dodecyl sulfate and cetyltrimethylammonium bromide were chemically pure grades, while BRIJ 52 (ethoxylated(2) cetyl alcohol) was an Atlas commercial sample. Solvents were the middle fraction of redistilled analytical grade chemicals. This was a requirement of the interfacial tension work because trace impurities were found to reduce surface tension.

Reactions were carried out at 24 ± 1 °C (room temperature) in a 21-mm diameter glass tube, containing a 10 × 3 mm magnet. Stirring was achieved using a Cole-Parmer Magne-4 in which four stirrers are driven by a common belt. Catalyst was 5 mol % with respect to substrate and ethyl bromide was in 50% molar excess. Reaction volumes were 5 mL organic, 1 mL aqueous. Samples of 0.1 mL were withdrawn every 15-60 min according to the rate and extent of reaction and added to 0.1 mL of dilute HCl and 0.5 mL of toluene. The upper phase was injected onto a GC column (HP-1 crosslinked methyl silicone gum, 30 m × 0.53 mm) at 195 °C in a Hewlett-Packard 5890A instrument. Typical retention times were as follows: starting material, 3.3 min; C-alkylated product, 3.9 min; O-alkylated product, 4.5 min. Initial peak identification was confirmed by NMR spectroscopy. Each reaction profile was constructed from 5-8 samples.

Interfacial tension measurements were performed by the Du Noy ring method using a Lauda Tensiometer. Using the "prevented rupture" technique, in which the interface is not broken during the measurement, readings were taken every 5 min until a stable value was obtained. Ten minutes was usually sufficient.

Registry No. BRIJ 52, 9004-95-9; TMeAB, 64-20-0; TEtAB, 71-91-0; TPrAB, 1941-30-6; TBuAB, 1643-19-2; PhCH(Et)COPh, 16282-16-9; PhCH=C(OEt)Ph, 13676-20-5; tetrahexylammonium bromide, 4328-13-6; tetraoctylammonium bromide, 14866-33-2; deoxybenzoin, 451-40-1; ethyl bromide, 74-96-4; sodium dodecyl sulfate, 151-21-3; cetyltrimethylammonium bromide, 57-09-0.

Direct Observation of an Intermediate in the Oxygen Atom Rearrangement of 2-Cyclopropylnitrobenzene in a Strong Acid

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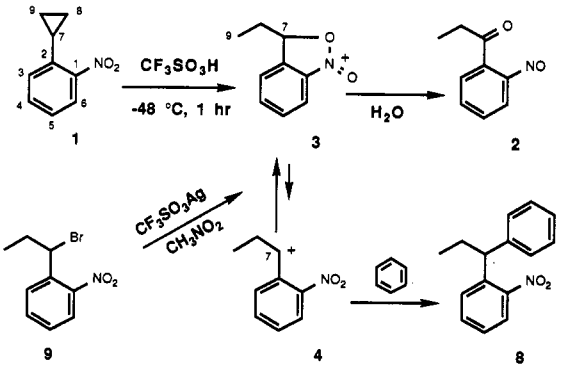
Direct spectroscopic observation revealed the formation of the 1,3-dihydro-3-ethyl-1-oxo-2,1-benzoxazolyl cation (**3**) from 2-cyclopropylnitrobenzene (**1**) in trifluoromethanesulfonic acid. This observation provided experimental evidence for the involvement of **3** as a discrete intermediate in the transfer of oxygen from nitrogen to carbon during the rearrangement of **1** to 2-nitrosopropiophenone.

The electron-donating effect of a cyclopropyl group on an aromatic ring is expected to stabilize a cation center more efficiently than that of a phenyl group.[1,2] This generalization led us to anticipate that a cyclopropyl group might exert a similar stabilizing influence on the cationic center NO_2H^+ (a protonated nitro group),[3] and we therefore undertook the investigation of the behavior of 2-cyclopropylnitrobenzene in a strong acid. 2-Cyclopropylnitrobenzene (**1**) in an excess of trifluoromethanesulfonic acid (TFSA) reacted to give *o*-nitrosopropiophenone (**2**) in 79% yield after aqueous workup (Scheme I). The reaction catalyzed by sulfuric acid has been reported,[4] and the involvement of the cyclic intermediate **3** in the formation of **2** has been proposed although no experimental evidence was provided. We present herein direct spectroscopic evidence for the involvement of the cyclic intermediate, 1,3-dihydro-3-ethyl-1-oxo-2,1-benzoxazolyl cation (**3**), in the oxygen atom rearrangement of 2-cyclopropylnitrobenzene to *o*-nitrosopropiophenone. The cyclic intermediate **3** was a discrete chemical species, stable

Scheme I



enough to be observed spectroscopically in TFSA at −30 °C. The ^1H and ^{13}C NMR data for **3** are summarized in Tables I and II, together with the data for the neutral precursor **1**. In the ^1H NMR spectrum of **3**, the H_7 proton was observed at 7.40 ppm as a double doublet, and in the ^{13}C NMR spectrum (Table II) the C_7 carbon atom resonated at 98.4 ppm. These chemical shifts are more readily interpreted in terms of formation of the C_7–O bond rather than the formation of the *free* cation center at the 7-position (**4**).[5] From structural considerations, **3** can be

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(2) Brown, H. C.; Cleveland, J. D. *J. Org. Chem.* **1976**, *41*, 1792. Hahn, R. C.; Corbin, T. F.; Shechter, H. *J. Am. Chem. Soc.* **1968**, *90*, 3404.

(3) Ohta, T.; Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1984**, 325. Ohwada, T.; Ohta, T.; Shudo, K. *J. Am. Chem. Soc.* **1986**, *108*, 3029.

(4) Dickinson, W. B. *J. Am. Chem. Soc.* **1964**, *86*, 3580. Shabarov, Y. S.; Mochalov, S. S.; Stepanova, I. P. *Dok. Akad. Nauk SSSR* **1969**, *189*, 1028. See also: Gravel, D.; Hebert, J.; Thoraval, D. *Can. J. Chem.* **1983**, *61*, 400.

(5) Olah, G. A.; Porter, R. D.; Kelly, D. P. *J. Am. Chem. Soc.* **1971**, *93*, 464. Forsyth, D. A.; Spear, R. J.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2512. Olah, G. A.; Westerman, P. W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3419. Olah, G. A.; Westerman, P. W.; Nakanishi, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548. In the 1-phenyl-1-ethyl cation, the benzyl proton resonated at 10.50 ppm, and the benzyl carbon atom at 230.4 ppm.

0022-3263/90/1955-2717$02.50/0

Table I. ^1H NMR Spectroscopic Data for Neutral Precursors and Ions[a]

compd	solvent	temp, °C	H_3	H_4	H_5	H_6	H_7	H_8	H_9
1	$CDCl_3$	23	7.16 (d, 7.7)	7.48 (dd, 7.5, 7.5)	7.29 (dd, 8.1, 7.5)	7.80 (d, 8.1)	2.40 (dd, 8.5, 5.5)	0.71 (m), 1.05 (m)	0.71 (m), 1.05 (m)
3	TFSA	-30	8.70 (d, 8.3)	9.06 (dd, 7.6, 7.6)	8.67 (dd, 7.8, 7.8)	9.00 (d, 8.6)	7.40 (dd, 7.8, 4.2)	2.90 (dq, 7.6, 7.6) 3.21 (dq, 4.2, 7.5)	1.81 (t, 7.1)

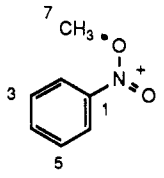
[a] Coupling modes and ^1H–^1H coupling constants in hertz are shown in parentheses: d = doublet, dd = double doublet, m = multiplet, q = quartet, dq = double quartet.

Table II. ^{13}C NMR Spectroscopic Data for Neutral Precursors and Ions[a]

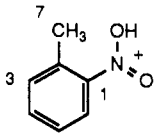
compd	solvent	temp, °C	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
1	$CDCl_3$	23	150.6	137.2	127.1	132.1	125.9	123.4	12.1	7.8	7.8
3	TFSA	-30	151.9	137.0	134.0 (171.7)	145.8 (167.3)	122.8 (179.0)	125.0 (178.6)	98.4 (164.4)	25.7 (132.0)	7.7 (128.1)
5[b]	SO_2	-60	142.9	128.8 (171.7)	132.8 (172.0)	146.2 (167.7)	132.8 (172.0)	128.8 (171.7)	67.5 (157.0)		
6	TFSA	-20	145.0	141.5	135.1 (167.1)	144.1 (167.3)	129.4 (171.7)	129.6 (164.3)	21.9 (133.0)		
7	$CDCl_3$	23	149.1	133.4	132.6 (164.3)	132.9 (164.3)	126.8 (165.8)	124.4 (167.3)	20.3 (129.1)		

[a] ^{13}C–^1H coupling constants are shown in parentheses in hertz. [b] Reference 6.

regarded as an O-monoalkylated nitrobenzene. This view is also supported by the correspondence of the reported ^{13}C NMR chemical shifts[6] of the ion of O-methylated nitrobenzenes **5** (in SO_2) with those of **3** (Table II). Furthermore, the ^{13}C chemical shifts of the aromatic ring of **3** are also related to those of O-protonated state (**6**) of *o*-nitrotoluene (**7**) in TFSA (Table II).[7] In the ^{15}N NMR spectrum of ^{15}N-enriched **1** in TFSA, the nitrogen signal of **3** was observed at -10.99 ppm (calibrated on the basis of $^{15}NH_2{}^{15}NO_2$ in D_2O as 0 ppm).[8] This chemical shift was in good accordance with that of O-monoprotonated nitrobenzene formed in TFSA (-9.20 ppm).[3]



5



6

In deuterated trifluoromethanesulfonic acid (CF_3SO_3D), **1** gave monodeuterated **2** in a 59% yield at -48 °C, where the terminal methyl group of **2** was deuterated. This result suggested predominant protonation of the cyclopropyl ring at the 8(or 9)-position in TFSA and rearrangement to **3**. Subsequent ring opening of **3** then occurs to yield the *o*-nitrobenzyl cation **4**. In the presence of benzene, **1** gave 2-(1-phenylpropyl)nitrobenzene (**8**) (12%) in addition to **2** (72%), catalyzed by TFSA. This acid-catalyzed reaction of **1** with benzene suggested the possible contribution of an acyclic cation **4**, which may be in equilibrium with cyclic **3** in TFSA. Alternatively, the cation **4** may be formed by silver ion (CF_3SO_3Ag) assisted ionization of 2-(1-bromopropyl)nitrobenzene (**9**) in nitromethane at -30 °C: the species thus formed gave a 65% yield of **2** after aqueous quenching. Even aqueous workup of the species formed by the treatment of the bromide by CF_3SO_3Ag gives essentially the same yield of **2** as does the reaction **1** → **2**. This suggests that the same intermediate (**3**) rather than the cation **4** may be involved in both cases. The same reaction of the bromide was also catalyzed by silver tetrafluoroborate ($AgBF_4$) in methylene chloride at -45 °C and yielded **2** (25%), together with recovered **9** (15%). This result excluded intervention of 2-((((trifluoromethyl)sulfonyl)oxy)propyl)nitrobenzene in the formation of **2** in the CF_3SO_3Ag-assisted reaction of **9** and therefore in the acid-catalyzed reaction of **1** in TFSA. The subsequent proton elimination (H_7) and N–O bond cleavage of **3** do not occur in TFSA; no absorption of **2** (or protonated **2**) can be detected in the NMR spectra of **1** in TFSA, and the nitrosobenzene itself is very unstable in TFSA. Basic treatment of the solution of **3** effected its transformation into nitrosobenzene **2**.

The reaction described herein represents an efficient intramolecular route to the formation of an O-alkylated nitroarene, which is in contrast to the severe conditions employed in the intermolecular O-methylation reactions of nitroarenes catalyzed by methylsulfoxonium fluoroantimonate.[6,9]

Experimental Section

General Methods. Proton NMR spectra were measured on either a JEOL FX 100 (100 MHz) NMR spectrometer or a JEOL GX 400 (400 MHz) NMR spectrometer with TMS as an internal reference in $CDCl_3$. Coupling constants (J_{HH}) are shown in parentheses in hertz.

^{13}C NMR spectra were recorded on either a JEOL FX 100 (at 25.5 MHz) or a JEOL GX 400 (at 100 MHz) in $CDCl_3$ and chemical shifts are reported in ppm, referenced by assignment of the middle resonance of deuteriochloroform as 77.0 ppm from TMS. Infrared spectra were measured on a Shimadzu IR 408 as a solid suspension in KBr. Column chromatography was performed by using silica gel (Wako Chemical Co., Wakogel C-200), and flash column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh) with the specified solvent. Combustion analyses were carried out in the microanalytical laboratory of this facility.

Materials. 2-Cyclopropylnitrobenzene (**1**) was prepared by nitration (Ac_2O/HNO_3) of cyclopropylbenzene[10] at 0 °C as described previously.[3] The crude cyclopropylnitrobenzenes (*o*/*p*

(6) Olah, G. A.; Fung, A. P.; Rawdah, T. N. *J. Org. Chem.* 1980, *45*, 4149.

(7) The assignments of the ^1H and ^{13}C NMR spectra of **7** were based on the 2D-CHCOSY spectra.

(8) We thank Drs. K. Kimura and K. Harada (the Central Research Laboratory of Yakult Co.) for providing facilities for measuring the ^{15}N NMR spectra on a JEOL GX400 spectrometer.

(9) Both intra- and intermolecular O-alkylations of an aliphatic nitro group, in particular nitroalkenes, are effectively catalyzed by a Lewis acid. Denmark, S. E.; Sternberg, J. A.; Leuoend, R. *J. Org. Chem.* **1988**, *53*, 1251.

(10) *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 328.

isomer ratio 4/1) were chromatographed on silica gel with CH_2Cl_2–*n*-hexane (1:10), followed by distillation under reduced pressure (111 °C/4 mmHg) to give 1 as a yellow oil in 39% yield. The ^1H and ^{13}C NMR spectroscopic data of 1 are shown in Tables I and II, respectively. 2-(1-Bromopropyl)nitrobenzene (**9**) was obtained by bromination (PBr_3 in CH_2Cl_2 at 0 °C, 1 h) of the corresponding 2-(1-hydroxypropyl)nitrobenzene[11] and purified by column chromatography (1:4 CH_2Cl_2–*n*-hexane) to give a pale yellow oil **9** (17%). **9**: a pale yellow oil, purified by molecular distillation (42 °C (external temperature)/0.8 mmHg). Anal. Calcd for $C_9H_{10}NO_2Br$: C, 44.28; H, 4.13; N, 5.74. Found: C, 44.08; H, 4.06; N, 5.44. ^1H NMR: 7.84 (1 H, d, d, 7.70, 1.47), 7.82 (1 H, d, d, 8.06, 1.47), 7.63 (1 H, t, d, 7.70, 1.47), 7.43 (1 H, t, d, 7.70, 1.47), 5.52 (1 H, d, d, 5.86, 8.43), 2.23 (2 H, m), 1.08 (3 H, t, 7.15). ^{13}C NMR: 147.9 (s), 136.7 (s), 130.4 (d, 161.4), 128.8 (d, 161.4), 124.2 (d, 162.9), 49.4 (d, 164.4), 33.4 (t, 132.1), 12.7 (q, 123.2). 2-(1-Hydroxypropyl)nitrobenzene: ^1H NMR: 7.90 (1 H, d, d, 2.25, 1.0), 7.80 (1 H, d, d, 2.5, 12.5), 7.64 (1 H, d, t, 2.25, 10.5), 7.40 (1 H, d, t, 2.5, 12.5), 5.16 (1 H, quintet, 5.0), 1.82 (2 H, m), 1.04 (3 H, t, 10.0). ^{13}C NMR: 147.0 (s), 139.6 (s), 132.7 (d), 127.2 (d), 123.4 (d), 69.7 (d), 30.9 (t), 9.9 (q). ^{15}N-Enriched 2-cyclopropylnitrobenzene was prepared by nitration with $[^{15}N]NaNO_3$ (98.8 atom % ^{15}N, MSD Isotopes) of cyclopropylbenzene (1.24 equiv) in trifluoroacetic acid at 0 °C. After 2 h of stirring at 0 °C, the usual aqueous workup, extraction with CH_2Cl_2 and evaporation of the solvent gave the crude mixture, which was purified by column chromatography (1:10 CH_2Cl_2–*n*-hexane) to yield ^{15}N-labeled 1 (14%) in addition to recovered cyclopropylbenzene (22%) and ^{15}N-labeled *p*-cyclopropylnitrobenzene (4%). Silver trifluoromethanesulfonate was obtained from Aldrich Chemical Co.

Reaction of 2-Cyclopropylnitrobenzene in TFSA. 2-Cyclopropylnitrobenzene (**1**) (137.6 mg, 0.844 mmol) was added in portions to 8.0 mL (100 equiv) of TFSA cooled in a dry ice–acetone bath at −48 °C, with vigorous stirring. After 1 h of stirring at the same temperature, the deep orange solution was added dropwise into ice water (100 mL) followed by extraction with CH_2Cl. The organic layer was washed with brine and dried over Na_2SO_4. The material obtained after evaporation of the solvent was purified by column chromatography (silica gel) with 1:3 CH_2Cl_2–*n*-hexane as the eluent to give 109 mg (79%) of 2-nitrosopropiophenone (**2**). **2**: mp 105.0 °C dec (recrystallized from CH_2Cl_2–hexane) as a colorless powder. Anal. Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58. Found: C, 65.95; H, 5.53; N, 8.52. ^1H NMR ($CDCl_3$): two components, owing to the equilibrium between the monomer and the dimer of the nitroso group, were observed in a ratio of 5:1, as estimated from the ^1H NMR spectrum. Major component: 7.76 (1 H, t, d, 7.7, 1.5), 7.61 (1 H, d, 7.88), 7.60 (1 H, t, nd), 7.17 (1 H, d, 7.33), 2.95 (2 H, q, 7.33), 1.31 (3 H, t, 7.33); minor component: 7.88 (1 H, d, 7.33), 7.87 (1 H, d, 7.7), 7.76 (1 H, t, 7.7), 7.63 (1 H, t, nd), 3.05 (2 H, q, 6.96), 1.25 (3 H, t, 6.97). IR (KBr, cm^{-1}): 1690, 1600, 1580, 1490 cm^{-1}.

Acid-Catalyzed Reaction of 2-Cyclopropylnitrobenzene in the Presence of Benzene. To an ice-cooled solution of 4.42 mL (10 equiv) of TFSA in 13.26 mL (30 equiv) of dry benzene, 814.7 mg (5 mmol) of 1 was added in portions. Stirring was continued at 1 °C (in an ice–water bath) for 1 h, followed by the aqueous workup as described above. Evaporation of the solvent and flash column chromatography with 1:3 CH_2Cl_2–*n*-hexane as the eluent gave 589.2 mg (72% yield) of 2-nitrosopropiophenone (**2**) and 142.0 mg (12%) of 2-(1-phenylpropyl)nitrobenzene (**8**) as a pale yellow oil. **8**: purified by molecular distillation (48 °C (external temperature)/0.3 mmHg). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.39; H, 6.27; N, 5.53. ^1H NMR ($CDCl_3$) 7.70 (1 H, d, d, 8.25, 1.47), 7.50 (1 H, t, d, 7.69, 1.46), 7.43 (1 H, d, d, 8.06, 1.46), 7.32–7.24 (5 H, m), 7.20 (1 H, t, t, 6.96, 1.47), 4.46 (1 H, t, 7.69), 2.08 (2 H, m), 0.91 (3 H, t, 7.33).

Silver Ion Assisted Reaction of 2-(1-Bromopropyl)nitrobenzene. A solution of 2-(1-bromopropyl)nitrobenzene (**9**) (244.0 mg) in 0.5 mL of nitromethane was added by portions (over 2 min) to a solution of 475.8 mg of $AgSO_3CF_3$ (1.58 equiv with respect to the bromide) in 2 mL of nitromethane at −30 °C in a dry ice–acetone bath with vigorous stirring. After 5 min at that temperature the mixture was poured into ice and water and worked up as described above. The crude products were chromatographed (1:1 CH_2Cl_2–*n*-hexane) to give 105.2 mg (60% yield) of 2-nitrosopropiophenone (**2**), accompanied with recovered bromide (40.1 mg, 16%). **2** obtained in this reaction was identical with an authentic sample (obtained from **1**), in terms of both the IR and NMR spectra.

Preparation and NMR Studies of Ions in TFSA. NMR spectra of ions were measured on a JEOL GX 400 spectrometer equipped with a variable-temperature apparatus. Coupling constants (J_{HH} and J_{CH}) are shown in parentheses. The digital resolutions in the observed NMR spectra are as follows: ±0.5 Hz in ^1H NMR spectra and ±2.9 Hz in ^{13}C NMR spectra. All samples of ions in TFSA were prepared below −30 °C in a dry ice–ethanol bath. The ^1H NMR spectra were obtained without deuterium locking, and the chemical shifts were calibrated as follows. The chemical shifts of the methyl groups of protonated acetone in these acid systems were referred to TMS in acetone-d_6 in a capillary: in TFSA (−30 °C), 3.26 ppm. The ^{13}C NMR spectra were also recorded without deuterium locking. The chemical shifts in TFSA were calibrated on the basis of the middle resonance of the quartet of CF_3SO_3H as 118.07 ppm from TMS in $CDCl_3$.

Registry No. 1-*o*, 10292-65-6; 1-*p*, 6921-44-4; 1 ^{15}N, 125643-11-0; **2**, 25804-26-6; **2** (dimer, 125643-12-1; **3**, 117972-82-4; **4**, 125643-14-3; **8**, 125643-13-2; **9**, 125643-10-9; cyclopropylbenzene, 873-49-4; 2-(1-hydroxypropyl)nitrobenzene, 90972-31-9.

(11) Chaudhuri, A. R.; Giiosh, T. N. *J. Indian Chem. Soc.* **1951**, *28*, 563.