Tetrahedron Letters,Vol.25,No.3,pp 325-328,1984
Printed in Great Britain

0040-4039/84 $3.00 + .00

DIPROTONATION OF NITROARENES

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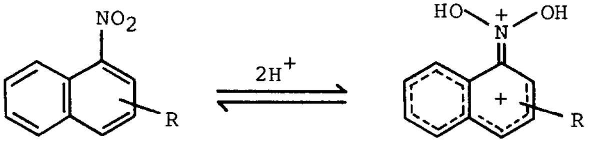
ABSTRACT: Cryoscopic measurement shows that 1-nitronaphthalene is diprotonated in trifluoromethanesulfonic acid (TFSA). The diprotonated nitronaphthalenes are N,N-dihydroxyiminium-naphthalenium dications, which is fully characterized by UV, ^{1}H-, ^{13}C and ^{15}N-NMR spectra.

While monoprotonation of nitroarenes in strongly acidic media is well established by various studies,[1] diprotonation has never been discussed. In this paper we describe a surprising feature of 1-nitronaphthalenes (1): they are diprotonated in trifluoromethanesulfonic acid (TFSA) to give N,N-dihydroxyiminium-naphthalenium dications (2).



1 2

a; R = H
b; R = 2-CH$_3$
c; R = 2,6-diCH$_3$
d; R = 4-CH$_3$
e; R = 4,8-diCH$_3$

TFSA solution of 1a (1; R=H) was deep-red colored, and was stable (even at 40°C) enough for spectroscopic measurements to be made (*vide infra*). When the colored solution after standing for 24 hr at room temperature was diluted with water, alcohol, or trifluoroacetic acid (TFA), 1a was quantitatively recovered. In order to determine whether this deep-red solution consists of monoprotonated 1-nitronaphthalene or of the diprotonated compound (2a), we performed cryoscopic measurement of the TFSA solution of 1a.[2] Since there is no report on the freezing point depression of TFSA,[3] the degree of the depression produced by 1a was compared with those of nitrobenzene (3) and 4-nitrotoluene (4). Observed freezing points were plotted against mole concentration of nitroarenes. Plots for 1a, 3 and 4 showed good linear correlation lines for molar concentrations between 0 and 6.5 x 10^{-2} mole/kg for 1a and between 0 and 10.5 x 10^{-2} mole/kg for 3 and 4. From the slopes of the plots, the molar freezing point depression values were 29.4 ± 2.2 (95% confidence interval) degree/mole·kg^{-1} for 1a, 20.1 ± 0.9 degree/mole·kg^{-1} for 3, and 19.5 ± 2.2 degree/mole·kg^{-1} for 4. Nitrobenzene in TFSA is monoprotonated, the reported dissociation constant of 3 in TFSA being 3.2 x 10^{3}.[1c] The UV and ^{1}H-NMR spectra of 4 and 5 in TFSA[4] also showed that they were monoprotonated in TFSA by comparison with reported data.[1b,d] Therefore, the cryoscopic i factor for each of 3 and 4 is 2 (eq. 1 and 2). As the molar freezing point depression of 1a is 1.46 times that of 3 and 1.51 times that of 4, the cryoscopic i factor for 1a is 3: thus, 1a is diprotonated in TFSA (eq. 3).

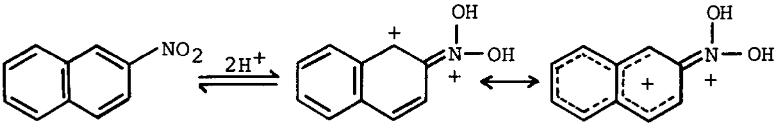
$$C_6H_5NO_2 + CF_3SO_3H \longrightarrow C_6H_5NO_2H^+ + CF_3SO_3^- \quad (i=2)\cdots(1)$$

$$CH_3\text{-}C_6H_4NO_2 + CF_3S)_3H \longrightarrow CH_3\text{-}C_6H_4NO_2H^+ + CF_3SO_3^- \quad (i=2)\cdots(2)$$

$$C_{10}H_7NO_2 + 2CF_3SO_3H \longrightarrow C_{10}H_7NO_2H_2{}^{2+} + 2CF_3SO_3{}^- \quad (i=3)\cdots(3)$$

In order to obtain information about the structural nature of 2, the UV and NMR spectra were measured. 2a had an absorption maximum in the visible region at 524 nm in TFSA (log ε = 4.05), and this is bathochromically shifted by more than 100 nm when compared with that of 1-protonated naphthalene (1-naphthalenium ion; naphthalene in HF-BF_3; λ_{max}(log ε) = 410 (sh) and 390 nm (4.04)).[5] The UV spectrum of protonated nitrobenzene in TFSA solution has λ_{max}(log ε) at 344 nm (4.03) and resembles that of the benzenium cation ($AlBr_3$-HBr; 325 nm).[6] A methyl group(s) substituted on the naphthalene ring (1b, c, d) shifts λ_{max} to shorter wave length by 4-12 nm, as was reported in the case with naphthalenium cations,[5] but compound 2e with a methyl group at 8 position, which is *peri* to the iminium group, had λ_{max} at 554 nm (log ε = 3.76).

The ^{1}H-NMR spectrum of 2a is shown in the figure (A). The spectrum eliminates the possibility of a protonation on the naphthalene ring, which cannot be ruled out by the result of cryoscopy. The nmr spectra in CF_3SO_3D never show any exchange of every proton of the naphthalene ring for more than 3 hr at -20°C, and the recovered 1a after quenching was not deuterated at all. Three protons are significantly deshielded, and they were assigned as H(2), H(4) and H(8) (*peri*) based on comparison with the spectra of mono- and dimethyl-1-nitronaphthalene (1b, c, d, e) in TFSA. Since the most highly deshielded absorption at δ 9.13 ppm of 2a disappeared in the spectra of 2b (R=2-CH_3) and 2c (R=2,6-diCH_3), this absorption of 2a can be assigned to H(2). One of the other two deshielded absorptions (8.59 and 8.53 ppm) disappeared in the spectrum of 2d (R=4-CH_3), and both disappeared in the spectrum of 2e (R=4,8-diCH_3): These two absorptions can therefore be assigned to H(4) and H(8). These spectra resemble those of protonated naphthalenes in superacid, reported by Olah,[7] except for the deshielded H(8) proton located at the *peri* position to the iminium group. Interestingly, H(3) of 2d and 2e is more shielded by 0.5 ppm than H(5), H(6) and H(7), just as is observed for 4-protonated 1-methylnaphthalene.[7a] In the spectrum of 2-nitronaphthalene (5) in TFSA, H(1) was highly deshielded at 9.23 ppm which shows that a large amount of the positive charge on the ring is located on the C (1) carbon (6a).



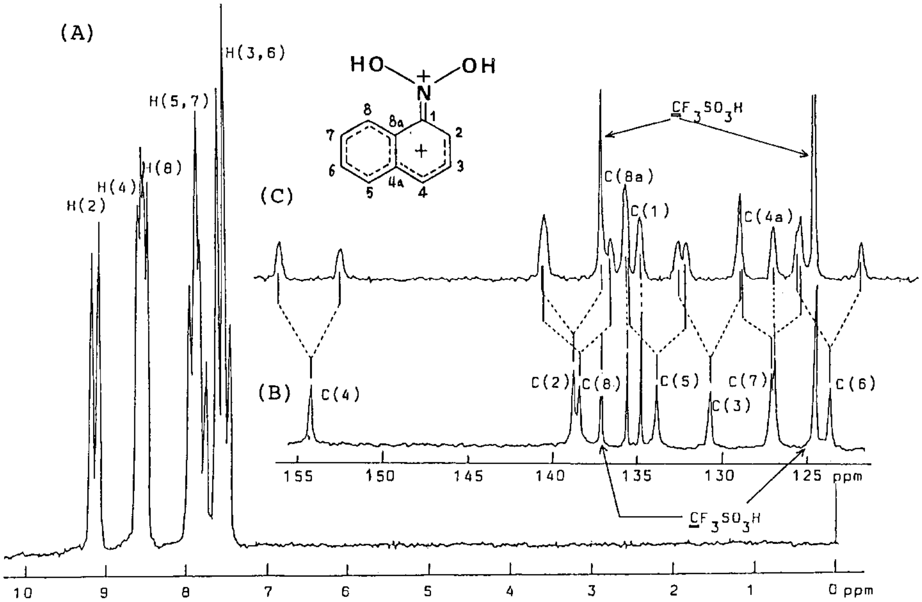
5 6a 6b

UV (in TFSA at 0°C)
λ_{max} nm (log ε):
547 (3.48), 411 (4.19)

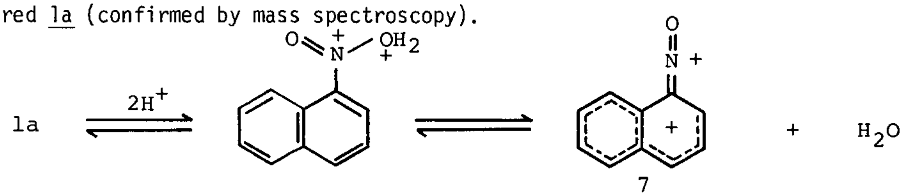
The ^{13}C-NMR spectrum of 2a also clearly showed the presence of a single species in TFSA solution, different from the cases of protonated nitrosobenzene[8] and nitrobenzene.[1d] A protonation on the naphthalene ring was also eliminated by an off-resonance proton decoupling experiment (Fig. B and C). The C(2), C(4) and C(8) carbons in 2a appeared at 138.8, 154.3 and 138.3 ppm, respectively, which are more deshielded by 15-20 ppm than those in TFA. The C(1) carbon appeared at 135.6 ppm as a singlet, which is more shielded by 12 ppm than in TFA.

The ^{15}N-NMR spectrum of 2a was obtained by diprotonation of 99% ^{15}N-enriched 1-nitronaphthalene with TFSA at -20°C. The ^{15}N absorption of 2a in TFSA appeared at 348.15 ppm from the external ammonia, which was spin-spin coupled with H(2) (J=2.2 Hz), while that of 1a in TFA appeared at 376.79 ppm.

Figure NMR Spectra of 2a in TFSA at -30°C (A) ^{1}H-NMR (100 MHz) (B) ^{13}C-NMR (25.0 MHz); Complete Decoupling (C) Off-Resonance Proton Decoupling



Finally, we eliminated the possibility of the oxo-iminium-naphthalenium ion (7), as the colored species in the TFSA solution of 1a. 7 can be formed by diprotonation followed by elimination of water in an analogous way to the Wallach rearrangement.[9] 7 seems to be eliminated from the result of the cryoscopic experiment (the cryoscopic *i* factor for the formation of 7 would be 5), though the UV and NMR spectra were not incompatible with 7. Conclusively, when TFSA solution of 1a was quenched with 95% ^{18}O-enriched water, no ^{18}O was incorporated into the recovered 1a (confirmed by mass spectroscopy).



The formation of diprotonated nitronaphthalenes, N,N-dihydroxyiminium-naphthalenium dication (2 and 6), is also supported by the existence of a phenylation reaction with benzene,[10] which acts as a nucleophile towards the dications, as in the TFSA-catalyzed phenylation reaction of N-phenylhydroxylamine and nitrosobenzene with benzene, which involves iminium-benzenium dications.[11] The TFSA-catalyzed reaction of nitrobenzene with benzene occurs under forcing conditions.[12] Nitronaphthalenes can be relatively easily diprotonated, because they lose a part of the naphthalenoid aromaticity on diprotonation, while nitrobenzene loses benzenoid aromaticity completely on diptotonation. The facile diprotonation on a nitro group is rather surprising from a conventional point of view, and the present fingings should contribute significantly to an understanding of the chemistry of iminium-benzenium dications.[9,11,13] Futher work on the protonation of nitro compounds is in progress.

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(10) From the reaction mixture of 1a, TFSA (30 eqt) and benzene (60 eqt) (after reaction for 2 hr at 0-5°C), 2-phenyl-, 4-phenyl- and 3,4-diphenyl-1-naphthylamine were identified in the yields of 5-10, 10-15 and 25-30%, respectively. From the corresponding reaction mixture of 2-nitronaphthalene, 1-phenyl-2-naphthylamine (50%) was isolated. No naphtylamine was found in either reaction. These isolated phenylated naphthylamines are secondary products from the initial phenylated products, as the formation requires reduction steps. We have found that phenylated intermediates of some stabilized iminium-benzenium dications suffer reduction, i.e. 4-biphenylhydroxylamine gives 4-aminobiphenyl as the major product, when treated with TFSA-benzene.[11] The results of a detailed products analysis will be published separately.

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(Received in Japan 3 October 1983)