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Reaction of β-Nitrostyrenes with Benzene Catalyzed by Trifluoromethanesulfonic Acid. Formation and Reaction of N,N-Dihydroxyiminium-Benzyl Dications.

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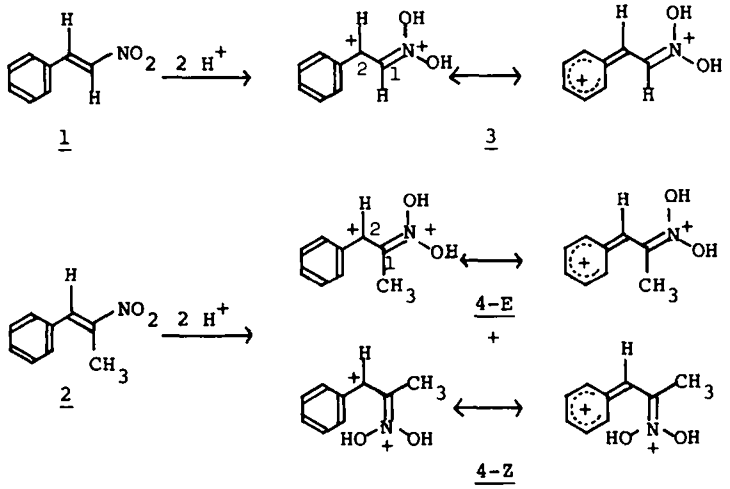
Abstract

β-Nitrostyrenes are diprotonated on the nitro group to yield N,N-dihydroxyiminium-benzyl dications in trifluoromethanesulfonic acid. These dications comprise a new class of reagents that can react with benzene. The reaction is dependent on the substituent (H or alkyl group) at the β position of nitrostyrene: β-nitrostyrene yields diphenylacetophenoneoxime, and β-methyl-β-nitrostyrene yields acetophenoneoxime and triphenylmethane. An essentially common mechanism is suggested to be involved in both reactions. These reactions are novel examples of acid-catalyzed reactions of nitro olefins.

Diprotonation of a nitro group was recognized for the first time in the case of nitronaphthalenes in a strongly acidic medium.[1] We also reported the diprotonation of β-nitrostyrenes in a strong acid[2]: β-nitrostyrenes (1, 2) form N,N-dihydroxyiminium-benzyl dications (3 and 4, respectively) in trifluoromethanesulfonic acid (TFSA). These findings encouraged us to clarify the formation and reactivities of diprotonated species of nitro olefins, since the diprotonation of nitroarenes seems to be a restricted phenomenon at the present stage. In this paper, we will describe the formation and the reactions of N,N-dihydroxyiminium-benzyl dications. This confirms the discrete existence of these dications evaluated by means of cryoscopic, spectroscopic and ^{18}O-isotope incorporation experiments. These dications are considered to be novel reactive electrophiles which comprise a new class of reagents that can react with non-activated benzenes. Another aim of the study was to establish the acid-catalyzed reaction of nitro olefins. Though nitro olefins



1

3

2

4-E

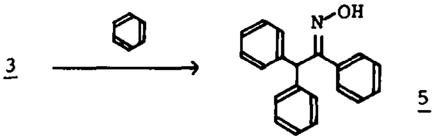
+

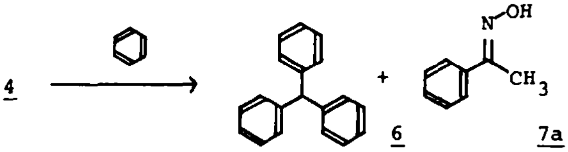
4-Z

have been extensively studied as Michael acceptors, the reactions often hinged on the nature of the catalytic Lewis acids and on the nucleophilicity of the Michael donors, and the nature of the reaction intermediates has remained ambiguous. The reaction of the discrete cation intermediates formed from nitrostyrenes should provide an interesting mechanistic contrast to the conventional Michael reactions of nitro olefins catalyzed by Lewis acids.

Results and Discussion

E-β-Nitrostyrene **1** forms the O,O-diprotonated dication **3** in TFSA at 0°C. E-β-Methyl-β-nitrostyrene **2** is also diprotonated, forming a similar dication. In the latter case two stereoisomers of the dication were observed; the ratio of **4-E** and **4-Z** was estimated from ^{1}H-nmr to be 95:5. The nmr spectra show only signals of the dications (**3** and **4**) in both cases (**1** and **2**), suggesting nearly complete formation of the dications. These dications are quite stable under appropriate conditions, and after aqueous work-up, the starting materials are quantitatively recovered. On the other hand, these dications exhibit high reactivities toward benzene. The reaction is dependent on the substituent (H or alkyl group) at the β position of the nitrostyrene. However, essentially common reaction intermediates are suggested to be involved (vide post); the final products are derived from two types of reaction pathway.





Reaction of β-Nitrostyrene

The O,O-diprotonated dication (**3**) was formed as a stable orange-colored solution when E-β-nitrostyrene **1** was dissolved in TFSA (10 eq) at -22 °C in a dry ice-CCl_4 bath. A large excess of benzene (30 eq with respect to **1**) was added to the TFSA solution of the dication **3** at the same temperature and the solution was maintained at 0-5 °C for 40 min with vigorous stirring. Work-up after aqueous quenching gave the diphenylated oxime **5** in 89% yield.[3] The consumption of the starting material was rapid and the reaction was clean. The isolated oxime **5** was recovered unchanged under similar reaction conditions (no Beckmann rearrangement product is formed). The same product **5** was obtained in a comparable yield (94%) when the reactants were added in the reverse order, that is, addition of β-nitrostyrene **1** to a mixture of benzene (30 eq) and TFSA (10 eq) at 0-5 °C for 40 min. The reaction did not proceed when the acid (TFSA) was replaced by trifluoroacetic acid (TFA). Diprotonation of **1** in TFA was conclusively excluded by uv spectroscopy: in TFA **1** has an absorption maximum at 327 nm ($\log \varepsilon_{\lambda_{max}}=4.80$), which is distinguished from the absorption of **3** in TFSA ($\lambda_{max}=440$nm , $\log \varepsilon_{\lambda_{max}}=4.38$).[2] Similarly, when equimolar TFSA (with respect to **1**) was employed in the reaction, **no**

Table 1 Results of the Reactions of para-Substituted β-Nitrostyrenes

entry	X	Starting Material	Product	Yield (%)[a]
1	H	1	5	94 (89)[b]
2	CH_3	15	22	87
3	Cl	16	23	94
4	OCH_3	17	24	98

a) Isolated yields obtained by the addition of a nitrostyrene to a solution of TFSA in benzene (method B).

b) Yields obtained by method A. See Experimental Section.

product (5 or others) was formed in spite of partial monoprotonation of 1 (quenching with water resulted in complete recovery of 1). When a 2-fold molar excess of TFSA was used, the diphenylated oxime 5 was obtained in 25% yield, in addition to recovery (67%) of 1. This amount of TFSA should not be acidic enough to diprotonate all the nitrostyrene 1, but 1 should be partially diprotonated. These observations strongly support the idea that the diprotonated dication 3 is the reactive electrophile involved in the reaction with benzene. If a monoprotonated nitrostyrene had sufficient reactivity, the product should be obtained even when equimolar TFSA is used. The reaction also occurred in 98% sulfuric acid, but resulted in a 32% yield of 5 (and 43% recovery of 1). Sulfuric acid is not sufficiently acidic; the nitrostyrene 1 was shown to be partially diprotonated in sulfuric acid by means of uv spectroscopy: in 98% sulfuric acid the uv absorptions are observed at 365 and 440 nm. The yield of the diphenylated oxime was comparable to that in the reaction catalyzed by two eq of TFSA. Therefore it seems reasonable to consider that the acidity of the reaction medium containing two eq of TFSA is approximately equivalent to that of 98% sulfuric acid (H_0=-9.4).

Reaction of β-Methyl-β-Nitrostyrene

The reaction of E-β-methyl-β-nitrostyrene 2 was investigated. As already described, 2 forms two O,O-diprotonated dications, 4-E and 4-Z, when dissolved in TFSA at 0°C. When the TFSA solution of the dications 4, cooled to -22°C in a dry ice-CCl_4 bath, was treated with benzene at the same temperature and stirring was continued at 8°C for 6 hr, triphenylmethane 6 and acetophenoneoxime 7a were obtained after aqueous work-up in 73% and 77% yields, respectively.[4] Although the starting material disappeared immediately after the addition of benzene, the complete formation of these products (6 and 7a) required a higher temperature and a prolonged reaction time. It is apparent that these products are formed by C-C bond cleavage between C1 and C2 carbons. As in the case of the reaction of β-nitrostyrene 1, the order of addition of reagents had no effect on the reaction: addition of the nitrostyrene 2 to a mixture of benzene (30 eq) and TFSA (10 eq) resulted in the formation of 6 and 7a in yields of 77% and 90%, respectively (8°C, 6 hr). In this reaction, one eq or less of TFSA (with respect to 2) did not catalyze the

Table 2 Results of the Reaction of β-Alkyl-β-Nitrostyrenes

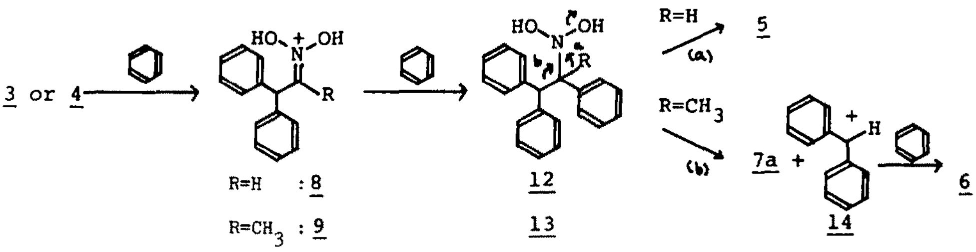
entry	Starting Material	Products	Yields (%)^a
1	**2**	**6**	77 (73)^b
		7a	90 (77)^b
2	**8**	**6**	73
		25a	50
		25b	22
3	**19**	**26**	61
		7a	78

a),b) See footnotes to Table 1. See also note 4.

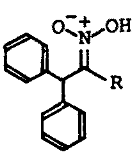
reaction: no product was formed and the starting material was recovered quantitatively after usual aqueous quenching. The use of two equivalents of TFSA provided **6**, **7a** and recovered **2** in yields of 26%, 16%, and 50%, respectively.[4] These results strongly indicate that the active intermediates is not a monoprotonated cation but the diprotonated dication **4**.

Reaction Mechanisms

From the above results and the reported spectral and cryoscopic evidence[2], it is concluded that in the reactions of both β-nitrostyrenes, the reaction intermediates that react with benzene are the N,N-dihydroxyiminium-benzyl dications. It is reasonable to assume that common reaction mechanisms are operative for the two nitrostyrenes (**1** and **2**), judging from the acidities of the reaction media. The first benzene reacts initially at the electron-deficient center (C_2) of the benzyl cation moiety of the dications, **2** and **4**, to form the intermediate N,N-dihydroxyiminium cations **8** and **9**, respectively. Of special significance is the concept that the electrophilic species reacting with the second benzene are not the aci-nitro compounds **10** and **11**, but the protonated aci-nitro compounds **8** and **9**. This conclusion can be derived from an analogy with the Nef reaction[5] (the Nef reaction has been shown kinetically to occur when the protonated aci-nitro species is formed)[6],



and was confirmed by the fact that sodium salt of 1-aci-nitro-2-phenylethane reacted with benzene to give α-phenylacetophenoneoxime in the presence of excess molar amount of TFSA. A similar mechanism has also been proposed for the reaction of the protonated aci-nitro compounds with nucleophilic halide



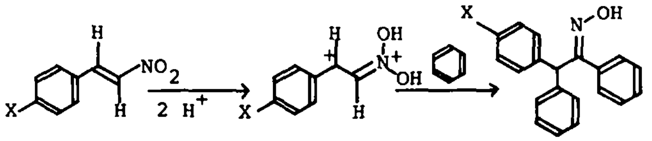
R=H: 10

R=CH_3: 11

ions.[7] In this context, the iminium carbon of the protonated aci-nitro compounds **8** and **9** reacts with the second benzene to afford the intermediates, N,N-dihydroxylamines **12** and **13**, respectively. In this process, it can be reasonably assumed that the electrophilicity of the protonated aci-nitro compound **9** is suppressed owing to the stabilization of the iminium cation by the electron-donating methyl substituent. This assumption is consistent with the experimental results that the reaction of the dication **4** with benzene was slower and required a higher temperature (8-15°C) and longer reaction time. These intermediates **12** and **13** might be further protonated at the hydroxy groups (and probably the nitrogen atom too) in the strongly acidic reaction medium. When the C1 carbon on the β-nitrostyrenes bears a mobile hydrogen atom (as in the case of β-nitrostyrene **1**), the N,N-dihydroxylamine intermediate **12** can afford the (protonated) oxime **5** by the elimination of water. When an alkyl group is present on the C1 carbon atom of β-nitrostyrenes (e.g. **2**), elimination of water from the transient N,N-dihydroxylamine **13** occurs, accompanied with C_1-C_2 bond cleavage, to result in the formation of the stable diphenylmethyl cation **14** and (protonated) acetophenoneoxime **7a**. The former cation reacts with another molecule of benzene to yield triphenylmethane **6**. It is to be expected that the elimination of water from the N,N-dihydroxylamine intermediates (**12** and **13**) would be enhanced by protonation under the acidic conditions. The reaction of the N,N-dihydroxyiminium-benzyl dications with benzene involves a novel reaction of a protonated aci-nitro compound (such as **8** and **9**) with a carbon nucleophile, benzene.

Generalization

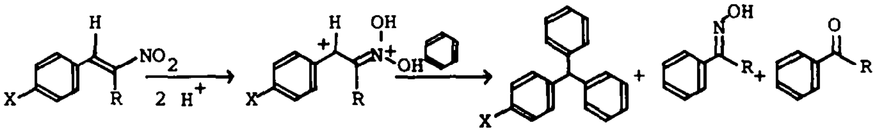
In order to generalize the reaction of β-nitrostyrenes, reactions of other substituted nitrostyrenes were investigated. The results are listed in Table 1 and Table 2, including the results for **1** and **2**. The yields shown in the tables were obtained by the addition of β-nitrostyrenes to the mixture of benzene and TFSA (Method B, Experimental Section), unless otherwise specified. The similar reactions of para-substituted β-nitrostyrenes having a C-1 hydrogen atom were investigated (Table 1). The addition of β-nitrostyrenes (**15**: p-CH_3; **16**: p-Cl; **17**: p-OCH_3) to the mixture of TFSA (10 eq) and benzene (30 eq) at 0 °C for 40 min resulted in the formation of the diphenylated oximes in high yields. The results of nmr spectroscopic investigations on the O,O-diprotonated dications of **15** and **16**



15 (X=CH_3) 22

16 (X=Cl) 23

17 (x=OCH_3) 24



X=H,R=C_2H_5: 18 20 6 25a 25b

X=Cl,R=CH_3: 19 21 26 7a 7b

in TFSA at low temperature have already been reported.[2] Although nmr spectroscopic evidence for the formation of the O,O-diprotonated dication from p-methoxy-β-nitrostyrene **17** has not been obtained owing to the extreme instability of **17** in TFSA even at low temperature, the result of the reaction of **17** with benzene catalyzed by TFSA strongly supports the formation of the O,O-diprotonated dication from **17** in TFSA.

Similar reactions of β-nitrostyrenes having an alkyl substituent were investigated (Table 2). It is apparent that E-β-ethyl-β-nitrostyrene **18** and p-Cl-β-methyl β-nitrostyrene **19** exhibit reactivities similar to those of **2**. Therefore, the O,O-diprotonated dications **20** and **21** should be formed in TFSA, as in the case of **4**.

Conclusion

The formation of N,N-dihydroxyiminium-benzyl dications was established by the cryoscopic and spectroscopic studies described in our earlier work.[2] Here additional evidence for the formation of the dications from β-nitrostyrenes in TFSA was obtained from the results of chemical reactions. The reactions are not catalyzed by a single equivalent of TFSA, and the initial reaction intermediates are so reactive that non-activated benzene can be attacked. This constitutes strong chemical evidence for the hypothesis that the reactive intermediates are O,O-diprotonated β-nitrostyrenes, but not monoprotonated cations. Further studies on the protonation of nitro groups are in progress.

Experimental Section

General Methods

All the melting points were measured with a Yanagimoto hot stage melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded with a JEOL FX100 spectrometer with tetramethylsilane as an internal reference and $CDCl_3$ as the solvent unless otherwise specified. Infrared spectra were measured on a JASCO D-S-402G spectrometer as a solid suspension in KBr. Mass spectra were recorded with a JEOL JMS-DX300. Column chromatography was performed by using silica gel (Wako Chemical Co., Wakogel C-200), and flash column chromatography[8] was performed over silica gel (Merck, Kieselgel 60, 230-400 mesh) with a specified solvent. Combution analyses were carried out in the microanalytical laboratory of this faculty.

Materials

All β-nitrostyrenes were prepared through condensation of the nitroalkanes with a corresponding benzaldehyde, and were purified by recrystallization from n-hexane or methanol, followed by sublimation or molecular distillation. All these compounds showed satisfactory spectroscopic properties and combution analyses; **1**: mp 55-55.5°C (lit. 58-59°C[9]); **2**: mp 63-64 ℃ (lit. 64-65°C[9]); **15** mp 104.5-105°C (lit. 101°C[9]); **16**: mp 112-113°C (lit. 112-112.5°C[10]); **17**: mp 86-86.5 ℃ (lit. 86-87 °C[9]); **18**: yellow oil. Purified by molecular distilation: 35 ℃ (external temp.)/1 mmHg> (lit. bp 100 °C/0.5 mmHg)[11]; **19**: mp 87 ℃ (lit. 85°C[13]). Trifluoromethanesulfonic acid (TFSA) was purchased from 3M Co., and was purified by distillation (68°C/17 mmHg). Trifluoroacetic acid (TFA) was obtained from Wako Chemicals and was used without further purification.

Acid-Catalyzed Reaction of β-Nitrostyrene 1 with Benzene

Method A A solution of 0.88 ml (10 mmol) of TFSA was cooled to -22°C in a dry ice-CCl_4 bath and

149 mg (1 mmol) of β-nitrostyrene 1 was added in portions with vigorous stirring. To the resultant orange-colored solution, 2.65 ml (30 mmol) of benzene was added with vigorous stirring. The whole was stirred for 40 min at 0-5°C in an ice bath. The resulting heterogenous mixture was poured into 200 ml of ice and water, and extracted with 2x200 ml portions of CH_2Cl_2. The extract was washed with brine, and dried over Na_2SO_4 and concentrated under reduced pressure to afford 256 mg (89%) of diphenylacetophenoneoxime 5 as a pure white powder: mp 181-182°C (recrystallized from benzene); Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.76; H, 6.0; N, 4.89.; mass spectrum: m/e 287 (M^+); ^{1}H-nmr: 8.9 (1H, s, OH), 5.5-5.0 (15H, m, aromatic),3.4 (1H, s); ^{13}C-nmr: 56.8 (d), 126.6 (d), 128.0 (dx2), 128.4 (d), 129.6 (d), 135.2 (sx2), 141.6 (s), 156.5 (s).

The product 5 was also obtained in a similar yield (94%) in the following manner.

Method B A solution of 2.65 ml (10 eq) of TFSA and benzene was cooled to 0-5°C in ice-water bath, and a solution of β-nitrostyrene 1 (447 mg, 3 mmol) dissolved in benzene (total amount of benzene used was 7.96 ml, 30 eq) was added in portions with vigorous stirring. The reaction mixture was kept at this temperature for 40 min. The aqueous work-up of the resultant mixture as described in Method A gave 650 mg (94 % yield) of 5.

Independent Preparation of Diphenylacetophenoneoxime 5

A solution of 0.88 ml (10 eq) of TFSA and 8.8 ml of benzene (100 eq) was cooled to 0°C (ice bath), and treated with 214 mg (1.01 mmol) of diphenylacetic acid. The mixture was stirred at 15°C for 15 hr, then the reaction was quenched with ice-water and the whole was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The crude products were isolated by flash chromatography (CH_2Cl_2/hexane 2:1) to give 186 mg (75%) of triphenylmethane and 28 mg (10%) of α,α-diphenylacetophenone. The latter ketone was converted to the oxime (5) in a usual way ($NH_2OH\cdot HCl$/EtOH/pyridine). The ir spectrum of this prepared oxime was identical with that of 5.

Acid-Catalyzed Reaction of Sodium Salt of 1-aci-Nitro-2-Phenylethane

To an ice-cooled solution of 2.65 ml (10 eq) of TFSA in 7.96 ml (30 eq) of benzene, the sodium salt of 1-aci-nitro-2-phenylethane[13] (514 mg) was added by portions. The solution was vigorously stirred at 0-5°C for 4 hr, followed by usual aqueous work-up. The obtained residue was flash-chromatographed with AcOEt/hexane (1:8) as the eluent to give 187 mg (26 %) of α-phenylacetone-oxime. The product was identified with the authentic sample in terms of the ir and nmr spectra. The yield of the phenylated product was not so high since the alternant reaction path to recover 1-nitro-2-phenylethane exists. Optimization of the reaction yield is under investigation , and the result is to be published as soon as possible.

Acid-Catalyzed Reaction of β-Methyl-β-Nitrostyrene 2 with Benzene (Method A)

A solution of 2.65 ml (30 mmol) of TFSA was cooled to -22°C in a dry ice-CCl_4 bath, and 489 mg (3 mmol) of 2 was added in portions with vigorous stirring. To the resultant red-colored solution, 7.96 ml (90 mmol) of dry benzene was added with vigorous stirring, and stirring was continued for 6 hr at 8°C (water bath). The reaction mixture was subjected to aqueous work-up, followed by extraction and evaporation as described in the procedure of the reaction of **1**. The crude reaction mixture was purified by flash column chromatography with AcOEt/hexane (1:7) as the eluent to afford 537 mg (73%) of triphenylmethane **6** and 312 mg (77%) of acetophenoneoxime **7a** as a pure white solid. **6**: mp 94°C (recrystallized from benzene); all spectral data (nmr, uv, mass and ir) were identical with those of an authentic sample of triphenylmethane. **7a**: mp 58°C (recrystallized from hexane); all spectral data were identical with those of an authentic sample.[4]

The same reaction occurred in similar yields by Method B: **6**: 77%, **7a**: 90% (8°C, 6 hr)[4].

Acid-Catalyzed Reaction of 15 with Benzene

The acid-catalyzed reaction of p-methyl-β-nitrostyrene **15** was performed by Method B as described in the procedure of the reaction of **1**. The pure diphenylated oxime **22** was obtained in 87% yield ; mp: 146-147 °C (recrystallized from benzene); Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.90; H, 6.41; N, 4.53; mass spectrum: m/e 301 (M^+); ^1H-nmr: 7.75 (1H, brd s, OH), 7.45-7.3 (14H, m), 5.40 (1H, s), 2.35 (3H, s, CH_3); ^{13}C-nmr: 20.4 (q), 56.3 (d), 125.6 (d), 127.0 (d), 127.3 (d), 128.1 (d), 128.5 (d), 134.0 (s), 135.0 (s), 136.9 (s), 140.4 (s), 156.8 (s)

Acid-Catalyzed Reaction of 16 with Benzene

The acid-catalyzed reaction of p-chloro-β-nitrostyrene **16** was performed by Method B as described in the procedure of the reaction of **1** . The pure diphenylated oxime **23** was obtained in 94% yield; mp 169-170 °C (recrystallized from benzene); Anal. Calcd for $C_{20}H_{16}NOCl$: C, 74.65; H, 5.00; N, 4.36. Found: C, 74.52; H, 4.93; N, 4.69.; mass spectrum: m/e 321,323 (M^+); ^1H-nmr: 8.10 (1H, br s, OH), 7.45-7.2 (14H, m), 5.35 (1H, s).; ^{13}C-nmr: 55.6 (d), 125.9 (d), 127.1 (d), 127.4 (d), 127.6 (d), 128.6 (d), 130.2 (d), 131.2 (s), 133.9 (s), 139.2 (s), 139.8 (s), 156.2 (s).

Acid-Catalyzed Reaction of 17 with Benzene

p-Methoxy-β-nitrostyrene **17** (537 mg, 3mmol) was reacted as usual with a solution of 2.65 ml (30 mmol) of TFSA in 7.96 ml (90 mmol) of benzene. The crude reaction product (1.22g) was purified by column chromatography (SiO_2) with CH_2Cl_2/hexane (1:1) as the eluent to give 930 mg (98%) of **24** as a white solid: mp 112-114°C (recrystallized from benzene); Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.83; H, 6.09; N, 4.31.; mass spectrum: m/e 317 (M^+); ^1H-nmr: 8.55 (1H, br s, OH), 7.7-7.0 (14H, m), 5.60 (1H, s), 4.0 (3H, s, CH_3O); ^{13}C-nmr: 55.1 (d), 56.6 (q), 113.7 (d), 126.5 (d), 127.7 (d), 127.9 (d), 128.2 (d), 128.4 (d),129.0 (d), 130.1 (d), 132.0 (d), 133.7 (s), 140.2 (s), 158.2 (s), 158.9 (s).

Acid-Catalyzed Reaction of 18 with Benzene

A solution of 2.2 ml (25 mmol) of TFSA in 4.6 ml of dry benzene was cooled to 0°C, and treated dropwise with a solution of 440 mg (2.5 mmol) of **18** in 2 ml of benzene (total benzene 75 mmol). Stirring was continued at 0-5°C for 6.5 hr before usual aqueous work-up. Evaporation of the solvent left a residue which was flash-chromatographed (SiO_2) with AcOEt/hexane (1:7) as the eluent to afford 450 mg (73%) of triphenylmethane **6**, and 190 mg (50%) of propiophenoneoxime **25a** and 70 mg (22%) of propiophenone **25b**, respectively. : **25a**: mp 50-51°C (recrystallized from hexane). All spectral data for **6**, **25a** and **25b** were identical with those of corresponding authentic samples.

Acid-Catalyzed Reaction of 19 with Benzene

A solution of 1.77 ml (20 mmol) of TFSA in 5.3 ml (60 mmol) of dry benzene was cooled to 0°C, and 390 mg (2 mmol) of nitrostyrene **19** was added. Stirring was continued for 6.5 hr at 0 °C. Evaporation of the solvent left a residue, which was flash-chromatographed with AcOEt/hexane (1:8) as the eluent to give 340 mg (61%) of **26** as a colorless oil, and 210 mg (78%) of acetophenoeoxime **7a** as a white solid. **26**: mass spectrum: m/e 278, 280 (M^+); ^1H-nmr: 7.4-6.8 (14H, m), 5.52 (1H, s); ^{13}C-nmr: 143.2 (s), 142.3 (s), 132.0 (d), 130.6 (d), 129.2 (d), 128.3 (d), 126.3 (d), 56.3 (d). **7a** obtained in this reaction was identical with an authentic sample in terms of the ir and nmr spectra.

References and Note

(1) Ohta,T; Shudo, K; Okamoto,T. Tetrahedron Let. 1984, 325.

(2) Ohwada, T.; Ohta, T.; Shudo, K. J. Am. Chem. Soc., 1986, 108, 3029.

(3) The same reaction occurred when the stoichiometric amount of benzene (2.2 eq) was used.

(4) In addition, acetophenone **7b**(10%) and another product ($C_{15}H_{13}NO$) (10%) was obtained. The latter product was tentatively assigned as 3-methyl-4-phenyl-4H-1,2-benzoxazine: HRMS. Calcd. for $C_{15}H_{13}NO$ (M^+) 223.09964, found 223.0973.; ^1H-nmr ($CDCl_3$) 5.92-6.16 (9H, m), 4.48 (1H, s), 2.0 (3H, s); ^{13}C-nmr ($CDCl_3$) 156.7 (s), 151.4 (s), 140.3 (s), 128.8 (d), 128.0 (d), 127.9 (d), 127.6 (d), 127.3 (d), 126.9 (d), 123.5 (d), 119.5 (s), 43.3 (d), 19.8 (q).
The same product ($C_{15}H_{13}NO$) was obtained (5% yield) together with acetophenone **7b** (6% yield), when the reaction was catalyzed by two eq of TFSA. (See text)

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