(88%) along with 15 (10%), after chromatography.

Registry No. 1, 140-39-6; **2a**, 2937-64-6; **2b**, 71118-97-3; **3**, 7143-16-0; **4a**, 878-00-2; **4b**, 123-08-0; **5a**, 2973-78-6; **5b**, 2973-77-5; **6a**, 121-33-5; **6b**, 121-32-4; **6c**, 71118-98-4; **6d**, 71118-99-5; **7a**, 13287-30-4; **7b**, 71119-00-1; **8a**, 5355-17-9; **8b**, 57726-26-8; **9a**, 71119-01-2; **9b**, 71119-02-3; **9c**, 71119-03-4; **9d**, 71119-04-5; **10a**, 5533-03-9; **10b** (R′ = Et), 5595-79-9; **10b** (R′ = *i*-Pr), 71119-05-6; **10b** (R′ = Bu), 71119-06-7; **10c**, 71119-07-8; **11**, 623-05-2; **12a**, 29922-56-3; **14**, 2432-14-6; **15**, 71119-08-9; **16**, 6638-05-7; a, 104-93-8; b, 104-21-2; c, 14202-31-4; d, 63866-99-9; e, 71155-68-5; 2-bromophenol, 95-56-7; 4-bromophenol, 106-41-2; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; butanol, 71-36-3; 2-methoxyphenol, 90-05-1; 4-methoxyphenol, 150-76-5.

Ion Radicals. 44. Reactions with 10-Phenylphenoxazine Cation Radical Perchlorate[1,2]

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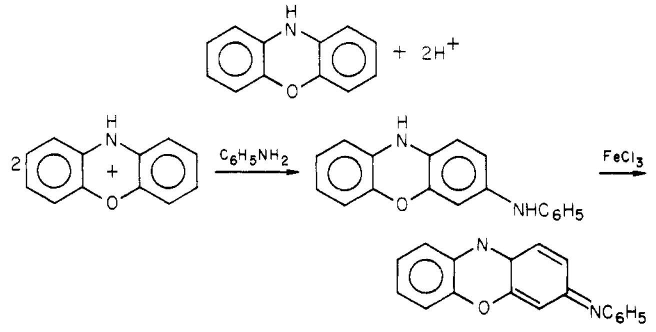
10-Phenylphenoxazine cation radical perchlorate ($1^{+\cdot},ClO_4^-$) was prepared by oxidation of 1 with $I_2/AgClO_4$. Reaction of $1^{+\cdot}$ with NO_2^-, SCN^-, and Br^- gave excellent yields of 3-nitro- (**2**), 3-thiocyano- (**3**), and 3-bromo-10-phenylphenoxazine (**4**). Reaction with Cl^- gave only 14% of 3-chloro-10-phenylphenoxazine (**6**). Reaction with Br^- gave also 1.9% of 3,7-dibromo-10-phenylphenoxazine (**5**), while reaction with Cl^- gave also 10% of 7,7′-dichloro-3,3′-bis(10-phenylphenoxazine) (**7**) and 74% of **1**. Reaction with H_2O and CH_3OH gave only **1** and 3,3′-bis(10-phenylphenoxazine) (**8**), the latter being in yields of about 45%. Reaction with CN^-, $O_2^{-\cdot}$, diethylamine, diisopropylamine, and butylamine gave mostly **1** (78–92%) and smaller amounts of **8**. Reaction with F^- gave mostly **1** with a small amount of **8** and monofluoro **8** (**9**). Authentic **2** was prepared, and from it authentic **4** and **6** were obtained. During the preparation of **2**, some peculiarities in the melting point of 3-nitrophenoxazine were observed but not resolved.

Oxidized states of phenoxazines are to be found in important dyestuffs and indicators (Meldola's blue, litmus) and in some naturally occurring antibiotics (actinomycins) and pigments.[3] Yet, little is known of the chemistry of the primary, one-electron oxidation states (the cation radicals) of phenoxazines. This is in contrast with what is known about the cation radicals of the analogous thianthrene, phenoxathiin, and phenothiazine.[4,5] The phenoxazine cation radical itself has, nevertheless, been known for many years, having been made by Kehrmann in the early 1900s by the oxidation of phenoxazine with Br_2 and $FeCl_3$.[6] The radical nature of the oxidation product was not, of course, recognized, although Kehrmann understood clearly that two stages of oxidation could occur and classified the products later, from oxidations with H_2O_2 in H_2SO_4 and H_2O_2 in $HClO_4$–acetic acid, as mono- and diacid salts. The monoacid salt solution had λ_{max} at 530 nm and the diacid salt solution at 460 nm,[7] which we would now attribute, respectively, to the mono- and dication resulting from one- and two-electron oxidation. The correct formulation of the cation radical was made by Weitz and Schwechten in 1926[8] and was confirmed experimentally later by others with the potentiometric titration of phenoxazine with $Pb(OAc)_4$ in acetic acid[9] and photoionization at low temperature.[10] Confirmation of the cation radical's structure by ESR spectroscopy followed, with low-resolution spectra in 1962[11] and complete-resolution spectra in later years.[12-14]

Scheme I



The only other phenoxazine cation radicals which have received attention are the 10-aryl ones. Detailed ESR characterization of a series of these has been made, in which the cation radicals were obtained by oxidation with nitromethane solutions of $AlCl_3$, $Tl(OAc)_3$, or H_2SO_4.[15] The 10-phenylphenoxazine cation radical has also been obtained by oxidation of the parent compound with $FeCl_3$ in acetic acid.[16]

Among these studies, however, no deliberate attempts have been made to study the chemistry of the cation radicals. Musso found that in neutral and alkaline solutions phenoxazine cation radical gave the 1,10′ and 3,10′ dimers of phenoxazine,[16,17] while Tsujino found that these

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[1] Part 43: *J. Org. Chem.* **1979**, *44*, 915.

[2] Supported by Grant No. D-028 from the Robert A. Welch Foundation.

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[10] Lewis, G. N.; Bigeleisen, J. *J. Am. Chem. Soc.* **1943**, *65*, 2419.

[11] Tuck, L. D.; Schiesser, D. W. *J. Phys. Chem.* **1962**, *66*, 937.

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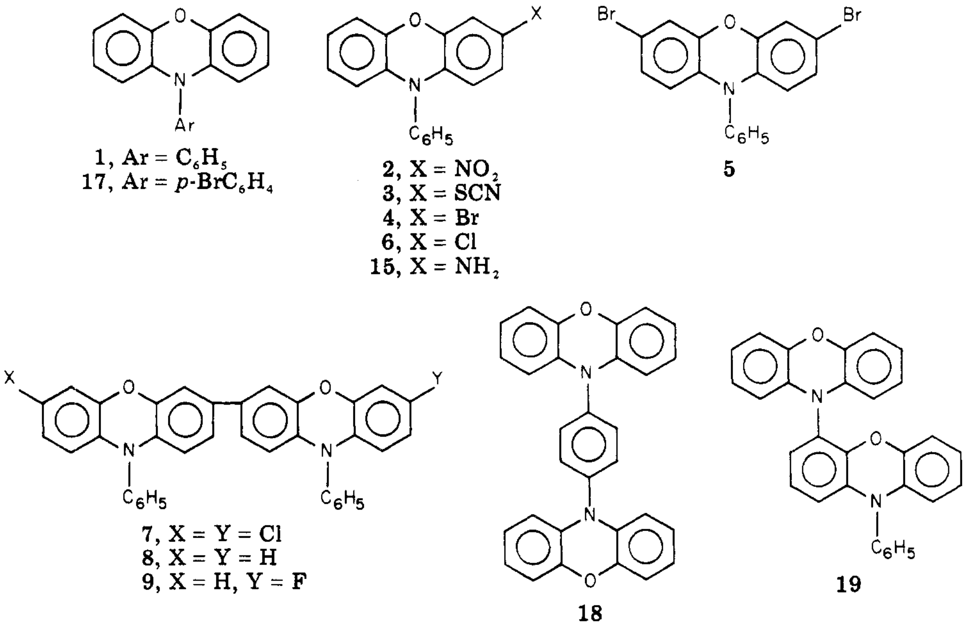
[14] Chiu, M. F.; Gilbert, B. C.; Hanson, P. *J. Chem. Soc. B* **1970**, 1700.

[15] Clarke, D.; Gilbert, B. C.; Hanson, P. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1078; **1976**, 114.

[16] Musso, H. *Chem. Ber.* **1959**, *92*, 2873.

Chart I



1, Ar = C_6H_5
17, Ar = p-BrC_6H_4

2, X = NO_2
3, X = SCN
4, X = Br
6, X = Cl
15, X = NH_2

5

7, X = Y = Cl
8, X = Y = H
9, X = H, Y = F

18

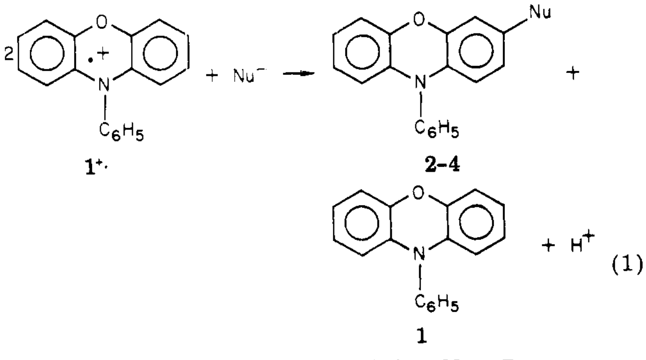
19

dimers are also obtained by oxidation of phenoxazine with Me_2SO–Ac_2O,[18] whereas the 3,10′ dimer only was obtained by oxidation with I_2 in Me_2SO.[19] A dimer of unspecified structure was obtained by Musso when 10-phenylphenoxazine was oxidized by $FeCl_3$ in acetic acid and the solution was poured into boiling water.[16]

To our knowledge the only reaction of a nucleophile with a phenoxazine cation radical which has been reported is that of aniline with phenoxazine cation radical. Oxidation of phenoxazine with $FeCl_3$ in the presence of aniline gave 3-(phenylimino)phenoxazine.[6] Kehrmann represented this reaction as of the phenoxazonium ion with aniline, but it may be that reaction was in fact with the cation radical (Scheme I).

In view of the lack of information on the chemistry of phenoxazine cation radicals we have undertaken such a study. We have turned first to 10-phenylphenoxazine cation radical ($1^{+\cdot}$).

Results and Discussion



$1^{+\cdot}$ 2-4 1 (1)

2, Nu = NO_2; 3, Nu = SCN; 4, Nu = Br

Results of the reaction of $1^{+\cdot}$ with nucleophiles show that only with three nucleophiles (NO_2^-, SCN^-, Br^-) is ring substitution substantial and in accord with the customary stoichiometry for nucleophilic substitution in aromatic cation radicals (eq 1). That is, good yields of 3-nitro-, 3-thiocyano-, and 3-bromo-10-phenylphenoxazine were obtained. Reactions of this kind have been characterized kinetically and for the most part follow the sequence of eq 2–4.[4] There is, however, always the possibility that

$$ArH^{+\cdot} + Nu^- \rightleftarrows (ArH/Nu)\cdot \qquad (2)$$

$$(ArH/Nu)\cdot + ArH^{+\cdot} \rightleftarrows (ArH/Nu)^+ + ArH \qquad (3)$$

$$B + (ArH/Nu)^+ \rightarrow ArNu + HB^+ \qquad (4)$$

substitution with some nucleophiles is, in fact, electrophilic, occurring after electron exchange between cation radical and nucleophile. This has been discussed earlier[4,5] and is of particular concern with such easily oxidized anions as Br^- and NO_2^-. In such cases the reaction's stoichiometry is not changed, but the reaction's pathway is entirely different (eq 5 and 6). We are unable to say at this stage

$$2ArH^{+\cdot} + 2Br^- \rightleftarrows 2ArH + Br_2 \qquad (5)$$

$$ArH + Br_2 \rightarrow ArBr + H^+ + Br^- \qquad (6)$$

which path is followed in reactions of $1^{+\cdot}$, particularly with Br^-. The half-wave potentials of Br^- and 1 in acetonitrile are respectively 0.4[20] and 0.36 V, so that it should not be difficult for reaching the redox system as in eq 5 with, say, 1 and Br_2. It is noteworthy also that when 1 was brominated with Br_2 in acetonitrile, the color of $1^{+\cdot}$ was seen initially; this again suggests that the redox system is readily achieved. Also noteworthy is the formation of 3,7-dibromo-10-phenylphenoxazine (5) from both the reaction of $1^{+\cdot}$ with Br^- and of 1 with Br_2. The simplest accounting for the formation of 5 is electrophilic bromination of first-formed 4. However, the half-wave oxidation potentials of 1 and 4 are sufficiently close (0.36 and 0.46 V) to suggest the possibility that electron exchange between $1^{+\cdot}$ and 4 may have occurred (eq 7) and that reaction of

$$1^{+\cdot} + 4 \rightleftarrows 1 + 4^{+\cdot} \qquad (7)$$

$4^{+\cdot}$ with Br^- (eq 1) led to 5. Analogous dihalogenations in reactions of cation radicals with halide ions have been observed and the ambiguity of the reaction pathways has been pointed out.[5,21,22]

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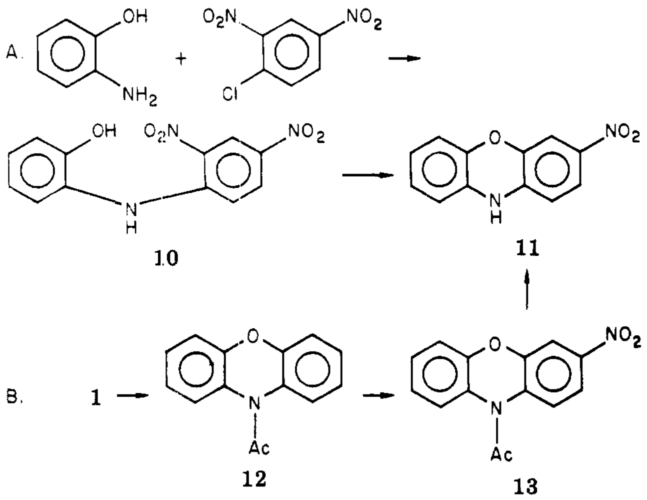
[17] Musso, H. *Chem. Ber.* **1959**, *92*, 2862.
[18] Tsujino, Y. *Tetrahedron Lett.* **1968**, 4111.
[19] Tsujino, Y. *Tetrahedron Lett.* **1969**, 763.
[20] Eberson, L. *J. Chem. Soc., Chem. Commun.* **1975**, 826. The data are for half-wave potentials and are for a Ag/Ag^+ (0.1 M) reference.
[21] Shine, H. J.; Silber, J. J.; Bussey, R. J.; Okuyama, T. *J. Org. Chem.* **1972**, *37*, 2691.

Scheme II



Biehl has found that bromination of 10-phenylphenothiazine gave 10-(*p*-bromophenyl)phenothiazine.[23] Therefore, a careful search for the formation of the analogous 10-(*p*-bromophenyl)phenoxazine (**17**) was made in our reactions, but none was found. Authentic **17** was made by reaction of *p*-bromoiodobenzene with phenoxazine. In the course of that reaction, 1,4-bis(10-phenoxazinyl)benzene (**18**) was also obtained.

Reaction of $1^{+\cdot}$ with SCN^- appears to be a very simple way of preparing 3-thiocyano-10-phenylphenoxazine (**3**). Reports of reactions between SCN^- and cation radicals in the literature are sparse. Zinc tetraphenylporphyrin cation radical gave the thiocyano derivative,[24] whereas 9,10-diphenylanthracene cation radical was reduced by SCN^-.[25] Some reports of anodic thiocyanation of arylamines and phenol in acetonitrile have also been given.[26] These reactions were carried out at potentials well below the oxidation potentials of the aromatics so that thiocyanation is thought to have been preceded by electron exchange[26] and appears to involve, in fact, either the SCN radical or dithiocyanogen.[26] The oxidation potential of SCN^- is 0.38 V[26] so that as with Br^-, electron exchange with appropriate cation radicals should be readily achievable. Consequently, the thiocyanation of $1^{+\cdot}$ may follow the exchange route, but we can only conjecture on that at this stage.

Reaction of $1^{+\cdot}$ with nitrite ion was clean, giving 3-nitro-10-phenylphenoxazine (**2**) quantitatively (eq 1). This compound served also as the basis for assigning the position of substitution in **4** and **6** and, by analogy, in **3**. That is, **2** was also made by the phenylation of 3-nitrophenoxazine (**11**), and the properties of the **2** made in this way and by the cation-radical reaction were identical. Conversion of **2** into **4** and **6** via 3-amino-10-phenylphenoxazine (**15**) showed that **4** and **6** made by diazotization of **15** were the same as **4** and **6** obtained from the cation-radical reaction. In this respect, it should be noted that attempts to diazotize **15** by standard mineral-acid techniques failed, and success was achieved only with the use of isoamyl nitrite.

In order to make **2** authentically, we had to prepare **11**. This compound has been made several times by others by either of two routes (see Scheme II): by the Turpin reaction of *o*-aminophenol with 1-chloro-2,4-dinitrobenzene, followed by closure of the 2-hydroxy-2′,4′-dinitrodiphenylamine (**10**),[27,28] and by Musso's method, the nitration of *N*-acetylphenoxazine, followed by removal of the acetyl group.[27] Previous workers have reported melting points for **11** of 199–201,[27] 195–197,[27] 200–201,[28] and 196–199 °C when **11** was made by the reaction of phenoxazine with ferric chloride and sodium nitrite in acetic acid.[29] The exception to this is the report by Kehrmann and Ramm,[30] in which **11**, made by the Turpin reaction, is described as dark brown, brass-like needles, which darken at 200 °C but do not melt even near 300 °C. Partly on the basis of these properties and partly, apparently, on the belief that 2-hydroxy-2′,4′-dinitrodiphenylamine (**10**) was not structurally suited for ring closure to give **11**, Kehrmann's work has been disputed as not having given **11**.[31,32] We have found a curious behavior of **11**, however. When first isolated from either Turpin's reaction or Musso's method, our red product had, indeed, a melting point like those in the literature. On crystallizing from benzene, however, the product became lustrous, brass-colored needles which, as reported by Kehrmann,[30] did not melt up to 360 °C. Nevertheless, all of our analytical and mass spectroscopic data[33] indicate that the high-melting compound is **11**. Phenylation gave **2** and some monophenyl dimer (**14**). It is notable also, in connection with our phenylation, that Kehrmann was able to convert his product into the 10-acetyl derivative (**13**). We have not resolved this curiosity in behavior. Musso has noted that **11** decomposes in benzene when exposed to sunlight for long periods, but the products are phenoxazone and 7-nitrophenoxazone,[34] so that this behavior appears to be unrelated to that of crystallization from benzene.

We found, interestingly, also that **2** could be made in excellent yield by the synchronous phenylation and ring closure of **10**, achieved by subjecting **10** to the standard phenylation procedure with iodobenzene.

Reaction of $1^{+\cdot}$ with Cl^- gave only a small yield (14%) of 3-chloro-10-phenylphenoxazine (**6**). However, 10% of the $1^{+\cdot}$ was also converted into the dimer of **6**, i.e., **7**. An amount (74%) of **1** was formed which was in large excess of the amount of **1** to be expected on the basis of the yields of **6** and **7** (see eq 1). The cause of this excessive formation of **1**, i.e., the source of the reducing agent, is not known. It is possible that Cl^- itself may have reduced $1^{+\cdot}$, but the somewhat higher oxidation potential of Cl^- (0.8 V)[20] makes this less likely. Reaction with Cl^- was very slow, so that ample opportunity existed for reduction of $1^{+\cdot}$ by the solvent system.

Extensive reduction of $1^{+\cdot}$ occurred in reaction with CN^-, $O_2^{-\cdot}$ and alkylamines, even though the amines have relatively high oxidation potentials ($E_{1/2}$ = 1.2 V[20]). Such reductions are not unusual in cation-radical reactions, and as has been discussed earlier, the fate of the nucleophiles such as CN^- and tertiary amines is as yet not known.[4]

A striking feature of the reactions of $1^{+\cdot}$ is the formation of dimers, which is quite different from reactions of

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[22] Shine, H. J.; Bandlish, B. K.; Stephenson, M. T. *Tetrahedron Lett.* **1978**, 733.

[23] Personal communication from Professor E. R. Biehl, Southern Methodist University.

[24] Padilla, A. G.; Wu, S.-M.; Shine, H. J. *J. Chem. Soc., Chem. Commun.* **1976**, 236.

[25] Sioda, R. E. *J. Phys. Chem.* **1968**, *72*, 2322.

[26] Cauquis, G.; Pierre, G. *C. R. Hebd. Seances Acad. Sci.*, **1971**, *272*, 609; **1968**, *266*, 883. The oxidation potential for SCN^- is vs. Ag/Ag^+ adjusted to 0.1 M Ag^+.

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[28] Sparks, A. K. U. S. Patent 3 389 124, June 18, 1968; *Chem. Abstr.*, **1968**, *69*, 36904.

[29] Karpishchenko, L. S.; Prosyanik, A. V.; Burmistrov, S. I. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1977**, 496.

[30] Kehrmann, F.; Ramm, M. *Ber. Chem. Dtsch. Ges.* **1920**, *53*, 2265.

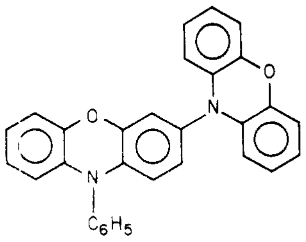
[31] Boothroyd, B.; Clark, E. R. *J. Chem. Soc.* **1953**, 1499.

[32] Brady, O. L.; Waller, C. *J. Chem. Soc.* **1930**, 1218.

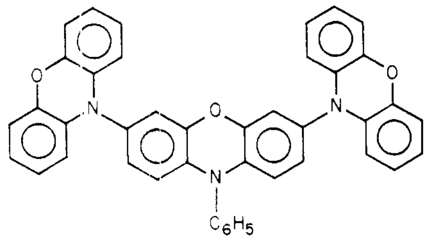
[33] We are indebted to Dr. L. Baczynskyj, The Upjohn Co., Kalamazoo, Mich., for assistance with the mass spectroscopic data.

[34] Musso, H. *Chem. Ber.* **1978**, *111*, 3012.

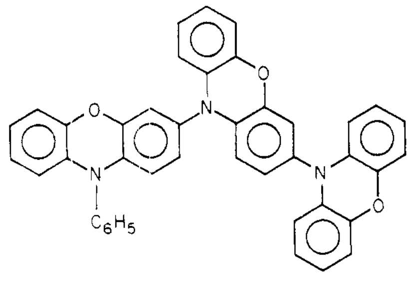
Chart II



20



21a



21b

analogous cation radicals, e.g., of thianthrene, phenoxathiin, and even 10-phenylphenothiazine.[4] Dimer formation was most marked in reactions with poor nucleophiles (H_2O, MeOH) which are not easily oxidized. These nucleophiles served, apparently, as bases in deprotonating the dimer of $1^{+}\cdot$. It is considered unlikely that deprotonation at the ring, leading to 3-(10-phenyl)-phenoxazinyl radicals, preceded dimerization. It is still not known why the more basic nucleophiles, the alkylamines, led to so much reduction and so little dimerization of $1^{+}\cdot$.

The dimer formed from $1^{+}\cdot$ is deduced to be the 3,3′ dimer (**8**), mp 264–265 °C. This was obtained also by Musso from oxidation of **1** by ferric chloride, but a structure was not assigned.[16] We have assigned the 3,3′ structure, partly on intuitive grounds but also from the ^{1}H NMR spectrum.

Reaction of $1^{+}\cdot$ with F^- gave primarily **1**. In some reactions of $1^{+}\cdot$ with F^-, up to 82% conversion into **1** was observed. It is quite unlikely that electron exchange with F^- ($E_{1/2}$ = 2.5 V) itself can occur, and again the source of electron donation is unknown. This has been observed in other cases, too.[4,5] Small amounts of **8** were obtained in reactions with F^-, and in one experiment some monofluorinated **8** was deduced by mass spectrometry to be present as a mixture with **8**.

The propensity for phenoxazines to dimerize was also observed in attempts to phenylate phenoxazine with bromobenzene instead of iodobenzene. A small amount (7%) of **1** was formed. In contrast, two dimers and a trimer of phenoxazine, each carrying one phenyl group, were obtained. The structures of these compounds are not known, although we suggest, from ^{1}H NMR data, that they are 10-phenyl-1,10′ (**19**, mp 195–196 °C), 10-phenyl-3,10′ (**20**, mp 162–164 °C), and 10-phenyl-3,10′:7,10″ (**21a**, mp 181–183 °C).

Experimental Section

Materials. Phenoxazine (mp 152–153 °C) was prepared by heating *o*-aminophenol in 0.5 equiv of hydrochloric acid.[35] 10-Phenylphenoxazine (**1**) (mp 138–139 °C) was prepared from phenoxazine and iodobenzene.[36] Acetonitrile was Eastman's anhydrous grade and was stored over molecular sieves in a septum-capped bottle. Solvents for column chromatography were redistilled, and solvent mixtures were prepared by volume. Either Merck (No. 7734) or ICN (No. 04657) silica gel was used for column chromatography. Thick-layer chromatography (ThLC) was performed with Merck (No. 7730) silica gel. All other chemicals were reagent grade and were used without further treatment.

10-Phenylphenoxazine Cation Radical Perchlorate ($1^{+}\cdot$,ClO_4^-). *Warning! Solid cation radical perchlorates are potentially explosive and great care should be used in handling them. Large-scale preparations are not recommended. Fritted-disc filter funnels should not be used.* To a stirred solution of 648 mg (2.50 mmol) of 10-phenylphenoxazine (**1**) in 5 mL of methylene chloride was added freshly mixed solutions of 316 mg (1.24 mmol) of powdered iodine in 15 mL of methylene chloride and 513 mg (2.48 mmol) of silver perchlorate in 5 mL of acetonitrile. The resulting reddish solution was stirred for 30 min and filtered from silver iodide which was washed with a small amount of methylene chloride. The filtrate was diluted with a twofold quantity of dry petroleum ether, flushed with nitrogen (to exclude moisture), and refrigerated for 4 h. Crystalline $1^{+}\cdot$,ClO_4^- was filtered, washed with dry petroleum ether, and dried under vacuum. Iodometric assay showed the product to contain 96% of the cation radical.

General Procedure for Reaction with Nucleophiles. Reactions were carried out in dry acetonitrile under a gentle current of nitrogen. Completion of a reaction was determined either by the disappearance of the peak for $1^{+}\cdot$ at 535 nm or by a negative response to starch-iodide paper. An excess of nucleophile was always used. At the completion of a reaction the mixture was filtered from undissolved nucleophile salt (if any) and evaporated to dryness in a rotary evaporator. The solids were dissolved in methylene chloride. The solution was washed with water, dried over an appropriate drying agent, and evaporated again. The weighed residue was then chromatographed on a column of silica gel.

Reaction of $1^{+}\cdot$,ClO_4^- with Nitrite Ion. Formation of 3-Nitro-10-phenylphenoxazine (2). Potassium nitrite (864 mg, 10.2 mmol) was stirred in 30 mL of acetonitrile for 1 h before the cation radical (681 mg, 1.90 mmol) was added. The reddish pink solution was stirred for 4 h and became red-brown. Workup and column chromatography followed. Elution with 90:10 petroleum ether–benzene (500 mL) gave 252 mg (0.973 mmol, 51%) of **1** (mp 138–139 °C), elution with an 80:20 mixture (900 mL) gave 4.2 mg of a yellow oil which was shown by TLC to be a mixture of the 3,3′ dimer of **1** and 3-nitro-10-phenylphenoxazine (**2**), and elution with a 70:30 mixture (1 L) gave 302 mg (0.993 mmol, 52%) of **2**, with mp 174–175 °C before crystallization from benzene and 175.5–176 °C after crystallization from benzene: ^{1}H NMR (acetone-d_6) δ 7.82–7.53 (m, 5 H, phenyl), 7.51–7.36 (m, 2 H, $H_{2,4}$), 6.86–6.64 (m, 3 H, H_{6-8}), 6.00 (d, 1 H, J = 9.0 Hz, H_1), 5.96 (d of d, 1 H, J = 9.0, 2.3 Hz, H_9); λ_{max} (acetonitrile) 446 nm (ϵ 1.38 × 10^4 M^{-1} cm^{-1}); *m/e* (relative intensity) 305 (27), 304 (100), 274 (28), 258 (79), parent peak at *m/e* 304.0865 ($C_{18}H_{12}N_2O_3$ requires *m/e* 304.0847).

Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 71.0; H, 3.95; N, 9.21. Found: C, 70.8; H, 3.80; N, 9.09.

Reaction of $1^{+}\cdot$,ClO_4^- with Thiocyanate Ion. Formation of 3-Thiocyano-10-phenylphenoxazine (3). The cation radical (340 mg, 0.948 mmol) was added to a stirred suspension of 404 mg (5.0 mmol) of sodium thiocyanate in 40 mL of acetonitrile. The solution became gray-brown immediately but was stirred 1 h before workup. Elution with 700 mL of 90:10 petroleum ether–benzene gave 145 mg (0.560 mmol, 59%) of **1**, mp 138.5–139.5 °C, and elution with 400 mL of benzene gave 130 mg

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(35) Granick, S.; Michaelis, L.; Schubert, M. P. *J. Am. Chem. Soc.* **1940**, *62*, 1802.

(36) Gilman, H.; Moore, L. O. *J. Am. Chem. Soc.* **1957**, *79*, 3485.

(0.411 mmol, 43%) of **3**, as a light yellow solid, mp 122–123 °C (benzene): ^{1}H NMR (CDCl$_3$) δ 7.74–7.37 (m, 5 H, phenyl), 6.86 (d, 1 H, J = 2.3 Hz, H$_4$), 6.81–6.56 (m, 4 H, H$_2$ and H$_{6-8}$), 6.02–5.86 (m, 2 H, H$_1$ and H$_9$); m/e (relative intensity) 317 (26), 316 (100), 290 (8), 284 (18), 239 (30), 181 (5).

Anal. Calcd for $C_{19}H_{12}N_2OS$: C, 72.1; H, 3.82; N, 8.85. Found: C, 72.3; H, 3.83; N, 8.57.

Reaction of 1$^{+\cdot}$,ClO$_4^-$ with Bromide Ion. Formation of 3-Bromo-10-phenylphenoxazine (4) and 3,7-Dibromo-10-phenylphenoxazine (5). Potassium bromide (1.11 g, 9.3 mmol) was stirred in 30 mL of acetonitrile for 30 min before the cation radical (716 mg, 2.0 mmol) was added. Workup was carried out after 8 h. Elution with 90:10 petroleum ether–benzene gave a mixture of components. Therefore chromatography was repeated. Elution with 1 L of petroleum ether gave 16 mg (0.0384 mmol, 1.9%) of white solid (**5**), mp 142.5–144 °C before crystallization from petroleum ether and 150–151 °C after crystallization from petroleum ether: ^{1}H NMR (CDCl$_3$) δ 7.70–7.26 (m, 5 H, phenyl), 6.80 (d, 2 H, J = 2.0 Hz, H$_{4,6}$), 6.67 (d of d, 2 H, J = 8.5, 2.0 Hz, H$_{2,8}$), 5.74 (d, 2 H, J = 8.5 Hz, H$_{1,9}$); m/e (relative intensity) 419 (50), 417 (100), 415 (50), 342 (22), 340 (44), 338 (22), parent peak at m/e 416.9192 ($C_{18}H_{11}Br_2NO$ requires m/e 416.9184).

Continued elution with petroleum ether (1.5 L) gave 282 mg (0.834 mmol, 42%) of a thick pale yellow oil which solidified after several days: mp 90–92 °C; ^{1}H NMR (CDCl$_3$) δ 7.70–7.28 (m, 5 H, phenyl), 6.80 (d, 1 H, J = 2.0 Hz, H$_4$), 6.74–6.50 (m, 4 H, H$_2$ and H$_{6-8}$), 5.92–5.84 (m, 1 H, H$_9$), 5.76 (d, 1 H, J = 8.5 Hz, H$_1$); m/e (relative intensity) 339 (98), 337 (100), 262 (73), 260 (75), 258 (13), parent peak at m/e 337.0057 ($C_{18}H_{12}BrNO$ (**4**) requires m/e 337.0099).

Finally, elution with 2 L of 95:5 petroleum ether–benzene gave 326 mg (1.26 mmol, 63%) of **1**, mp 138–139 °C.

Reaction of 1$^{+\cdot}$,ClO$_4^-$ with Chloride Ion. Formation of 3-Chloro-10-phenylphenoxazine (6) and Its 7,7′ Dimer (7). Potassium chloride (598 mg, 8.03 mmol) and the cation radical (539 mg, 1.50 mmol) were used as above. The reddish pink color of 1$^{+\cdot}$ remained for 10 days, and the reaction mixture was worked up after 19 days. Elution with 200 mL of 95:5 petroleum ether–benzene gave 62 mg (0.210 mmol, 14%) of **6** as a pale brown oil which solidified on standing: mp 83–84.5 °C; ^{1}H NMR (CDCl$_3$) δ 7.70–7.26 (m, 5 H, phenyl), 6.76–6.46 (m, 5 H, H$_{2,4}$ and H$_{6-8}$), 6.00–5.86 (m, 1 H, H$_9$), 5.80 (d, 1 H, J = 8.5 Hz, H$_1$); m/e (relative intensity) 295 (44), 293 (100), 258 (5), 218 (20), 216 (62), parent peak at m/e 293.0572 ($C_{18}H_{12}ClNO$ requires m/e 293.0604). Elution with 1.4 L of 95:5 petroleum ether–benzene gave 287 mg (1.11 mmol, 74%) of **1**, mp 138–139 °C, and elution with 100 mL of 60:40 petroleum ether–benzene gave 45 mg (0.0762 mmol, 10%) of a yellow-brown solid, mp 270–270.5 °C, thought to be **7**: ^{1}H NMR (CDCl$_3$) δ 7.72–7.32 (m, 12 H, two phenyl groups and H$_{2,2'}$), 6.83 (d, 2 H, J = 1.8 Hz, H$_{4,4'}$), 6.70 (d, 2 H, J = 2.3 Hz, H$_{6,6'}$), 6.55 (d of d, 2 H, J = 8.5, 2.3 Hz, H$_{8,8'}$), 5.86 (2 d as t, 4 H, J = 8.5 Hz, H$_{1,1'}$ and H$_{9,9'}$); parent peak at m/e 584.1046 ($C_{36}H_{22}N_2O_2Cl_2$ requires m/e 584.1052).

Reaction of 1$^{+\cdot}$,ClO$_4^-$ with Methanol. Formation of 1 and Its 3,3′ Dimer (8). The cation radical (575 mg, 1.60 mmol) was dissolved in 10 mL of acetonitrile to which was added, over a period of 7 h, 31 mL of methanol, previously distilled over magnesium and iodine. The solution was stirred for 6 days and worked up. Elution with 350 mL of 90:10 petroleum ether–benzene gave 115 mg (0.443 mmol, 28%) of **1**, mp 138–139 °C. Continued elution (500 mL) gave 61 mg (0.118 mmol, 15%) of **8** as a yellow solid, mp 249–250 °C: mp 264–265 °C after three crystallizations from benzene–methanol (lit. mp 262–265 °C (structure unspecified)[16]); ^{1}H NMR (CDCl$_3$) δ 7.70–7.26 (m, 10 H, two phenyls), 6.84 (d, 2 H, J = 2.0 Hz, H$_{4,4'}$), 6.78–6.50 (m, 8 H, H$_{2,2'}$ and H$_{6-8,6'-8'}$), 5.90 (d, 4 H, J = 8.5 Hz, H$_{1,9,1',9'}$); m/e (relative intensity) 517 (64), 516 (100), 439 (28), 362 (6), 258 (14), parent peak at m/e 516.1876 ($C_{36}H_{24}N_2O_2$ requires m/e 516.1838). Continued elution with 450 mL of methylene chloride gave a further 128 mg (0.248 mmol, 31%) of the dimer: mp 264–265 °C (benzene–methanol); m/e 516.1876.

Reaction of 1$^{+\cdot}$,ClO$_4^-$ with Water, Cyanide Ion, Superoxide Ion, and Alkyl Amines. Formation of 1 and 8. In each of the following reactions the only products obtained were, in various yields, **1** and its dimer (**8**). Details of the workup were similar to those of the methanol reaction and are therefore not given. From 675 mg (1.88 mmol) of the cation radical and 5 mL of H$_2$O in 20 mL of acetonitrile were obtained 161 mg (0.622 mmol, 33%) of **1** and 211 mg (0.409 mmol, 47%) of **8**. From 589 mg (1.64 mmol) of the cation radical and a suspension of 464 mg (7.1 mmol) of potassium cyanide in 40 mL of acetonitrile, stirred previously for 2 h, were obtained 391 mg (1.51 mmol, 92%) of **1** and 54 mg (0.105 mmol, 13%) of crude **8**, mp 247–248 °C (mp 264–265 °C after several crystallizations). From 563 mg (1.57 mmol) of the cation radical and 215 mg (3.0 mmol) of potassium superoxide in 30 mL of acetonitrile were obtained 316 mg (1.22 mmol, 78%) of **1** and 10 mg (0.0198 mmol, 2.5%) of **8**. In the reactions with amines, to approximately 390–760 mg (1.1–2.1 mmol) of the cation radical in 20 mL of acetonitrile was added a slight excess of amine (1.7–3.0 mmol). In each case the mixture turned gray-brown immediately, and workup after 30 min gave **1** and **8** as follows: butylamine, 83%, 2.4%; diisopropylamine, 85%, 8.2%; triethylamine, 92%, 2.4%.

Reaction of 1$^{+\cdot}$,ClO$_4^-$ with Fluoride Ion. Formation of 1, 8, and a Fluoro Dimer (9). Several reactions of the cation radical with fluoride ion were carried out and led mainly to **1**, but in variable amounts. The reactions were very slow. In one reaction mass spectrometric evidence for a fluorinated dimer was obtained, as follows. A suspension of 175 mg (3.02 mmol) of potassium fluoride was stirred for 12 days in a solution of 596 mg (1.66 mmol) of the cation radical in 40 mL of acetonitrile, before working up. Elution with 1.2 L of 90:10 petroleum ether–benzene gave 228 mg (0.880 mmol, 53%) of **1**. Elution with 600 mL of 70:30 petroleum ether–benzene gave 23.5 mg of a yellow solid: mp 255–257 °C; m/e (relative intensity) 535 (5), 534 (11), 517 (58), 516 (100), 457 (3), 439 (33), 362 (26), 258 (27); mass matched peaks m/e 534.1682 and 516.1871 ($C_{36}H_{23}FN_2O_2$ requires m/e 534.1738 and $C_{36}H_{24}N_2O_2$ requires m/e 516.1838, suggesting that **8** and a monofluoro **8** were present). Separation of the dimers by ThLC and further column chromatography were not successful.

Direct Bromination of 1. (A) In Acetonitrile. To a stirred solution of 782 mg (3.02 mmol) of **1** in 20 mL of acetonitrile, under a gentle flow of nitrogen, was added 0.17 mL (3.1 mmol) of bromine from a microsyringe. The solution became red-pink (the color of 1$^{+\cdot}$) immediately but soon turned green, then purple, and finally black. Hydrogen bromide was evolved during reaction. After 1 h the solution was poured into aqueous sodium bicarbonate, the mixture was extracted with benzene, and the benzene solution was worked up to give 158 mg (0.379 mmol, 12.6%) of **5** (mp 150–151 °C (petroleum ether); m/e 416.9249), 520 mg of **4** as a thick yellow oil which later solidified (mp 89–91 °C), and 168 mg (0.649 mmol, 21.5%) of recovered **1** (mp 138–139 °C). The ^{1}H NMR spectra of the products **4** and **5** corresponded with those obtained from reaction of 1$^{+\cdot}$ with bromide ion.

(B) In Acetic Acid. Reaction of 474 mg (1.83 mmol) of **1** with 0.10 mL (1.83 mmol) of bromine in 30 mL of acetic acid gave 25% of **5**, 46.5% of **4**, and 20.7% of **1**.

Preparation of Authentic Compounds. 3-Nitrophenoxazine(11). (A) Turpin Reaction. A solution of 4.15 g (104 mmol) of sodium hydroxide in 60 mL of 50% ethanol was added dropwise to a stirred solution of 4.51 g (41.4 mmol) of *o*-aminophenol and 8.5 g (42.0 mmol) of 1-chloro-2,4-dinitrobenzene in 80 mL of 95% ethanol. The mixture was boiled for 100 min and filtered. The gray-brown solid was washed with 10% sodium hydroxide and then ethanol and dissolved in benzene. Concentrating the benzene solution gave 7.6 g (27.5 mmol, 66.5%) of reddish brown 2-hydroxy-2′,4′-dinitrodiphenylamine (**10**): mp 200.5–202 °C (lit.[28] mp 200.5–202 °C); ^{1}H NMR (acetone-d_6) δ 9.94 (bd s, 1 H, NH), 9.04 (d, 1 H, J = 2.7 Hz, H$_{3'}$), 8.26 (d of d, 1 H, J = 9.50, 2.7 Hz, H$_{5'}$), 7.50–6.88 (m, 6 H, OH, H$_{3-6}$, H$_{6'}$); m/e (relative intensity) 276 (14), 275 (100), 183 (22), parent peak at m/e 275.0520 ($C_{12}H_9N_3O_5$ requires m/e 275.0540).

To a stirred solution of 550 mg (2.0 mmol) of **10** in 30 mL of Me$_2$SO was added a solution of 251 mg (3.1 mmol) of sodium acetate in 10 mL of Me$_2$SO. The mixture was heated at 96 °C for 16 h and poured into 500 mL of ice-cold water. The precipitated solid was filtered, washed with water, and dissolved in acetone. The aqueous solution was extracted with methylene chloride, and the combined organic solutions were dried and evaporated. Trituration of the residue with a little benzene and ethanol gave 284 mg (1.25 mmol, 62.5%) of crude, red-brown **11**, mp 190–192 °C (lit. mp 195–197,[27] 200–201 °C[28]). Crystallization from benzene gave lustrous, brass-colored needles, mp >360 °C.

(B) Musso's Method. 10-Acetylphenoxazine (**12**) was prepared from phenoxazine and acetic anhydride, mp 145.5–146 °C (lit.[37] mp 142 °C). This was nitrated giving a 92% yield of 3-nitro-10-acetylphenoxazine (**13**), mp 134–135 °C (lit.[27] mp 136–137 °C), which was hydrolyzed as described[27] to give gray-brown **11** in 96% yield: mp 198–198.5 °C; *m*/*e* (relative intensity) 229 (13), 228 (100), 198 (11), 182 (87), parent peak at *m*/*e* 228.0484 ($C_{12}H_8N_2O_3$ requires *m*/*e* 228.0533). Crystallization from benzene gave lustrous, brass-colored needles, mp >360 °C. Nevertheless, all analytical data were consistent with **11**: *m*/*e* (relative intensity) 229 (11), 228 (100), 198 (13), 182 (77), parent peak at *m*/*e* 228.0554; ^{1}H NMR (acetone-d_6) δ 8.30 (bd s, 1 H, NH), 7.67 (d of d, 1 H, *J* = 9.0, 2.3 Hz, $H_{2,8}$), 7.39 (d, 1 H, 2.3 Hz, H_4), 6.90–6.66 (m, 4 H, H_{6-9}), 6.58 (d, 1 H, *J* = 9.0 Hz, H_1). The NMR data are in good agreement with literature data[38] for **11**, prepared[39,40] by heating the sodium salt of **10** in DMF as described by Musso,[27] but the melting point is not recorded.[38-40]

Anal. Calcd for $C_{12}H_8N_2O_3$: C, 63.2; H, 3.54; N, 12.3. Found (mp >360 °C): C, 63.3; H, 3.54; N, 12.1.

3-Nitro-10-phenylphenoxazine (2). (A) From 11. A mixture of 916 mg (4.02 mmol) of **11** (mp >360 °C), 69.3 mg (5.0 mmol) of potassium carbonate, 2.41 g (11.8 mmol) of iodobenzene, and 250 mg of activated Cu powder in 20 mL of DMF was boiled for 36 h and filtered. The residue was washed with hot benzene, and the combined filtrate and washings were evaporated. The residue was dissolved in methylene chloride, washed with water, dried, and concentrated. Attempts to crystallize from methylene chloride and ethanol failed. The residue was therefore chromatographed on a column of silica gel. Elution with 70:30 petroleum ether–benzene gave first (250 mL) a small amount of oil and next (700 mL) 278 mg (0.914 mmol, 22.7%) of **2**, mp 173–174 °C, whose ^{1}H NMR and mass spectra were almost identical with **2** obtained from reaction of $1^{+\cdot}$ with nitrite ion.

Continued elution with 40:60 petroleum ether–benzene gave first (250 mL) 8 mg of **2** and next (850 mL) 231 mg (0.436 mmol, 21.7%) of a red-brown solid, mp 282–283 °C, which is deduced to be 3,3′-dinitro-10-phenyl-7,10′-biphenoxazine (**14**): mp 290–291 °C (benzene); *m*/*e* (relative intensity) 531 (37), 530 (100), 500 (3), 484 (11), parent peak at *m*/*e* 530.1292 ($C_{30}H_{18}N_4O_6$ requires *m*/*e* 530.1222). Owing to poor solubility, the ^{1}H NMR (Me_2SO-d_6) had poor resolution: δ 7.82–7.56 (m, 5 H, phenyl), 7.56–7.36 (m, 3 H, $H_{2,2',4}$), 7.01 (d, 1 H, *J* = 2.3 Hz, $H_{4'}$), 6.88–6.54 (m, 5 H, $H_{6,8}$ and $H_{6'-8'}$), 6.22–5.94 (m, 4 H, $H_{1',9,9'}$). The IR spectrum (Nujol) gave no indication of an N–H stretch and is the basis for designating **14** *as a* 7,10′ dimer.

Anal. Calcd for $C_{30}H_{18}N_4O_6$ (**14**): C, 67.9; H, 3.42; N, 10.6. Found: C, 68.0; H, 3.30; N, 10.4.

Continued elution with 500 mL of benzene gave 215 mg of a black-red solid, mp 170 °C (dec). TLC showed this to be a mixture, and by ThLC, using 40:60 petroleum ether–benzene, 162 mg (0.306 mmol, 15.2%) of **14**, mp 290–291 °C, was obtained, after extracting the band with methylene chloride. Four other bands remained, but no attempt to identify them was made.

(B) From 10. A mixture of 1.37 g (4.98 mmol) of **10**, 1.43 g (7.04 mmol) of iodobenzene, 0.834 g (6.0 mmol) of potassium carbonate, and 0.309 g of activated Cu powder in 20 mL of DMF was boiled for 48 h. The evolution of nitrogen dioxide was observed. After the mixture was filtered, the residue was washed with hot benzene. Evaporation of the filtrate and washings gave 1.09 g (3.58 mmol, 72%) of crude **2**, mp 163–164 °C. The following data were obtained after crystallization: mp 172.5–173 °C; λ_{max} (acetonitrile) 446 nm (ϵ 1.37 × 10^4). All other spectroscopic data agreed with those of **2** made from $1^{+\cdot}$ and from **11**.

3-Amino-10-phenylphenoxazine (15). A warm solution of 416 mg (1.37 mmol) of **2** in 40 mL of ethyl acetate was added dropwise to a stirred suspension of 2.08 g (32 mmol) of Zn dust in 10 mL of 50% ethanol. The mixture was stirred at 45 °C and to it was added 20 mL of concentrated hydrochloric acid over a period of 20 min. The solution was cooled, stirred for 4 h, neutralized with sodium hydroxide, and filtered. The solids were washed five times each with 30 mL of methylene chloride. The methylene chloride solution was washed, dried, and evaporated to give 393 mg of blue-gray solid. This was chromatographed on silica gel. Elution with 700 mL of 70:30 petroleum ether–benzene gave a small amount of solid, and elution next with 700 mL of *benzene gave 322 mg (1.18 mmol, 86%) of* **15**: mp 154–155 °C (benzene–methanol); *m*/*e* (relative intensity) 275 (22), 274 (100), 197 (41), parent peak at *m*/*e* 274.1079 ($C_{18}H_{14}N_2O$ requires *m*/*e* 274.1103); ^{1}H NMR ($CDCl_3$) δ 7.68–7.28 (m, 5 H, phenyl), 6.76–6.50 (m, 3 H, H_{6-8}), 6.17 (d, 1 H, *J* = 2.5 Hz, H_4), 6.06–5.86 (m, 2 H, $H_{2,9}$), 5.75 (d, 1 H, *J* = 8.5 Hz, H_1), 3.27 (bd s, 2 H, NH_2).

3-Bromo-10-phenylphenoxazine (4). The conversion of **15** into **4**, and into the 3-chloro derivative (**6**), by the customary diazotization techniques using mineral acid and sodium nitrite was unsuccessful. Limited success was achieved by using isoamyl nitrite. To a solution of 40 mg (0.146 mmol) of **15** and 1 mL of concentrated sulfuric acid in 5 mL of ethanol was added 0.02 mL (0.144 mmol) of isoamyl nitrite. The mixture was cooled to 0 °C and to it was added slowly an excess of a solution of freshly prepared cuprous bromide in 48% hydrobromic acid. The mixture was removed from the ice bath, allowed to warm to room temperature, and then warmed at 50 °C until nitrogen evolution ceased. The mixture was poured into water and extracted with methylene chloride. The methylene chloride solution was dried, concentrated, placed on ThLC plates, and developed with petroleum ether. The uppermost band gave 17.3 mg (0.051 mmol, 35%) of a thick oil which later solidified, mp 89–92 °C. Mass spectroscopy showed this to be **4** contaminated with a small amount of **5**: parent peak at *m*/*e* 337.0047 ($C_{18}H_{12}NOBr$ requires *m*/*e* 337.0099); ^{1}H NMR ($CDCl_3$) δ 7.70–7.28 (m, 5 H, phenyl), 6.80 (d, 1 H, *J* = 2.0 Hz, H_4), 6.74–6.51 (m, 4 H, $H_{2,6-8}$), 6.00–5.84 (m, 1 H, H_9), 5.76 (d, 1 H, *J* = 8.5 Hz, H_1).

3-Chloro-10-phenylphenoxazine (6). A similar procedure with 45 mg (0.164 mmol) of **15**, 0.03 mL (0.217 mmol) of isoamyl nitrite, and freshly prepared cuprous chloride in ice-cold hydrochloric acid gave 16.4 mg (0.056 mmol, 34%) of **6** as a thick oil which later solidified: mp 82–83.5 °C; parent peak at *m*/*e* 293.0633 ($C_{18}H_{12}NOCl$ requires *m*/*e* 293.0604); ^{1}H NMR ($CDCl_3$) δ 7.70–7.26 (m, 5 H, phenyl), 6.76–6.46 (m, 5 H, $H_{2,4,6-8}$), 6.00–5.88 (m, 1 H, H_9), 5.81 (d, 1 H, *J* = 8.5 Hz, H_1).

2-Chloro-10-phenylphenoxazine (16). A mixture of 1.06 g (4.86 mmol) of 2-chlorophenoxazine,[41] 2.42 g (11.9 mmol) of *iodobenzene, 652 mg (4.94 mmol) of potassium* carbonate, and 226 mg of activated Cu powder was boiled for 2 days. The mixture was filtered, the residue was washed with hot benzene, and the combined solutions were evaporated to dryness. The residue was crystallized from cyclohexane to give 751 mg (2.56 mmol, 52.7%) of **16**, as colorless cubes: mp 84.5–86 °C, mixture melting point with **6** 63–68 °C; ^{1}H NMR ($CDCl_3$) δ 7.72–7.20 (m, 5 H, phenyl), 6.74–6.46 (m, 5 H, $H_{3,4,6-8}$), 5.96–5.80 (m, 2 H, $H_{1,9}$).

Anal. Calcd for $C_{18}H_{12}NOCl$ (**16**): C, 73.6; H, 4.11; N, 4.77; Cl, 12.1. Found: C, 73.7; H, 4.05; N, 4.79; Cl, 12.1.

Concentration of the mother liquor gave a further 566 mg (1.93 mmol, 39.7%) of crude **16**, mp 79–82 °C.

10-(*p*-Bromophenyl)phenoxazine (17) and 1,4-Bis(10-phenoxazinyl)benzene (18). A mixture of 391 mg (2.14 mmol) of phenoxazine, 628 mg (2.27 mmol) of *p*-bromoiodobenzene, 304 mg (2.2 mmol) of potassium carbonate, and 424 mg of activated Cu powder was boiled in 10 mL of DMF for 60 h. Chromatographic workup gave 166 mg (0.491 mmol, 23%) of **17** (mp 199–200.5 °C (hexane) (lit.[36] mp 200–202); parent peak at *m*/*e* 337.0114 ($C_{18}H_{12}NOBr$ requires *m*/*e* 337.0099)) and 101 mg (0.230 mmol, 21.5%) of crude **18** (mp 240–241 °C (lit.[36] mp 249–250.5 °C); parent peak at *m*/*e* 440.1548 ($C_{30}H_{20}N_2O_2$ requires *m*/*e* 440.1520)).

Reaction of Phenoxazine with Bromobenzene. Formation of 1, Two Dimers, and a Trimer. A mixture of 545 mg (2.98 mmol) of phenoxazine, 1.52 g (9.7 mmol) of bromobenzene, 694 mg (5.0 mmol) of potassium carbonate, and 159 mg of activated Cu powder was boiled for 4 days and filtered. The filtrate and

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[41] We thank Dr. C. Zirkle and Mr. A. Pavloff, Smith, Kline and French Laboratories, for a generous gift of this compound.

benzene washings were concentrated and cooled to give 150 mg (0.341 mmol, 23%) of a white solid, mp 195–196 °C (benzene). This solid is thought to be 10-phenyl-1,10′-biphenoxazine (**19**): parent peak at *m/e* 440.1461 ($C_{30}H_{20}N_2O_2$ requires *m/e* 440.1520); ^1H NMR ($CDCl_3$) δ 7.37 (s, 3 H, aromatic), 7.05 (s, 4 H, aromatic), 6.92–6.32 (m, 10 H, aromatic), 6.19 (d of d, 1 H, $J = 7.0, 2.0$ Hz, H_9), 6.04–5.84 (m, 2 H, $H_{1',9'}$). The IR (Nujol) spectrum did not show an N–H stretch.

Anal. Calcd for $C_{30}H_{20}N_2O_2$ (**19**): C, 81.8; H, 4.55; N, 6.36. Found: C, 81.6; H, 4.65; N, 6.14.

The filtrate was evaporated and chromatographed on silica gel. Elution with 500 mL of 90:10 petroleum ether–benzene gave 55.5 mg (0.214 mmol, 7.2%) of **1**, mp 138–139 °C. Elution with 200 mL of 70:30 petroleum ether–benzene gave 146 mg (0.332 mmol, 22.3%) of a white solid: mp 162–164 °C (benzene); *m/e* (relative intensity) 441 (33), 440 (100), 363 (11), 259 (3), 182 (18); ^1H NMR ($CDCl_3$) δ 7.66–7.34 (m, 2 H, *o*-phenyl), 7.06 (s, 3 H, *m,p*-phenyl), 6.92–6.32 (m, 11 H, ring H), 6.26–6.07 (m, 2 H, $H_{1,9}$), 6.02–5.88 (m, 2 H, $H_{1',9'}$). The IR (Nujol) spectrum showed no N–H stretch. This compound is thought to be 10-phenyl-3,10′-biphenoxazine (**20**). Elution with 100 mL of 70:30 petroleum ether–benzene gave 52 mg of a mixture (ThLC) of two compounds, *m/e* 621 and 440. Elution with 250 mL of 50:50 petroleum ether–benzene gave 139 mg (0.224 mmol, 22.5%) of a white solid, mp 181–183 °C, thought to be 10-phenyl-3,10′:7(or 3′),10″-terphenoxazine (**21a** or **21b**). Parent peak at *m/e* 621.1926 ($C_{42}H_{27}N_3O_3$ requires *m/e* 621.2046); ^1H NMR ($CDCl_3$) δ 7.80–7.40 (m, 2 H, *o*-phenyl), 7.38 (s, 3 H, *m,p*-phenyl), 7.22–7.04 (m, 2 H, $H_{4,6(\text{or } 4')}$), 6.98–6.46 (m, 14 H, ring H), 6.46-5.90 (m, 6 H, $H_{1,1',1'',9,9',9''}$).

Half-wave oxidation potentials of **1**–**4** and **16** were measured by cyclic voltammetry in acetonitrile with tetrabutylammonium perchlorate as the electrolyte. The acetonitrile was Eastman's anhydrous grade and was further dried by being passed through a column of predried alumina. The reference electrode was Ag/Ag^+ (0.1 M) and was calibrated against an SCE electrode. Half-wave potentials were measured at increasing scan rates and leveled off as follows: **1**, 0.36 V; **2**, 0.64 V; **3**, 0.50 V; **4**, 0.46 V; **16**, 0.46 V.[42]

Registry No. 1, 37832-25-0; $1^{+\cdot},ClO_4^-$, 67728-02-3; **2**, 71041-09-3; **3**, 71041-10-6; **4**, 71041-11-7; **5**, 71041-12-8; **6**, 71041-13-9; **7**, 71041-14-0; **8**, 71041-15-1; **9**, 71041-16-2; **10**, 6358-23-2; 11, 20464-44-2; **12**, 6192-43-4; **13**, 71041-17-3; **14**, 71041-18-4; **15**, 71041-19-5; **16**, 71041-20-8; **17**, 71041-21-9; **18**, 71041-22-0; **19**, 71041-23-1; **20**, 71041-24-2; **21a**, 71041-25-3; 1-chloro-2,4-dinitrobenzene, 97-00-7; *o*-aminophenol, 95-55-6; iodobenzene, 591-50-4; 2-chlorophenoxazine, 56821-03-5; phenoxazine, 135-67-1; *p*-bromoiodobenzene, 589-87-7; bromobenzene, 108-86-1; NO_2^-, 14797-65-0; SCN^-, 302-04-5; Br^-, 24959-67-9; Cl^-, 16887-00-6; CH_3OH, 67-56-1; H_2O, 7732-18-5; CN^-, 57-12-5; O_2^-, 11062-77-4; butylamine, 109-73-9; diisopropylamine, 108-18-9; triethylamine, 121-44-8; F^-, 16984-48-8.

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[42] We thank Mr. Michael T. Stephenson for making these measurements.

Bizarre Reactions of 2-Butyne during the Addition of Hydrogen Chloride[1]

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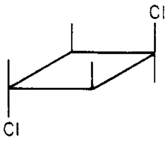
Liquid-phase reactions of anhydrous hydrogen chloride with 2-butyne at ambient temperatures were studied. In addition to the normal reaction products 13 compounds have been identified. They are chlorinated and nonchlorinated cyclic and acyclic dimers and trimers of 2-butyne.

In previous papers we have reported that liquid-phase reactions of anhydrous hydrogen bromide[2,3] and hydrogen chloride [2,4,5] with a series of monoalkylacetylenes resulted partly in 2 + 2 cycloadditions to afford products having four-membered ring structures. By contrast, in the reaction of excess hydrogen chloride with the dialkylacetylene 2-butyne under similar conditions, only 2,2-dichlorobutane was reported as a product.[6]

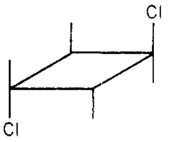
In continuation of our studies on electrophilically induced cycloaddition reactions, we have now reexamined this reaction with particular attention to the occurrence of nonconventional products.

Results

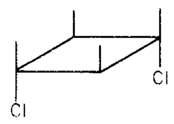
Reactions of hydrogen chloride with 2-butyne in a relative molar ratio of 5:1 at ambient temperatures gave complete conversions of the substrate within 10 days. GLC analysis of the crude, liquid reaction mixture showed the presence of at least 12 components, of which 11 could be identified. They are 2,2-dichlorobutane (major product, 60–70%), 2-chloro-1-butene,[7] (*Z*)- and (*E*)-2-chloro-2-butene,[7] pentamethylbenzene, hexamethylbenzene, and the hitherto unknown compounds **1**–**5**.[8]



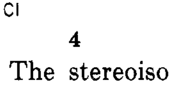
1



2



3



4

$$CH_3CCl{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}C(CH_3)\overset{CH_3}{\overset{|}{C}}HCHClCH_3$$

5

The stereoisomeric 1,3-dichloro-1,2,3,4-tetramethylcyclobutanes **1**–**4** are colorless, crystalline solids. Their stereochemistry was assigned on the basis of the following ^1H NMR data (Table I). Isomer **1** exhibited one doublet

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[1] Presented by H.S. at the 17th Hauptversammlung der Gesellschaft Deutscher Chemiker, München, 1977.

[2] K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Am. Chem. Soc.*, 87, 3151 (1965).

[3] K. Griesbaum, W. Seiter, H. Schneider, M. El Abed, and Z. Rehman, *Justus Liebigs Ann. Chem.*, in press.

[4] K. Griesbaum, Z. Rehman, and U.-I. Zâhorszky, *Angew. Chem.*, 82 841 (1970); *Angew. Chem., Int. Ed. Engl.*, 9, 273 (1970).

[5] K. Griesbaum and M. El Abed, *Chem. Ber.*, 106, 2001 (1973).

[6] Belgian Patent 666930 (1965), *Chem. Abstr.*, 65, 7056e (1965).

[7] These unsaturated adducts may have been partly or totally formed by dehydrohalogenation of 2,2-dichlorobutane during GLC analysis, since they were also detected when pure 2,2-dichlorobutane was analyzed under the same conditions.

[8] The single bonds originating from the cyclobutane rings represent methyl groups.