166–167 °C); IR 1580, 1529 (aromatic C=C), 1339, 1167 cm^{-1} (SO_2).

3,3,4,5,6,7-Hexachloro-2,3-dihydrobenzothiophen-2-one (17). Hexachlorobenzothiophene (**16**; 10.23 g, 0.03 mol) was suspended in 100 mL of acetic acid and stirred and heated on a steam bath. Chromium trioxide (15 g, 0.15 mol) was added in portions, and heating was continued for 40 min. The mixture was then poured into ice and water. The product was filtered off and recrystallized from acetone to give 3.11 g (29%) of the thiolactone **17**: mp 144.8–145 °C; IR 1745 (C=O), 1558 cm^{-1} (conjugated C=C). The mass spectrum showed the following peaks of sequential decomposition: *m/e* 354 (parent), 319 (-Cl), 291 (-CO), 256 (-Cl), 221 (-Cl), 151 (-Cl).

Anal. Calcd for C_8Cl_6OS: C, 26.02; Cl, 59.60; S, 8.98. Found: C, 27.09; Cl, 59.42; S, 8.90.

Hydrolysis of 17. 3,3,4,5,6,7-Hexachloro-2,3-dihydrobenzothiophen-2-one (**17**; 3.41 g, 0.01 mol) and a solution of 0.88 g (0.022 mol) of sodium hydroxide in 25 mL of water were heated on a steam bath. The lactone soon dissolved, and, on cooling the solution, the sodium salt of the product crystallized out. It was dissolved by adding water, and the free acid was precipitated with hydrochloric acid. The product was filtered off, air-dried, and recystallized from carbon tetrachloride to give 2.25 g (66.5%) in two crops of 2,3,4,5,8-pentachloro-7-thiabicyclo[4.2.0]-1,3,5-octatriene-8-carboxylic acid (**18**): mp 183–184 °C; NMR ($CDCl_3$) 9.60 ppm (s); IR 3333–2500, 1730 (C=O, typical of COOH), 1475 cm^{-1} (aromatic C=C). The mass spectrum showed peaks at *m/e* 336 (parent, strong), 301 (-Cl), 291 (-COOH), and 654 (weak, anhydride).

Anal. Calcd for $C_8HCl_5O_2S$: C, 28.39; H, 0.30; Cl, 52.38. Found: C, 28.43; H, 0.46; Cl, 52.36.

3,3,4,5-Tetrachloro-2,3-dihydrothiophen-2-one (19). A solution of 22.2 g (0.1 mol) of tetrachlorothiophene[14] in 120 mL of acetic acid was warmed and stirred on a steam bath. The heat was removed, and 20 g (0.2 mol) of chromium trioxide was added in portions. The reaction was vigorous. The solution was cooled and poured into 600 mL of ice and water. The oil was separated, and the aqueous layer was extracted once with ether. The combined oil and ether extract were dried ($MgSO_4$) and distilled to give 11.6 g of product: bp 75–77 °C (1.8 mm); n^{25}_D 1.5913–1.5918. The product was purified by GLC over 25% fluoroalkyl pyromellitate on Gas Chrom R. Tetrachlorothiophene came off at 18.4 min and the product (3.86 g, 16%) at 35 min. The product (**19**) was redistilled: bp 75 °C (2.2 mm); n^{25}_D 1.5920; IR 1733 (C=O), 1608 cm^{-1} (C=C).

Anal. Calcd for C_4Cl_4OS: C, 20.19; Cl, 59.61; S, 13.48. Found: C, 20.51; Cl, 59.81; S, 13.57.

Octachlorodibenzothiophene. Dibenzothiophene (9.2 g, 0.05 mol), 150 mL of carbon tetrachloride, 1 g of iodine, and 32 g (0.9 mol) of chlorine were charged into a 360-mL Hastelloy C shaker tube and heated 4 h at 100 °C. The octachlorobenzothiophene (20.3 g, 88%) was filtered off. Recrystallization from xylene left 19.3 g (84%) of product, mp 304–307.5 °C (lit.[20] mp 302 °C).

Anal. Calcd for $C_{12}Cl_8S$: Cl, 61.69. Found: Cl, 61.46.

Acknowledgment. I am indebted to Drs. D. A. Pensak, the late W. A. Sheppard, H. E. Simmons, and B. E. Smart for helpful discussions, to E. W. Matthews for interpretations of IR spectra, to C. B. Matthews for GLC analyses, to R. L. Harlow for X-ray diagrams, and to L. C. Hovsepian for thermal analyses. Technical assistance was provided by F. A. Blissick.

Registry No. **1**, 18043-32-8; **2**, 73308-46-0; **3**, 7294-43-1; **4**, 380-40-5; *cis*-**5**, 73308-47-1; *trans*-**5**, 73308-48-2; *cis*-**6**, 73308-49-3; *trans*-**6**, 73308-50-6; *cis*-**7**, 3934-26-7; *trans*-**7**, 3832-15-3; **8**, 73308-51-7; **9**, 73308-52-8; **10**, 11095-43-5; **11**, 73308-53-9; **12**, 73308-54-0; **13**, 54087-31-9; **15**, 29082-74-4; **16**, 54087-24-0; **17**, 73308-55-1; **18**, 73308-56-2; **19**, 73308-57-3; tetrachlorothiophene, 6012-97-1; dibenzothiophene, 132-65-0; octachlorodibenzothiophene, 7683-05-8; hexachlorocyclobutene, 6130-82-1; hexachlorobutadiene, 87-68-3.

Quinone Chemistry. Reaction of 2,3-Dichloro-1,4-naphthoquinone with *o*-Aminophenols under Various Conditions

Nand L. Agarwal and Wolfram Schäfer*

Max-Planck-Institut für Biochemie, D-8033 Martinsried bei München, Germany

Received December 19, 1979

The reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) and *o*-aminophenols (**2**) under various reaction conditions was reinvestigated. Despite earlier literature, **1** and **2a** in alcohol react to give a mixture of 6-chloro-12a-hydroxy-5*H*-benzo[*c*]phenoxazin-5-one (**4a**), 6-chloro-12a-alkoxy-5*H*-benzo[*c*]phenoxazin-5-one (**5**), 6-chloro-5*H*-benzo[*a*]phenoxazin-5-one (**7a**), 2-amino-3*H*-phenoxazin-3-one (**8**) and triphenodioxazine (**9a**). Contradictory to earlier findings, **1** and **2a** in MeOH/KOH afford **7a** but the highest yield of the compound is achieved by using EtOH or MeOH and anhydrous potassium acetate. A probable mechanism for the formation of all reaction products is presented and detailed spectroscopic data of all compounds are given.

Most of the reported methods for the synthesis of phenoxazones[1-9] from quinones and *o*-aminophenols involve the initial attack of the amino group of the *o*-aminophenol on the quinone substituent (OH, OCH_3, halogen, etc.) and subsequent ring closure. An *o*-aminophenol exchange reaction or a rearrangement leads finally to the phenoxazone system.

Van Allan and co-workers have reported that 2,3-dichloro-1,4-naphthoquinone (**1**) reacts with *o*-aminophenol (**2a**) in ethanol to give 6-chloro-5-hydroxybenzo[*a*]phenoxazine (A) (47%),[10] and in methanol they described 2-chloro-3-(2-hydroxyanilino)-1,4-naphthoquinone (**3a**)[11] as the main reaction product (93%). They have assigned the structure of these compounds by elemental analysis and infrared spectra. From our experience[1-8] in phenoxazone

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Scheme I

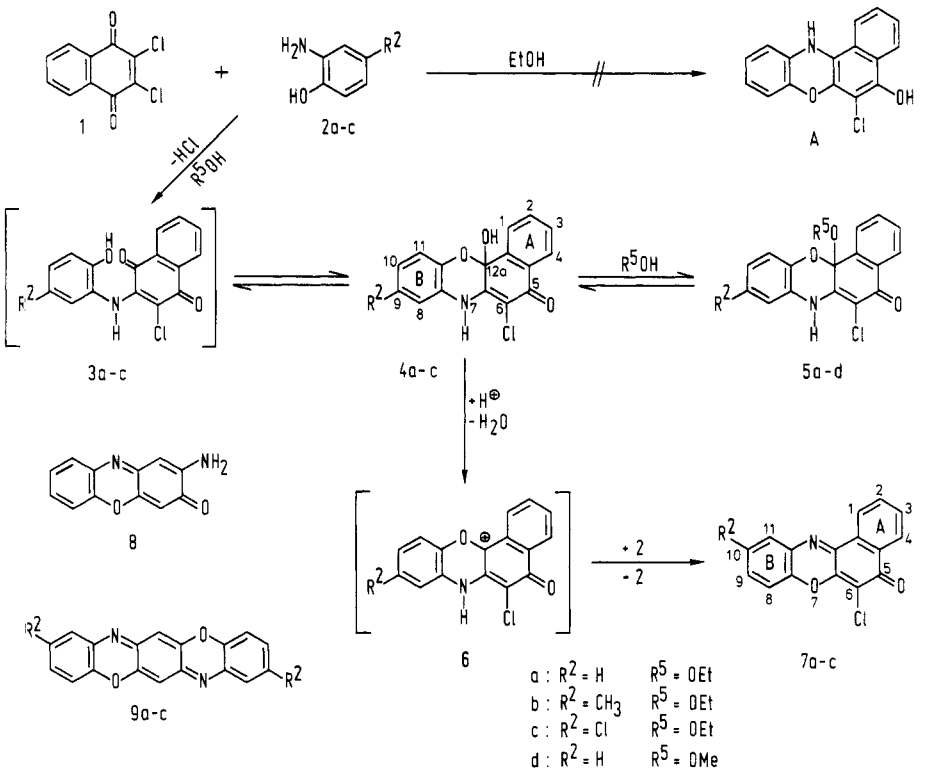

Table I. Reaction of 2,3-Dichloro-1,4-naphthoquinone (1) and o-Aminophenols (2)

reactants	solvent	compd (% yield)					
1 + 2a	EtOH	4a (10.5)	5a (50)	7a (1.5)	8 (3)	9a (4.8)	1 (2)
1 + 2b	EtOH	4b (9)	5b (70)	7b (2)		9b (5)	
1 + 2c	EtOH	4c (21)	5c (44)	7c (2.8)		9c (2)	1 (8)
1 + 2a	MeOH	4a (18)	5d (61)	7a (1.4)	8 (2.5)	9a (4.5)	1 (2)

chemistry, it seemed surprising that different pathways should operate in the reaction of 1 and 2a in solvents of a similar nature. In addition to this, the formation of A in high yield from 1 and 2a did not appear reasonable, because hydroxyphenoxazines are highly unstable.[3] Therefore, we reinvestigated the reaction of 1 and 2 under various reaction conditions.

Despite numerous attempts, we have not been able to find any evidence for the existence of A and 3a under the cited conditions.[10,11] From the reaction of 1 and 2a in ethanol (absolute or 95%), 5a was obtained as the main product (see Scheme I). Other products were 1, 4a, 7a, 8 and 9a. All these compounds were separated by chromatography and structures were established by elemental analysis, UV, IR, ^{1}H NMR, and mass spectra, chemical reactions, or comparison with authentic samples. The IR and UV spectral data of 4a, 5a and 7a are in close agreement with the spectral characteristics of analogous heterocycles.[1,2,12] On o-aminophenol exchange reaction, 4a and 5a yield 7a. The structures of 1, 8, 7a, and 9a were confirmed by comparing their IR and mass spectra and mixture melting points with those of standard samples prepared by known methods.[3,13,14] From these data there is no doubt that the assigned structures are correct. The reaction of 1 and 2a in methanol (absolute or 95%) under the mentioned conditions[11] gave 5d as the main product, accompanied by the same products as in the case of ethanol. Two other substituted o-aminophenols were examined with the intention of determining the generality of the above reaction. Under similar conditions they gave the expected products; the yields of these derivatives are summarized in Table I.

We assume that the reaction of 1 and 2 in ethanol and methanol starts with nucleophilic attack of the amino group of 2 on the halogen atom of 1 with the elimination of hydrogen chloride to give 3. In 3, addition of the hydroxyl group to the quinone carbonyl group in equilibrium reaction leads to the formation of the hemiketal 4, which, due to the presence of hydrogen chloride in the reaction mixture, is etherified to the ketal 5, the main product of the reaction. It was reported that the position of this equilibrium 3⇄4 depends upon the substitution of the o-aminophenols as well as the pH and polarity of the solvent;[2] e.g., in the reaction of 2-hydroxy-1,4-naphthoquinone and 2a in ethanol, 2-(2-hydroxyanilino)-1,4-naphthoquinone (12) (12 = 3a without Cl) was obtained; a hemiketal of type 4 could not be isolated. The UV spectrum of 12 in 1 N HCl confirmed the formation of a hemiketal.[2] When 12 was treated with concentrated HCl in ethanol, 12 and ketal 5e (5e = 5a without Cl) were obtained, but a hemiketal of type 4 could not be isolated. In contrast to this 1 and 2a react in ethanol to form hemiketal 4a and ketal 5a (61% yield), but the open form 3a could not be isolated. From these results it appears that in addition to the above mentioned effects, a substituent in the C-3 position of the quinone also markedly influences the equilibrium.

Due to the presence of hydrogen chloride, carbonium ion 6 is generated by elimination of the hydroxy group in

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4. This reacts with a second molecule of *o*-aminophenol to form the phenoxazone **7** with loss of the *o*-aminophenol added initially. The relatively small amount of hydrogen chloride explains well the formation of **4**, **5**, and **7**. An alternative possibility for the formation of **7a** from a Smiles rearrangement[15] was ruled out, as **4a** or **5a** in acidic medium does not rearrange to **7a**.

The hemiketal structure and the proposed mechanism are further supported by the following reasons: (i) The hemiketals **4** and the ketals **5** have an absorption maximum[2] in the 380–400-nm region only, while quinones of type **3** have a maximum at 450–480 nm.[2] (ii) The hemiketal structure **4a** was confirmed by its etherification in a separate experiment to give the ketal **5a**. (iii) 2-Amino-4-chlorophenol (**2c**) reacts with **4a** and **5a** in acetic acid to give **7c** with the elimination of **2a**.

The formation of **8** from the oxidative condensation of **2a** by use of **1** as oxidizing agent is well-understood.[16] The isolation of triphenodioxazine **9** as a byproduct under the conditions of phenoxazone synthesis is also well-known and mechanistically explained.[16]

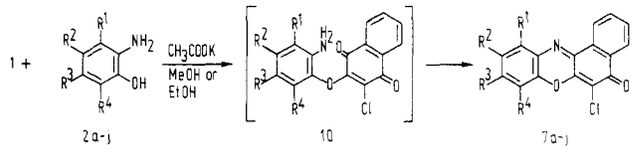
Several attempts to synthesize A from **7a** have been made. Reduction of **7a** using palladium charcoal/hydrogen or sodium dithionite in acetone under a nitrogen atmosphere afforded a light yellow solution (probably the phenoxazine), which on filtration and removal of the solvent, even under a dry nitrogen atmosphere, gave a mixture of **7a** (mol wt 281) and the phenoxazine (mol wt 283). This again supports indirectly the assumption that the phenoxazine cannot be the product of reaction of **1** and **2a** in ethanol under normal conditions.

Van Allan et al. also reported[10] that **1** and **2a** in the presence of potassium hydroxide gave 5*H*-benzo[*a*]phenoxazin-5-one (**7a**, but without chlorine). In this reaction, the formation of **7a** seems possible, but the chlorine-free phenoxazone could only result by replacement of the chlorine atom by a hydrogen, and this appears to be unreasonable under the described conditions. So this unusual reaction seemed to us to be worthy of further investigation. We repeated the reaction[10] several times and could not find evidence for the existence of the well-known phenoxazone. Indeed, we isolated **7a** in 40% yield. The structure was strongly supported by elemental analysis, spectroscopic data, and reductive acetylation. The presence of chlorine is clearly indicated, especially from the mass spectrum. So there is no doubt that the product of this reaction is **7a** and that no reductive dehalogenation occurs under the reported reaction conditions.

It was noticed from these experiments that the presence of potassium hydroxide in the reaction of **1** and **2a** greatly increased the yield of **7a**. This observation suggests that **7a** is formed under the above mentioned conditions by another path. It appears that the *o*-aminophenoxide anions exist[17,18] in basic medium and react with the quinone by initial attack of the phenoxide anion to give the presumed intermediate (**10**), which on subsequent ring closure leads to the phenoxazone (see Scheme II).

On the other hand, potassium hydroxide also reacts with **1** and **7a** to give 2-hydroxy-3-chloro-1,4-naphthoquinone[19] and thus lowers the yield of **7a**. One may expect, therefore, a very high yield of **7**, provided one could find a reagent which produces only phenoxide anions from **2**. Indeed,

Scheme II



2a-j 10 7a-j

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	CH_3	H	H
c	H	Cl	H	H
d	H	H	CH_3	H
e	H	NO_2	H	H
f	H	H	NO_2	H
g	H	Cl	H	Cl
h	Cl	Cl	H	Cl
i	$COCH_3$	H	H	H
j	H	COOH	H	H

Table II. Substituted 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-ones (7)[i]

compd	mp,[d] °C	yield, %	reflux time, h
7a	203	89[e]	0.5
7b	229	82[e]	2
7c	234	95[e]	2
7d	224	74[f]	2
7e	291	78[f]	2
7f	249	76[g]	2
7g	263	87[f]	20
7h	302	87[f]	20
7i	253	77[g]	20
7j	>300	60[h]	20
7k[a]	206	95[f]	2
7l[b]	282	18[c]	2

[a] 11-Aza-6-chloro-5*H*-benzo[*a*]phenoxazin-5-one. [b] 6-Chloro-5*H*-dibenzo[*a*,*i*]phenoxazin-5-one. [c] Purified by column chromatography. [d] TLC I and II. [e] Recrystallized from benzene–hexane. [f] Recrystallized from chloroform–hexane. [g] Recrystallized from ethylacetate–hexane. [h] Recrystallized from concentrated H_2SO_4–H_2O. [i] Satisfactory analytical values (±0.3% for C, H, N, and some Cl) were reported for all compounds.

when **1** was condensed with **2** in the presence of anhydrous potassium acetate in ethanol and methanol or in triethylamine alone, phenoxazones are formed in excellent yields (Table II). Several attempts to isolate the presumed intermediate **10** were unsuccessful. This represents a new synthesis of phenoxazone from a quinone and *o*-aminophenol in high yields, which starts with the formation of an ether bridge.

^{1}H NMR Studies. Ketals 5 and Hemiketals 4. The NMR data of the ketals **5**, measured in dimethyl sulfoxide and in chloroform, are listed in Table III. It is remarkable to note that in dimethyl sulfoxide there is found one exchangeable proton in the region δ 10.38–10.88, whereas in chloroform this proton is shifted to higher field δ 7.34–8.82. We view this large difference in the shift of the NH protons as a solvent effect.[20] This argument is supported, as the ^{13}C NMR spectra of **5a** in $CDCl_3$ (C-5, δ 175.9) and in Me_2SO-d_6 (C-5, δ 175.2) are quite similar and rule out the alternative 5-OH tautomeric form of **5**. The IR spectra of **4** and **5** in methylene chloride also show only NH

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Table III. ^{1}H NMR Spectra of Substituted 12a-(OH, OCH_3, OC_2H_5)-5*H*-benzo[*c*]phenoxazin-5-ones[g]

compd	7-NH (s)	12a-OH/OCH_3/OC_2H_5	aromatic protons of ring A: 1-H (m)	aromatic protons of ring A: 4-H (m)	aromatic protons of ring A: 2-H + 3-H	aromatic protons of ring B: 8-H	aromatic protons of ring B: 9-H	aromatic protons of ring B: 10-H	aromatic protons of ring B: 11-H	other protons
4a[e]	10.54	8.06 (s)	8.01-8.09		7.06-7.8	7.46-7.8 (m)	7.05		7.24 (m)	-
4b[e]	10.38	7.96 (s)	7.97-8.06		7.61-7.85	7.3 (d)[b]	-	6.86 (dd)	7.05 (d)[c]	9-CH_3, 2.30 (s)
4c[e]	10.56	8.20 (s)	7.97-8.06		7.61-7.86	7.53 (d)	-	7.08 (dd)	7.23 (d)[c]	-
5a[e]	10.66	0.71 (t,[a] 3 H, CH_3), 3.19 (mc, 2 H, OCH_2)	8.01-8.14		7.66-7.80	7.05			7.56 (m)	-
5a[f]	7.65	0.85 (t, 3 H, CH_3), 3.33 (mc, 2 H, OCH_2)	7.97-8.07	8.19-8.28	7.48-7.76	7.06			7.20 (m)	-
5b[e]	10.55	0.71 (t, 3 H, CH_3), 3.25 (mc, 2 H, OCH_2)	8.05-8.17		7.66-7.86	7.28 (d)		6.99 (dd)	7.13 (d)[c]	9-CH_3, 2.31 (s)
5b[f]	7.48	0.85 (t, 3 H, CH_3), 3.31 (mc, 2 H, OCH_2)	7.96-8.06	8.18-8.28	7.49-7.74	6.87 (d)		6.86 (not resolved)	7.14 (m)	9-CH_3, 2.35 (s)
5c[e]	10.71	0.73 (t, 3 H, CH_3), 3.25 (mc, 2 H, OCH_2)	8.02-8.10		7.74-7.86	7.51 (d)	-	7.16 (dd)	7.34 (d)[c]	-
5c[f]	7.45	0.87 (t, 3 H, CH_3), 3.30 (mc, 2 H, OCH_2)	7.94-8.04	8.18-8.28	7.57-7.70	7.08-7.10 (m)	-	7.08 (not resolved)	7.10 (m)	-
5d[e]	10.68	2.96 (s, 3 H, OCH_3)	8.03-8.13		7.68-7.83	7.05			7.56 (m)	-
5d[f]	7.34	3.06 (s, 3 H, OCH_3)	7.98-8.08	8.21-8.29	7.59-7.72	7.07			7.17 (m)	
5e[e]	10.88	0.73 (t, 3 H, CH_3), 3.22 (mc, 2 H, OCH_2)	7.95-8.09		7.61-7.75	7.00			7.23 (m)	6-H, 5.65 (s)
5e[f]	8.82[d]	0.84 (t, 3 H, CH_3), 3.30 (mc, 2 H, OCH_2)	7.98-8.23		7.53-7.66	6.99			7.15 (m)	6-H, 5.88 (s)

[a] J = 7 Hz. [b] $J_{8,10}$ = 2 Hz. [c] $J_{10,11}$ = 8 Hz. [d] Broad; s, singlet; m, multiplet; d, doublet; dd, doublet of doublets; t, triplet; mc, multiplet center. [e] Solvent Me_2SO-d_6. [f] Solvent $CDCl_3$. [g] Chemical shifts in parts per million, coupling constants in hertz.

Table IV. ^{1}H NMR Data of Substituted 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-ones (7) in $CDCl_3$[e]

compd	1-H (m)[a]	4-H (m)	2-H + 3-H (m)	11-H	8-H	9-H	10-H	substituents
7a	8.29-8.39	8.65-8.75	7.72-7.88	7.72-7.88 (m)	7.37		7.54 (m)	
7b	8.25-8.34	8.56-8.65	7.67-7.77	7.54 (s, AMX)	7.27 (s)		-	10-CH_3, 2.43 (s)
7c	8.3-8.39	8.64-8.73	7.74-7.84	7.74-7.84 (m)	7.28	7.46 (m)	-	
7d	8.25-8.35	8.58-8.67	7.61-7.77	7.61-7.77 (m)	7.16-7.2 (m)	-	7.16-7.2 (m)	9-CH_3, 2.49 (s)
7e	8.34-8.47	8.70-8.76	7.8-7.9	8.70-8.76 (m)	7.58 (d, $J_{8,9}$ = 9 Hz)	8.34-8.7 (m)	-	
7f	8.34-8.43	8.70-8.80	7.79-7.94	7.99 (dd, $J_{10,11}$ = 9, $J_{8,11}$ = 0.88 Hz)	8.33 (s)	-	8.27 (dd, $J_{8,10}$ = 2.3 Hz)	
7g	8.34-8.44	8.65-8.76	7.84-7.90	7.76 (d, AX, $J_{9,11}$ = 2 Hz)	-	7.57 (d)	-	
7h	8.36-8.46	8.77-8.58	7.83-7.93	-	-	7.69 (s)	-	
7i	8.38-8.48	8.62-8.71	7.83-7.87	ABC -	7.56		7.81 (m)	11-C(O)CH_3, 2.96 (s)
7j[b]	8.21-8.35	8.63-8.73	7.88-7.98	8.34 (d, AMX, $J_{9,11}$ = 2 Hz)	7.69 (d, $J_{8,9}$ = 9 Hz)	7.88-8.28 (m)[d]	-	
7k	8.28-8.37	8.77-8.87	7.76-7.84	-	7.76-7.84 (m)	7.49 (dd, $J_{9,10}$ = 6, $J_{8,9}$ = 8 Hz)	8.64 (dd, $J_{8,10}$ = 1.5 Hz)	
7l	8.30-8.41[c]	8.70-8.80	-					7.49-7.94 (m, 7 H, 2-H, 3 H, 8-H to 12-H)

[a] s, singlet; d, doublet; dd, doublet of doublets; m, multiplet. [b] In dimethyl sulfoxide. [c] 1-H and 13-H. [d] Mixed with 1-H to 4-H protons. [e] Chemical shifts in parts per million, coupling constants in hertz.

stretching vibrations. In dimethyl sulfoxide (Table III), the resonance at δ 7.96–8.20 for 4 is attributed to the 12a-OH protons, because analogous *N*-methyl derivatives show the 12a-OH signal in the same region.[12] The C-1 and C-4 protons of **4** and **5** occur at lowest field, due to the presence of the carbonyl group and the benzo[*c*] skeleton. They could be resolved only in a few cases. The C-2 and C-3 protons may be assigned at δ 7.06–7.86. In the case of 12a-ethoxy-substituted derivatives, the methyl protons of the ethoxy group appeared as a triplet (J = 7 Hz) in the region δ 0.71–0.87. The two methylene protons are not equivalent and show a multiplet of 16 lines centered in the region δ 3.19–3.33. In the range of B ring protons, the highest field proton (C-10) appears as a doublet of doublets. The low-field doublet is attributed to the C-8 proton, due to the meta coupling constant ($J_{8,10}$), while the next low-field doublet may belong to the C-11 proton ($J_{10,11}$). The signals from the protons of the methyl group occur at δ 2.30–2.35, which agrees with data reported[21] for numerous methyl-substituted heterocyclic compounds.

Phenoxazones (7). The aromatic protons of ring A are comparable to an ABCD pattern; the hydrogen atoms at C-1 and C-4 are clearly distinguishable. The proton of C-4 in all derivatives appeared at the lowest field (δ 8.56–8.88) in comparison to the other protons of the ring system. It is probably due to a combined effect of anisotropy and the electron-withdrawing character of the carbonyl group. The resonance of the C-1 proton is assigned in the region δ 8.21–8.48, while the protons at C-2 and C-3 appeared at δ 7.61–7.98 and could not be separated. The above assignment of protons is fully supported by the integration curve. The long-range deshielding effect arising from replacing an electron-donating group (CH_3) by electron-attracting groups (NO_2, Cl, $COCH_3$, etc.) in ring B is thought to be responsible for the C-1 and C-4 protons occurring at lower field. In derivatives substituted at C-9 or C-10, the ring-proton spectrum may be analyzed as an AMX pattern. It is quite interesting to note that the C-11 proton of **7c** could not be resolved individually, due to the presence of the chloro group at C-10, whereas the C-11 proton of **7b** showed a singlet at δ 7.54, due to the electron-donating nature of the methyl group. This assignment is further supported as the C-11 proton in **7d** could not be resolved individually, due to the absence of the methyl group at the C-10 position.

The NMR spectra of positional isomers **7e** and **7f** are interesting and distinguishable. In **7e** the C-11 proton appeared at δ 8.70–8.76, due to the electron-donating nature of the nitro group, and it was mixed with the C-4 proton. The C-8 proton is assigned at the highest field position as a doublet centered at δ 7.58, $J_{8,9}$ = 9 Hz, because it is at a position meta to the nitro group. In contrast to this, in **7f** the proton C-8 occurs at the lowest field position as almost a singlet at δ 8.33, due to the small coupling constant of $J_{8,10}$ and $J_{8,11}$. The highest field proton (C-11) of ring B appeared as a doublet of doublets at δ 7.99 and the C-10 proton appeared as a doublet of doublets centered at δ 8.27. The coupling constants are in agreement with the proposed assignment. On similar grounds, the protons of ring B for **7g–7j** were assigned and are listed in Table IV.

The NMR spectrum of 11-aza-6-chloro-5*H*-benzo[*a*]-phenoxazin-5-one (**7k**) is unique and may be rationalized on as an ABC pattern. The C-10 proton occurs at the lowest field as a doublet of doublets δ 8.64, $J_{9,10}$ = 6 and $J_{8,10}$ = 1.5 Hz. The ring proton at C-9 is found at the highest field at δ 7.49, $J_{8,9}$ = 8 and $J_{9,10}$ = 6 Hz. However, the proton at C-8 is mixed with ring protons C-2 and C-3. This analysis is in close agreement with that of reported phenoxazines.[22a] The major IR, UV, and mass spectral data of the phenoxazones **7** are listed in Table V (see Supplementary Material).

Experimental Section

Melting points were determined on a Dr. Tottoli apparatus in open capillaries and are uncorrected. UV spectra were recorded with a Beckman DK-2 spectrophotometer. IR spectra were taken on a Perkin-Elmer 225 spectrometer as KBr pellets or in CH_2Cl_2. ^1H NMR spectra (reported in δ) were recorded on Varian HA 100 and Brucker WH 90 spectrometers with tetramethylsilane as the internal reference. Mass spectra were obtained with a Varian CH-7 (electron energy 70 eV, ion source temperature 200 °C) mass spectrometer. Purity of the compounds was checked by ascending TLC on Merck precoated silica gel F-254 plates (0.25 mm) with fluorescent backing, using the following solvent systems: I, benzene; II, chloroform; III, chloroform–acetone (1:1); IV, benzene–acetone (8:2). Spots were visualized in daylight or UV light. Elemental analyses were performed by the Peptide Chemistry Division of the Max-Planck-Institute of Biochemistry, Munich.

Reaction of 1 with 2a in Ethanol. 6-Chloro-12a-hydroxy-5*H*-benzo[*c*]phenoxazin-5-one (4a), 6-Chloro-12a-ethoxy-5*H*-benzo[*c*]phenoxazin-5-one (5a), 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (7a), 2-Amino-3*H*-phenoxazin-3-one (8), and Triphenodioxazine (9a). A mixture of **1** (2.75 g, 12.1 mmol) and **2a** (2.75 g, 25.2 mmol) in 25 mL of ethanol (absolute or 95%) was heated at 95–100 °C for 3 h with stirring. It was poured into 700 mL of ice-cold water and filtered, and the residue was dried over phosphorus pentoxide. It was column chromatographed (silica gel, 10% H_2O deactivated) and eluted with benzene to yield the following fractions: The first yellow band provided **1** (53 mg, 2%), mp 192 °C. The second orange-yellow band furnished a mixture of **7a** and **9a**; these substances were separated by preparative TLC (silica gel, 0.5 mm) with benzene as the eluant. The faster moving yellow band gave **7a** (52 mg, 1.5%), mp 203 °C, TLC I, which was crystallized from benzene–hexane and found to be identical in every respect with an authentic sample prepared by the method reported in ref 13. The second pinkish band gave **9a** (115 mg, 4.8%), mp >300 °C, TLC I, which was found to be identical in every respect with an authentic sample.[3]

After **9a** was eluted from the column, elution was continued with chloroform. The yellow zone afforded **5a** (1.98 g, 50%), which was crystallized from chloroform–hexane to yield yellow crystals: mp 201 °C; TLC IV; IR (KBr) 3220 (m, NH and OH), 3060 (w, aromatic CH), 1620 (m, C=O), 741 (m), 748 (s)[22b] cm^{-1}; UV (dioxane) λ_{max} nm (log ε) 256 (4.35), 379 (4.24); mass spectrum, m/e (relative intensity) 329 (17), 327 (M^+, 48), 300 (4), 298 (10), 291 (14), 285 (5), 284 (22), 283 (16), 282 (57), 263 (100), 256 (2), 254 (5), 248 (4), 235 (9), 219 (8). Anal. Calcd for $C_{18}H_{14}ClNO_3$: C, 65.94; H, 4.30; N, 4.27. Found: C, 66.07; H, 4.33; N, 4.40. The column was then eluted with chloroform–acetone (2:1) to give a violet-color zone of **8** (80 mg, 3%), which was crystallized from chloroform–hexane, mp 198 °C, TLC IV, and was identical with an authentic sample of known[14] orientation. The next yellow colored band afforded **4a** (380 mg, 10.5%); several crystallizations from chloroform–hexane provided an analytical sample of **4a** as light yellow crystals: mp 198 °C dec; TLC III; IR (KBr) 3360 (vw), 3280 (s, NH and OH), 3070 (vw, aromatic CH), 1620 (s, C=O), 748 (s), 741 (m)[22b] cm^{-1}; UV (ethanol) λ_{max} nm (log ε) 255 (4.39), 390 (4.28); mass spectrum, m/e (relative intensity) 301 (17), 299 (M^+, 47), 284 (1), 282 (3), 264 (97), 263 (100), 247 (1), 246 (3), 236 (13), 235 (13), 219 (5), 218 (4), 208 (11), 207 (8), 190 (6). Anal. Calcd for $C_{16}H_{10}ClNO_3$: C, 64.11; H, 3.36; N, 4.67. Found: C, 63.88; H, 3.34; N, 4.63.

Reaction of 1 and 2a in methanol. 4a,6-Chloro-12a-methoxy-5*H*-benzo[*c*]phenoxazin-5-one (5d), 7a, 8, and 9a. A mixture of **1** (2.27 g, 10 mmol) and **2a** (2.18 g, 20 mmol) in 20 mL

(21) D. W. Mathieson, *Nucl. Magn. Reson. Org. Chem.*, 184 (1967).

(22) (a) N. Giulieri, M. Rouillard, R. L. Mital, and M. Azzaro, *Bull. Soc. Chim. Fr.* 4194 (1972). (b) Characteristic ring vibration of 5-benzo[*c*]phenoxazone systems.

of methanol (95% or absolute) was refluxed on a steam bath for 2 h. The mixture was diluted with 500 mL of water, and the product was isolated by filtration and dried. The crude material was column chromatographed (silica gel, 10% H_2O deactivated) and worked up as described above to provide the following derivatives: 1 (28 mg, 2%), mp 192 °C; **7a** (40 mg, 1.4%), mp 203 °C, TLC I; and **9a** (85 mg, 4.5%), mp >300 °C, TLC I. **5d** (1.91 g, 61%) was crystallized several times from chloroform–hexane to yield yellow crystals of **5d**: mp 187 °C; TLC II; IR (KBr) 3294 (m), 3220 (m, NH and OH), 3064 (w, aromatic CH), 1620 (s, C=O), 746 (s), 739 (s)[22b] cm^{-1}; IR (CH_2Cl_2) 3380 (NH) cm^{-1}; UV (dioxane) λ_{max} nm (log ϵ) 257 (4.35), 379.5 (4.24); mass spectrum, *m/e* (relative intensity) 315 (25), 313 (M^+, 71), 285 (9), 284 (38), 283 (30), 282 (100), 277 (55), 256 (4), 254 (13), 249 (21), 248 (28), 221 (8), 220 (15), 219 (19). Anal. Calcd for $C_{17}H_{12}ClNO_3$: C, 65.08; H, 3.85; N, 4.46. Found: C, 65.03; H, 3.80; N, 4.30.

8 (53 mg, 2.5%), mp 198 °C, TLC IV, and **4a** (0.53 g, 18%), mp 198 °C dec, TLC III, were also isolated.

Reaction of 1 with 2b in Ethanol. 6-Chloro-12a-hydroxy-9-methyl-5*H*-benzo[*c*]phenoxazin-5-one (4b), 6-Chloro-12a-ethoxy-9-methyl-5*H*-benzo[*c*]phenoxazin-5-one (5b), 6-Chloro-10-methyl-5*H*-benzo[*a*]phenoxazin-5-one (7b), and 2,9-Dimethyltriphenodioxazine (9b). A mixture of **1** (2.27 g, 10 mmol) and **2b** (1.23 g, 10 mmol) in 25 mL of ethanol (absolute or 95%) was heated to 95–100 °C for 3 h with stirring. The reaction mixture was poured into 800 mL of cold water and the crude material filtered and dried over phosphorus pentoxide. It was column chromatographed (silica gel, 10% H_2O deactivated) and eluted with benzene to yield some impurities. The next yellow zone provided **7b** (59 mg, 2%) which was crystallized from chloroform–hexane, mp 224 °C, TLC II. The mixture melting point and IR and mass spectra matched those of the sample prepared by another method. The column was then run with chloroform–benzene (1:1) to give **9b** (104 mg, 5%), mp >300 °C, identical in every respect with the sample prepared by a known method.[23] Further elution with the same solvent gave a yellow band which was discarded. Finally the column was eluted with chloroform to give a main yellow zone which provided **5b** (2.39 g, 70%). Three recrystallizations from acetonitrile–ether afforded **5b** as yellow needles: mp 195 °C; TLC III; IR (KBr) 3225 (ms, NH and OH), 2975 (vw, aromatic CH), 1612 (m, C=O), 758 (m), 765 (m)[22b] cm^{-1}; UV (ethanol) λ_{max} nm (log ϵ) 257.5 (4.33), 395 (4.24); mass spectrum, *m/e* (relative intensity) 343 (10), 341 (M^+, 31), 314 (2), 312 (5), 305 (16), 298 (13), 296 (38), 290 (9), 277 (100), 276 (18), 262 (3), 260 (1), 249 (8), 248 (7), 221 (3), 220 (5). Anal. Calcd for $C_{19}H_{16}ClNO_3$: C, 66.00; H, 4.71; N, 4.1. Found: C, 66.11; H, 4.75; N, 4.34.

The next yellow band furnished **4b** (281 mg, 9%). Repeated recrystallization from chloroform–hexane afforded yellow crystals: mp 188 °C; IR (KBr) 3260 (s, NH and OH), 3065 (vw, aromatic CH), 1610 (s, C=O), 768 (m), 758 (m)[22b] cm^{-1}; UV (dioxane) λ_{max} nm (log ϵ) 262 (4.26), 382 (4.29); mass spectrum, *m/e* (relative intensity) 315 (12), 313 (M^+, 36), 298 (1), 296 (2), 278 (100), 277 (85), 250 (12), 249 (8), 232 (6), 222 (6), 221 (5), 194 (2), 193 (4). Anal. Calcd for $C_{17}H_{12}ClNO_3$: C, 65.07; H, 3.83; N, 4.46. Found: C, 64.56; H, 4.14; N, 4.40.

Reaction of 1 and 2c in Ethanol. 6,9-Dichloro-12a-hydroxy-5*H*-benzo[*c*]phenoxazin-5-one (4c), 6,9-Dichloro-12a-ethoxy-5*H*-benzo[*c*]phenoxazin-5-one (5c), 6,10-Dichloro-5*H*-benzo[*a*]phenoxazin-5-one (7c), and 2,9-Dichlorotriphenodioxazine (9c). A mixture of **1** (2.27 g, 10 mmol) and **2c** (1.43 g, 10 mmol) in 25 mL of ethanol (absolute or 95%) was heated to 95–100 °C for 3 h with stirring. The reaction mixture was cooled to ambient temperature and then poured into 1000 mL of ice-cold water. The resulting precipitate was collected, dried over phosphorus pentoxide, and column chromatographed (silica gel, 10% H_2O deactivated). The column was eluted with benzene to provide **1** (181 mg, 8%), mp 192 °C. The next yellow band afforded **7c** (88 mg, 2.8%), mp 234 °C, TLC II; its spectral properties (IR, mass spectrum) and mixture melting point are identical with those of a sample prepared by another method. Further elution with the same solvent gave an orange-pinkish band which provided **9c** (48 mg, 2%), mp >360 °C, TLC II, identical in every respect with a sample prepared by a known method.[24] After this fraction was eluted, the column was eluted with chloroform which provided a main yellow band of **5c** (1.59 g, 44%), TLC IV. An analytical sample was obtained by recrystallization with chloroform–hexane to yield shining yellow crystals: mp 212 °C; IR (KBr) 3222 (m, NH and OH), 3065 (w, aromatic CH), 1622 (m, C=O), 760 (m)[22b] cm^{-1}; UV (dioxane) λ_{max} nm (log ϵ) 259 (4.35), 377 (4.16); mass spectrum, *m/e* (relative intensity) 365 (3), 363 (21), 361 (30), 336 (1), 334 (5), 332 (6), 328 (2), 327 (6), 326 (5), 325 (18), 320 (4), 318 (23), 316 (34), 300 (9), 299 (38), 298 (31), 297 (100), 296 (10), 269 (9), 268 (3), 241 (3), 240 (4). Anal. Calcd for $C_{18}H_{13}Cl_2NO_3$: C, 59.67; H, 3.61; N, 3.86. Found: C, 59.52; H, 3.50; N, 3.80.

The next yellow band on elution with the same solvent afforded **4c** (0.7 g, 21%). Repeated recrystallization with chloroform–ether provided **4c** as yellow crystals: mp 210 °C (color change at 200 °C); TLC III; IR (KBr) 3462 (m), 3298 (s, NH and OH), 3065 (vw, aromatic CH), 1618 (s, C=O), 765 (s), 731 (m)[22b] cm^{-1}; UV (dioxane) λ_{max} nm (log ϵ) 262 (4.28), 372.5 (4.01); mass spectrum, *m/e* (relative intensity) 337 (4), 335 (M^+, 23), 333 (34), 320 (0.5), 318 (1), 316 (2), 300 (26), 299 (51), 298 (100), 297 (100), 272 (3), 271 (5), 270 (9), 269 (10), 244 (2), 243 (2), 242 (5), 241 (5), 235 (7), 234 (6), 207 (3), 206 (5), 178 (8), 177 (5), 151 (6), 150 (5). Anal. Calcd for $C_{16}H_9Cl_2NO_2$: C, 57.50; H, 2.69; N, 4.19. Found: C, 57.93; H, 3.03; N, 4.40.

12a-Ethoxy-5*H*-benzo[*c*]phenoxazin-5-one (5e). To a solution of 2-(2-hydroxyanilino)-1,4-naphthoquinone (0.265 g, 1 mmol) in ethanol (50 mL) was added concentrated hydrochloric acid (50 mL), and the mixture was kept for 48 h at ambient temperature. The resulting suspension was extracted with a large volume of chloroform–acetone (1:1), and the organic phase was washed with a saturated aqueous solution of sodium bicarbonate and water and then dried (Na_2SO_4). Evaporation of the solvent yield 0.22 g of crude material. This was dissolved in the minimum quantity of acetone–chloroform (1:1) and column chromatographed (silica gel, 10% H_2O deactivated, 1.5 × 170 cm). On elution with chloroform, 0.125 g of starting material was isolated. Elution with chloroform–acetone (3:1) gave **5e** (0.099 g, 33.7%). Several recrystallizations from chloroform–hexane provided a clean product as yellow crystals: mp 182–184 °C; TLC III; IR (KBr) 3270 (w), 3178 (m, NH and OH), 3060 (w, aromatic CH), 1630 (s, C=O), 751 (s)[22b] cm^{-1}; UV (ethanol) λ_{max} nm (log ϵ) 208.5 (4.46), 255 (4.37), 387.5 (4.23); mass spectrum, *m/e* (relative intensity) 293 (M^+, 54), 264 (100), 249 (42), 248 (19), 236 (7), 220 (9), 208 (6). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.60; H, 5.16; N, 4.77. Found: C, 73.10; H, 4.92; N, 4.40.

Exchange Reaction of 6-Chloro-12a-ethoxy-5*H*-benzo[*c*]phenoxazin-5-one (5a) with 2-Amino-4-chlorophenol (2c) in Acetic Acid. 6,10-Dichloro-5*H*-benzo[*a*]phenoxazin-5-one (7c). A mixture of **5a** (0.362 g, 1 mmol) and **2c** (0.143 g, 1 mmol) in 5 mL of glacial acetic acid was heated to reflux for 3 h. The resulting suspension was chilled overnight in the refrigerator, and the product was collected, washed well with water, and dried. It was purified by preparative thin-layer chromatography (silica gel) with benzene as the developing system to give **7c** (126 mg, 40%), mp 234 °C. An analytical sample was obtained by crystallization with chloroform–hexane. It was identical in every respect with an authentic sample of **7c** prepared by another method.

Equilibrium of 4a with 5a in Ethanol in the Presence of Dilute HCl. A mixture of **4a** (0.299 g, 1 mmol) in 15 mL of ethanol and 2 N HCl (15 mL) was kept with stirring at a temperature of 90–100 °C for 2 h. On TLC (chloroform–acetone 1:1) the resulting solution shows the presence of hemiketal **4a** and ketal **5a**. It was diluted to 500 mL with water and extracted with chloroform–acetone (2:1). The organic phase was washed with water and dried (Na_2SO_4) to give 320 mg of crude product. This was column chromatographed (silica gel, 14% H_2O deactivated) with chloroform and chloroform–acetone (2:1) as the eluants, respectively, to give the following compounds: **5a** (0.218 g, 66.6%), mp 201 °C, identical with an authentic sample; **4a** (0.099 g, 33.3%), mp 198 °C dec, identical with a standard sample. In a separate experiment **4a** in methanol and dilute HCl was shown to exist in the same equilibrium (1:2) with **5d**.

(23) J. F. Corbett, *Spectrochem. Acta*, **21**, 1081 (1965).

(24) P. C. Taunk and R. L. Mital, *Ann. Soc. Sci. Bruxelles*, **88**, 259 (1974); *Chem. Abstr.*, **83**, 61613n (1975).

Reaction of 1 with 2a in Methanol in the Presence of Potassium Hydroxide. 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (7a). A mixture of 1 (11.3 g, 49.7 mmol) and **2a** (5.5 g, 50.4 mmol) containing potassium hydroxide (6 g, 107 mmol) in 150 mL of methanol (absolute or 95%) was refluxed for 3 h with stirring, then poured into water (1200 mL), and neutralized with 2 N HCl. The resulting suspension was extracted with chloroform–acetone (2:1), and the organic phase was dried over anhydrous sodium sulfate and evaporated to dryness. The resulting product was column chromatographed (alumina, neutral V) and eluted with benzene to give **7a** as orange-yellow crystals (chloroform–hexane), 5.59 g (40%), mp 203 °C. It was identical in every respect with an authentic sample of **7a** prepared by another method.

Anal. Calcd for $C_{16}H_8ClNO_2$: C, 68.20; H, 2.86; N, 4.98; Cl, 12.59. Found: C, 68.11; H, 2.90; N, 5.16; Cl, 12.39.

General Procedure for Preparation of Substituted 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-ones (7). A mixture of 1 (2.27 g, 10 mmol), the corresponding substituted *o*-aminophenol **2** (10 mmol), and anhydrous potassium acetate (1.56 g, 20 mmol) in 95% or absolute ethanol or methanol (25 mL or 50 mL) was heated with stirring at 90–100 °C for some hours. The resulting suspension was chilled, filtered, washed with water followed by a little cold ethanol, and dried over phosphorus pentoxide. Repeated recrystallization of the product or column chromatography afforded analytical-grade phenoxazin-5-one. Analytical data, physical constants, solvent of recrystallization, and times of heating of the compounds are collected in Table II.

6,8,9,11-Tetrachloro-5*H*-benzo-[*a*]phenoxazin-5-one (7h). A solution of **2h** (2.01 g, 10 mmol) was prepared in 30 mL of dry chloroform containing triethylamine (5.16 g, 40 mmol) and heated to 50–60 °C for 1 h. To this was added a suspension of 1 (2.27 g, 10 mmol) in 10 mL of dry chloroform over a period of 5 min. After the addition, the reaction mixture was heated to 90–110 °C for 1 h. It was cooled to −2 °C for 5 h. The precipitate was filtered, washed thoroughly with 50% sodium bicarbonate solution and 500 mL of water, and dried to yield light yellow **7h** (3 g, 78%), mp 302 °C, TLC IV. It was identical by IR and mixture melting point with a sample prepared by another method.

5-Acetoxy-6-chloro-12*H*-benzo[*a*]phenoxazine (11). A mixture of **7a** (0.281 g, 1 mmol), acetic anhydride (50 mL) and pyridine (5 mL) was stirred with zinc dust (2 g) for 15 min and then heated on a boiling-water bath for 5 min. The pale yellow solution was separated from the excess zinc dust by filtration and poured into ice for 24 h to yield a light yellow precipitate. This was filtered, washed with water, and dried to yield **11** (0.19 g, 68%), mp 208–210 °C, TLC IV. An analytical sample was obtained by repeated crystallization with benzene–hexane: IR (KBr) 3374 (s, NH), 1748 (s, aromatic acetate) cm^{-1}; UV (dioxane) λ_{max} nm (log ϵ) 269 (4.39), 319.5 (3.68), 396 (3.68); ^1H NMR (Me_2SO-d_6) 8.41 (s, NH, D_2O exchangeable), 2.49 (s, 3 H), 6.66–8.12 (m, 8 H); mass spectrum, *m/e* (relative intensity) 325 (M^+, 15), 285 (35), 284 (28), 283 (100), 282 (30), 248 (12), 219 (20), 218 (13), 191 (10), 190 (32), 163(9), 162 (9). Anal. Calcd for $C_{18}H_{12}ClNO_3$: C, 66.37; H, 3.71; N, 4.30. Found: C, 65.99; H, 3.61; N, 4.27.

Reaction of 6-Chloro-5*H*-benzo[*a*]phenoxazin-5-one (7a) with Potassium Hydroxide in Methanol. A solution of **7a** (0.281 g, 0.001 mol) in 30 mL of methanol containing potassium hydroxide (0.04 mol, 2.24 g) was heated with stirring at 90–100 °C for 3 h. The mixture was cooled to room temperature and filtered, and the residue was washed with hexane, dissolved in 200 mL of warm water, filtered, and neutralized with 2 N HCl. The resulting solid was isolated by extraction with chloroform–acetone (1:1) and dried over anhydrous sodium sulfate to give 0.105 g (50%) of 2-chloro-3-hydroxy-1,4-naphthoquinone.[19] An analytical sample was obtained by recrystallization from acetone–hexane, mp 215 °C.

Registry No. 1, 117-80-6; **2a**, 95-55-6; **2b**, 95-84-1; **2c**, 95-85-2; **2d**, 2835-98-5; **2e**, 99-57-0; **2f**, 121-88-0; **2g**, 527-62-8; **2h**, 6358-15-2; **2i**, 4502-10-7; **2j**, 1571-72-8; **4a**, 73396-99-3; **4b**, 73397-00-9; **4c**, 73397-01-0; **5a**, 73397-02-1; **5b**, 73397-03-2; **5c**, 73397-04-3; **5d**, 73397-05-4; **5e**, 73397-06-5; **7a**, 73397-07-6; **7b**, 73397-08-7; [7c], 73397-09-8; **7d**, 73397-10-1; **7e**, 73397-11-2; **7f**, 73397-12-3; **7g**, 73397-13-4; **7h**, 73397-14-5; **7i**, 73397-15-6; **7j**, 73397-16-7; **7k**, 73397-17-8; **7l**, 73397-18-9; **8**, 1916-59-2; **9a**, 258-72-0; **9b**, 1496-98-6; **9c**, 52829-20-6; **11**, 73397-19-0; **12**, 19073-35-9; 3-hydroxy-2-pyridinamine, 16867-03-1; 3-hyroxy-2-naphthalenamine, 5417-63-0; 2-chloro-3-hydroxy-1,4-naphthoquinone, 1526-73-4.

Supplementary Material Available: UV, IR, and mass spectral data for **7a–l** (3 pages). Ordering information is given on any current masthead page.

Ring Expansion Reaction of Cyclopropylcarbene to Cyclobutene[1]

Wolfgang W. Schoeller

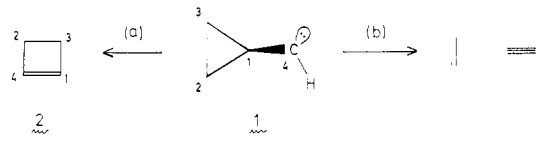
Fakultät für Chemie, Universität Bielefeld, 48 Bielefeld, Federal Republic of Germany

Received February 8, 1980

The ring expansion reaction of cyclopropylcarbene in its singlet ground state $^1(\sigma^2)$ to cyclobutene is initiated by an electrophilic attack of the empty p AO at the carbene site on the most electron-rich carbon atom of the three-membered ring. The reaction is completed by participation of the nucleophilic σ orbital. In the transition state, charge density is accumulated at C_4 and depleted at C_2 and C_1. The stereochemical integrity at the attacked carbon atom is maintained.

Cyclopropylcarbene (1) rearranges thermally[2] primarily to cyclobutene (**2**, route a; see Scheme I), while to a minor

Scheme I



extent the fragmentation to ethylene and acetylene is observed (route b). This side reaction is more probable in the gas phase[3] than in solution. The ring expansion is also stereospecific.[4] When a choice exists, the stronger

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