powder. Anal. Found: C, 82.78; H, 7.60; Cu, 3.76; N, 0.45; Cl, 0.27; Ca, 0.20 (detection limit is 0.20%).

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Registry No. BrLi, 7550-35-8; copper cyanide, 544-92-3.

Formylation of Aromatic Compounds with CO in HSO_3F–SbF_5 under Atmospheric Pressure

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The formylation of aromatic compounds such as benzene, toluene, xylenes, mesitylene, indan, tetralin, fluorobenzene, chlorobenzene, and bromobenzene was carried out in HSO_3F–SbF_5 under atmospheric CO pressure at 0 °C. In HSO_3F–SbF_5, both formylation and sulfonation took place to give formyl and sulfonyl compounds. In the case of alkylbenzenes, including toluene, xylenes, mesitylene, and tetralin, formylalkylbenzenesulfonyl fluorides, new compounds, were obtained by a one-pot reaction as well as alkylbenzaldehydes, alkylbenzenesulfonyl fluorides, and bis(alkylphenyl) sulfones. The direct introduction of a formyl and sulfonyl group was achieved in alkylbenzenes. The reaction path of the new compounds is a two-step reaction comprised of formylation as the first step and sulfonation as the second step. The product composition was strongly dependent on the acid strength of the HSO_3F–SbF_5 systems. The formyl compounds became predominant with increasing acidity of the HSO_3F–SbF_5 system. On the other hand, only sulfonyl compounds were produced when the acidity of the HSO_3F–SbF_5 system was low.

Introduction

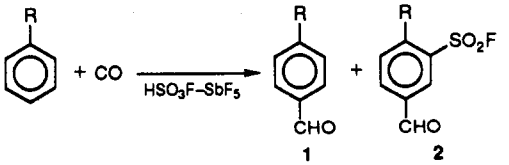
The formylation reactions of aromatic compounds with acid catalysts and CO are well-known as Gattermann–Koch reactions.[1] After Gattermann and Koch published their original paper concerning the synthesis of *p*-tolualdehyde from toluene and CO in the HCl–$AlCl_3$–Cu_2Cl_2 system,[2] other catalyst systems such as HF–BF_3,[3] HF–SbF_5,[4] HF–CF_3SO_3H–BF_3,[5,6] and CF_3SO_3H[7] have been extensively investigated for this reaction. In most cases, these formylations have been carried out under high pressure CO. There is continuing interest in the formylation of aromatic compounds with CO under milder conditions.

It has been demonstrated that HSO_3F is the strongest Brønsted acid and has become a widely used superacid solvent.[8] The systems such as HSO_3F–SbF_5 and HSO_3F–SbF_5–SO_3 have been recognized as the most highly acidic media;[9,10] however, the HSO_3F–SbF_5 system has not been used as a formylation catalyst. This paper investigates whether the HSO_3F–SbF_5 system can be used as a catalytic system in the formylation of aromatic compounds and reveals which specific reactions occur.

In this paper, we wish to report the formylation of aromatic compounds in HSO_3F–SbF_5 under atmospheric CO pressure at 0 °C and the formation of the new compounds, formylalkylbenzenesulfonyl fluorides as well as alkylbenzaldehydes, alkylbenzenesulfonyl fluorides, and bis(alkylphenyl) sulfones by a one-pot reaction. The composition of these four products based on reaction conditions was also investigated.

Results and Discussion

When alkylbenzene was slowly added to a mixture of HSO_3F and SbF_5 with vigorous stirring under atmospheric CO pressure at 0 °C, formylalkylbenzenesulfonyl fluoride **2** as well as alkylbenzaldehyde **1** was obtained by a one-pot reaction as follows:



R = alkyl group

Attempts to extend this reaction to a variety of aromatic

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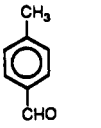
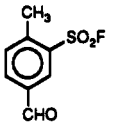
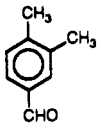
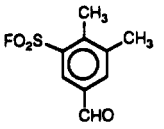
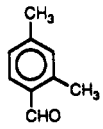
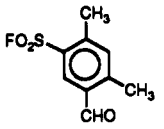
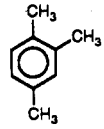
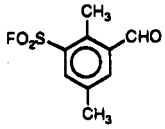
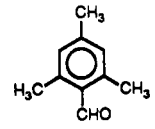
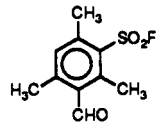
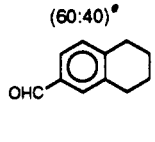
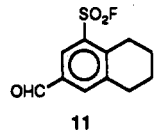
Table I. Synthesis of Formylalkylbenzenesulfonyl Fluorides[a]

substrate	reactn time (h)	SbF_5 (mmol)	product, yield (%)	
toluene	168	138	 2	 7 90 (76:24)[b]
o-xylene	96	138	 6	 8 78 (95:5)[c]
m-xylene	24	69	 0	 4 93
p-xylene	96	138	 6	 9 79 (95:5)[d]
mesitylene	48	69	 48 (60:40)[e]	 10 34
tetralin	24	138	 2	 11 21 (90:10)[f]

[a] The reaction was carried out using 20 mmol of substrate and 174 mmol of HSO_3F under atmospheric pressure of CO. The structures of main products are shown. [b] Isomer ratio of 3-formyl-6-methylbenzenesulfonyl fluoride:3-formyl-4-methylbenzenesulfonyl fluoride. [c] Isomer ratio of 5-formyl-2,3-dimethylbenzenesulfonyl fluoride:5-formyl-2,4-dimethylbenzenesulfonyl fluoride. [d] Isomer ratio of 3-formyl-2,5-dimethylbenzenesulfonyl fluoride:5-formyl-2,4-dimethylbenzenesulfonyl fluoride. [e] Isomer ratio of 2,4,6-trimethylbenzaldehyde:2,4,5-trimethylbenzaldehyde. [f] Isomer ratio of 5-(fluorosulfonyl)-7-formyltetralin:7-(fluorosulfonyl)-5-formyltetralin.

compounds gave several new compounds with the results summarized in Table I. The formyl group was exclusively introduced into the para position of the alkyl group in all cases. It has been known that the Gattermann–Koch formylation is an electrophilic substitution reaction and that the formyl group is introduced into the para position of an alkyl group with high positional selectivity.[4,6] This characteristic has been interpreted as being due to steric hindrance where the para substitution is greatly favored if the transition state of highest energy of the reaction is like the intermediate arenium ion (σ-complex), where a

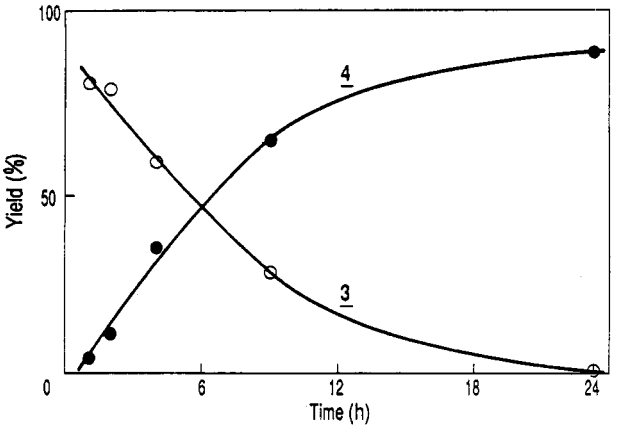


Figure 1. Time dependence of composition of products. The reaction was carried out using 20 mmol of *m*-xylene, 174 mmol of HSO_3F, and 69.0 mmol of SbF_5 under atmospheric pressure of CO at room temperature: (3) 2,4-dimethylbenzaldehyde; (4) 2,4-dimethyl-5-formylbenzenesulfonyl fluoride.

Table II. Formylation of Aromatics[a]

substrate	SbF_5 (mmol)	yield of aldehyde (%)	substrate	SbF_5 (mmol)	yield of aldehyde (%)
benzene	138	74	indan	138	71 (91:9)[g]
toluene	69	95 (90:10)[b]	tetralin	138	78 (87:13)[h]
o-xylene	69	99 (93:7)[c]	fluorobenzene	138	92 (99:1)[b]
m-xylene	69	83 (100:0)[d]	chlorobenzene	138	90 (93:7)[b]
p-xylene	69	98	bromobenzene	138	88 (88:12)[b]
mesitylene[e]	69	53 (90:10)[f]			

[a] The reaction was carried out using 20 mmol of substrate and 174 mmol of HSO_3F under atmospheric pressure of CO at 0 °C for 1 h. [b] Isomer ratio of para-substituted benzaldehyde:ortho-substituted benzaldehyde. [c] Isomer ratio of 3,4-dimethylbenzaldehyde:2,3-dimethylbenzaldehyde. [d] Isomer ratio of 2,4-dimethylbenzaldehyde:2,6-dimethylbenzaldehyde. [e] The reaction was carried out for 24 h. [f] Isomer ratio of 2,4,6-trimethylbenzaldehyde:2,4,5-trimethylbenzaldehyde. [g] Isomer ratio of 5-formylindan:4-formylindan. [h] Isomer ratio of 6-formyltetralin:5-formyltetralin.

p-alkyl group is more stabilizing than an *o*-alkyl group.[4,6] The sulfonyl group was introduced into the meta position of the formyl group. The new compounds were obtained from alkylbenzenes such as toluene, xylenes, mesitylene, and tetralin. From benzene, fluorobenzene, chlorobenzene, and bromobenzene, only aldehydes were produced. When the reaction mixture from benzene was heated to 100 °C, the slight formation of formylbenzenesulfonyl fluoride was observed. Consequently, the introduction of both the formyl and sulfonyl group was difficult because of the low reactivity of these aromatics. In the case of indan and tetralin, the decomposition of the saturated ring gave unidentifiable products during the reactions in superacid[11] and resulted in low yield, especially with indan. It became apparent that HSO_3F–SbF_5 was useful for the introduction of two different functional groups, the formyl and sulfonyl group, into alkylbenzenes in the presence of CO by a one-pot reaction.

The time dependence of the product composition from *m*-xylene was investigated in order to verify the reaction path of the new compounds. As shown in Figure 1, 2,4-dimethylbenzaldehyde (3) was formed first, and the yield of 5-formyl-2,4-dimethylbenzenesulfonyl fluoride (4) increased in proportion to the length of reaction time and with a decrease in 3. In control experiments, no formylation of 2,4-dimethylbenzenesulfonyl fluoride (5) and bis(2,4-dimethylphenyl) sulfone (6) was observed with the

(11) Olah, G. A.; Lukas, J. *J. Chem. Soc.* **1967**, *89*, 2227.

Table III. Relation between Products Composition and Acidity[a]

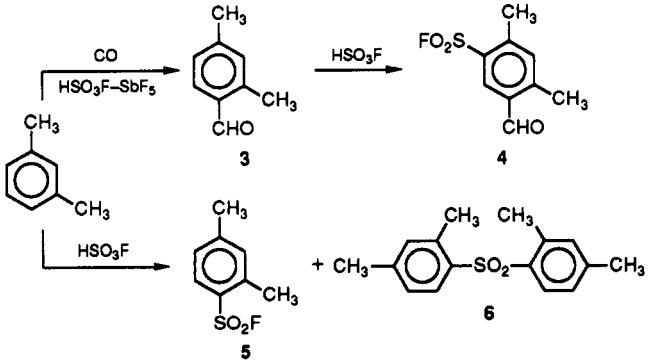
SbF_5 (mmol)	acidity $-H_o$[b]	product yield (%) 1	2	3	4
0	15.1	0	0	50 (83:17)[c]	48 (78:22)[d]
13.8	18.3	17 (100:0)[c]	0	41 (80:20)[c]	36 (79:21)[d]
69.0	22.4	83 (100:0)[c]	4	6 (100:0)[c]	2 (100:0)[d]
138	22.7	79 (100:0)[c]	15	0	0

[a] The reaction was carried out using 20 mmol of *m*-xylene and 174 mmol of HSO_3F under atmospheric pressure of CO at 0 °C for 1 h. [b] The value of H_o was estimated from the data of ref 10. [c] Isomer ratio of 2,4-dimethylbenzene derivative:2,6-dimethylbenzene derivative. [d] Isomer ratio of bis(2,4-dimethylphenyl) sulfone:2,2',4,6'-tetramethyldiphenyl sulfone.

same reaction conditions used in the formylation experiments. It is clear that the reaction path of the new compounds is a two-step reaction comprised of formylation as the first step and sulfonation as the second step.

Aromatic aldehydes could be obtained in high yield with a short reaction time using HSO_3F–SbF_5 under atmospheric CO pressure at 0 °C. These results are listed in Table II. All aromatic compounds were quickly formylated with high yield except for mesitylene. The formyl group was predominantly introduced into the para position of a substituent in all cases. In the case of mesitylene, the formylation proceeded slowly, and the 1,2-shift of the methyl group was observed. It is known that mesitlyene is protonated to form an arenium ion in strong acidic medium[12] because of its high basicity[13] and the arenium ion is considered to be the intermediate for the 1,2-shift of the methyl group.[14] In control experiments, sulfonation of mesitylene using HSO_3F–SbF_5 proceeded more slowly with increasing acidity of the HSO_3F–SbF_5 system. Therefore, protonation of mesitylene prevented formylation and caused the 1,2-shift of the methyl group.

The influence of acid strength, the molar ratio of SbF_5:HSO_3F, on the formylation of *m*-xylene was studied with various compositions of HSO_3F–SbF_5. Both formylation and sulfonation took place, and four kinds of products were produced as follows:



The results are given in Table III. The Hammett acidity function, H_o, as reported in the literature was added to Table III for comparison. When the acidity of the HSO_3F–SbF_5 system was low, only sulfonyl compounds **5** and **6** were obtained. However, formyl compounds **3** and **4** became predominant with the increase in acidity of the HSO_3F–SbF_5 system. A several-fold molar excess of SbF_5 as compared with *m*-xylene was advantageous for formylation in the HSO_3F–SbF_5 system. The Gattermann–Koch formylation was strongly promoted by increasing the acidity of the catalyst systems. This result is based on the fact that a high acidity is necessary for formylation in order to produce electrophilic reactive species such as protonated CO, $[HCO^+]$. The role of SbF_5 in HSO_3F is to increase the acidity of the system and to produce the formyl cation.

$$HSO_3F + SbF_5 \rightleftharpoons [H^+] + [SO_3F^-]\cdot SbF_5$$

$$[H^+] + CO \rightleftharpoons [HCO^+]$$

Formylation of toluene was carried out using analogous catalyst systems such as HSO_3F–$SbCl_5$, HSO_3Cl–SbF_5, and HSO_3Cl–$SbCl_5$. In all cases, tolualdehyde was not obtained, and only sulfonyl compounds were formed. These results seemed to suggest that these systems did not have sufficient acidity for formylation.

In conclusion, the HSO_3F–SbF_5 system is useful not only for formylation but also for the convenient one-pot synthesis of formylalkylbenzenesulfonyl fluorides, new compounds, under mild conditions. Diaryl sulfones have also been produced by a one-pot reaction, and detailed studies are now in progress.

Experimental Section

All aromatic starting materials were of highest available purity and were used without further purification. HSO_3F (Moritaka-gaku), SbF_5 (Aldrich), and CO (Nihonsanso) were all commercial reagents. A Yanagimoto G-3800 and G-6800 gas chromatograph equipped with an on-line automatic integrator was used for GC analysis. A 25-m capillary column (OV-1701) and a 3-m packed column (FFAP) were used for isomer separations, whereas a 1.5-m packed column (OV-17) was utilized for yield determinations. MS analysis (GC-MS) was performed on a Hitachi M-2000 instrument fitted with a 50-m capillary column (OV-1701). ^{1}H-NMR spectra were recorded on a Hitachi R-24B spectrophotometer and ^{13}C-NMR spectra were recorded on a Nihondenshi FX-200 spectrophotometer. Infrared analysis was accomplished on a Nihonbunko IRA-1 instrument.

Formylation Reaction Procedures. The required amounts of HSO_3F and SbF_5 were added into a 300-mL three-necked flask equipped with a CO gas buret under atmospheric pressure at 0 °C. The aromatics were added slowly (40 mmol per h) into a HSO_3F–SbF_5 mixture with vigorous stirring. After the addition of aromatic compounds was complete, the temperature was raised to room temperature. The reaction mixture was quenched in ice–water and extracted by benzene. Products were analyzed by GC and characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectra and elemental analysis after isolation by a vacuum distillation or a recrystallization in benzene-*n*-hexane systems.

4: IR (KBr) 1680 (CO), 1400, 1200 (SO_2F) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.75 (s, 3 H, CH_3), 2.80 (s, 3 H, CH_3), 7.50 (s, 1 H, Ph proton), 8.60 (s, 1 H, Ph proton), 10.35 (s, 1 H, CHO); ^{13}C-NMR ($CDCl_3$) δ 19.7, 20.4 (CH_3), 132.6, 133.0, 134.0, 136.6, 144.1, 148.2 (Ph carbons), 189.9 (CHO); mass M^+ = 216; mp 68–69 °C. Anal. Found (calcd): H = 4.13 (4.20); C = 49.63 (49.99).

7: IR (KBr) 1680 (CO), 1395, 1175 (SO_2F) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.85 (s, 3 H, CH_3), 7.6–8.7 (m, 3 H, Ph protons), 10.30 (s, 1 H, CHO); ^{13}C-NMR ($CDCl_3$) δ 20.8 (CH_3), 131.8, 133.4, 133.9, 134.9, 145.6 (Ph carbons), 189.2 (CHO); mass M^+ = 202; mp 36–37 °C. Anal. Found (calcd): H = 3.61 (3.49); C = 47.91 (47.52).

8: IR (KBr) 1690 (CO), 1405, 1195 (SO_2F) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.55 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 8.17 (s, 1 H, Ph proton), 8.53 (s, 1 H, Ph proton), 10.27 (s, 1 H, CHO); ^{13}C-NMR ($CDCl_3$) δ 17.1, 20.6 (CH_3), 129.0, 129.6, 134.1, 134.3, 136.0, 141.6, 144.1 (Ph carbons), 189.5 (CHO); mass M^+ = 216; mp 71–72 °C. Anal. Found (calcd): H = 4.19 (4.20); C = 49.92 (49.99).

9: IR (KBr) 1690 (CO), 1410, 1200 (SO_2F) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.59 (s, 3 H, CH_3), 3.07 (s, 3 H, CH_3), 8.0–8.7 (m, 2 H, Ph protons), 10.80 (s, 1 H, CHO); ^{13}C-NMR ($CDCl_3$) δ 14.6, 20.7 (CH_3), 134.4, 134.8, 135.2, 136.2, 137.6, 137.7, 138.2 (Ph carbons), 190.2 (CHO); mass M^+ = 216; mp 63–64 °C. Anal. Found (calcd): H = 4.11 (4.20); C = 50.24 (49.99).

10: IR (KBr) 1695 (CO), 1400, 1200 (SO_2F) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.58 (s, 3 H, CH_3), 2.70 (s, 3 H, CH_3), 2.79 (d, 3 H, CH_3,

(12) Olah, G. A. *J. Am. Chem. Soc.* **1965**, *87*, 1103.
(13) (a) McCaulay, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1951**, *73*, 2013. (b) Kilpatrick, M.; Luborsky, F. E. *J. Am. Chem. Soc.* **1953**, *75*, 577.
(14) Olah, G. A.; Olah, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1839.

J = 2.4 Hz), 7.22 (s, 1 H, Ph proton), 10.74 (s, 1 H, CHO); ^{13}C-NMR ($CDCl_3$) δ 17.2, 17.3, 20.6, 23.2 (CH_3), 131.7, 132.1, 134.3, 134.5, 141.9, 143.8, 145.9 (Ph carbons), 192.7 (CHO); mass M^+ = 230; mp 22-23 °C. Anal. Found (calcd): H = 4.76 (4.81); C = 51.80 (52.16).

11: IR (KBr) 1680 (CO), 1380, 1195 (SO_2F) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.7–2.1 (m, 4 H, CH_2), 2.8–3.4 (m, 4 H, CH_2), 7.95 (s, 1 H, Ph proton), 8.37 (s, 1 H, Ph proton), 10.05 (s, 1 H, CHO); ^{13}C-NMR ($CDCl_3$) δ 21.6, 21.9, 27.2, 30.1 (CH_2), 129.1, 129.3, 130.0, 133.8, 136.2, 142.0, 144.6 (Ph carbons), 189.7 (CHO); mass M^+ = 242; mp 64–66 °C. Anal. Found (calcd): H = 4.55 (4.58); C = 54.21 (54.53).

Registry No. 1 (R = Me), 104-87-0; **3**, 15764-16-6; **4**, 128203-58-7; **5**, 445-15-8; **6**, 5184-75-8; **7**, 139650-04-7; **8**, 139689-26-2; **9**, 139650-06-9; **10**, 139650-07-0; **11**, 139689-27-3; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; mesitylene, 108-67-8; tetralin, 119-64-2; antimony pentafluoride, 7783-70-2; 3,4-dimethylbenzaldehyde, 5973-71-7; 2,5-dimethylbenzaldehyde, 5779-94-2; 2,4,6-trimethylbenzaldehyde, 487-68-3; 6-formyltetralin, 51529-97-6; benzene, 71-43-2; indan, 496-11-7; fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; benzaldehyde, 100-52-7; 5-formylindan, 30084-91-4; 4-formylindan, 51932-70-8; 5-formyltetralin, 41828-13-1; *p*-fluorobenzaldehyde, 459-57-4; *o*-fluorobenzaldehyde, 446-52-6; *p*-chlorobenzaldehyde, 104-88-1; *o*-chlorobenzaldehyde, 89-98-5; *p*-bromobenzaldehyde, 1122-91-4; *o*-bromobenzaldehyde, 6630-33-7; *o*-tolualdehyde, 529-20-4; 2,3-dimethylbenzaldehyde, 5779-93-1; 2,4,5-trimethylbenzaldehyde, 5779-72-6; 2,6-dimethylbenzenesulfonyl fluoride, 61153-14-8; 2,2′,4,6′-tetramethyldiphenyl sulfone, 139689-28-4; 3-formyl-4-methylbenzenesulfonyl fluoride, 139689-29-5; 5-formyl-2,4-dimethylbenzenesulfonyl fluoride, 128203-58-7; 7-(fluorosulfonyl)-5-formyltetralin, 139689-30-8; fluorosulfonic acid, 7789-21-1.

α-Alkoxy Ketones from the Nucleophilic Substitution on the Peroxide Bond of 3,3-Disubstituted 1,2-Dioxetanes by Enamines

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The reaction of 1,2-dioxetanes with enamines as π-nucleophiles was investigated. 3,3-Dibenzyl-1,2-dioxetane (**1**) was allowed to react with enamines **2a–c** in methylene chloride to afford after hydrolysis the corresponding α-alkoxylated ketones **4a–c**. Additionally, the reaction of the dimedone-derived enamine **3** with dioxetane **1** yielded the oxidized enamine adduct **4**. Nucleophilic attack of the enamine β-carbon (S_N2 reactivity) on the sterically less hindered site of the dioxetane peroxide bond is proposed to constitute the initial step of the reaction.

The high thermal lability of 1,2-dioxetanes and their cumbersome synthesis are mainly responsible for the limited scope of chemical transformations of these highly reactive and biologically significant molecules.[1] Besides their thermolysis, which yields efficiently triplet-excited carbonyl products, only few reactions of these four-membered ring peroxides have been reported: reduction by lithium aluminum hydride,[2] mercaptans,[3] and biologically relevant reductands,[4] biphilic insertion reactions of phosphines,[5] arsines, and stibines,[6] and the deoxygenation by sulfides[7] and sulfoxylates.[7b]

Recently, we observed the novel S_N2-type reactivity of 3,3-disubstituted dioxetanes with π-nucleophiles[8] such as alkenes and enol ethers, with carbanions[9] and with heteroatom nucleophiles,[10] e.g., amines, sulfides and cyanide, thiocyanate, halide, and even hydroxide ions. To extend the S_N2 chemistry of electrophilic 3,3-disubstituted dioxetanes, it was of interest to explore their reaction with enamines. These ambident π-nucleophiles should react at their β-carbon to produce after hydrolysis β-keto β′-hydroxy ethers.

Results and Discussion

The readily available 3,3-dibenzyl-1,2-dioxetane[9,11] **1** was chosen for the S_N2 reactions with the three morpholino- and piperidino-substituted enamines **2a–c**. The transformations of **1** with **2** were performed in methylene chloride at low temperature (−20 to 0 °C). The primary reaction products were not isolated but hydrolyzed in situ under acidic conditions. The corresponding β-keto β′-

Table I. Reaction of Dioxetane 1 with Enamines 2[a]

enamine	T (°C)	time (h)	yield[b] (%) adduct[c]	yield[b] (%) ketone[d]
2a	−20	2	64 (**4a**)	11
2b	0	3	38 (**4b**)	30
2c	−20	0.5	67 (**4c**)	6

[a] In methylene chloride, up to 10% excess of enamine. [b] Isolated yields of pure products after hydrolysis, column chromatography, and recrystallization. [c] The type of adduct is specified in parentheses. [d] 1,3-Diphenylacetone, isolated together with the ketone derived from enamine hydrolysis.

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