nitrogen in a controlled atmosphere glovebox.

Dry silver tosylate (2.78 g, 0.01 mol) was mixed with acetonitrile (freshly distilled from P_2O_5) in a quantity just sufficient to effect solution, and **2** (1.38 g, 0.005 mol, freshly recrystallized from CH_3NO_2) was likewise dissolved in a minimum quantity of dry CH_3CN . The latter solution was added dropwise to the former over a period of about 10 min. After an additional 10 min, the AgCl which had precipitated was isolated, dried, and weighed (0.94 g, 65.5%). The clear, yellow filtrate, when it was allowed to stand overnight, *did not* yield phenylhydroxytosyloxyiodine (**4a**).

The filtrate was then concentrated in vacuo to a yellow, waxy solid (2.98 g): NMR (CD_3CN) δ 1.9 (s, CH_3CN impurity), 2.75 (s, 66 mm), 7.1–7.9 (m, 123 mm), 13.7 (s, 14 mm). A portion (0.48 g) was redissolved in CH_3CN , an observation which indicates clearly that the *insoluble 4a* was not present in the crude product. A sample (2.00 g) of the crude product was triturated with ether, and 0.80 g of an ether-insoluble, water-soluble, tan-gray solid was obtained and found to consist primarily of unreacted silver tosylate: duplicate gravimetric silver analyses (by the NaCl precipitation method) gave values of 23.1 and 27.1% for the percentage by weight of silver. The ether solution from the trituration experiment was concentrated to a colorless to pale yellow semisolid (0.85 g) which rapidly changed to a black oil. After several days, the oil crystallized *partially* to a brown solid: NMR (CD_3CN) δ 1.2 and 3.6 (t and q of occluded ether), 2.40 (s, 14.5 mm), 7.0–8.0 (m, 25.5 mm), 10.82 (s, 7 mm).

Anal. C, 41.43; H, 4.98; I, 35.22.

The brown solid is water soluble and gives a brown, cloudy, acidic solution (pH ~2–3). Titration of those solutions with NaOH (0.099 N) gave an equivalent weight of ~300. The solid material is only slightly soluble in CHCl_3 , but “recrystallization” of a portion from that solvent gave a solid, mp 102–105 °C, identified by NMR analysis as toluenesulfonic acid.

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Registry No.—1, 3240-34-4; 2, 932-72-9; 4a, 27126-76-7; 4b, 61477-31-4; 4c, 61477-32-5; 4d, 61477-33-6; *p*-toluenesulfonic acid, 104-15-4; benzenesulfonic acid, 98-11-3; *p*-chlorobenzenesulfonic acid, 98-66-8; *p*-nitrobenzenesulfonic acid, 138-42-1; silver *p*-toluenesulfonate, 16836-95-6; silver benzenesulfonate, 39938-06-2; silver *p*-chlorobenzenesulfonate, 39938-10-8; silver *p*-nitrobenzenesulfonate, 39938-18-6; iodobenzene, 591-50-4.

References and Notes

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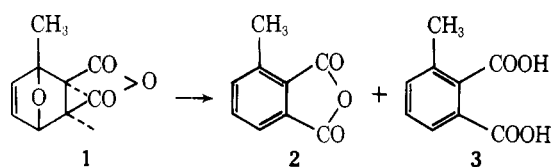
Improved Synthesis of 3-Methylphthalic Anhydride¹

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The Diels–Alder reaction of furans with maleic anhydride (MA) is known to occur in excellent yield in many cases.³ However, the aromatization of these adducts to derivatives of phthalic anhydride is less well documented. In an early paper *exo-cis*-1-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (1), the adduct of 2-methylfuran and MA, 2, was converted to 3-methylphthalic anhydride (2) by treatment with hydrogen bromide in acetic acid but no details or yields were given.⁴



In this laboratory, 3,6-dimethylphthalic anhydride was prepared in 45% yield⁵ by adding the 2,5-dimethylfuran–MA adduct to 90% sulfuric acid at -6 to 0 °C. Similarly, 3-meth-

ylphthalic anhydride was prepared from 1 in 38% yield.⁶ The adduct of 2-acetoxymethylfuran and MA was converted into 3-acetoxymethylphthalic anhydride in 57% yield by heating with acetic anhydride containing sulfuric acid.⁷ In this paper we report on our efforts to improve the yield of 2 by treatment of 1 with acidic reagents. In addition to the isolation of 2, we also examined the reaction mixtures for 3-methylphthalic acid (3) and other compounds, but the side products, when isolated, proved to be tars, except in one experiment (no. 5, Table I). No attempt was made to isolate highly water-soluble compounds.

Of the acidic reagents tried, 98% sulfuric acid proved the most promising. The best result (expt 2), a 66% yield, was obtained when the mixing of reagents was done at very low temperatures. In order to attain a low-temperature liquid medium with sulfuric acid a cosolvent, sulfolane, was needed. The desirability of having a low temperature may be explained by assuming that one reason for getting a low yield in these reactions is that an acid-catalyzed reversal of the Diels–Alder reaction^{8,9} competes with acid-catalyzed dehydration to the desired product. This reversal of the Diels–Alder reaction is less important at lower temperatures and hence a higher yield of dehydration product results. In support of this concept, the fact that a 25% yield of 5-acetyl-2-methylfuran¹⁰ was obtained in a $\text{BF}_3\text{-Ac}_2\text{O-AcOH}$ medium (expt 5, Table I) is pertinent. This compound undoubtedly arises from acetylation of the 2-methylfuran formed by reversion of the Diels–Alder adduct to its components. In other acidic media used any 2-methylfuran formed was converted either into water-soluble products or tars.

Experimental Section¹¹

exo-cis-1-Methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (1). In the best of several large-scale runs, 216 g (2.20 mol) of freshly distilled maleic anhydride was dissolved in 600 mL of dry ether freshly distilled from Grignard reagent.¹² To this solution 4 g of hydroquinone and 200 g (2.44 mol) of freshly distilled 2-methylfuran were added at room temperature. After 4 h the mixture was placed in a refrigerator overnight. The crystals (322 g, 81.3% based on MA) which had separated were collected and washed with an ether–petroleum ether mixture and melted at $80\text{--}81$ °C. Further cooling of the combined filtrates yielded 48.6 g (12.3%) of 1, mp $79\text{--}80$ °C.¹³ The total yield was thus 94.6% based on MA and 85% based on 2-methylfuran. In order to obtain such high yields it is important that all reactants and solvents be freshly distilled. As we never tried a run without hydroquinone we do not know if the presence of hydroquinone is necessary.

3-Methylphthalic Anhydride (2). The highest yields obtained are represented by expt 3, Table I. On a large scale 250 mL of concentrated H_2SO_4 (98%) was dissolved in 100 mL of freshly distilled sulfolane¹⁴ and the solution was cooled to -55 °C (alcohol thermometer) with dry ice–isopropyl alcohol. Finely powdered, freshly

Table I. Conversion of 1 to 2^a

Expt	Acid medium	Conditions	Yield, %		
			2	3	Tar, other
1 ^a	98% H_2SO_4	-20 to -10 °C, 4 h 25 °C, 1 h	38	0	0
2	85% H_2SO_4	$0\text{--}26$ °C, 2 h	1	25	0
3 ^a	98% H_2SO_4 in sulfolane	-55 to -45 °C, 3 h -45 to 26 °C, 3 h	66	0	0
4 ^a	HF (liq)	-78 to 26 °C, 24 h	30	5	65
5	$\text{BF}_3\text{-Ac}_2\text{O}$, HOAc	25 °C, 3 h	0	0	25 ^b
6	80% H_3PO_4 , 20% H_2SO_4	$0\text{--}27$ °C, 2 h	5	5	0
7	71% $\text{CH}_3\text{SO}_3\text{H}$, P_2O_5 ^c	$0\text{--}26$ °C, 5 h	10	0	0
8	71% $\text{CH}_3\text{SO}_3\text{H}$	$0\text{--}26$ °C, 5 h	0	0	100 ^d
9	Dry HCl in ether	$0\text{--}25$ °C, 3 h	0	0	100 ^d

^a The reactions were carried out in general with 5–10 g of 1 and appropriate volumes of the acidic reagents, e.g., 50–100 mL. All productive experiments were run in duplicate with excellent agreement of results. ^b 5-Acetyl-2-methylfuran. ^c 1 equiv of P_2O_5 added for the 29% of H_2O . ^d Starting material, 1.