

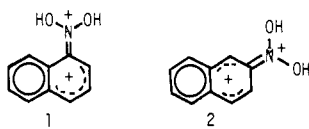
# Protonation of Nitro Groups. Diprotonation of $\beta$ -Nitrostyrenes in Trifluoromethanesulfonic Acid

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**Abstract:** Dissolving (*E*)- $\beta$ -nitrostyrene in trifluoromethanesulfonic acid (TFSA) resulted in a stable orange-colored solution. Quenching the solution with water quantitatively yielded the starting  $\beta$ -nitrostyrene. The nature of the chemical entity in the TFSA solution was deduced from the results of cryoscopy and NMR spectroscopy. The molal freezing point depressions of TFSA by triphenylmethanol, mesitoic acid, potassium nitrate, nitrobenzene, nitrotoluene, and 1-nitronaphthalene gave a reliable value for the cryoscopic constant,  $K_f = 10.06$  °C, of TFSA. The molal freezing point depressions of (*E*)- $\beta$ -nitrostyrene and (*E*)- $\beta$ -methyl- $\beta$ -nitrostyrene were found to be  $30.37 \pm 2.61$  and  $30.98 \pm 2.39$  °C, respectively. That is, the nitrostyrene yielded three particles in TFSA and thus are diprotonated. The sites of protonation were analyzed by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. The facts that no carbon bears two hydrogens and no deuterium exchange occurs in d-TFSA exclude the formation of O,C-diprotonated and C,C-diprotonated dications. The species formed in TFSA from  $\beta$ -nitrostyrenes are O,O-diprotonated dications (*N,N*-dihydroxyiminium benzyl dications), where roughly one positive charge is delocalized on the benzyl cation system and the rest of the positive charge is localized on the iminium nitrogen.

Very extensive research has been carried out on the generation of a diverse array of cations,<sup>1</sup> whose existence has generally been deduced from the kinetics or by direct observation by spectroscopic methods. From the historical point of view, cryoscopic studies on acid solutions of ionizing materials have played a significant role in the determination of the structures of novel cations.<sup>2</sup> There has been considerable interest in the protonation of nitro groups in strongly acidic media. Generally nitro compounds are weak bases in a strong acid. Nitrobenzene is partially monoprotated in sulfuric acid<sup>3</sup> and nearly completely monoprotated in  $\text{FS-O}_3\text{H-SbF}_5$  (NMR)<sup>4</sup> and in trifluoromethanesulfonic acid (TFSA) (conductivity<sup>5</sup> and cryoscopy<sup>6</sup>). Nitroalkanes are also monoprotated in a strong acid.<sup>4</sup> On the other hand, 1- and 2-nitronaphthalenes are diprotonated in TFSA.<sup>6</sup> This was shown by careful cryoscopy, and the protonated structures **1** and **2** were elucidated from  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR analyses. We have expanded the chemistry of protonated nitro compounds to the protonation of nitrostyrenes in TFSA. In this paper we present the results of our investigation on the formation of stable cations by protonation of nitrostyrenes in TFSA. In order to determine the stoichiometry in the solution, cryoscopic experiments were performed. The structures of the protonated species in TFSA were also elucidated from direct NMR spectral evidence.



## Results and Discussion

Dissolving (*E*)- $\beta$ -nitrostyrene (**3**) in TFSA at  $-20$  °C resulted in an orange-red solution (UV:  $\lambda_{\text{max}} = 440$  nm,  $\log \epsilon_{\text{max}} = 4.86$ ) which is stable at  $0$  °C for more than 3 h. Quenching the solution

(1) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279. Parakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 390. Pagni, R. M. *Tetrahedron* **1984**, *40*, 4161.

(2) The significant contributions of cryoscopy to the chemistry of cations are well documented in the following: Gillespie, R. J.; Robinson, E. A. "Carbonium Ions"; Olah, G. A., Schleyer, P. von R., Eds.; Wiley-Interscience: New York, 1968; Vol. 1, pp 111-134. Gillespie, R. J.; Leisten, J. A. *Q. Rev. (London)* **1956**, *8*, 40. Scorrano, G.; Walter, W. *J. Chem. Educ.* **1979**, *56*, 728.

(3) Cryoscopic measurements on nitro compounds: Gillespie, R. J. *J. Chem. Soc.* **1950**, 2542. Gillespie, R. J.; Robinson, E. A. *Ibid.* **1957**, 4233. Ultraviolet spectroscopic studies: Brand, J. C. D. *Ibid.* **1950**, 997. Brand, J. C. D.; Horning, W. C.; Thornly, M. B. *Ibid.* **1952**, 1374.

(4) Olah, G. A.; Kiovsky, T. E. *J. Am. Chem. Soc.* **1968**, *90*, 6461. Olah, G. A.; Fung, A. P.; Rawdah, T. N. *J. Org. Chem.* **1980**, *45*, 4149.

(5) Russell, D. G.; Senior, J. B. *Can. J. Chem.* **1980**, *58*, 22.

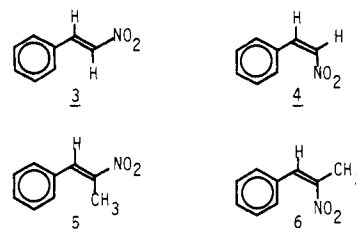
(6) Ohta, T.; Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1984**, 325.

**Table I.** Determination of the Cryoscopic Constant  $K_f$  of TFSA and Evaluation of  $i$  Factors of Nitrostyrenes from the Freezing Point Depressions

compound	molal freezing point depression, °C/(mol·kg <sup>-1</sup> )	$i$	$K_f$
nitrobenzene	$20.1 \pm 0.9^a$	2	10.06
4-nitrotoluene	$20.05 \pm 1.24^b$	2	10.03
1-nitronaphthalene	$29.4 \pm 2.2^a$	3	9.8
triphenylmethanol	$41.11 \pm 1.57$	4	10.28
mesitoic acid	$40.12 \pm 1.25$	4	10.03
potassium nitrate	$60.85 \pm 1.43$	6	10.14
			av 10.06
( <i>E</i> )- $\beta$ -nitrostyrene ( <b>3</b> )	$30.37 \pm 2.61$	$3.02 \pm 0.26$	
( <i>E</i> )- $\beta$ -methyl- $\beta$ -nitrostyrene ( <b>5</b> )	$30.98 \pm 2.39$	$3.08 \pm 0.24$	

<sup>a</sup>Reference 6. <sup>b</sup>This value was previously reported<sup>6</sup> to be  $19.5 \pm 2.2$  °C/(mol·kg<sup>-1</sup>).

with water after standing at  $0$  °C for 3 h quantitatively yielded the starting compound. A solution of (*Z*)- $\beta$ -nitrostyrene (**4**) in TFSA is spectroscopically (UV and NMR) indistinguishable from that of **3** in TFSA, and aqueous quenching yielded (*E*)- $\beta$ -nitrostyrene quantitatively. Dissolving (*E*)-(**5**) and (*Z*)- $\beta$ -methyl- $\beta$ -nitrostyrene (**6**)<sup>7</sup> similarly gave spectroscopically indistinguishable solutions, which on quenching with water gave (*E*)- $\beta$ -methyl- $\beta$ -nitrostyrene in quantitative yield. For the conclusive determination of the stoichiometry in the solution, cryoscopic experiments were carried out on  $\beta$ -nitrostyrenes.



**Cryoscopic Studies.** The procedure for determining freezing points involved the drawing of cooling curves as described.<sup>8</sup> Temperature was measured with a copper-constantan thermocouple with a reference junction at  $0$  °C. The measured molal concentration was within the range of  $0$  to  $5.0 \times 10^{-2}$  mol/kg for

(7) (*Z*)- $\beta$ -Nitrostyrenes were prepared by photoisomerization of corresponding (*E*)-nitrostyrenes in cyclohexane. See the Experimental Section.

(8) Determination of freezing points was achieved through the use of the time-temperature curve (cooling curve) method. Aston, J. G.; Fink, H. L.; Tooke, J. W.; Cines, M. R. *Anal. Chem.* **1947**, *19*, 218.

**Table II.**  $^1\text{H}$  NMR Chemical Shifts<sup>a</sup> and  $^1\text{H}$ - $^1\text{H}$  Coupling Constants<sup>b</sup> of O,O-Diprotonated  $\beta$ -Nitrostyrenes in TFSA at  $-20^\circ\text{C}$ 

	H <sub>2</sub>	H <sub>1</sub>	H <sub>0</sub>	H <sub>m</sub>	H <sub>p</sub>	CH <sub>3</sub>
7	9.27 (d, 12.7)	8.58 (d, 13.2)	8.17 (d, 7.3)	7.78 (dd, 7.6, 7.6)	8.09 (dd, 6.9, 6.9)	
11	9.65 (s)		8.14 (d, 8.1)	7.81 (dd, 7.3, 7.3)	8.03 (dd, 7.1, 7.1)	2.79 (s)
12	9.74 (s)		8.65 (d, 7.7)	7.99 (dd, 7.7, 7.7)	8.41 (dd, 7.1, 7.1)	2.50 (s)
			8.52 (d, 7.0)	7.95 (dd, 8.4, 8.4)		
15	9.22 (d, 12.7)	8.53 (d, 12.7)	8.12 (d, 8.3)	7.98 (d, 8.3)		2.67 (s)
16	9.44 (d, 13.2)	8.77 (d, 12.8)	8.34 (d, 8.8)	7.98 (d, 8.3)		

<sup>a</sup> Chemical shifts are in ppm from external capillary Me<sub>4</sub>Si in acetone-*d*<sub>6</sub>. <sup>b</sup> Coupling modes and  $^1\text{H}$ - $^1\text{H}$  coupling constants in Hz are shown in parentheses: d = doublet, dd = double doublet, s = singlet.

**Table III.**  $^{13}\text{C}$  NMR Chemical Shifts<sup>a</sup> and  $^{13}\text{C}$ - $^1\text{H}$  Coupling Constants<sup>b</sup> of O,O-Diprotonated  $\beta$ -Nitrostyrenes at  $-20^\circ\text{C}$ 

	C <sub>2</sub>	C <sub>1</sub>	C <sub>ipso</sub>	C <sub>o</sub>	C <sub>m</sub>	C <sub>p</sub>	CH <sub>3</sub>
7	165.1 (161.1)	128.3 (200.2)	130.9	136.4 (159.9)	130.8 (167.3)	143.1 (146.0)	
11	161.8 (161.4)	142.5	132.3	137.7 (157.5)	130.9 (159.9)	141.0 (164.8)	13.9 (133.1)
12	204.4 (191.5)	128.4	131.2	145.7 (168.7)	131.7 (170.2)	148.7 (163.6)	15.0 (133.5)
				133.5 (166.5)	131.5 (170.2)		
15	164.8 (162.3)	126.2 (197.7)	129.7	132.3 (164.8)	132.3 (164.8)	160.8	22.2 (134.2)
16	163.2 (163.6)	128.3 (203.9)	129.4	137.2 (166.0)	131.5 (172.1)	151.6	

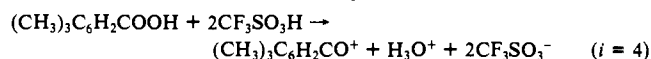
<sup>a</sup> Chemical shifts (in ppm) are calibrated from Me<sub>4</sub>Si in CDCl<sub>3</sub>. <sup>b</sup>  $^{13}\text{C}$ - $^1\text{H}$  coupling constants are shown in parentheses in Hz.

all compounds (except nitrobenzene, 0 to  $1 \times 10^{-1}$  mol/kg). Molal freezing point depressions were calculated from the regression line between molal concentrations and freezing point depressions, and the ranges shown are the 95% confidence intervals of the slopes. Good linearity between the molality of the solutes and the freezing point depressions was obtained with correlation coefficients ( $r > 0.99$  in every case). The recovery of the starting compounds from the solution was complete after the cryoscopic experiments. The freezing point was not time-dependent, and all the experiments showed excellent reproducibility. The cryoscopic constant of TFSA was obtained from the molal freezing point depressions of TFSA by triphenylmethanol ( $41.11 \pm 1.57^\circ\text{C}$ ,  $i = 4$ ),<sup>9</sup> mesitoic acid ( $40.12 \pm 1.25^\circ\text{C}$ ,  $i = 4$ ),<sup>10</sup> and potassium nitrate ( $60.85 \pm 1.43^\circ\text{C}$ ,  $i = 6$ ),<sup>11</sup> non-nitro compounds with known, definite  $i$

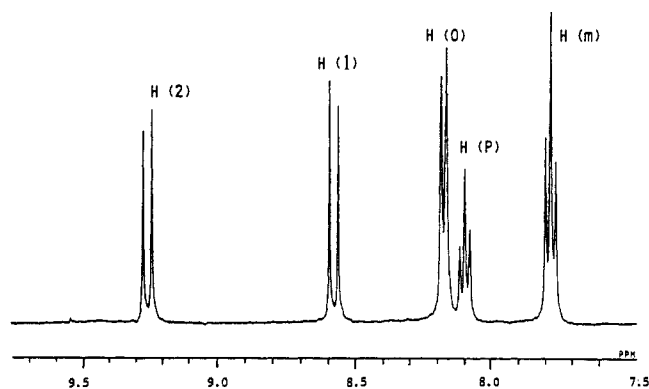
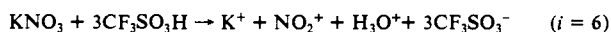
(9) Cryoscopic, NMR, and UV spectroscopic studies have established that triphenylmethanol ionizes in acidic media to form the triphenylmethyl cation. (a) Cryoscopy: Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1933**, *55*, 1900. Craig, R. A.; Garrett, A. B.; Newman, M. S. *Ibid.* **1950**, *72*, 163. (b) NMR and UV studies: Moodie, R. B.; Connor, T. M.; Stewart, R. *Can. J. Chem.* **1959**, *37*, 1402. Harmon, K. M.; Harmon, A. B. *J. Am. Chem. Soc.* **1961**, *83*, 865. The NMR and UV spectra showed that the species formed from triphenylmethanol in TFSA was the triphenylmethyl cation.



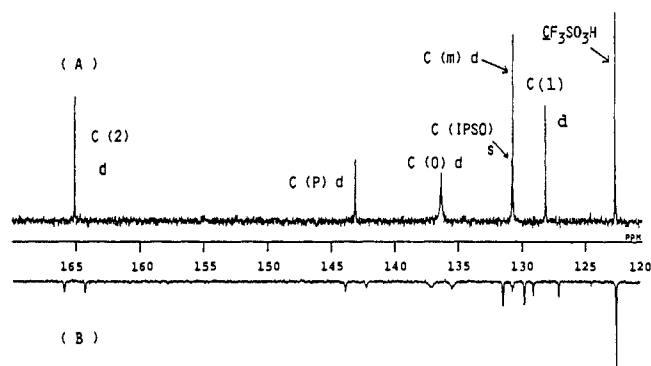
(10) Cryoscopy and NMR and UV spectroscopy revealed the formation of the acylium ion,  $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{-CO}^+$ , from mesitoic acid in sulfuric acid or 60% sulfur trioxide: Treffers, H. P.; Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 1708. Schubert, W. S.; Donohue, J.; Gardner, J. D. *Ibid.* **1954**, *76*, 9. Deno, N. C.; Pittman, C. U.; Wisotsky, M. J. *Ibid.* **1964**, *86*, 4370. Complete ionization of mesitoic acid to the acylium ion in TFSA was confirmed by UV and NMR spectroscopy.



(11) Cryoscopy in sulfuric acid (Gillespie, R. J.; Millen, D. J. *Q. Rev.* **1948**, *2*, 277) and conductivity in FSO<sub>3</sub>H (Gillespie, R. J.; Milne, J. B.; Senior, J. B. *Inorg. Chem.* **1966**, *5*, 1233) showed that potassium nitrate forms the nitronium ion in a strong acid. Russell and Senior (ref 5) measured the conductivity of potassium nitrate in TFSA and concluded that potassium nitrate ionizes to the nitronium ion according to the following equation.



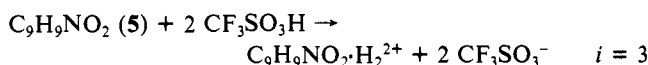
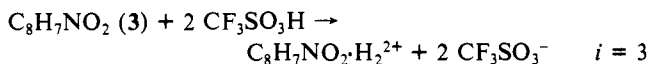
**Figure 1.** The 400-MHz  $^1\text{H}$  NMR spectrum of  $\beta$ -nitrostyrene (3) in TFSA at  $-20^\circ\text{C}$ . Five sets of absorptions in the ratio of 1:1:2:1:2 can be seen.



**Figure 2.** The 100-MHz  $^{13}\text{C}$  NMR spectrum of  $\beta$ -nitrostyrene (3) in TFSA at  $-20^\circ\text{C}$ : (A) proton complete decoupled, (B) proton off-resonance decoupled spectrum. No secondary carbon is observed.

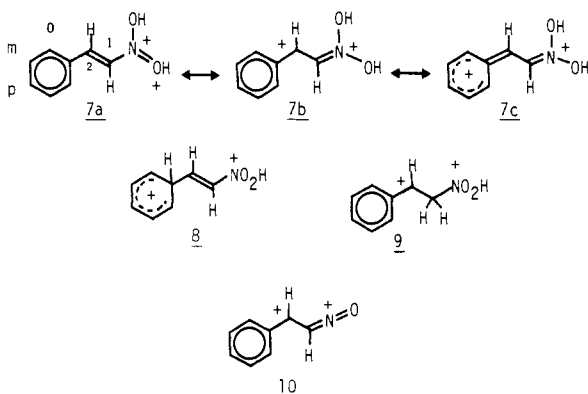
factors, in conjunction with the molal freezing point depressions for nitrobenzene ( $i = 2$ ),<sup>12</sup> 4-nitrotoluene ( $i = 2$ ),<sup>12</sup> and 1-nitro-

naphthalene ( $i = 3$ ), obtained in the previous work.<sup>6</sup> The cryoscopic constant  $K_f$  of TFSA was refined to 10.06 °C on the basis of all these cryoscopic data (Table I). Thus, nitrostyrenes were investigated cryoscopically: the molal freezing point depression for (*E*)- $\beta$ -nitrostyrene (**3**) was found to be  $30.37 \pm 2.61$  °C and that of (*E*)- $\beta$ -methyl- $\beta$ -nitrostyrene (**5**) was  $30.98 \pm 2.39$  °C. Consequently, the experimental  $i$  factors for **3** and **5** in TFSA are consistent with the following equations:



That is, the nitrostyrenes are concluded to be diprotonated in TFSA.

**Nuclear Magnetic Resonance Studies.** The structures of the diprotonated species in TFSA were deduced from the NMR spectra. The possible structures of the diprotonated  $\beta$ -nitrostyrene are O,O-diprotonated (**7**), O,C-diprotonated (e.g., **8** and **9**), or C,C-diprotonated. The <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figures 1 and 2) were obtained at -30 to 0 °C, where the solutions were sufficiently stable and the spectra were independent of time and temperature. The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of protonated

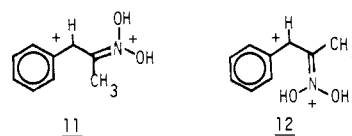


$\beta$ -nitrostyrenes in TFSA at -20 °C are listed in Tables II and III, respectively, which also include <sup>1</sup>H-<sup>1</sup>H coupling constants ( $J$ ) and <sup>13</sup>C-<sup>1</sup>H coupling constants ( $J_{\text{CH}}$ ).

Both (*E*)- $\beta$ -nitrostyrene (**3**) and (*Z*)- $\beta$ -nitrostyrene (**4**) gave identical spectra when dissolved in TFSA. These spectra are consistent with the conclusion that no carbon atom bears two hydrogens: if the benzenium ion such as **8** was formed, an absorption of a proton on an  $\text{sp}^3$ -hybridized carbon atom might be observed.<sup>13</sup> If protonation of the olefin occurred (e.g., **9**), aliphatic methylene absorptions might be observed. Thus, no O,C-diprotonated or C,C-diprotonated structures can be assigned. The O,O-diprotonated structure **7** is consistent with the <sup>1</sup>H NMR and the proton complete decoupled and proton off-resonance decoupled <sup>13</sup>C NMR spectra. The  $\text{H}_2$  proton (at 9.27 ppm; 1.27 ppm deshielded from neutral **3**) and the  $\text{C}_2$  carbon (at 165.1 ppm; 26.3 ppm deshielded from neutral **3**) exhibit the largest deshielding upon protonation, due to the strong electron deficiency at the  $\text{C}_2$  position. The absorptions of the aromatic moiety remained sharp and well-resolved and were also deshielded in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra in comparison with those of the neutral material. The assignments of the other absorptions are shown in Tables II and III. Therefore, the diprotonated species can be represented by a hybrid structure of **7a-7c**, where roughly one positive charge is delocalized on the benzyl system and the rest of the positive

charge is localized mostly on the iminium nitrogen. The <sup>13</sup>C NOE experiments showed that the <sup>13</sup>C-H coupling constants of the  $\text{C}_2$  and  $\text{C}_1$  positions were 161.1 and 200.2 Hz, respectively. With use of the empirical relationships<sup>14</sup> between  $J_{\text{C-H}}$  and the fraction of  $s$  character in the C-H bond, the fractions of  $s$  character of the  $\text{C}_2$  and  $\text{C}_1$  carbons can be calculated to be 0.32 and 0.40, respectively. These values are comparable with those in the neutral **3** ( $s_2 = 0.32$ ,  $s_1 = 0.39$ ) and also support the idea that the  $\text{C}_2$  and  $\text{C}_1$  carbons are  $\text{sp}^2$ -hybridized. The large coupling constant ( $J = 13$  Hz) between the  $\text{H}_1$  and  $\text{H}_2$  protons suggests planar entgegen stereochemistry about the  $\text{C}_1$ - $\text{C}_2$  bond of **7**. The facile isomerization of (*Z*)- $\beta$ -nitrostyrene to the *E* isomer in TFSA may be attributed to the presumed lower  $\text{C}_1$ - $\text{C}_2$  bond order in the protonated species as compared with a normal double bond. No deuterium exchange of protons at -30 to 0 °C was observed in  $\text{CF}_3\text{SO}_3\text{D}$ , suggesting that there is no equilibrium among **7**, **8**, and **9**. Another structure **10**, which may be consistent with the NMR data, is eliminated by the  $i$  factors<sup>15</sup> and by the fact of non-incorporation of oxygen-18 into the recovered **3** on quenching with  $\text{H}_2^{18}\text{O}$ .

A similar NMR spectroscopic investigation was also performed on  $\beta$ -methyl- $\beta$ -nitrostyrene. Both (*E*)-(**5**) and (*Z*)- $\beta$ -methyl- $\beta$ -nitrostyrene (**6**) gave identical <sup>1</sup>H and <sup>13</sup>C NMR spectra consisting of two components in a ratio of 95:5. Since the chemical shifts (Tables II and III) attributed to the major component are similar to those of the O,O-diprotonated dication **7** and since the NOE between  $\text{H}_0$  and  $\text{CH}_3$  protons was observed, entgegen stereochemistry (**11**) was suggested. The signals attributed to the minor component can be reasonably interpreted as being due to the diprotonated *Z*-isomer **12** from the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. Nonequivalence of the aromatic atoms may be attributed to the restricted rotation about the  $\text{C}_2$ - $\text{C}_{\text{ipso}}$  bond. No deuterium exchange of protons of either the major isomer or the minor isomer was observed in  $\text{CF}_3\text{SO}_3\text{D}$  at -30 to 0 °C. Another structure, **10**, was also excluded by the result of the oxygen-18 incorporation experiment. The ratio of two isomers, which was estimated from proton NMR spectral peak areas, essentially did not change in the temperature range from -30 to 0 °C. The presence of the stereoisomers in the O,O-diprotonated  $\beta$ -methyl- $\beta$ -nitrostyrene may be partially attributed to the larger steric repulsion between the phenyl group and the methyl group than that between the phenyl group and the hydrogen atom.



A similar NMR spectroscopic investigation was conducted on para-substituted  $\beta$ -nitrostyrenes (Tables II and III). The para-substituted (*Z*)- $\beta$ -nitrostyrenes ( $p$ - $\text{CH}_3$ : **13**; and  $p$ - $\text{Cl}$ : **14**) exhibit chemical shifts similar to those of the O,O-diprotonated  $\beta$ -nitrostyrene **7** in TFSA at -20 °C, supporting the formation of *E*-O,O-diprotonated  $\beta$ -nitrostyrenes **15** and **16**, respectively. The proton-proton coupling constants between  $\text{H}_1$  and  $\text{H}_2$ ,  $J = 13$  Hz, in both cases, and the  $J_{\text{C-H}}$  coupling constants listed were confirmatory evidence for the proposed stereochemistry. These compounds were also stable enough at low temperature (-30 to 0 °C) to be recovered unchanged in quantitative yields after aqueous quenching. In the <sup>1</sup>H NMR spectra, the ortho protons in **15** were observed at 8.1 ppm as broad peaks at -30 °C, which sharpened to clean doublets ( $J = 8$  Hz) at -18 °C. This may be attributed to restricted rotation at the lower temperature about the  $\text{C}_2$ - $\text{C}_{\text{ipso}}$  bond, which has more double bond character due to

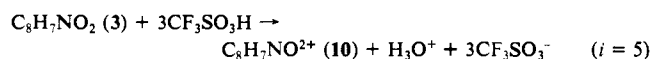
(12) Nitrobenzene and 4-nitrotoluene were practically completely mono-protonated in TFSA. This conclusion was based on the UV and NMR spectroscopic evidence in TFSA, in comparison with the data described in ref 3 and 5.



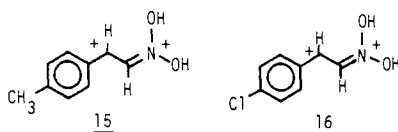
(13) Olah, G. A.; Schlosberg, R. H.; Poter, E. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034.

(14) Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 768, 1471. Shooley, J. N. *Ibid.* **1959**, *31*, 1427.

(15) **10** can be formed in TFSA by diprotonation of **3** followed by dehydration. The  $i$  factor on cryoscopy would be not 3 but 5, according to the following equation, if **10** were formed.



the significant mesomeric contribution of the electron-donating methyl group.



### Conclusion

The results of cryoscopy and NMR spectroscopy show that the stable species formed by the protonation of  $\beta$ -nitrostyrenes in TFSA are the O,O-diprotonated dicationic (*N,N*-dihydroxyiminium benzyl dicationic). The finding of diprotonation on the nitro groups of nitronaphthalenes and nitrostyrenes is unexpected and represents a new aspect of the chemistry of the nitro group. Owing to the higher acidity, the lower freezing point ( $-43.5^\circ\text{C}$ ), and the lower nucleophilicity of TFSA as compared with sulfuric acid, long-lived stable ions should be more easily obtained than in sulfuric acid. In addition, the lower viscosity and the large cryoscopic constant ( $10.06^\circ\text{C}$ ) of TFSA are important advantages in cryoscopy and NMR spectroscopy. The cryoscopic method in TFSA was confirmed to be versatile and to provide reliable evidence in relation to the protonation chemistry.

### Experimental Section

**Materials.** Melting points were obtained on a Yanagimoto micro melting point apparatus and were not corrected. All (*E*)- $\beta$ -nitrostyrenes (**3**, **5**, **13**, **14**) were prepared through condensation of nitroalkanes with a corresponding benzaldehyde and were purified by recrystallization from *n*-hexane or methanol, followed by sublimation. All these compounds showed satisfactory spectroscopic properties and elemental analyses: **3**: mp  $55\text{--}55.5^\circ\text{C}$  (lit.<sup>16</sup> mp  $58\text{--}59^\circ\text{C}$ ); **5**: mp  $63\text{--}64.5^\circ\text{C}$  (lit.<sup>16</sup> mp  $64\text{--}65^\circ\text{C}$ ); **13**: mp  $104.5\text{--}105^\circ\text{C}$  (lit.<sup>16</sup> mp  $101^\circ\text{C}$ ); **14**: mp  $112\text{--}113^\circ\text{C}$  (lit.<sup>17</sup> mp  $112\text{--}112.5^\circ\text{C}$ ). (*Z*)- $\beta$ -Nitrostyrenes (**4**, **6**) were synthesized according to Miller, Flanagan, and Shechter<sup>18</sup> with some modifications: the *E* isomers of  $\beta$ -nitrostyrenes (**3** and **5**) in cyclohexane, when irradiated in a Pyrex tube with a 400-W high-pressure mercury lamp for 8 h, gave mixtures containing the *Z* isomers **4** and **6**, respectively, in 60–70% yield. Isolation by silica column chromatography (flash column: Merck Kieselgel 60, 230–400 mesh; AcOEt/*n*-hexane) followed by molecular distillation (**4**:  $37\text{--}40^\circ\text{C}/(1\text{ mmHg})$  external temperature; **6**:  $40^\circ\text{C}/(1\text{ mmHg})$  external temperature) gave isomerically pure **4** as a volatile yellow oil and **6** (mp  $42.5\text{--}43^\circ\text{C}$ ; lit.<sup>18</sup> mp  $43\text{--}44^\circ\text{C}$ ) as yellow crystals. These compounds gave satisfactory spectroscopic data.<sup>18</sup> Trifluoromethanesulfonic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ) was obtained from 3M Co. and was purified by repeated distillation ( $62.5^\circ\text{C}$  ( $15\text{ mmHg}$ )). Deuteriumtrifluoromethanesulfonic acid ( $\text{CF}_3\text{SO}_3\text{D}$ ) was prepared by heating of a mixture of deuterium oxide (99.7 atom % D) and an equivalent amount of trifluoromethanesulfonic anhydride, prepared as described,<sup>19</sup> at  $80^\circ\text{C}$  for 2 h, followed by distillation ( $68^\circ\text{C}$  ( $17\text{ mmHg}$ )). Triphenylmethanol was recrystallized from benzene-*n*-hexane, mp  $167\text{--}168^\circ\text{C}$  (lit.<sup>9</sup> mp  $164^\circ\text{C}$ ). Mesitoic acid was repeatedly recrystallized from  $\text{CCl}_4$ , mp  $154\text{--}155^\circ\text{C}$  (lit.<sup>10</sup> mp  $152\text{--}153^\circ\text{C}$ ). Potassium nitrate (99.999% pure) was purchased from Aldrich Chemical Co. and was used after drying in an oven under vacuum.

**Recovery Experiment by Quenching of Ion Solutions with Water.** (*E*)- $\beta$ -Nitrostyrenes were stable in TFSA at low temperature ( $-30$  to  $0^\circ\text{C}$ ), and quenching with water yielded the starting materials in 99–100% yields. Quantitative recovery after treatment with typical concentrations ( $5.0 \times 10^{-2}$  mol/kg) and temperatures ( $-40$  to  $0^\circ\text{C}$ , 3 h) used for

cryoscopy was confirmed. After standing at  $-20^\circ\text{C}$  or a specified temperature for 3 h, the TFSA solution was poured dropwise into ice-water, followed by extraction with methylene chloride. The material obtained after evaporation of the solvent proved to be the pure starting material (or the isomerized compound in the case of (*Z*)- $\beta$ -nitrostyrenes, as described in the text) and recovery was quantitative.

**Cryoscope and Procedures for Cryoscopic Studies.** Temperature was measured with a copper-constantan thermocouple with a reference junction at  $0^\circ\text{C}$ . A Yokokawa precision digital multimeter (Model 2501) was used to measure potential with a precision of  $10^{-3}$  mV. The freezing points of TFSA and TFSA solutions were obtained with an accuracy of  $0.01^\circ\text{C}$ , and the procedure was as follows: Electromotive force (*E*, mV) was measured, and to calculate the experimental freezing point (*T*,  $^\circ\text{C}$ ), the reported relation,  $-T = 29.331 \times E - 2.910$ , was used in the range of  $-40$  to  $-50^\circ\text{C}$  without calibration. The apparatus was dried in an oven and cooled under vacuum with protection from moisture. TFSA and materials for solutes were stored with a drying agent ( $\text{P}_2\text{O}_5$ ). The weighed solute was placed in the bottom of a flat-bottomed glass tube (diameter = 1.7 cm) which could be tightly sealed with a Teflon cap. To this tube, weighed TFSA (ca. 9 mL) was added quickly, and the tube was cooled at  $-22^\circ\text{C}$  in a dry ice- $\text{CCl}_4$  bath. Immediately after addition of TFSA, the tube was sealed with a tight-fitting Teflon cap equipped with a copper-constantan thermocouple enclosed in glass. The tube was fitted with an air jacket in which the air pressure was reduced to 20 mmHg by a vacuum pump. The cryoscope was cooled at  $-75^\circ\text{C}$  in a dry ice-ethanol bath under thorough stirring by a well-controlled magnetic stirrer. The initial cooling rate was set at  $2.2^\circ\text{C}/\text{min}$ . Immediately after crystallization (monitored from the cooling curve), the stirring was stopped so as to obtain equilibrium. The freezing points were obtained from the cooling curves as described.<sup>8</sup> The lowering of the freezing point of the solution due to the increment in the molality of the solute (the molal freezing depression) was calculated from the slope of the relationship between the freezing point depressions ( $\Delta T$ , the ordinate) and the molalities of the solute ( $\Delta m$ , the abscissa). The 95% confidence interval of the slopes was also calculated. Good linearity was always obtained (correlation coefficient  $r > 0.99$ ), and the lines passed through the origin in all cases.

**Preparation and NMR Studies of Ions in TFSA.** NMR spectra were measured on JEOL GX400 or FX100 spectrometers equipped with a variable-temperature apparatus. All samples were prepared at  $-22^\circ\text{C}$  in a dry ice- $\text{CCl}_4$  bath, under protection from moisture. The  $^1\text{H}$  NMR data (400 and 100 MHz) were obtained by using an internal lock (acetone- $d_6$  in a capillary) or without locking, and the chemical shifts were referred to  $\text{Me}_4\text{Si}$  in acetone- $d_6$ . The  $^{13}\text{C}$  NMR spectra (100 and 25.5 MHz) were measured by using an external lock ( $\text{D}_2\text{O}$ ) or internal lock ( $\text{CF}_3\text{SO}_3\text{D}$  as a solvent), and the chemical shifts were calibrated on the basis of  $\text{Me}_4\text{Si}$  in  $\text{CDCl}_3$ . In the case of internal locking by using  $\text{CF}_3\text{SO}_3\text{D}$ , the absence of deuterium exchange of any proton was confirmed.

**Oxygen-18 Incorporation Experiment.** Mass ratios were determined with a JEOL JMS DX300 gas chromatography-mass spectrometer. All samples were introduced into the mass spectrometer via the gas chromatograph (column: OV 17.1%, 1 m). Weighed  $\beta$ -nitrostyrene (0.113 mmol) was added to the pre-cooled TFSA (1.13 mmol) at  $-22^\circ\text{C}$  in a dry ice- $\text{CCl}_4$  bath. After standing for 10–15 min at this temperature, the TFSA solution was poured onto crushed ice, which was prepared by freezing 100 or 150 equivalent (for nitrostyrenes) amounts of  $\text{H}_2\text{O}^{16}$  or  $\text{H}_2\text{O}^{18}$  in a dry ice- $\text{CCl}_4$  bath. Extraction with 3 mL of dry  $\text{CH}_2\text{Cl}_2$ , followed by drying over anhydrous  $\text{Na}_2\text{SO}_4$ , gave the samples for gas chromatographic analysis. The mass ratio of  $M + 2/M$  (*M* is the parent molecular ion of  $\beta$ -nitrostyrenes) was determined from the peak areas obtained from mass fragmentography. These analyses revealed that no trace of oxygen-18 was incorporated into the recovered  $\beta$ -nitrostyrenes, (*E*)- $\beta$ -nitrostyrene (**3**), and (*E*)- $\beta$ -methyl- $\beta$ -nitrostyrene (**5**).

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**Registry No.** **3**, 5153-67-3; **4**, 15241-23-3; **5**, 18315-84-9; **6**, 58321-79-2; **13**, 101671-00-5; **14**, 101671-01-6; trifluoromethanesulfonic acid, 1493-13-6; triphenylmethanol, 76-84-6; mesitoic acid, 480-63-7; potassium nitrate, 7757-79-1.

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