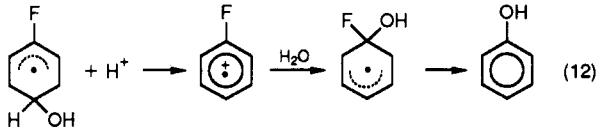
The effect of pH on the hydroxylation of fluorobenzene and anisole is also in accordance with previous results on the radiation-induced hydroxylations.[16d] In the hydroxylation of fluorobenzene the yield of phenol increases with decreasing pH (Table II, experiments 11 and 12):



(12)

The main position of attack by H_2O on the radical cation of fluorobenzene is at the ipso position, giving phenol as the main product in agreement with SCF MO calculations.[15] In the hydroxylation of anisole (Table III, experiments 10 and 11) and nitrobenzene (Table V, experiment 13) on the other hand, a low pH gives only small amounts of phenol and nitrophenols, due to the irreversibility of the dehydration.[15,25]

In conclusion we have shown that the hydroxylations of aromatics by Cu^+–H_2O_2 proceeds via OH radicals (reactions 1 and 3) and not via a Cu^{3+}(aq) species (reactions 2 and 4).

Experimental Section

General Procedure. Triply distilled water (500 mL) containing Cu^{2+} was deoxygenated by bubbling Ar through the solution for 30 min. After deoxygenation 500 μL of the aromatic was added, and the solution shaken to dissolve the aromatic. Then Cu^+ ($Cu(CH_3CN)_4ClO_4$) was added, and 10 mL of a 0.3% H_2O_2 solution (0.88×10^{-3} mol) was injected through a rubber stopper. The solution was shaken for 30 min and then extracted once with 200 mL and three times with 100 mL ether. The ether extracts were dried over Na_2SO_4 for 24 h and then concentrated to 10 mL in a rotary evaporator.

Preparation of Cu^+. The $Cu(CH_3CN)_4ClO_4$ was prepared according to the procedure described by Hemmerich and Sigwart.[26]

Analysis. The concentrated extracts were analyzed by gas chromatography using a 6-ft FFAP column (10% on Chromosorb W, AWDMCS) at 150 °C for phenol and fluorophenols and 170 °C for hydroxyanisoles. The nitrophenols were first reacted with 10 mL of diazomethane solution (prepared from Diazald, Aldrich Chemical Co.). Analysis was carried out using the same column as above at 165 °C and a flow rate of 20 mL of He/min. In the experiment using oxygen as oxidizing agent oxygen was bubbled through the solution before addition of Cu^+ and H_2O_2. Standards containing known amounts of products were worked up and analyzed under the same conditions as the experimental samples.

Acknowledgment. This work was supported, in part, by the National Institutes of Health (Grant No. SO6 RR 08224-04).

Registry No. Cu^+, 17493-86-6; H_2O_2, 7722-84-1; fluorobenzene, 462-06-6; anisole, 100-66-3; nitrobenzene, 98-95-3; benzene, 71-43-2.

(25) Shevchuck, L. G.; Vysotskaya, N. A. *Zh. Org. Khim.* **1968**, *4*, 1936.

(26) Hemmerich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488.

Reactions of an *o*-Quinone Monoimide with Anthracenes, Phencyclone, and 1,3-Diphenylisobenzofuran

Harold W. Heine,* Joseph A. Suriano, Chris Winkel, Andrea Burik, and Carol M. Taylor

Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

Elizabeth A. Williams*

General Electric Company, Corporate Research and Development, Schenectady, New York 12309

Received April 3, 1989

The *o*-quinone monoimide *N*-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (**1**) reacts at ambient temperature and in the absence of light with anthracene, 9-substituted anthracenes, and 9,10-diphenylanthracene to give the $4\pi + 4\pi$ cycloadducts dibenz[*b*,*f*][1,4]oxazocines (**6**). Compounds **6** when treated with acid isomerize into 9,10-disubstituted anthracenes. Compound **1** also undergoes $4\pi + 4\pi$ cycloaddition with 1,3-diphenylisobenzofuran and phencyclone. Admixing of 9,10-dimethylanthracene with **1** results in an abstraction of a hydrogen from one of the methyl groups by the nitrogen of **1** followed by the bonding of the oxygen of **1** with the erstwhile methyl carbon to give the ether **17**. A similar reaction occurs between **1** and hexamethylbenzene. The adduct of **1** with 1,3-diphenylisobenzofuran, namely, **26**, undergoes an isomerization to **28** in refluxing benzene.

The only known example of a thermal $4\pi + 4\pi$ cycloaddition of anthracene involves its interaction with the *o*-quinodimethane **2** (generated from **1**) to produce 9,10-*endo*-*o*-xylylene-9,10-dihydroanthracene (**3**) in 12% yield (Scheme I).[1] Photochemically induced $4\pi + 4\pi$ cycloadditions of anthracene are more common. For example, irradiation of a mixture of anthracene and 1,3-cyclohexadiene gave **4**[2] (Scheme I). Similar photochemical additions occur between anthracene and 2,5-dimethyl-2,4-hexadiene,[2] 1,3-diphenylisobenzofuran,[3] and derivatives of 1,3-cyclohexadienes.[4] This paper describes the relatively easy $4\pi + 4\pi$ thermal cycloadditions of anthracene and some 9-substituted anthracenes when the latter are treated with the *o*-quinone monoimide *N*-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (**5**). Compound **5** also forms $4\pi + 4\pi$ thermally generated cycloadducts when it is admixed with 1,3-diphenylisobenzofuran and phencyclone.

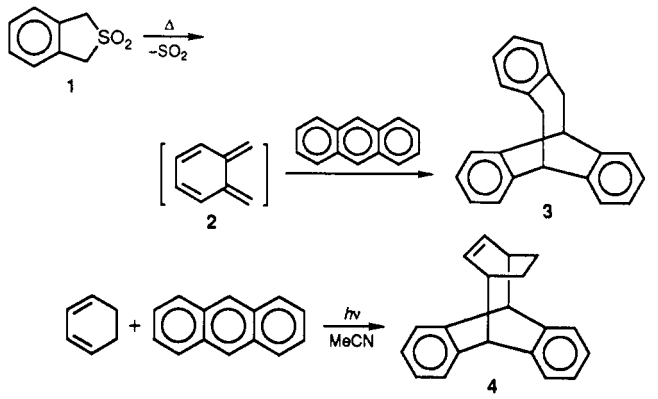
(1) Sisido, K.; Udo, Y.; Nozaki, H. *J. Org. Chem.* **1961**, *26*, 584.
(2) Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1972**, *94*, 1405.
(3) Kaupp, G.; Grüter, H.-W.; Teufel, E. *Chem. Ber.* **1983**, *116*, 618.
(4) Yang, N. C.; Chen, M. J.; Chen, P.; Mak, K. T. *J. Am. Chem. Soc.* **1982**, *104*, 853.

Results and Discussion

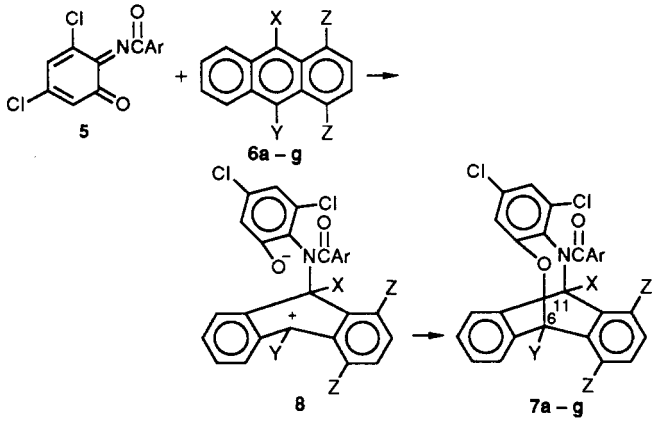
The addition of **5** to methylene chloride solutions of anthracene, 9-methyl-, 9-phenyl-, 9-bromo-, 9-*trans*-styryl-, 1,4-dimethoxy-, and 9,10-diphenylanthracenes (**6a–g**) produced dark-colored reaction mixtures. The color faded gradually (1–2 days), and removal of the solvent left good yields of the $4\pi + 4\pi$ cycloadducts dibenz[*b*,*f*][1,4]oxazocines (**7a–g**) (Scheme II). Reaction of **5** with **6a–g** in the

0022-3263/89/1954-5926$01.50/0

Scheme I



Scheme II



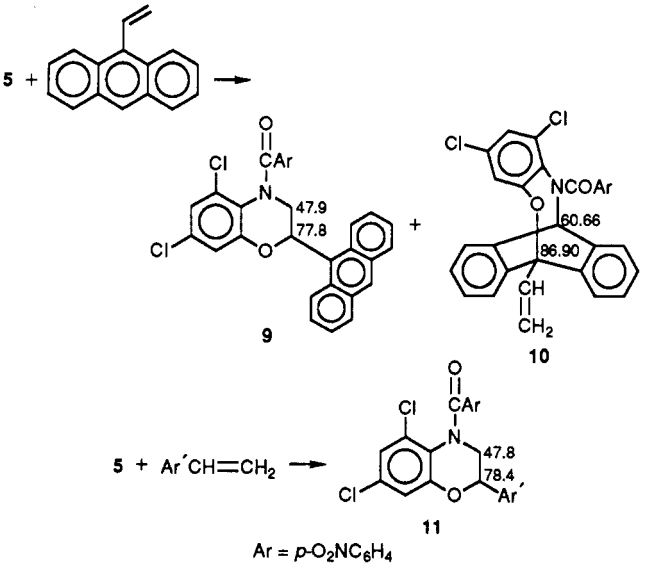
6a, 7a, X = Y = Z = H; **6b, 7b**, X = Z = H, Y = Me; **6c, 7c**, X = Z = H, Y = Ph; **6d, 7d**, X = Z = H, Y = Br; **6e, 7e**, X = Z = H, Y = *trans*-PhCH=CH; **6f, 7f**, X = Y = H, Z = OMe; **6g, 7g**, X = Y = Ph, Z = H
Ar = *p*-$O_2NC_6H_4$

dark also formed **7a–g**. No reaction occurred between **5** and 9-nitroanthracene or 9-anthracenecarbonitrile. X-ray crystallographic analysis established the structures of **7b** and **7c** and documented that the C-10 carbon of 9-methyl- and 9-phenylanthracenes had bonded to the imido nitrogen of **5**. Structural assignments for **7a–d–g** were based on the comparison of ^1H and ^{13}C NMR spectra with those of **7b,c**. In particular, for compounds **7a–g** the C-11 carbons exhibit a chemical shift of 56–61 ppm.

It is unlikely, given the predictions of Woodward–Hoffmann orbital symmetry rules, that the $4\pi + 4\pi$ adducts **7a–g** are formed by a concerted process. Several other mechanistic routes are feasible. The dark color that develops at the outset of the reaction suggests the formation of a charge-transfer complex between **5** and the anthracene which could subsequently lead to **8**, the immediate precursor to **7a–g**. Alternatively, the charge-transfer complex could dissociate into the reactants which by a two-electron transfer from anthracene to **5** could form **8** directly.

Reaction of **5** with 9-vinylanthracene gave a mixture of the 2,3-dihydro-4*H*-[1,4]benzoxazine **9** and the $4\pi + 4\pi$ cycloadduct **10** (Scheme III). ^{13}C NMR spectroscopy provided evidence for the assignment of structures to **9** and **10**. Compound **9** exhibited chemical shifts at 47.9 and 77.8 ppm, indicating the presence of a methylene group attached to a nitrogen atom and a methine carbon bound to an oxygen atom, respectively. The chemical shifts compared favorably with those found for a series of 2,3-dihydro-[1,4]benzoxazines (**11**) formed by the reaction of **5** with styrenes[5] (Scheme III). The ^{13}C NMR spectrum of

Scheme III



10 showed chemical shifts for the C-11 and C-6 atoms at 60.60 and 86.90 ppm, respectively. These values are about the same as the chemical shifts of 60.66 and 86.98 ppm found for the C-11 and C-6 atoms of the $4\pi + 4\pi$ cycloadduct of 9-*trans*-styrylanthracene, namely **7e**.

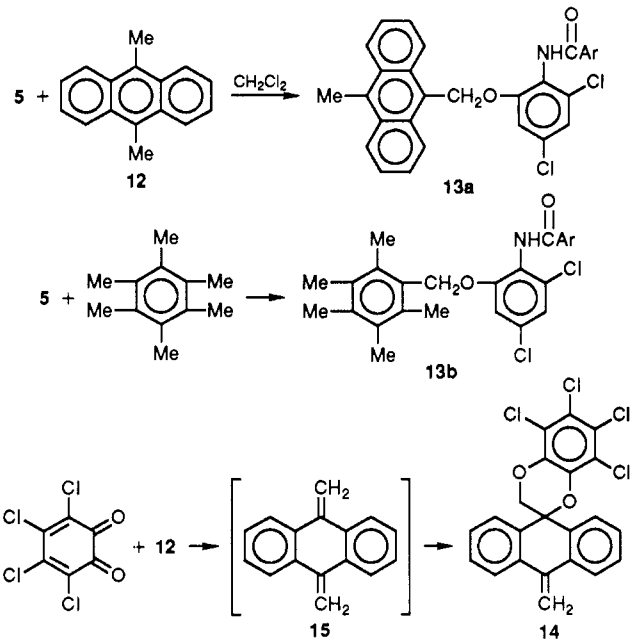
Steric factors appear to determine whether a 9-alkenylanthracene and **5** forms a 2,3-dihydro-[1,4]benzoxazine or a dibenz[*b,f*][1,4]oxazocine. Thus 9-vinylanthracene produced both heterocyclic systems, but the more hindered 9-*trans*-styrylanthracene formed only the $4\pi + 4\pi$ cycloadduct **7e**.

Although 9-methyl- and 9,10-diphenylanthracene reacted with **5** to form $4\pi + 4\pi$ cycloadducts, 9,10-dimethylanthracene (**12**) and **5** produced the ether **13a** (Scheme IV). The structure of **13a** was deduced by spectral means. The ^1H NMR spectrum clearly indicated the presence of a methylene group and a methyl group by chemical shifts at 6.13 and 3.05 ppm, respectively. The ^{13}C NMR spectrum exhibited chemical shifts at 64.52 and 14.03 ppm for the methylene ether carbon and the methyl group. A similar reaction occurred when **5** was reacted with hexamethylbenzene. Compound **13b** was obtained in 89% yield. Ethers analogous to **13a,b** have been isolated when hexamethylbenzene (and similar substrates) were treated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ).[6] It was proposed that the latter reaction proceeds by a hydride ion transfer from the methyl group to the DDQ to produce a carbocation and a quinolanion, which then react to form the ether.[6] A similar mechanism can be put forth for the formation of **13a,b**. Interestingly, reaction of 9,10-dimethylanthracene with excess *o*-chloranil gave **14** in 18% yield (Scheme IV).[7] The formation of **14** was suggested to occur by the addition of *o*-chloranil to the postulated intermediate anthraquinodimethane **15**.[7]

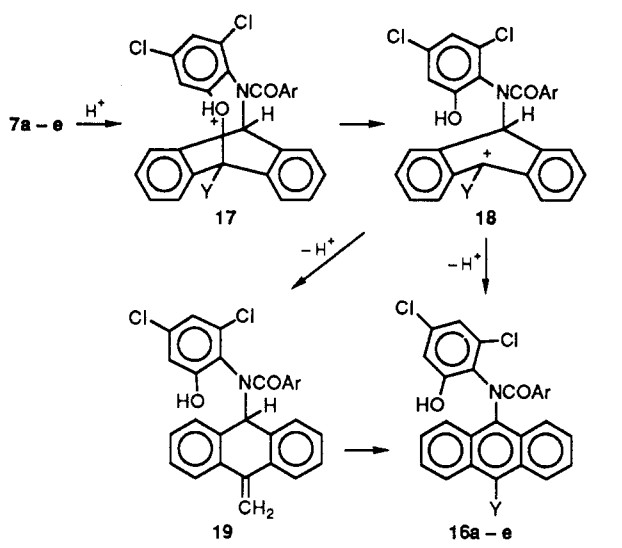
The $4\pi + 4\pi$ cycloadducts **7a–e** were readily isomerized in methylene chloride solutions containing small quantities of trifluoroacetic acid into the 9,10-disubstituted anthracenes **16a–e** (Scheme V). The structures of **16** were confirmed by ^{13}C NMR spectroscopy. The chemical shifts for the aliphatic carbons at C-6 and C-11 of the dibenz[*b,f*][1,4]oxazocines (**7a–e**) were not present in the ^{13}C

(5) Heine, H. W.; Barchiesi, B.; Williams, E. A. *J. Org. Chem.* **1984**, *49*, 2560.
(6) Foster, R.; Horman, I. *J. Chem. Soc. B* **1966**, 1049.
(7) Lown, J. W.; Aidoo, A. S. K. *Can. J. Chem.* **1966**, *44*, 2507.

Scheme IV



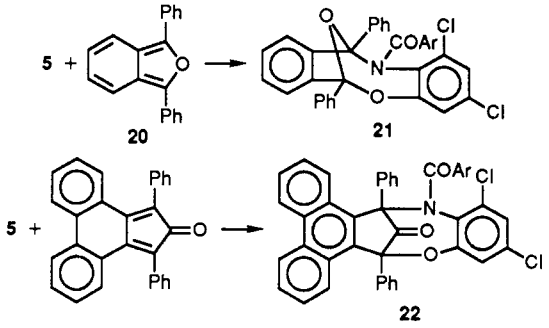
Scheme V



NMR spectra of **16a–e**. The presence of the phenolic group was shown by the preparation of the *p*-nitrobenzoate esters of **16b,c**. The formation of **16** is thought to occur via the intermediate **17**, which can either aromatize directly to **16** or isomerize to **18**. Evidence for the intermediacy of **18** is the isolation of **19** when **7b** (Y = Me) is dissolved in methylene chloride containing traces of trifluoroacetic acid or hydrogen chloride (Scheme V). Dissolution of **7b** or **19** into methylene chloride containing larger quantities of trifluoroacetic acid yields **16a**.

Other examples of the formation of $4\pi + 4\pi$ cycloadducts involve reactions of **5** with 1,3-diphenylisobenzofuran (**20**) and phencyclone. Compound **20** reacted instantaneously with **5** in methylene chloride to produce **21** (Scheme VI). Structural elucidation of **21** was based on X-ray crystallography, which showed that the eight-membered ring was in the chair conformation. Analogues of **21** had been prepared previously by reaction of **20** with *o*-chloranil[8,9a,b] and with *N,N'*-bis(arylsulfonyl)- and *N,N'*-dibenzoyl-*o*-quinone diimines.[10] The $4\pi + 4\pi$ cycloadduct **22** was isolated when **5** was added to a methylene chloride solution of phencyclone (Scheme VI). The structure of **22** was based on the ^{13}C NMR chemical shifts at 80.5 and 93.0 ppm, which were attributed to the aliphatic carbons linked respectively to the nitrogen and oxygen atoms.

Scheme VI



Experimental Section

12-(*p*-Nitrobenzoyl)-1,3-dichloro-11,12-dihydro-6,11-[1′,2′]-benzeno-6*H*-[*b*,*f*][1,4]oxazocine (7a). To a solution of 162 mg (0.5 mmol) of **5** in 3 mL of CH_2Cl_2 was added 89 mg (0.5 mmol) of anthracene. The reaction mixture turned black upon the addition of the anthracene. The solvent was evaporated after 3 days and the gummy orange residue was triturated three times with MeOH and filtered. The crude **7a** (237 mg, 94%) melted at 148–159 °C °C. Recrystallization from EtOH yielded **7a**, mp 198–201 °C. Anal. Calcd for $C_{27}H_{16}Cl_2N_2O_4$: C, 64.43; H, 3.20; N, 5.57. Found: C, 64.22; H, 3.53; N, 5.65.

12-(*p*-Nitrobenzoyl)-1,3-dichloro-6-methyl-11,12-dihydro-6,11[1′,2′]-benzeno-6*H*-dibenz[*b*,*f*][1,4]oxazocine (7b). Compound **5** (324 mg, 1.0 mmol) was added to a solution of 192 mg (1.0 mmol) of 9-methylanthracene in 3 mL of dichloromethane. Within 3 h at ambient temperature the color of the reaction mixture changed from black-green to yellow. Evaporation of the solvent gave **7b** as a gummy residue. Trituration with MeOH and collection of the residue provided 503 mg (97% of **7b**, mp 157–159 °C). Thrice recrystallized **7b** from MeCN yielded an analytical sample melting at 185–188 °C. Anal. Calcd for $C_{28}H_{18}Cl_2N_2O_4$: C, 64.99; H, 3.48; N, 5.42. Found: C, 64.77; H, 3.77; N, 5.56. The structure of **7b** was determined by X-ray diffraction studies.

12-(*p*-Nitrobenzoyl)-1,3-dichloro-6-phenyl-11,12-dihydro-6,11[1′,2′]-benzeno-6*H*-dibenz[*b*,*f*][1,4]oxazocine (7c) was obtained by adding **5** (324 mg, 1.0 mmol) to 245 mg (1.0 mmol) of 9-phenylanthracene in 3 mL of CH_2Cl_2. Over 4 days the color of the reaction mixture turned from black to orange. The solvent was evaporated, and the gummy residue was triturated with MeOH and filtered to give **7c** (536 mg, 93%), mp 175–185 °C. Recrystallization from MeCN/THF formed crystals melting at 216–220 °C. Anal. Calcd for $C_{33}H_{20}Cl_2N_2O_4$: C, 68.40; H, 3.48; N, 4.84. Found: C, 67.92; H, 3.60; N, 4.86. The structure of **7c** was affirmed by X-ray crystallography.

12-(*p*-Nitrobenzoyl)-1,3-dichloro-6-bromo-11,12-dihydro-6,11[1′,2′]-benzeno-6*H*-dibenz[*b*,*f*][1,4]oxazocine (7d). To a solution of 1 (324 mg, 1.0 mmol) in 3 mL of CH_2Cl_2 was added 9-bromoanthracene (257 mg, 1.0 mmol). The solvent was removed after 24 h, and the residue was triturated with MeOH and filtered. The crude **7d** (557 mg, 98%, mp 175–181 °C) was suspended in hot MeCN, and THF was added until dissolution occurred. This procedure was repeated three times and gave **7d** melting at 184–188 °C. Anal. Calcd for $C_{27}H_{15}BrCl_2N_2O_4$: C, 55.70; H, 2.60; N, 4.81. Found: C, 55.55; H, 3.02; N, 4.59.

12-(*p*-Nitrobenzoyl)-1,3-dichloro-6-*trans*-styryl-11,12-dihydro-6,11[1′,2′]-benzeno-6*H*-dibenz[*b*,*f*][1,4]oxazocine (7e)

(8) Horspool, W. M.; Tedder, J. M.; Din, Z. U. *J. Chem. Soc. C* **1969**, 1692, 1694.

(9) (a) Friedrichsen, W. *Tetrahedron Lett.* **1969**, 4425. (b) Friedrichsen, W.; Kallweit, I.; Schmidt, R. *Justus Liebigs Ann. Chem.* **1977**, 116.

(10) Friedrichsen, W.; Rohe, M.; Debaerdemaeker, T. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, 632.

was obtained by the addition of **5** (324 mg, 1.0 mmol) to a solution of 9-*trans*-styrylanthracene (280 mg, 1.0 mmol) in 4 mL of CH_2Cl_2. After 1 h the color of the reaction mixture changed from dark brown to light yellow. Removal of the solvent gave a quantitative yield of **7e**, mp 167–173 °C. Two recrystallizations from 1-PrOH gave **7e** melting at 200–204 °C. Anal. Calcd for $C_{35}H_{22}Cl_2N_2O_4$: C, 69.43; H, 3.66; N, 4.63. Found: C, 69.74; H, 3.86; N, 4.54.

12-(*p*-Nitrobenzoyl)-1,3-dichloro-7,10-dimethoxy-11,12-dihydro-6,11[1′,2′]-benzeno-6*H*-dibenz[*b*,*f*][1,4]oxazocine (7f). To a solution of **5** (162 mg, 0.5 mmol) in 3 mL of CH_2Cl_2 was added 1,4-dimethoxyanthracene (119 mg, 0.5 mmol). After 3 days the solvent was evaporated, and the residue was triturated with MeOH and filtered. The crude **7f** (280 mg, 99%, mp 133–147 °C) was partially purified by heating in MeOH and filtering the undissolved **7f**. Recrystallization three times from MeCN gave **7f** melting at 208–210 °C. Anal. Calcd for $C_{29}H_{20}Cl_2N_2O_6$: C, 61.82; H, 3.58; N, 4.97. Found: C, 61.47; H, 3.70; N, 4.98.

12-(*p*-Nitrobenzoyl)-1,3-dichloro-6,11-diphenyl-11,12-dihydro-6,11[1′,2′]-benzeno-6*H*-dibenz[*b*,*f*][1,4]oxazocine (7g) was obtained by admixing **5** (324 mg, 1.0 mmol) and 9,10-diphenylanthracene (330 mg, 1.0 mmol) in 4 mL of CH_2Cl_2. After 3 days at ambient temperature the solvent was removed, and the residue was triturated with methanol. The crude **7g** (641 mg, 98%, mp 148–150 °C) was recrystallized several times from MeCN to give material melting at 202–205 °C. A final recrystallization from MeCN/THF gave an analytical sample of **7g**, mp 212–215 °C. Anal. Calcd for $C_{39}H_{24}Cl_2N_2O_4$: C, 71.46; H, 3.69; N, 4.27. Found: C, 71.33; H, 3.80; N, 4.25.

Reaction of 5 with 9-Vinylanthracene. Synthesis of 9 and 10. To a solution of 9-vinylanthracene (204 mg, 1 mmol) in 4 mL of CH_2Cl_2 was added **5** (324 mg, 1 mmol). The color of the reaction mixture changed from black to light yellow within a few hours. After 24 h the mixture was filtered to give **9** (153 mg, 29%, mp 201–212 °C). Recrystallization from MeCN gave **9**, mp 245–246.5 °C. Anal. Calcd for $C_{29}H_{18}Cl_2N_2O_4$: C, 65.90; H, 3.44; N, 5.30. Found: C, 65.85; H, 3.77; N, 5.22. Evaporation of the filtrate afforded 364 mp of residue, which when triturated with C_6H_6 and filtered gave additional **9** (146 mp , mp 204–212 °C). Evaporation of the benzene yielded **10** (218 mg, 41%, mp 162–175 °C). Recrystallization from 1-PrOH gave **10**, mp 197–201 °C. Anal. Calcd for $C_{29}H_{18}Cl_2N_2O_4$: C, 65.90; H, 3.44; N, 5.30. Found: C, 65.41; H, 3.15; N, 5.46.

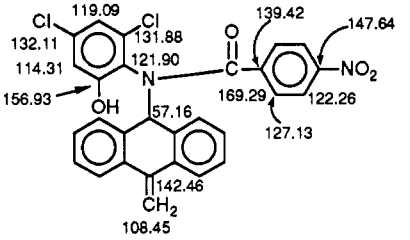
***N*-[2,4-Dichloro-6-[(10-methyl-9-anthracenyl)methoxy]-phenyl]-4-nitrobenzamide (13a)** was formed by the addition of 9,10-dimethylanthracene (103 mg, 0.5 mmol) to a solution of **5** (324 mg, 1.0 mmol) in 3 mL of $CHCl_3$. The reaction mixture turned a black-green color immediately after admixture of the reactants. A yellow precipitate began to form after 10 min. The reaction mixture was filtered after standing 24 h to give **13a** (188 mg, 71%), which melted into a red globule at 198–205 °C. Evaporation of the filtrate and trituration of the residue with MeOH gave more **13a** (48 mg, 18%). Three crystallizations from chlorobenzene followed by slurrying with MeOH and filtering gave **13a** that again melted into a red globule at 204–207 °C. High-resolution mass spectroscopy m/z calcd for $C_{29}H_{20}Cl_2N_2O_4$ 530.0798, found 530.0810.

***N*-[2,4-Dichloro-6-[(2,3,4,5,6-pentamethylphenyl)methoxy]phenyl]-4-nitrobenzamide (13b)** was obtained by admixture of hexamethylbenzene (32 mg, 0.20 mmol), 2.0 mL CH_2Cl_2, and **5** (66 mg, 0.20 mmol). The reaction mixture after standing at ambient temperature for 24 h was filtered. The crude **13b** (63 mg, mp 226–230 °C) was recrystallized from MeCN to give **13b** melting at 234–236 °C. Evaporation of the CH_2Cl_2 filtrate gave an additional 32 mg of **13b**. The total crude yield of **13b** was 97%. Anal. Calcd for $C_{25}H_{24}Cl_2N_2O_4$: C, 61.61; H, 4.96; N, 5.75. Found: C, 61.53; H, 5.33; N, 5.99.

Synthesis of *N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(9-anthracenyl)-4-nitrobenzamide (16a). A mixture of **7a** (240 mg, 0.48 mmol), 9 mg of CF_3CO_2H, and 3 mL of CH_2Cl_2 was kept at ambient temperature for 48 h. The solvent was removed, and the residue was slurried thrice with 5-mL portions of MeOH. Filtration gave **16a** (240 mg, 100%, mp 180–192 °C). Purification was brought about by heating **16a** in cyclohexane and adding 1-chloropentane until dissolution occurred. Cooling the solution precipitated **16a**, mp 223–225 °C. Anal. Calcd for $C_{27}H_{16}Cl_2N_2O_4$: C, 64.43; H, 3.20; N, 5.57. Found: C, 64.43; H, 3.80; N, 4.95.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(10-methyl-9-anthracenyl)-4-nitrobenzamide (16b)** was obtained by admixing **7b** (258 mg, 0.5 mmol) and trifluoroacetic acid (10 mg) in 4 mL of CH_2Cl_2. After 4 h the CH_2Cl_2 was evaporated, and the residue was slurried with 5 mL of MeOH and filtered. The crude **16b** (214 mg, 83%), mp 206–219 °C was recrystallized from MeCN to give **16b**, mp 236–237 °C. Anal. Calcd for $C_{28}H_{18}Cl_2N_2O_4$: C, 65.00; H, 3.51; N, 5.42. Found: C, 65.08; H, 3.64; N, 5.45. The *p*-nitrobenzoate of **16b** melted at 269–271 °C. Anal. Calcd for $C_{35}H_{21}Cl_2N_3O_7$: C, 63.07; H, 3.18; N, 6.31. Found: C, 62.66; H, 3.49; N, 6.33.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(9,10-dihydro-10-methylene-9-anthracenyl)-4-nitrobenzamide (19).** To a solution of 9-methylanthracene (96 mg, 0.5 mmol) in 4 mL of CH_2Cl_2 were added 6 mg of CF_3CO_2H and **5** (162 mg, 0.5 mmol). After standing for 24 h the mixture was poured on a watchglass, and the solvent was evaporated. The gummy residue was slurried with MeOH and filtered. The crude **19** (243 mg, 94%) melted at 125–143 °C. Recrystallization from EtOH gave **19** that melted with ebullition at 152–156 °C. Anal. Calcd for $C_{28}H_{18}Cl_2N_2O_4 \cdot H_2O$: C, 62.81; H, 3.76; N, 5.23. Found: C, 62.66; H, 3.63; N, 5.18. Mol ion m/z 516. The pertinent chemical shifts in natural abundance ^{13}C NMR spectrum of compound **19** are summarized in the following structure.



***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(10-phenyl-9-anthracenyl)-4-nitrobenzamide (16c).** A solution of **7c** (459 mg, 0.79 mmol) in 3 mL of CH_2Cl_2 containing 14 mg of CF_3CO_2H was allowed to stand for 1 day during which time a precipitate of **16c** formed. Filtration gave **16c** (357 mg, 78%, mp 197–205 °C). Two recrystallizations from MeCN gave **16c**, mp 213–216 °C. Anal. Calcd for $C_{33}H_{20}Cl_2N_2O_4$: C, 68.40; H, 3.48; N, 4.84. Found: C, 68.69; H, 3.71; N, 4.81. The *p*-nitrobenzoate of **16c** melted at 267–270 °C ($MeCN/H_2O$). Anal. Calcd for $C_{47}H_{23}Cl_2N_3O_7$: C, 65.93; H, 3.18; N, 5.77. Found: C, 66.15; H, 3.53; N, 5.75.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(10-bromo-9-anthracenyl)-4-nitrobenzamide (16d)** was obtained by adding **7d** (260 mg, 0.45 mmol) to 3 mL of CH_2Cl_2 containing 9 mg of CF_3CO_2H. Filtration of the reaction mixture after 1 day gave **16d** (242 mg, 93%, mp 197–200 °C). Purification was effected by dissolving **16d** in a minimum of hot 1-PrOH, cooling and adding H_2O until the solution was slightly turbid. The **16d** so obtained melted at 221–225 °C. Anal. Calcd for $C_{27}H_{15}BrCl_2N_2O_4$: C, 55.70; H, 2.60; N, 4.81. Found: C, 55.81; H, 2.87; N, 4.62.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(10-*trans*-styryl-9-anthracenyl)-4-nitrobenzamide (16e).** A mixture of **7e** (302 mg, 0.5 mmol), 9 mg of CF_3CO_2H, and 4 mL of CH_2Cl_2 was allowed to stand for 10 h. The solvent was removed, and the gummy residue was triturated with MeOH several times. Filtration gave **16e** (263 mg, 87%, mp 233–236 °C) Recrystallization from $CHCl_3$ gave **16e**, mp 250–253 °C. Anal. Calcd for $C_{35}H_{22}Cl_2N_2O_4$: C, 69.54; H, 3.50; N, 4.63. Found: C, 69.76; H, 3.53; N, 4.70.

1,3-Dichloro-11,12-dihydro-12-(4-nitrobenzoyl)-6,11-diphenyl-6,11-epoxy-6*H*-dibenz[*b*,*f*][1,4]oxazocine (21) was prepared by admixing 1,3-diphenylisobenzofuran (54 mg, 0.20 mmol) and **5** (65 mg, 0.2 mmol) in 5 mL of CH_2Cl_2. The orange color of **5** was discharged within 1 min. After 24 h the solvent was evaporated, and the residue was triturated with MeOH. The crude **21** (117 mg, 98%, mp 115–125 °C) was filtered and was recrystallized from MeCN to give **21**, mp 180–183 °C. Anal. Calcd for $C_{33}H_{20}Cl_2N_2O_5$: C, 66.57; H, 3.39; N, 4.70. Found: C, 66.15; H, 3.50; N, 4.77.

12,14-Dichloro-15,16-dihydro-15-(4-nitrobenzoyl)-9,16-diphenyl-9,16-methano-9*H*-benzo[*b*]phenanthro[9,10-*f*][1,4]-oxazocin-17-one (22). To a solution of phencyclone (76 mg, 0.2

mmol) in 7 mL of CH_2Cl_2 was added **5** (65 mg, 0.2 mmol). The reaction mixture changed from black to deep red in color after 24 h. The solvent was removed, and the residue was triturated with MeOH and filtered. The crude rust-colored **22** (140 mg, 99%) melted at 199–215 °C. Purification was effected by dissolving **22** in DMF and then adding H_2O until turbidity resulted. Filtration gave **22**, mp 244–253 °C. Anal. Calcd for $C_{42}H_{24}Cl_2N_2O_5$: C, 71.29; H, 3.42; N, 2.96. Found: C, 71.82; H, 3.90; N, 3.78.

Acknowledgements are made to the donors of the Petroleum Research Fund, administered by the Amercian Chemical Society, and to the National Science Foundation for Grant CHE-84058555. We thank Dr. Mary F. Garbauskas and Carolyn Hejna for the X-ray crystallographic studies on compounds **7b,c** and **21**, William A. Bubnis for the initial study on **7e**, Kathryn F. Pileggi for investigating the reaction of **1** with hexamethylbenzene, and John Ramphal for the preliminary work on **21**. Dr. Robert White, Senior Advisor, Chemical Abstracts Service, kindly provided the nomenclature for compounds **7**, **21**, and **22**.

Supplementary Material Available: Atomic coordinates and all relevant details of X-ray crystallography of compounds **7b,c** and **21** (37 pages). Ordering information is given on any current masthead page.

Sodium Perborate: A Mild and Convenient Reagent for Efficiently Oxidizing Organoboranes

George W. Kabalka,* Timothy M. Shoup, and Naganna M. Goudgaon

Departments of Chemistry and Radiology, University of Tennessee, Knoxville, Tennessee 37996-1600

Received November 18, 1988

Sodium perborate, a readily available and inexpensive reagent, efficiently oxidizes organoboranes. The reagent permits the oxidation of a wide variety of functionally substituted organoboranes. In nearly every instance, the product yields exceed those obtained using standard oxidation procedures.

Organoboranes have proven to be versatile intermediates in a number of synthetic sequences. The utility of the borane reagents is centered on the stereodefined nature of their reactions and on the fact that they can be prepared containing a wide variety of important functional groups, e.g. carboxylic acid esters, nitriles, etc.[1] Interestingly, nearly every synthesis involving organoborane reagents includes an oxidation reaction to remove organoborane byproducts or to generate the target molecule.[2] Currently, the most effective method for oxidizing organoboranes involves heating the boron reagent with 30% hydrogen peroxide and 3 N sodium hydroxide at 50 °C.[3] The harsh nature of this standard oxidation reaction is often incompatible with the functional groups present in the target molecules.

In an attempt to minimize side reactions of functionally substituted organoboranes, researchers have resorted to modifying the standard oxidation procedure. Successful methods include the simultaneous addition of the base and peroxide[4] and the use of milder bases.[5,6] Other modifications include the use of oxidizing reagents other than hydrogen peroxide; these reagents are often expensive,[7] inconvenient to handle,[8,9] difficult to prepare,[10] or are themselves reactive toward certain functional substituents.[7-11]

Scheme I

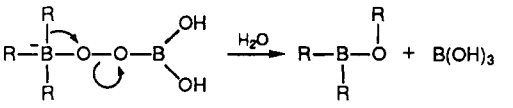


Table I. Comparison of the Efficiencies of the Sodium Perborate and Hydrogen Peroxide Oxidation Procedures

		yield, %	
organoborane	product	sodium perborate	hydrogen peroxide
tri-*n*-hexylborane	1-hexanol	94	94
tris(2-methylpentyl)-borane	2-methyl-1-pentanol	99	98
tris(1-ethylbutyl)-borane	3-hexanol	99	98
tricyclohexylborane	cyclohexanol	98	98
trinorbornylborane	*exo*-norborneol	98	98

[a] Yields determined via GLC analysis. [b] Conversion based on tri-*n*-hexylborane. [c] Oxidation was performed using 1 equiv of NaOH with heating to 50 °C for 30 min.

(1) (a) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press Inc. (Best Synthetic Methods): New York, 1988. (b) Brown, H. C. *Organic Synthesis via Boranes*; Wiley Interscience: New York, 1975. (c) Pelter, A.; Smith, K. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: New York, 1979. (d) Kabalka, G. W. *Acc. Chem. Res.* **1984**, *17*, 215.

(2) (a) Brown, H. C.; Prasad, J. V. N. V. *J. Am. Chem. Soc.* **1986**, *108*, 2049. (b) Evans, D. A.; Takacs, J. M.; McGee, L. R.; Ennis, M. D.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560–78. (d) Ikeda, N.; Arai, I.; Yamamoto, H. *J. Am. Chem. Soc.* **1986**, *108*, 483. (e) Matteson, D. S.; Peterson, M. L. *J. Org. Chem.* **1987**, *52*, 5116. (f) Masamune, S.; Sato, T.; Kim, B.; Wollman, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 8279. Masamune, S.; Kennedy, R. M.; Peterson, J. S.; Houk, K. N.; Wu, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7404. (h) Paquette, L. A.; Okazaki, M. E.; Caille, J. C. *J. Org. Chem.* **1988**, *53*, 477. (i) Pelter, A.; Buss, D.; Pitchford, A. *Tetrahedron Lett.* **1985**, *26*, 5093. (j) Roush, W. R.; Palkowitz, A. D.; Palmer, M. J. *J. Org. Chem.* **1987**, *52*, 316. (k) Uenishi, J.; Beau, J. M.; Armstrong, R. W.; Kishi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 4756. (l) Zweifel, G.; Shoup, T. M. *Synthesis* **1988**, 129.

(3) Zweifel, G.; Brown, H. C. *Org. React.* **1963**, *13*, 1.

(4) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 1512.

(5) Brown, H. C.; Kabalka, G. W.; Rathke, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 4528.

(6) Brown, H. C.; Knights, E.; Coleman, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 2144.

(7) (a) Kabalka, G. W.; Hedgecock, H. C. *J. Org. Chem.* **1975**, *40*, 1776. (b) Soderquist, J. A.; Najafi, M. R. *J. Org. Chem.* **1986**, *51*, 1330. (c) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.* **1986**, *27*, 3961.

(8) Brown, H. C.; Midland, M. M.; Kabalka, G. W. *Tetrahedron* **1986**, *42*, 5523.

(9) Pelter, A.; Hutchings, M. G.; Smith, K. *J. Chem. Soc. D* **1970**, 1529.

(10) (a) Midland, M. M. Preston, S. B. *J. Org. Chem.* **1980**, *45*, 4514. (b) Evans D. A.; Vogel, E.; Nelson, J. V. *J. Am. Chem. Soc.* **1979**, *101*, 6120. (c) Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1975**, *43*, 188.

(11) Koster, R.; Morita, Y. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 580.

0022-3263/89/1954-5930$01.50/0