hexane/EtOAc, 85/15) of the residue gave 0.531 g of the product mixture. Preparative TLC (hexane/EtOAc, 85/15; R_f 0.57–0.66) afforded 0.122 g of pure **32**: mp 68–70 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 18 H, $SiCH_3$), 1.29 (t, J = 7.1 Hz, 6 H, CH_3), 2.99 (s, 4 H, CH_2), 4.25 (q, J = 7.1 Hz, 4 H, OCH_2), 6.63 (s, 2 H, =CH); ^{13}C NMR ($CDCl_3$) δ –1.62 ($SiCH_3$), 13.9 (CH_3), 40.7 (CH_2), 62.2 (OCH_2), 118.4 (CN, $^3J_{CN-H}$ = 17 Hz), 122.4 (=C), 157.1 (=CH), 168.8 (CO); IR (neat) 2980, 2970, 2910, 2225 (CN), 1730 (CO), 1585, 1450, 1370, 1280, 1255, 1205, 1190, 1120, 1065, 1045, 1015, 850, 770, 755, 695 cm^{-1}; mass spectrum, m/e 434 (M^+). Anal. Calcd for $C_{21}H_{34}N_2O_4Si_2$: C, 58.03; H, 7.88; N, 6.44. Found: C, 58.53; H, 8.00; N, 6.47.

5-Phenyl-2-[(trimethylsilyl)methylene]-4-hexynenitrile (33). This compound was prepared from 1-phenyl-1,4-pentadiyne (0.35 g, 2.5 mmol) and Me_3SiCN (0.67 mL, 5 mmol) according to the general procedure. After the solvent was removed in vacuo, bulb-to-bulb distillation (110–120 °C (0.4 mmHg)) gave a 0.463 g of a crude product. The distillate was purified by gel permeation LC to give 0.249 g of pure **33**. The spectral data were obtained on this mixture: ^{1}H NMR ($CDCl_3$) δ 0.27 (s, Z isomer) and 0.25 (s, E isomer) [total 9 H, $SiCH_3$], 3.46 (d, J = 1.7 Hz, Z isomer) and 3.40 (d, J = 0.5 Hz, E isomer) [total 2 H, CH_2], 6.86 (t, J = 1.7 Hz, Z isomer) and 6.69 (d, J = 0.5 Hz, E isomer) [total 1 H, =CH], 7.30–7.33 (m, 3 H, Ph), 7.43–7.46 (m, 2 H, Ph); IR (neat) 3080, 3060, 3040, 2960, 2910, 2220 (CN), 2200 (CN), 1595, 1575, 1490, 1445, 1415, 1320, 1255, 1070, 1430, 850, 760, 690 cm^{-1}; mass spectrum, m/e 239 (M^+).

2,3-Diphenyl-3-(trimethylsilyl)prop-2-enenitrile (34): mp 102–103 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9 H, $SiCH_3$), 6.81 (d, J = 7.0 Hz, 2 H, Ph), 7.10–7.22 (m, 8 H, Ph); ^{13}C NMR ($CDCl_3$) δ –0.93 ($SiCH_3$), 119.6 (CN), 123.3, 126.6, 126.9, 128.0, 128.2, 128.3, 129.2, 135.1, 140.8 (Ph, =CCN), 165.0 (=CSi); IR ($CDCl_3$) 3150, 3060, 3030, 2960, 2900, 2210 (CN), 1595, 1490, 1445, 1265, 1255, 1025, 850, 695, 645 cm^{-1}; mass spectrum, m/e 277 (M^+). Anal. Calcd for $C_{18}H_{19}NSi$: C, 77.93; H, 6.90; N, 5.05. Found: C, 78.12; H, 6.89; N, 4.87.

5-[Bis(trimethylsilyl)amino]-3,4-diphenyl-1*H*-pyrrole-2-carbonitrile (36). In a 10-mL flask were placed diphenylacetylene (0.45 g, 2.5 mmol), Me_3SiCN (2.0 mL, 15 mmol), and $PdCl_2$ (18 mg, 0.1 mmol). The mixture was refluxed with stirring for 20 h under nitrogen. The excess Me_3SiCN was evaporated in vacuo. Column chromatography (silica gel; hexane/EtOAc, 85/15) of the residue afforded 0.887 g of a pale yellow solid (88% yield), which was essentially pure. A sample for the spectral data was obtained by recrystallization of the solid from hexane: mp 186–187 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 18 H, $SiCH_3$), 7.09–7.27 (m, 10 H, Ph), 8.80 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.59 ($SiCH_3$), 92.7 (CN), 139.5 (NCN); IR (Nujol) 3330 (NH), 2200 (CN) cm^{-1}; mass spectrum, m/e 403 (M^+). Anal. Calcd for $C_{23}H_{29}N_3Si_2$: C, 68.43; H, 7.24; N, 10.41. Found: C, 68.66; H, 7.10; N, 10.42.

Acknowledgment. This work was supported in part by Grant-in-Aid for Scientific Research provided by the Ministry of Education, Science, and Culture, Japan (No. 60750788 and 61750807). We gratefully acknowledge the ISIR Material Analysis Center in Osaka University for the measurement of ^{1}H and ^{13}C NMR, mass spectrum, and elemental analyses and for the determination of X-ray structure. We acknowledge Shin-Etsu Chem. Ind. Ltd. for generous gift of chlorosilanes.

Lower Nitrogen Oxide Species as Catalysts in a Convenient Procedure for the Iodination of Aromatic Compounds

Finn Radner

Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Received December 28, 1987

A simple method for the iodination of aromatic compounds, using I^- as the iodine source and O_2 and catalytic amounts of $NO^+BF_4^-$ as the oxidant, is presented. The reactions are performed at 25 °C in CF_3COOH/CH_2Cl_2 or CF_3COOH/CH_3COOH mixtures and compounds with as different reactivities as the halobenzenes and 1-methoxynaphthalene can be iodinated in very good yields. A set of relative rates, isotope effects, and isomer distributions in accordance with the electrophilic action of an "I^+" species are presented. The formation of "I^+" is discussed in terms of possible outer-sphere and inner-sphere electron-transfer steps. Aromatic bromination and to a lesser extent chlorination can be performed by using similar methods.

Introduction

Although aryl iodides have been successfully used in organic synthesis for more than a century, e.g., in the syntheses of Ullman[1a] and Heck,[1b] more extensive progress has been retarded due to the lack of simple and reliable methods of their preparation.[2] Aromatic compounds can generally be iodinated by iodine[3] only in the presence of a Lewis acid,[5] a hydrogen iodide trap,[6] or, most commonly, an oxidizing agent[7-11] (Scheme I).

Scheme I. Various Mechanisms of Electrophilic Aromatic Iodination

$$\begin{array}{lrl}
\text{activation:} & I_2 + L \longrightarrow \text{“}I^+\text{”} + LI^- & (1) \\
 & I_2 + Ag^+ \longrightarrow \text{“}I^+\text{”} + AgI & (2) \\
 & 0.5I_2 + \text{ox} \longrightarrow \text{“}I^+\text{”} + \text{red}^- & (3) \\
\text{oxidation of } I^-\text{:} & I^- + \text{ox} \longrightarrow 0.5I_2 + \text{red}^- & (4) \\
\text{iodination:} & \text{“}I^+\text{”} + ArH \longrightarrow Ar(H)I^+ \xrightarrow[-H^+]{\text{slow}} ArI & (5) \\
\text{overall reaction:} & I_2 + ArH \longrightarrow ArI + HI & (6) \\
 & \text{ox} + 0.5I_2 + ArH \longrightarrow ArI + H^+ + \text{red}^- & (7)
\end{array}$$

A variety of oxidants have been used to bring about the transformation of eq 3. HNO_3/H_2SO_4, as used in the

---

(1) (a) Fanta, P. E. *Synthesis* **1974**, 9. (b) Heck, R. F. *Org. React.* (*N.Y.*) **1982**, *27*, 345.

(2) Merkushev, E. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1984**, *53*, 583.

(3) Other reagents for direct iodination include ICl and *N*-iodo amides. Indirect methods for aromatic iodination include initial thallation,[4a] mercuration,[4b] and diazotation. For an extensive summary, see ref 2.

(4) (a) McKillop, A.; Hunt, J. D.; Zelesko, M. J., Fowler, J. S.; Taylor, E. C.; McGillivray, G.; Kienzle, F. *J. Am. Chem. Soc.* **1971**, *93*, 4841. Braun, S. L.; Dürmeyer, E.; Jacob, K.; Vogt, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 696. (b) Barluenga, J.; Campos, P. J.; Gonzales, J. M.; Asensio, G. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2623.

(5) Boote, R.; Dial, C.; Conaway, R.; Pagni, R. M.; Kabalka, G. W. *Tetrahedron Lett.* **1986**, *27*, 2207.

(6) Kobayashi, Y.; Kumadaki, I.; Yoshida, T. *J. Chem. Res. Synop.* **1977**, 215.

(7) (a) Sedov, A. M.; Novikov, A. N. *J. Org. Chem. USSR* (*Engl. Transl.*) **1971**, *7*, 524. (b) Chaikovskii, V. K., Novikov, A. N. *Ibid.* **1984**, *20*, 1350. (c) Chaikovskii, V. K.; Novikov, A. N.; Sarycheva, T. A. *Ibid.* **1985**, *21*, 1783. (d) Chaikovskii, V. K.; Novikov, V. T.; Novikov, A. N.; Garifullina, F. S. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1985**, *55*, 797.

(8) (a) Chaikovskii, V. K.; Novikov, A. N.; *Zh. Prikl. Khim.* **1984**, *57*, 134; *Chem. Abstr.* **1984**, *100*, 191452g. (b) Suzuki, H. *Bull. Soc. Chem. Jpn.* **1970**, *43*, 481. (c) Uemura, S.; Onoe, A.; Okano, M. *Ibid.* **1974**, *35*, 147.

Table I. $NO^+BF_4^-$**-Catalyzed Iodination of Aromatic Compounds with** NH_4I **and** O_2 **in** CF_3COOH/CH_2Cl_2 **([ArH] = 0.050–0.075 M, [**NH_4I**] = 0.050–0.075 M, [**$NO^+BF_4^-$**] = 0.005–0.010 M)**[a]

substrate	method[c]	reactn time, h	ArI yield, %[d,e]	isomer distrbtn (%)[e,f]	k_{rel}[g]
benzotrifluoride	A	140	0		
phenyl acetate		40	53	2 (5); 4 (95)	
iodobenzene		40	92	2 (10); 4 (90)	
bromobenzene		40	87	2 (10); 4 (90)	0.035
chlorobenzene		40	82	2 (9); 4 (91)	0.050
fluorobenzene		40	86	2 (3); 4 (97)	0.45
benzene	B	20	93		1.00
tert-butylbenzene		20	100	2 (2); 4 (98)	450
toluene		20	99	2 (37); 4 (63)	500
p-xylene		2	100		2000
biphenyl	C	20	88	2 (2); 4 (98)	400
diphenyl ether		20	91	2 (2); 4,5 (98)	
naphthalene		2	74	1 (>99)	
mesitylene		2	98		24000
anisole		2	100	2 (5); 4 (95)	
thiophene	D	2	78[h]	2 (>99)	90000
1-methoxynaphthalene		2	5[i]	4 (>99)	

[a] The iodinations were carried out by adding $NO^+BF_4^-$ to a suspension of NH_4I/ArH in CF_3COOH[b]/CH_2Cl_2 at room temperature under O_2. [b] Containing 3–6% $(CF_3CO)_2O$. [c] Method A: molar ratio of $ArH:NH_4I:NO^+BF_4^-$ = 1.0:1.5:0.2; 0 vol % CH_2Cl_2. Method B: 1.1:1.0:0.1; 0 vol %. Method C: 1.1:1.0:0.1; 10 vol %. Method D: 1.5:1.0:0.1; 25 vol %. [d] Yields are based on ArH for method A and on NH_4I for methods B–D. [e] Determined by GLC. [f] Isomers eventually formed in minor amounts, e.g., 1,3-disubstituted benzenes were not found as separate peaks. 3-Iodotoluene and 3-iodoanisole were established to be formed in <0.1% yield. [g] For experimental details, see Experimental Section.[14a] [h] 2,5-Diiodothiophene (18%) was also formed. [i] The major product was 4,4′-dimethoxy-1,1′-binaphthyl (80%).

Tronov–Novikov method,[2,7] has been most widely applied, but HIO_3/H_2SO_4,[7b,d,8a] $KMnO_4$,[7d,8b] $SbCl_5$,[8c] metal ions, e.g., Co(III),[9a] Ce(IV),[9a,b] Cu(II),[9c,e] and V(V),[9f] CH_3COOOH,[10a] $C_6H_5I(OCOCF_3)_2$,[10b] and anodic oxidation[11] have all been used with appreciable success. Some of these methods suffer from the disadvantage of the drastic conditions employed (oxidizing media and/or elevated temperatures), and all[12] have the drawback of the large (i.e., stoichiometric) amounts of oxidant required.

I recently reported on the use of catalytic amounts of NO^+ as the oxidant of a novel biaryl synthesis[13] (eq 8). In

$$2ArH + 0.5O_2 \xrightarrow[H^+]{NO^+} ArAr + H_2O \qquad (8)$$

this paper the use of NO^+ and other lower nitrogen oxide species as catalytic oxidants, in a very mild and convenient procedure for the direct synthesis of aryl iodides from I^- and oxygen (eq 9), is described.

$$ArH + I^- + H^+ + 0.5O_2 \xrightarrow{NO^+} ArI + H_2O \qquad (9)$$

Results

General Procedure. The simple experimental setup described earlier for the biaryl synthesis[13] was used. Thus the reaction flask, containing a stirred solution of NH_4I and the aromatic compound in CF_3COOH/CH_2Cl_2 at room temperature was exposed to air or oxygen, and a catalytic amount of $NO^+BF_4^-$ was added. A number of aromatic compounds selected from a wide reactivity range were examined, and only the strongly deactivated ones, e.g., benzonitrile and benzotrifluoride, failed to react. By varying the reaction period and the ratio of CF_3COOH:CH_2Cl_2, compounds with as different reactivity as the halobenzenes and thiophene could be satisfactorily iodinated (Table I).

Table II. Preparative Iodinations[a]

substrate	isoltd yield, %[b]
fluorobenzene	86
benzene[c]	78
biphenyl	90[f]
diphenyl ether[d]	82[f]
naphthalene[e]	93
p-xylene[e]	90
mesitylene[e]	95[f]

[a] 20.5–25 mmol of ArH, 20 mmol of NH_4I, 0.4–0.8 mmol of $NO^+BF_4^-$ in 60–80 mL of CF_3COOH and 1.5–2.5 mL of $(CF_3CO)_2O$ under O_2 at 25 °C. Reaction period, 50 h, last two entries, 20 h. [b] Calculated from the total amount of iodoaromatics collected after chromatography. [c] 50 mmol of ArH. [d] Air via a drying tube in place of O_2. [e] 10 mL of CH_2Cl_2 was added. [f] After recrystallization (small volumes of ethanol), 83% 4-iodo-1,1′-binaphthyl, 74% 4-iodo-diphenyl ether, and 90% iodomesitylene, respectively, could be collected.

Table III. Isotope Effects[a]

substrates	k_H/k_D determined by MS	k_H/k_D determined by GLC
naphthalene/naphthalene-d_8	2.91	
bromobenzene/bromobenzene-d_5	2.95	2.90[b]
toluene/toluene-d_8	2.89	2.84[b]

[a] For experimental details, see Experimental Section.[14b] Estimated accuracy, ±5 %. [b] For para substitution.

Preparative Iodinations. When the reactions were performed on a larger scale, good to excellent yields of the aryl iodides were obtained. In many cases, the iodoaromatics could be isolated essentially pure, directly after a simple workup procedure. Further purification by chromatography gave the results presented in Table II. The catalytic efficiency of NO^+ in these experiments was quite impressive; e.g. 0.6 mmol of NO^+ caused the for-

---

(9) (a) Makhonkov, D. I.; Cheprakov, A. V.; Rodkin, M. A.; Beletskaya, I. P. *J. Org. Chem. USSR* (*Engl. Transl.*) **1986**, *22*, 1003. (b) Sugiyama, T. *Bull. Soc. Chem. Jpn.* **1981**, *54*, 2847. (c) Baird, W. C., Jr.; Surridge, J. H. *J. Org. Chem.* **1970**, *35*, 3436. (d) Sugita, T.; Idei, M.; Ishibashi, K.; Takegami, Y. *Chem. Lett.* **1981**, 1481. (e) Horiuchi, C. A.; Satoh, J. Y. *Bull. Soc. Chem. Jpn.* **1984**, *57*, 2691. (f) Schimizu, A.; Yamataka, K.; Isoya, T. *Ibid.* **1985**, *58*, 1611.

(10) (a) Ogata, Y.; Urasaki, I.; Ishibashi, T. *J. Chem. Soc., Perkin Trans. 1* **1972**, 180. (b) Merkushev, E. B.; Yudina, N. D. *J. Org. Chem. USSR* (*Engl. Transl.*) **1981**, *17*, 2320.

(11) (a) Miller, L. L.; Watkins, B. F. *J. Am. Chem. Soc.* **1976**, *98*, 1515. (b) Lines, R.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *34*, 47.

(12) Reference 9f describes a nonstoichiometric iodination of benzene using I_2 and $NaVO_3$ (molar ratio 24:3:1) in CF_3SO_3H under O_2 at 100 °C.

(13) Radner, F. *J. Org. Chem.* **1988**, *53*, 702. The reaction may schematically be expressed as follows: $ArH + NO^+ \rightarrow ArH^{\bullet+} + NO$; $ArH^{\bullet+} + ArH \rightarrow ArAr$; $NO + O_2 + H^+ \rightarrow NO^+$.

Table IV. Iodination of *p*-Xylene under Different Conditions ([ArH] = 0.069 M, [NH_4I] = 0.063 M, [$NO^+BF_4^-$] = 0.006 M)[a]

atm	yield, %[b]	remarks
O_2	100	
O_2	76	no $(CF_3CO)_2O$ present
Ar	0.1	
O_2	<0.01	no $NO^+BF_4^-$ added
air	11	via a drying tube

[a] Reactions performed in 16 mL of CF_3COOH (with/without 0.8 mL of $(CF_3CO)_2O$) at 25 °C. Reaction period, 2 h. [b] Determined by GLC.

Table V. Iodination of Mesitylene in Different Solvents ([ArH] = 0.15 M, [NH_4I] = 0.10 M, [$NO^+BF_4^-$] = 0.008–0.010 M)[a]

solvent	reactn time, h	yield, %[b]
CH_3SO_3H	1	100
CCl_3COOH	1	99
CF_3COOH/CH_3COOH (1:3)	1	95
CH_3COOH	1	1
CH_3COOH	20	96
CF_3COOH/CH_3COOH (1:9)	3	96
CF_3COOH/CH_2Cl (1:9)	16	99

[a] Reaction in 10 mL of solvent containing 0.5 mL of $(CH_3CO)_2O$ at 25 °C. [b] Determined by GLC.

mation of 45 mmol of 2-iodo-*p*-xylene, corresponding to a yield of 7500% based on NO^+.

Relative Rates and Isotope Effects. The set of relative rates included in Table I must be treated with some caution since the individual values have not been measured in the same reaction media.[14a] Solubility effects, complexation of I_2 with the solvent and/or the substrate, and other factors resulted in unreliable values of k_{rel} for some substrates, e.g., naphthalene and anisole.[15]

Values of kinetic isotope effects were obtained from competition experiments between bromobenzene, toluene, and naphthalene and their fully deuteriated analogues (Table III). Note the direct determination of k_H/k_D by capillary GLC, e.g., base line separation of 2-iodotoluene, 2-iodotoluene-d_7, 4-iodotoluene, and 4-iodotoluene-d_7 was achieved.[14b]

The Role of $NO^+BF_4^-$ and O_2. In order to establish the key role of NO^+ and O_2, *p*-xylene was iodinated under different conditions as summarized in Table IV. Since iodination was not promoted by NO^+ in the absence of O_2, the possibility of NO^+ acting as a Lewis acid catalyst could be ruled out. The catalytic efficiency of NO^+ was determined by adding decreasing amounts of $NO^+BF_4^-$ to mesitylene/NH_4I in CF_3COOH/CH_2Cl_2.[14c] The results suggest the use of at least 5 mol % of NO^+ in small-scale experiments; on a larger scale 1–2 mol % generally will be sufficient.

Sources of "I" and H^+. No significant change from the approximately quantitative yield obtained with NH_4I was found when the following sources of "I" were used: NaI, KI, $(C_4H_9)_4NI$, and I_2.[14d] When CF_3COOH was replaced with CH_3SO_3H, CCl_3COOH, and CF_3COOH/CH_3COOH (1:3) no significant change in the yields was observed, but in CH_3COOH a much slower reaction was observed (Table V). The possibility of using CH_3COOH or CH_2Cl_2 as diluents for CF_3COOH is shown in the last two entries of Table V.

Table VI. Iodination of Aromatic Compounds in CH_3COOH/CF_3COOH and CH_3COOH/H_2SO_4 ([ArH] = 0.15 M, [NH_4I] = 0.13 M, [$NO^+BF_4^-$] = 0.005 M)[a]

substrate	vol % CF_3COOH in CH_3COOH	reactn time, h	yield, %
benzene	50	16	0.1
toluene	50	16	67
pyrene	10	70[e]	36[f]
p-xylene	10	70	15
anisole	10	20	97
1,3-dimethoxybenzene	10	4	86
1-methoxynaphthalene	10	4	83
thiophene	10	1.5	91[g]
toluene	3[c]	24	98
bromobenzene	*c,d*	48	75

[a] Reaction in 20 mL of solvent containing 2 mL of CH_2Cl_2 and 1 mL of $(CH_3CO)_2O$ under O_2 at 25 °C. [b] Determined by GLC. [c] H_2SO_4 in place of CF_3COOH. [d] Solvent system: 13 mL of CH_3COOH, 1 mL of $(CH_3CO)_2O$, 5 mL of H_2SO_4, 2 mL of CH_2Cl_2; 0.8 mmol of $NO^+BF_4^-$ added. [e] A second portion of $NO^+BF_4^-$ was added after 30 h. [f] Unreacted ArH (60%) was detected, together with 3% 1-nitropyrene. [g] 7% 2,5-diiodothiophene was also formed.

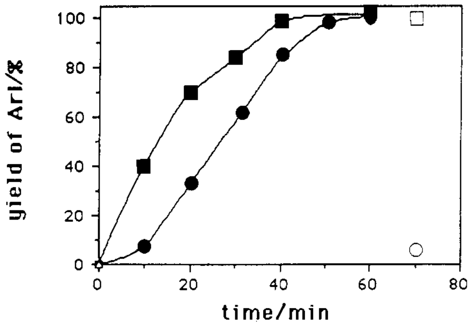

Figure 1. Iodination of mesitylene (0.14 M) with $NO^+BF_4^-$ (0.004 M) and I_2 (0.057 M) (■, ●) or NH_4I (0.11 M) (□, ○) in 14 mL of CH_3COOH, 5 mL of CF_3COOH, 2 mL of CH_2Cl_2, 1 mL of $(CH_3CO)_2O$ (squares) or in 14 mL of CH_3COOH, 2 mL of $(CH_3CO)_2O$ (circles) under O_2 at 25 °C.

Iodination in CF_3COOH/CH_3COOH. When mesitylene was iodinated on the 0.1-mol scale in 10:1 CH_3COOH/CF_3COOH an extremely clean reaction was observed and a nearly quantitative yield of iodomesitylene was isolated.[14e] In the same solvent system some of the more reactive substrates could be satisfactorily iodinated (Table VI), while toluene, but not benzene, was converted in a 1:1 acid mixture. Note that complete omission of CF_3COOH lowers the yield in small-scale experiments and inhibits iodination on a larger scale. H_2SO_4 can be used in place of CF_3COOH and is particularly effective with the less reactive substrates.

Iodination of Reactive Aromatics. The difficulties associated with the iodination of reactive aromatics in oxidizing media is demonstrated in the case of 1-methoxynaphthalene (Table I, last entry). In the system CF_3COOH/CH_2Cl_2 (3:1), substrate oxidation almost completely suppressed iodide/iodine oxidation, and hence the main product was 4,4'-dimethoxy-1,1'-binaphthyl. Under the milder reaction conditions (CF_3COOH/CH_3COOH, 1:10) employed in the experiments of Table VI only iodination was observed and a convenient synthesis of 1-iodo-4-methoxynaphthalene could be achieved.[14f] Iodination of thiophene in undiluted CF_3COOH resulted in significant byproduct formation, whereas in CF_3COOH/CH_2Cl_2 (Table I) reasonable yields of 2-iodothiophene could be obtained. However, about 20% of 2,5-diiodothiophene invariably formed, but with the method in Table

---

(14) See Experimental Section; special procedures: (a) A; (b) B; etc.

(15) Naphthalene exhibited a reactivity 0.5–1.5 times that of *p*-xylene. With anisole even larger discrepancies were observed ($k_{anisole}/k_{p\text{-xylene}}$ was 113, $k_{mesitylene}/k_{p\text{-xylene}}$ was 12, but $k_{mesitylene}/k_{anisole}$ was 28 and not 0.1 as expected from the former two values). A possible explanation involves the initial rapid formation of an I_2–anisole complex[16] in the case of the anisole/*p*-xylene pair.

(16) Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1987**, *52*, 2690.

Table VII. Iodination of Mesitylene with I_2 and NH_4I ([ArH] = 0.15 M, ["I"] = 0.13 M, [$NO^+BF_4^-$] = 0.003-0.040 M)[a]

iodine source	[$NO^+BF_4^-$], M	oxygen added[b]	yield, %[c,d]
I_2	0.004	yes	100
	0.004	no	23
	0.009	no	35
	0.034	no	41
	0.030[e]	no	17
NH_4I	0.003	yes	98
	0.003	no	0.02
	0.008	no	0.3
	0.040	no	36
	0.030[e]	no	0.3

[a] Reaction of 3 mmol of mesitylene in 14 mL of CH_3COOH/4 mL of CF_3COOH/2 mL of $(CH_3CO)_2O$ with 1.25 mmol of I_2 for 3 h (first five entries) or 2.50 mmol NH_4I for 20 h (last five entries) at 25 °C. [b] Reactions performed either under O_2 or in tightly stoppered flasks. [c] Based on "I". [d] Determined by GLC. [e] Flushed with Ar prior to addition of $NO^+BF_4^-$.

Table VIII. Iodination of Aromatics with Different Sources of NO_x

substrate	NO_x source	molar ratio NO_x:NH_4I	yield, %[a] ArI	yield, %[a] $ArNO_2$
mesitylene[c]	NO_2/N_2O_4[g]	0.08	98	2
	$NaNO_2$	0.08	96	2
	$NaNO_3$	0.08	96	2
	$NaNO_3$ + NaN_3[h]	0.08	0.3	3
	HNO_3 (conc)	0.08	92	3
	HNO_3 (fuming)	0.10	97	3
	HNO_3 (fuming)	1.00	79	20
mesitylene[d]	$NaNO_3$	0.01	98[b]	
toluene[e]	$NaNO_3$	0.01	10	
toluene[f]	$NaNO_3$	0.01	80	

[a] Determined by GLC. [b] Isolated yield. [c] Reaction of 3 mmol of ArH, 2.5 mmol of NH_4I in 14 mL of CH_3COOH, 3 mL of CF_3COOH, 2 mL of CH_2Cl_2, 1 mL of $(CH_3CO)_2O$ for 60 min under O_2. [d] Reaction of 100 mmol of ArH, 105 mmol of NaI, 1 mmol of $NaNO_3$ in 140 mL of CH_3COOH, 30 mL of CF_3COOH, 20 mL of CH_2Cl_2, 15 mL of $(CH_3CO)_2O$ for 16 h under O_2. [e] As in footnote d but with 70 mL of CH_3COOH, 70 mL of CF_3COOH, and 120-h reaction period. [f] As in footnote e but 5 mL of concentrated H_2SO_4 was also added. Reaction period, 24 h. [g] Added in CH_2Cl_2 solution. [h] Molar ratio NaN_3:NO_x = 1:1.

Table IX. $NO^+BF_4^-$-Catalyzed Aromatic Bromination and Chlorination

substrate	halogen source	ArX yield, %[a]
naphthalene[b]	NH_4Br	98
	NH_4Cl	58
	NH_4F	0
mesitylene[c]	NH_4Br	97
	NH_4Cl	17
	NH_4F	0

[a] Determined by GLC. [b] Reaction of 2 mmol of ArH with 1.0 mmol of NH_4X and 0.1 mmol of $NO^+BF_4^-$ in 12 mL of CF_3COOH, 0.3 mL of $(CF_3CO)_2O$, 3 mL of CH_2Cl_2 for 20 h under O_2 at 25 °C. [c] Reaction of 1.5 mmol of ArH with 1.0 mmol of NH_4X and 0.1 mmol of $NO^+BF_4^-$ in 10 mL of CF_3COOH, 0.3 mL of $(CF_3CO)_2O$, 1 mL of CH_2Cl_2 for 2 h under O_2 at 25 °C.

VI bisiodination could be reduced to 7%. Pyrene represents a special problem. This normally very reactive compound forms a molecular complex with I_2, and no method for its direct monoiodination has been reported.[17] With the method described in Table VI, 1-iodopyrene could be obtained in 36% yield.

Iodination with I_2. As mentioned above, I_2 can be used as the source of "I". I_2 was found to iodinate mesitylene somewhat faster than NH_4I and, in the absence of CF_3COOH (i.e., in CH_3COOH), very large differences in the rates were found (Figure 1). The effects of NO^+ and O_2 on the reaction are demonstrated in Table VII. Obviously some O_2 was initially present in the reaction mixtures, and when the solutions were flushed with argon prior to addition of $NO^+BF_4^-$, the yield of ArI was decreased.

Catalytic Action of Other NO_x Species. The rapid interconversion between NO_x species on the oxidation levels II, III, and IV was demonstrated in the case of the biaryl synthesis by the successful replacement of $NO^+BF_4^-$ with NO_2/N_2O_4.[13] In Table VIII the catalytic actions of a number of sources of NO_x species are shown. On the preparative scale $NaNO_3$ was found to be an efficient catalyst for the iodination of mesitylene,[18] and even toluene could be satisfactorily iodinated after the addition of H_2SO_4 (Table VIII, last three entries).

Chlorination and Bromination. Aromatic bromination and, to a lesser extent, chlorination could be carried out by the same method (Table IX). Assuming that the key step of the reaction involves oxidation of X^- to X_2, chlorination should be more difficult than bromination, while fluorination should be impossible as indeed was observed.

Discussion

The first step of the reaction necessarily involves oxidation of I^- (eq 10), as good yields of I_2 are obtained in

$$I^- + NO^+ \rightarrow 0.5I_2 + NO \qquad (10)$$

solvents containing CF_3COOH in the absence of a sufficiently reactive aromatic compound. The mechanism of the reoxidation of NO will at present only be schematically represented by eq 11. In order to account for the relative

$$NO + 0.5O_2 \rightarrow NO_2 \xrightarrow{NO} N_2O_3 \xrightarrow{2H^+} 2NO^+ + H_2O \qquad (11)$$

rates, isomer distributions, and isotope effects presented above, a mechanism of the electrophilic aromatic substitution type as shown in eq 5 (rate-determining proton loss) seems most reasonable. The unusually high $k_{\text{toluene}}/k_{\text{benzene}}$[19] and the high preference for para iodination suggests the existence of a source of electrophilic iodine of low reactivity and high selectivity along the reaction path (eq 12a). The existence of "I^+" as a kinetically in-

$$0.5I_2 + NO^+ \rightarrow \text{"}I^+\text{"} + NO \qquad (12a)$$

dependent species is possible only in strongly acidic media,[20] and the nature of the present "I^+" species cannot be stated with much certainty, a general problem in the field of aromatic iodination.[2] However, some clues are given by the observations presented above. (a) 1-Methoxynaphthalene (1-OMN) was mainly oxidized in CF_3COOH/CH_3COOH (3:1) and completely iodinated in CF_3COOH/CH_3COOH (1:10) (Tables I and VI). (b) NH_4I

---

(17) The standard preparation of 1-iodopyrene proceeds via diazotation. Lund, H.; Berg, A. *Chem. Abstr.* **1946**, *40*, 6072. By the addition of water diiodopyrenes were obtained when pyrene was treated with $I_2/HIO_3/H_2SO_4$, but no successful synthesis of monoiodopyrenes was achieved.[7b,c] The addition of donor solvents like DMF had a beneficial effect on the diiodination of fluoranthene, but the addition of DMF to the solvent systems presented here has this far not proven successful.

(18) In the absence of CF_3COOH no conversion into ArI was observed. When CF_3COOH was replaced by CH_3SO_3H iodomesitylene could be isolated in 90% yield after 16 h.

(19) $k_{\text{toluene}}/k_{\text{benzene}}$ was found to be 105,[8c] 9.5,[7a] and 21[11a] respectively in the $I_2/SbCl_5/CCl_4$, $HNO_3/H_2SO_4/CH_3COOH$, and electrochemical systems employed.

(20) Arotsky, J.; Symons, M. C. R. *Q. Rev.* **1962**, *16*, 282. See also ref 2.

(21) A variety of species has been suggested as possible sources of electrophilic iodine:[2] e.g., CH_3COOI, CF_3COOI,[9a] CH_3CNI^+,[11a] and $I_2^{\bullet+}$.[11b]

Scheme II. Possible ET Mechanisms of Aromatic Iodination at High (Left) or Low (Right) CF_3COOH Concentrations[a]

$$\mathrm{ArH} + \mathrm{NO^+BF_4^-} \xrightarrow{A_1} \mathrm{ArH^{\bullet+}} + \mathrm{BF_4^-} + \mathrm{NO} \tag{13}$$

$$\mathrm{I_2} \rightleftharpoons 2\mathrm{I} \tag{14}$$

$$\mathrm{I} + \mathrm{NO^+BF_4^-} \xrightarrow{A_2} \text{“}\mathrm{I^+}\text{”} + \mathrm{BF_4^-} + \mathrm{NO} \tag{12b}$$

$$\mathrm{ArH} + \mathrm{NO^+BF_4^-} \xrightarrow{B} \text{no reaction}$$

$$\mathrm{I_2} + \mathrm{NO^+BF_4^-} \rightarrow [\mathrm{I{-}I/NO}]^+\mathrm{BF_4^-} \tag{15}$$

$$[\mathrm{I{-}I/NO}]^+\mathrm{BF_4^-} \xrightarrow{C} \text{“}\mathrm{I^+}\text{”} + \mathrm{BF_4^-} + \mathrm{INO} \tag{12c}$$

$$\mathrm{INO} \rightarrow 0.5\mathrm{I_2} + \mathrm{NO} \tag{16}$$

$$\mathrm{ArH} + \text{“}\mathrm{I^+}\text{”} \rightarrow \mathrm{ArI} + \mathrm{H^+} \tag{5}$$

$$\mathrm{NO} \rightarrow \rightarrow \mathrm{NO^+} \tag{11}$$

[a] (A_1, A_2) outer-sphere ET steps (A_1 occurs only when ArH is readily oxidizable); (B) reaction inhibited due to low oxidizing power of NO^+ and/or formation of ArH/I_2 complex; (C) inner-sphere ET step.

was converted to I_2 much more slowly than I_2 was oxidatively activated in the absence of CF_3COOH. In CF_3COOH/CH_3COOH (1:3) the rate of iodination (and hence the rate of oxidation of I^-) was similar when either NH_4I or I_2 was used (Figure 1). These facts suggest that NO^+ oxidizes I^- and 1-OMN in a similar manner, since the oxidizing power of NO^+ is known to increase with increasing acid strength of the reaction media.[13,22a] Hence the oxidation of I^-[24a] can be suspected to proceed via the same kind of outer-sphere electron transfer (ET) process as the oxidation of 1-OMN does (eq 13).[23]

On the other hand, the oxidative activation of I_2 cannot proceed via the simple outer-sphere process shown in eq 12a since this reaction does not exhibit a similar pronounced sensitivity to the acid strength. The results under section (a) above suggest that 1-OMN[25] is preferentially oxidized under conditions where NO^+ is a powerful ET oxidant. However, in CH_3COOH-based media the rate of the ET step (eq 13) appears to be too slow to compete with the oxidative activation of I_2. Therefore another mechanism must be operating and one possibility, involving inner-sphere ET, is shown in eq 12c. Here the energy gained in the breaking of the I–I bond can be used to overcome the otherwise unfavourable energetics of the ET step.[26] The reaction is continued by the decomposition of INO[24b,27] as summarized in Scheme II.

By applying the concept of inner-sphere ET to the mechanism of the Tronov–Novikov reaction a possible explanation becomes available as to how NO_2^+, a much less efficient outer-sphere ET oxidant than NO^+,[22] can be capable of oxidatively activating I_2.[7a] Moreover, the key to the usefulness of the method may be found in the formation of a NO_2^+–I_2 complex analogous to eq 15. In such a complex, NO_2^+ would not be such a powerful nitrating agent, explaining why iodoaromatics and not nitroaromatics are formed as the main products.[28]

The catalytic action of $NaNO_3$ and HNO_3 (Table VIII) can be attributed either to the decomposition of N(V) into lower NO_x species or to the action of NO_2^+ as discussed above. The inhibition of iodination by the powerful nitrous acid scavenger NaN_3 can be taken as evidence in favor of the former possibility. However, two other explanations, reaction of N_3^- with NO_2^+[29] or I^+, cannot at present be ruled out.

Despite the many uncertainties regarding the mechanism discussed above, the synthetic value of the reaction is considerable. Especially by the $CH_3COOH/NaNO_3$- or $NaNO_2$-based reactions of Table VIII convenient ways of making aryl iodides are available, hopefully opening up a way to their more extensive use in organic synthesis.

Experimental Section

Materials and Methods. Dichloromethane (Merck) was dried and stored over 3-Å molecular sieves. Other solvents, acids, and acid anhydrides were of pa quality and used as supplied. Stock solutions of trifluoroacetic acid anhydride in trifluoroacetic acid were made up to minimize handling of the former. Aromatic compounds were used as supplied or purified by chromatography (purity >98%). Toluene-d_8 (Merck Uvasol, >99% D), naphthalene-d_8 (Aldrich, 98+% D) and bromobenzene-d_5 (Ciba, >99% D) were used as supplied. Iodine and all inorganic salts were commercial samples and used as supplied, as were sulfuric acid (Merck, pa, 95–97%), nitric acid (Merck, pa >65%), 65%), and fuming nitric acid (Merck, >96%). Solutions of dinitrogen tetraoxide in dichloromethane were made up as described previously.[30a]

Column chromatography was performed on 20 × 700 mm columns on silica gel 60 (Merck, 230–400 mesh) using heptane with 0–20% chloroform as eluent. GLC analyses were performed on capillary columns (A, 25 m × 0.2 mm OV 1701, or B, 25 m × 0.2 mm Superox 10) on a Varian 3400 gas chromatograph equipped with a Varian 4270 integrator or, in the cases of 1-methoxynaphthalene[13] and pyrene,[30b] by the conditions previously described.

^1H NMR spectra were recorded at a Varian XL300 spectrometer. Mass spectra were recorded on a Finnegan 4021 instrument at 70 eV or, in the case of the isotope effect studies, at 15 eV.

Products were identified by comparison of GLC retention times with authentic samples or by their mass and NMR spectra. GLC yields were determined via internal or external standard methods using 4-bromonitrobenzene as the reference compound. Isomer distributions were determined by GLC and certain minor isomers (3-iodoanisole, 3-iodotoluene) were sought but not found (i.e., formed in less than 0.1% yield).

General Iodination Procedure. The aromatic compound and NH_4I were weighed into an Erlenmeyer flask, and the solvents were added (CH_2Cl_2, when present, was added first). After

---

[22] (a) Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *20*, 53; (b) *Acta Chem. Scand., Ser. B* **1984**, *38*, 861. (c) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987; pp 14, 48, 91.

[23] The slow conversion of NH_4I to I_2 in CH_3COOH (especially on the larger scale) was caused either by a lower value of $E°(NO^+/NO)$ (and hence a lower value of k_{ET}[22a]) in media of lower acid strength or by a change in mechanism (for one possibility, see ref 24b).

[24] (a) Stanbury, D. M.; Wilmarth, W. K.; Khalaf, S.; Po, H. N.; Byrd, J. E. *Inorg. Chem.* **1980**, *19*, 2715. (b) The mechanism of the reaction between nitrous acid and I^- has been suggested to follow either of the two following pathways: (i) $H^+ + HNO_2 + I^- \rightarrow NOI + H_2O$, $NOI + HNO_2 \rightarrow HN_2O_3I$, $HN_2O_3I + H^+ + I^- \rightarrow H_2O + 2NO + I_2$; (ii) $H^+ + HNO_2 + I^- \rightarrow NOI + H_2O$, $NOI + I^- \rightarrow NO + I_2^-$, $I_2^- + HNO_2 + H^+ \rightarrow NO + I_2 + H_2O$. Ferranti, F.; Indelli, A. *Gazz. Chim. Ital.* **1980**, *110*, 273.

[25] Pyrene would be expected to be even more readily oxidized than 1-OMN. However, in these reactions pyrene apparently largely exists in the shape of an oxidation-resistant ArH–I_2 complex.

[26] Compare with an analogous proposal: the energy gained by breaking the C–N bond of the σ-complex was suggested to compensate for the otherwise unfavorable energetics of the ET step of the inner-sphere ET mechanism of aromatic nitration.[22a,c]

[27] INO decomposes rapidly at temperatures above 35 K. Feuerhahn, M.; Hilbig, W.; Minkwitz, R.; Engelhart, U. *Spectrochim. Acta A, Part* **1978**, *34A*, 1065. Weiss, R.; Wagner, K. G. *Chem. Ber.* **1984**, *117*, 1973. Two main pathways for the decomposition have been suggested: (a) $I + INO \rightarrow I_2 + NO$; (b) $2INO \rightarrow I_2 + 2NO$. van den Bergh, H.; Troe, J. *J. Chem. Phys.* **1976**, *64*, 736. Basco, N.; Hunt, J. E. *Int. J. Chem. Kinet.* **1978**, *10*, 733.

[28] Benzene was nitrated by the system $CH_3COOH/HNO_3/H_2SO_4$ in the absence of I_2, while no nitrobenzene was formed in its presence.[7a]

[29] Masek, J. *Collect. Czech. Chem. Commun.* **1962**, *27*, 667.

[30] (a) Eberson, L.; Jönsson, L.; Radner, F. *Acta Chem. Scand., Ser. B* **1978**, *32*, 749. (b) Radner, F. *Ibid.* **1983**, *37*, 65.

flushing with O_2 for 1 min, a small, constant overpressure of O_2 was kept over the magnetically stirred reaction mixture.[31] A few crystals of $NO^+BF_4^-$ were rapidly added, and stirring was continued for the appropriate reaction period at room temperature; in many cases colorless solutions were obtained at the end of reaction. The reaction mixture was poured onto aqueous $Na_2S_2O_3/CHCl_3$ and the aqueous layer washed with $CHCl_3$, and the combined organic layers were washed with water, aqueous $NaHCO_3$, and water and dried ($MgSO_4$). After evaporation and passage through a short column the yield was determined by GLC or workup continued by chromatography (and/or recrystallization in some cases) as described in the tables.

Special Procedures. A. Relative Rates. Values of k_{rel} were determined by allowing NH_4I to be competed for by a tenfold excess of the aromatic compounds (ratio 1:1 or 10:1) in any of the systems A–D in Table I. The relative rates of 27 different pairs were determined.

B. Isotope Effects. Values of k_H/k_D were determined by allowing 1.00 mmol each of, e.g., toluene and toluene-d_8 to compete for 0.20 mmol of NH_4I in 17 mL of CF_3COOH/1 mL of $(CF_3CO)_2O$ (in the naphthalene case 2 mL of CH_2Cl_2 was added) under O_2 at 25 °C for 2–3 h. After workup the values of k_H/k_D were calculated either from the mass spectrometric data or directly from the gas chromatograms obtained on column A.

C. Catalytic Efficiency. The catalytic efficiency of $NO^+BF_4^-$ was determined by treating 1.5 mmol of *p*-xylene and 1.0 mmol of NH_4I in 10 mL of CF_3COOH, 0.5 mL of $(CF_3CO)_2O$, and 1.0 mL of CH_2Cl_2 under O_2 for 5 h with 0.01–0.09 mmol of $NO^+BF_4^-$. Results [mmol of $NO^+BF_4^-$ (% yield)]: 0.09 (95); 0.068 (98); 0.048 (97); 0.025 (90); 0.019 (72); 0.011 (35).

D. Sources of "I". The yields of iodomesitylene from essentially the procedure as in C albeit with 0.08–0.10 mmol of $NO^+BF_4^-$ and a 1.5-h reaction period were in the 95–100% range for NH_4I, NaI, KI, $(n\text{-}C_4H_9)_4NI$, and I_2.

E. Synthesis of Iodomesitylene. Mesitylene (0.11 mol) and NH_4I (0.10 mol) were treated with $NO^+BF_4^-$ (0.001 mol) in 150 mL of CH_3COOH, 15 mL of CF_3COOH, and 10 mL of $(CH_3CO)_2O$ under O_2 at 25 °C for 48 h. At the end of reaction the solution turned colorless, and after workup as described above iodomesitylene (0.095 mol, 95%, recrystallized from a small volume of ethanol) was obtained.

F. Synthesis of 1-Iodo-4-methoxynaphthalene. A mixture of 1-methoxynaphthalene (8.2 mmol), NH_4I (7.5 mmol), CH_3COOH (30 mL), CF_3COOH (4 mL), and $(CH_3CO)_2O$ (2 mL) was stirred under O_2, and $NOBF_4$ (0.15 mmol) was added. After 16 h, the mixture was worked up, yielding 1-iodo-4-methoxynaphthalene (6.4 mmol, 85%): mp (ethanol) 54–56 °C (lit.[32a] mp 54–55 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 4.00 (s, 3), 6.60 (d, 1), 7.55 (m, 2), 7.95 (d, 1), 8.03 (d, 1), 8.23 (d, 1); mass spectrum, *m/e* (relative intensity) 284 (45), 269 (24), 241 (26), 157 (10), 142 (20), 128 (10), 127 (20), 126 (22), 114 (100).

Acknowledgment. I thank Professor Lennart Eberson for stimulating discussions and the Swedish Natural Science Research Council for financial support.

---

[31] When O_2 was replaced by air (furnished via a drying tube) aryl iodides generally were formed, albeit at lower rates, from substrates more reactive than toluene.

[32] (a) Baddar, G. F.; El-Assal, L. S.; Baghos, V. B. *J. Chem. Soc.* **1958**, 986. (b) Bergmann, E. D.; Shahak, I. *Ibid.* **1959**, 1418.

Selective Oxidation of Alcohols by a H_2O_2–$RuCl_3$ System under Phase-Transfer Conditions

Gabriela Barak, Jihad Dakka, and Yoel Sasson*

Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Received November 29, 1987

The selective oxidation of primary aliphatic alcohols to carboxylic acids (60–70% selectivity), secondary alcohols to ketones (100% selectivity), and primary benzylic alcohols to aldehydes (95–100% selectivity) or carboxylic acids as well as the selective oxidation of allylic alcohol to ketones (80% selectivity) was performed in a H_2O_2–$RuCl_3{\cdot}3H_2O$ phase transfer catalyst (PTC) system at a high substrate:$RuCl_3$ (625:1) ratio. It has also been found that the PTC not only has a role in the extraction of $RuCl_3$ and H_2O_2 in the organic phase but also protects the metallic catalyst against reduction. Other metallic catalysts as $PdCl_2$, $RhCl_3{\cdot}3H_2O$, $MnCl_2{\cdot}4H_2O$, and $CoCl{\cdot}6H_2O$ show poor conversion and selectivity.

The metal-promoted hydrogen peroxide oxidation of various alcohols to aldehydes, ketones, or carboxylic acids is usually performed in the presence of a polar solvent in order to overcome the solubility problems of both the metal salt catalyst and hydrogen peroxide.

Solvents like acetone,[1,2] methanol,[3] and even water[4] (for water-soluble glycols) are cited in literature, but the use of those is quite limited. For example, under the reaction conditions, acetone can form very explosive dimeric or trimeric peroxides[5] and methanol can be oxidized by itself.

It has recently been found that phase-transfer catalysts (PTC) can effectively replace the polar solvents in these reactions, when catalyzed by molybdate or tungstate anions.[6-9] However, these procedures are of limited preparative value since they use high catalyst:substrate ratios (1:10 to 1:40) and sometimes high hydrogen peroxide concentrations[6] (up to 70%).

We now report that aqueous 30% hydrogen peroxide solution in conjunction with catalytic amounts of $RuCl_3$ (catalyst:substrate ratio 1:625) under PTC conditions

---

[1] Jpn. Pat. Appl. 79-9639; *Chem. Abstr.* **1981**, *94*, 467836.

[2] Gore, E. S. *Platinum Met. Rev.* **1983**, *27*, 111.

[3] Sheldon, R. A. *Bull. Soc. Chim. Belg.* **1985**, *94*, 651.

[4] Venturello, C.; Ricci, M. *J. Org. Chem.* **1986**, *51*, 1599.

[5] Bretherick, L. *Handbook of Reactive Chemical Hazards*, 2nd ed.; Butterworths: London, 1979.

[6] Bortolini, O.; Conte, V.; di Furia, F.; Modena, G. *J. Org. Chem.* **1986**, *51*, 2661.

[7] Bortolini, O.; Conte, V.; di Furia, F.; Modena, G. *Nouv. J. Chim.* **1985**, *9*, 147.

[8] Trost, B. M.; Masuyama, Y. *Isr. J. Chem.* **1984**, *24*, 134.

[9] Trost, B. M. Masuyama, Y. *Tetrahedron Lett.* **1984**, *25*, 173.