Anal. Calcd for $C_{17}H_{14}N_4O_2$: C, 66.72; H, 4.57. Found: C, 66.72; H, 4.67.

General Procedure for the Reaction of 1 with Ylide 10. A solution of 3.3 mmol of **1** in 50 ml of CH_2Cl_2 at 0 °C was added dropwise to 3.3 mmol of **9** in 50 ml of CH_2Cl_2. After the mixture was stirred at 25 °C for 1 h the solvent was evaporated and **14** was obtained as a white solid and recrystallized from CH_2Cl_2–pentane.

Ylide **14a** was prepared in 82% yield from **1a** and **10a:** mp 145–146 °C; ^1H NMR ($CDCl_3$) τ 2.93–3.06 (m); ir (KBr) 3320–3420 (NH), 1745 and 1695 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 68.03 and 73.17 (C–P, J_{CP} = 129.5 Hz), 150.24 and 151.27 (N_2C=O), and 188.19 and 189.07 ppm ((R–C=O, J_{CP} = 22 Hz); mass spectrum *m/e* M^+, 293 ($M^+ - Ph_3P$), and 262 (Ph_3P).

Product **14b** was prepared in 78% yield from **1b** and **10a:** mp 134–136 °C; ^1H NMR ($CDCl_3$) τ 7.45 (s, 3 H), 1.9–2.79 (m, 20 H), and 1.68–1.87 (br s, 1 H, exchangeable with D_2O); ir (KBr) 3320–3420 (NH), 1750 and 1700 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 24.56 (N–CH_3), 68.50 and 73.50 (C=P, J_{CP} = 126 Hz), 151.78 and 152.96 (N_2C=O), 187.6 and 188.5 ppm (R–C=O, J_{CCP} = 22 Hz); mass spectrum no M^+, *m/e* 262 (Ph_3P) and 231 ($M^+ - Ph_3P$).

Adduct **14c** was obtained in 85% yield from **1b** and **10b:** mp 120–122.5 °C; ^1H NMR ($CDCl_3$) τ 8.02 (s, 3 H), 7.33 (s, 3 H), 1.98–2.64 (m, 16 H); ir (KBr) 3310–3420 (NH), 1740 and 1695 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 23.70 and 24.20 (NCH_3 and CH_3C=O), 65.37 and 70.53 (C=P, J_{CP} = 129.5 Hz), 151.50 and 152.67 (N_2C=O), 189.66 and 190.61 ppm (R–C=O, J_{CCP} = 24 Hz); mass spectrum no M^+, *m/e* 262 (Ph_3P), 169 ($M^+ - Ph_3P$).

Acknowledgment. We are grateful for support of this research by a grant from the National Science Foundation.

Registry No.—**1a,** 4233-33-4; **1b,** 3274-43-6; **5a,** 16717-64-9; **5b,** 28022-21-1; **5c,** 34910-42-4; **5d,** 40168-86-3; **6a,** 58249-36-8; **6b,** 58249-37-9; **6c,** 58280-92-5; **6d,** 58249-38-0; **10a** charged form, 20913-05-7; **10a** neutral form, 859-65-4; **10b** charged form, 29942-64-1; **10b** neutral form, 1439-36-7; **14a** charged form, 58249-39-1; **14a** neutral form, 58249-40-4; **14b** charged form, 58249-41-5; **14b** neutral form, 58249-42-6; **14c** charged form, 58249-43-7; **14c** neutral form, 58249-44-8.

References and Notes

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(3) The red color of **1a** is discharged rapidly even at 0 °C in the reaction of **5a–c. 5c** reacted at least five times faster than **5b** at −15 °C and with **5d** the color discharge proceeded much more slowly even at 25 °C.
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(7) (a) G. Aksnes, *Acta Chem. Scand.*, **15**, 692 (1961); (b) C. Osuch, J. E. Franz, and F. B. Zienty, *J. Org. Chem.*, **29**, 3721 (1964); (c) H. Hoffmann, *Chem. Ber.*, **94**, 1331 (1961).
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Carbon-13 Nuclear Magnetic Resonance Chemical Shifts of Substituted Phenazines

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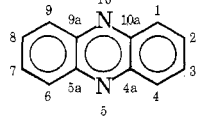
The ^{13}C chemical shifts of 16 phenazines, substituted in the 1, 1,6, and 1,9 positions, are reported. Signals are assigned by means of substituent effects on benzene shifts, by intensities, by molecular symmetry considerations, and by nuclear Overhauser enhancement for protonated carbons. Substituent effects of the substituent at carbon 1 are determined for carbons 1, 2, 3, and 4 and compared with those for benzene.

The ^{13}C NMR spectra of phenazines are of biological as well as of theoretical interest. Presently some 30 substituted phenazines have been isolated from microorganisms.[1] They possess antibiotic properties due to their interaction with deoxyribonucleic acid. Their ^{13}C spectra are useful in the elucidation of their biosynthesis. The electronic structure of phenazines, being diaza analogues of anthracene, is furthermore of interest and can be studied by ^{13}C NMR.[2]

We have measured the ^{13}C NMR spectra of 16 phenazines (**1**) in $CDCl_3$, Me_2SO-d_6, and mixtures thereof. The phenazines were substituted with various substituents in the 1, 1,6, or 1,9 position. Assignments were made by means of known benzene substituent effects,[3] by intensities, by molecular symmetry considerations, and by nuclear Overhauser enhancement for protonated carbons.



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Phenazine itself measured in $CDCl_3$ as well as in $(CD_3)_2SO$ showed slightly lower chemical shifts than those reported in the literature.[2] The protonated carbons were measured at 0.70 ppm and the nonprotonated carbons at 0.55 ppm upfield from the reported values. The methyl substituent effects on benzene shifts (α, ortho, meta, para) were used in the assignment of the methylated phenazines. Similarly the benzene –OH, $-OCH_3$, –COOH, $-NO_2$, $-NH_2$, and $-COOCH_3$ substituent effects served to assign the correspondingly substituted phenazines. The symmetrically 1,6- or 1,9-disubstituted phenazines showed the expected reduced number of 6 instead of 12 skeleton signals for the mono- or unsymmetrically substituted phenazines. Nuclear Overhauser enhancement aided in distinguishing the protonated from the nonprotonated carbons. 1,6-Dimethylphenazine was only sparingly soluble in $CDCl_3$ and showed a signal:noise ratio for the quaternary carbons of less than 3:1. In 1,6-dimethoxyphenazine 5-oxide

Table I. ^{13}C Chemical Shifts of Substituted Phenazines (—δ in ppm Relative to Internal Me_4Si) Measured at 15.08 MHz

Registry no.	Compd	Solvent, temp, °C	C-1	C-2	C-3	C-4	C-4a	C-5a	C-6	C-7	C-8	C-9	C-9a	C-10a	CH_3	CH_3O	COO
92-82-0	Phenazine	$CDCl_3$ 30	130.25	129.6	129.6	130.25	143.45	143.45	130.25	129.6	129.6	130.25	143.45	143.45			
1016-59-7	1-Methyl-	$CDCl_3$ 30	138.0	130.15	129.45[a]	127.6	143.15	143.15[b]	130.15[a]	129.45	129.8	130.3[a]	142.8[b]	143.7	17.6		
528-71-2	1-Hydroxy-	$CDCl_3$ 30	151.9	109.0	130.8[a]	120.1	144.3	144.0[b]	130.45[a]	129.25	129.85	131.85[a]	141.55[b]	135.15			
3225-19-2	1-Carbomethoxy-	$CDCl_3$ 30	133.7	130.9	129.55[a]	133.4	142.8	143.4[b]	131.05[a]	128.95	130.4	131.85[a]	143.7[b]	147.6		52.75	167.15
58718-43-7	1,6-Dimethyl-	$CDCl_3$ 30	137.55	129.9	129.7	127.75	142.95	143.5	137.55	129.9	129.7	127.75	142.95	143.5	17.50		
58718-44-8	1,9-Dimethyl-	$CDCl_3$ 30	138.4	130.35	129.15	127.3	142.25	142.25	127.3	129.15	130.35	138.4	143.35	143.35	17.4		
69-48-7	1,6-Dihydroxy-	$CDCl_3$ 35	153.4	110.6	131.3	119.3	142.2	135.85	153.4	110.6	131.3	119.3	142.2	135.85			
13398-79-3	1,6-Dimethoxy-	$CDCl_3$ 35	155.4	107.1	130.1	121.85	143.4	130.75	155.4	107.1	130.1	121.85	143.4	130.75		56.5	
23531-24-0	1,6-Dicarbomethoxy-	$CDCl_3$ 35	131.55	134.35	129.6	132.9	143.15	143.15	131.55	134.35	129.6	132.9	143.15	143.15		52.7	166.95
58718-45-9	1-Methyl-9-carbomethoxy-	$CDCl_3$ 30	138.65	131.4	129.05	127.5	143.25	140.1	133.05	130.05	131.4	131.4	142.55	143.75	17.25	52.45	167.8
58718-46-0	1-Methyl-9-carboxyl-	$CDCl_3$ 30	137.5	131.85	130.3	128.15	143.15	139.65	134.95	130.3	132.65	131.85	144.5	143.15	17.65		166.1
13925-10-5	1,6-Dimethoxy 5-oxide	$CDCl_3$ 30	155.95	108.25	129.8	123.35	130.0	120.35	153.15	108.45	130.45	111.1	131.3	131.3	C-1: 56.75 C-6: 57.05		
58718-47-1	1,9-Dicarbomethoxy-	$CDCl_3$ 29	132.4	133.2	130.0	132.6	142.75	142.75	132.6	130.0	133.2	132.4	141.1	141.1		52.6	167.25
58718-48-2	1,9-Dinitro-	Me_2SO-d_6/ $CDCl_3$ 30	147.95	126.65	130.6	133.75	146.6	146.6	133.75	130.6	126.65	147.95	142.25	142.25			
36848-41-6	1,6-Dinitro-	Me_2SO-d_6 30	146.7	126.85	130.85	133.85	145.0	142.35	146.9	126.85	130.85	133.85	145.0	142.35			
16582-03-9	1,6-Diamino-	Me_2SO-d_6 30	145.35	106.4	131.6	114.6	141.4	134.7	145.35	106.4	131.6	114.6	141.4	134.7			

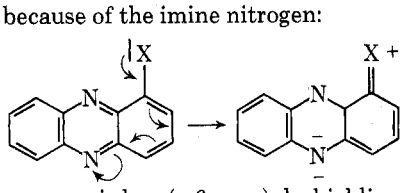
[a,b] Assignments interchangeable for equally labeled shifts in any horizontal row.

Table II. Comparison of Substituent Effects on Phenazine with Those on Benzene ($-\delta_{subst}$) − ($-\delta_{unsubst}$) in ppm

Carbon (relative to substituent)	1 (α)	2 (o)	3 (m)	4 (p)	
1-Methyl	7.75	0.55	−0.15	−2.65	
1,6-Dimethyl	7.30	0.3	0.1	−2.5	
1,9-Dimethyl	8.15	0.75	−0.45	−2.95	
1-Methyl-9-carbomethoxy	8.4	1.8	−0.55	−2.75	
1-Methyl-9-carboxyl	7.25	2.25	0.7	−2.1	
Benzene	9.3	0.6	0.0	−3.1	
1-Hydroxy	21.65	−20.6	1.2	−10.15	
1,6-Dihydroxy	23.25	−19.0	1.7	−10.95	
Benzene	26.9	−12.7	1.4	−7.3	
1-Carbomethoxy	3.45	1.3	−0.05	3.15	
1,6-Dicarbomethoxy	1.3	4.95	0.0	2.65	
1-Methyl-9-carbomethoxy	1.6	3.05	0.7	4.7	
1,9-Dicarbomethoxy	2.15	3.6	0.4	2.35	
Benzene	2.1	1.2	0.0	4.4	
1,6-Dimethoxy	25.15	−22.5	0.5	−8.4	
1,6-Dimethoxy 5-oxide	25.7	−21.35	0.2	−6.9	(1-methoxy)
	22.9	−21.15	0.85	−19.15	(6-methoxy)
Benzene	30.2	−14.7	0.9	−8.1	
1-Methyl-9-carboxyl	1.6	3.05	0.7	4.7	
Benzene	2.4	1.6	−0.1	4.8	
1,9-Dinitro	17.7	−2.95	1.0	3.5	
1,6-Dinitro	26.45	−2.75	1.25	3.6	
Benzene	19.6	−5.3	0.8	6.0	
1,6-Diamino	15.1	−23.2	2.0	−15.65	
Benzene	19.2	−12.4	1.3	−9.5	

the resonance effects of $-OCH_3$ and N^+-O^- on the ^{13}C shift of C-9 was taken into consideration. Both substituents will increase the electron density, hence shield the carbon. The carbons 4a and 5a in 1,9-dicarbomethoxyphenazine could be distinguished from carbons 9a and 10a due to the nearby protons at C-4 and C-6 and the weak nuclear Overhauser enhancement resulting therefrom.

Table I lists the chemical shifts of various phenazines. The chemical shifts of those compounds measured in $CDCl_3$ are comparable to those measured in Me_2SO-d_6 since the solvent shift between these two solvents is not more than ±0.1 ppm as can be shown for phenazine. Table II shows a comparison of the substituent effects on phenazine with those on benzene. While there is general agreement there are some marked differences also. The methyl group in phenazine acts less deshielding in the 1 (α) position and slightly more shielding at the 4 (para) position than in benzene. The hydroxy group is less deshielding at C-1, more shielding at C-4, and considerably more shielding (~7 ppm) at C-2 compared to benzene. The carbomethoxy group is more deshielding at C-2 and less deshielding at C-4 with respect to benzene. The methoxy group shows a pattern similar to the hydroxy group: less deshielding at C-1 and considerably more shielding (~7 ppm) at C-2. The carboxy group is less deshielding at C-1 and more deshielding at C-2. The nitro group is considerably more deshielding (~7–8 ppm) at C-1, less deshielding at C-4, and more shielding at C-2. For the phenazines with X = OH, OCH_3 polar resonance structures seem to contribute to a larger extent than in benzene because of the imine nitrogen:



The amino group is less (~6 ppm) deshielding at C-1 and considerably more shielding at C-2 and C-4 (~11 and ~6 ppm, respectively).

Experimental Section

All ^{13}C NMR spectra were taken in $CDCl_3$, $(CD_3)_2SO$, or mixtures thereof, at 30 or 35 °C, with tetramethylsilane as internal reference. A Bruker WP-60 instrument, operating at 15.08 MHz for ^{13}C and 60 MHz in the proton decoupling channel, was used and the pulse Fourier transform technique was applied. The accumulated 8K interferograms were Fourier transformed by a Bruker BNC-128 computer (8K, 20 bit) to the phase corrected real parts of the ^{13}C NMR spectra (spectral width 3000 Hz or 200 ppm). The ^2H signal of the deuterated solvent served for field/frequency stabilization at 8.67 MHz. All chemical shifts were calculated from the digitized spectra by the computer. The digital resolution was ±0.05 ppm.

All new compounds had satisfactory elemental analyses. Melting points were determined on a Kofler hot stage apparatus. Electronic spectra were determined on a Cary 14 spectrophotometer, mass spectra on a Du Pont 21-491 instrument, and ^1H NMR spectra in $CDCl_3$ with Me_4Si as internal standard on a Varian EM-360 spectrometer.

Phenazine. Phenazine, technical, was purchased from Aldrich, mp 171–173 °C.

1-Methylphenazine. The synthesis of 1-methylphenazine has been described in the literature.[4] It was recrystallized from benzene, mp 109–110 °C.

1-Hydroxyphenazine. 1-Hydroxyphenazine was made according to the literature.[5,6] Phenazine methosulfate, Aldrich 99%, 2 g, was dissolved in 2 l. of water and left in sunlight for 8 h. After addition of 40 ml of 10% sodium carbonate the blue solution was extracted with chloroform. The chloroform solution was dried and concentrated to 20 ml. Addition of 20 ml of hexane gave upon cooling crude pyocyanine which was recrystallized from 60 ml of water, mp 124–126 °C (lit.[5] 133 °C). Pyocyanine, 100 mg, was dissolved in 120 ml of water, 8.4 ml of 8 N sodium hydroxide was added to the solution, and the mixture was left at room temperature for 16 h. The maroon solution was filtered and the filtrate was extracted with ether. After acidifying the aqueous solution with glacial acetic acid it was extracted with ether yielding crude yellow 1-hydroxyphenazine. Sublimation at 115 °C (0.1 mm) gave 70% pure 1-hydroxyphenazine, mp 158 °C (lit.[6] 159–160 °C).

1-Carbomethoxyphenazine. Phenazine-1-carboxylic acid was obtained from *Pseudomonas aureofaciens*[1] or synthesized. To 1 g of 1-methylphenazine in 3 ml of glacial acetic acid was added a solution of 1 g of chromium trioxide in 0.3 ml of water and 7.7 ml of glacial acetic acid. The solution was refluxed for 1 h, diluted with water, and

continuously extracted with chloroform. After evaporation to dryness the residue was taken up in 1 N sodium hydroxide. Continuous extraction with chloroform removed unoxidized 1-methylphenazine which was resubjected to oxidation. Acidification and continuous chloroform extraction yielded crude phenazine-1-carboxylic acid which was recrystallized from isopropyl alcohol, yield 73%, mp 242 °C (lit.[8] 243 °C). Phenazine-1-carboxylic acid, 101 mg, was suspended in 20 ml of methanol. At 0 °C 50 ml of ethereal diazomethane (5 mmol) was added with stirring. The temperature was allowed to rise to room temperature while the acid dissolved. A quantitative yield of 1-carbomethoxyphenazine was obtained. Recrystallization from cyclohexane gave mp 126–128 °C. Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.74; H, 4.32; N, 11.58.

1,6- and 1,9-Dimethylphenazine. A solution of 10 g of 3-nitro-2-aminotoluene[9] in 200 ml of ethyl acetate was reduced with 3 ml of Raney nickel slurry at 40 atm during 24 h. After removal and washing of the catalyst by filtration the colorless filtrate was evaporated to dryness, yielding 95% of slightly colored 2,3-diaminotoluene, mp 61 °C (lit.[10] 61–62 °C). The product was ground together with 10 g of 2,3-dihydroxytoluene (K & K Laboratories) and placed in three Pyrex tubes which were sealed and heated at 200–220 °C for 48 h in a manner analogous to that described for the preparation of 1-methylphenazine.[4] The purple material was dissolved in ether and washed with 2 N NaOH until the aqueous layer was almost colorless. The ether layer was washed with water, dried, and evaporated to dryness. The residue was dissolved in 20 ml of benzene and treated with 5 g of active manganese dioxide[11] for 48 h under reflux. Manganese dioxide was removed by filtration and washed with 250 ml of hot benzene. Evaporation of benzene yielded a yellow mixture of crude 1,6- and 1,9-dimethylphenazine. It was dissolved in 200 ml of benzene and chromatographically separated on an Al_2O_3 (Woelm I) column. 1,6-Dimethylphenazine was eluted first: mp 235 °C (lit.[16] 221–222 °C); NMR 7.4–8.1, m, 6 H; 2.8 ppm, s, 6 H; mass spectrum *m/e* 208. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.65; H, 5.69; N, 13.64. The second yellow band, which was eluted with benzene/ether, contained 1,9-dimethylphenazine: mp 142 °C; NMR 7.4–8.0, m, 6 H; 2.8 ppm, s, 6 H; mass spectrum *m/e* 208. Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.84; H, 5.76; N, 13.64. The two isomers could also be separated by fractional crystallization from benzene. 1,6-Dimethylphenazine is the less soluble component. A total yield of 2 g, 10%, was obtained with about equal amounts of the two isomers.

1,6-Dihydroxyphenazine. 1,6-Dihydroxyphenazine 5,10-dioxide (iodinin) was obtained from *Chromobacterium iodinum*.[12] Iodinin (200 mg) in 100 ml of dioxane (AR) was added to 200 mg of reduced platinum oxide in 50 ml of dioxane. Reduction at atmospheric pressure and room temperature was complete in 30 min after an uptake of 3 mol of hydrogen. The colorless solution, presumably of 1,6-dihydroxy-5,10-dihydrophenazine, was filtered whereupon it rapidly turned yellow. Upon passing oxygen through the solution a golden yellow color was soon attained, yield 171 mg (98%) of gold-brown crystals of 1,6-dihydroxyphenazine, mp 278 °C (lit.[13] 274 °C), no depression on admixture with 1,6-dihydroxyphenazine obtained from 1,6-dimethoxyphenazine.[14]

1,6-Dimethoxyphenazine. 1,6-Dimethoxyphenazine was synthesized according to the literature.[14] A mixture of 10 g of *o*-anisidine (Eastman), 10 g of *o*-nitroanisole (Eastman), and 30 g of powdered potassium hydroxide was kept at 50 °C for 3 days. Unreacted material was removed by steam distillation and the residue was extracted with chloroform. The chloroform solution was extracted with dilute hydrochloric acid, and the hydrochloric acid layer was neutralized with ammonia and extracted with chloroform. Upon evaporation crude 1,6-dimethoxyphenazine was chromatographically purified in chloroform on aluminum oxide (Woelm I). Recrystallization from benzene gave 3 g (20%) of pure 1,6-dimethoxyphenazine, mp 260 °C (lit.[14] 251 °C).

1,6-Dicarbomethoxyphenazine. A mixture of 5.0 g of 2-chloro-3-nitrobenzoic acid (Aldrich), 3.33 g of *m*-aminobenzoic acid (Aldrich), 3.50 g of potassium carbonate, 3.0 ml of amyl alcohol, and 360 mg of copper powder (Baker) was refluxed for 30 min. After 20 ml of 0.5 N sodium hydroxide was added the suspension was filtered and washed with chloroform. The aqueous solution was acidified whereupon a yellow precipitate formed. Filtration gave 5.5 g (75%) of 6-nitrodiphenylamine-2,3′-dicarboxylic acid, mp 297–299 °C (lit.[15] 287–290 °C). According to the literature[15] 6-nitrodiphenylamine-2,3′-dicarboxylic acid (600 mg) was dissolved in 15 ml of absolute ethanol containing 560 mg of dissolved sodium and 390 mg of sodium borohydride. The solution was refluxed for 30 h, turning into a greenish-brown suspension. After addition of water the ethanol was evaporated under reduced pressure. Acidification gave a dark green microcrystalline precipitate of phenazine-1,6-dicarboxylic acid which was isolated by filtration, yield 357 mg (67%), mp (from dimethylformamide) 325 °C dec (lit.[15] >290 °C), λ_{max} (EtOH) 253, 368 nm. Phenazine-1,6-dicarboxylic acid (60 mg) was suspended in methanol and treated with excess ethereal diazomethane at 0 °C. Evaporation gave 1,6-dicarbomethoxyphenazine which was recrystallized from ethyl acetate, mp 228–230 °C (lit.[17] 229–230 °C).

1-Methyl-9-carboxyphenazine and 1-Methyl-9-carbomethoxyphenazine. 1,9-Dimethylphenazine (1 g) was oxidized with 2 g of chromium trioxide in 16 ml of 99% aqueous acetic acid by reflux for 1 h. After addition of ether the solution was extracted with dilute sodium hydroxide. The ether layer gave 317 mg of unreacted 1,9-dimethylphenazine. After acidification and ether extraction of the alkaline solution 440 mg of 1-methyl-9-carboxyphenazine was obtained. It was recrystallized from 2-propanol: mp 235 °C; λ_{max} (EtOH) 248, 378 nm. Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 81.53; H, 4.89; N, 13.59. Found: C, 81.43; H, 4.80; N, 13.71. A suspension of the acidic compound in methanol was treated with ethereal diazomethane giving 1-methyl-9-carbomethoxyphenazine. The product was purified over a Florisil column yielding 398 mg of crystals which were recrystallized from 2-propanol: mp 110–112 °C; NMR 7.2–8.3, m, 6 H; 3.9, s, 3 H; 2.8 ppm, s, 3 H. Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 81.79; H, 5.49; N, 12.72. Found C, 81.83; H, 5.35; N, 12.89.

1,6-Dimethoxyphenazine 5-Oxide. According to the literature[18] 1,6-dimethoxyphenazine (260 mg) suspended in 20 ml of benzene was oxidized with 550 mg of *m*-chloroperbenzoic acid (85%) in 15 ml of benzene during 24 h at room temperature. The residue after evaporation was chromatographed on 60 g of silica gel in chloroform/ethanol (99:1). The first red band gave 217 mg of red-orange material which after recrystallization from benzene/pentane yielded 60 mg of pure 1,6-dimethoxyphenazine 5-oxide, mp 185 °C (lit.[18] 180–182 °C).

1,9-Dicarbomethoxyphenazine. 2-Chloro-3-nitrobenzoic acid (Aldrich) (4.17 g), 3.02 g of anthranilic acid (Aldrich), 10 g of potassium carbonate, and a small amount of copper powder (Baker) were thoroughly mixed and placed in a round-bottom flask with 7.5 ml of amyl alcohol. The mixture was heated with magnetic stirring until it melted and the amyl alcohol refluxed. After about 45 min when the red mixture turned into a semisolid, it was cooled and dissolved in water. Copper powder was removed by filtration and the basic solution was washed with chloroform to remove amyl alcohol and impurities. The basic solution was added slowly to an excess of 1 N hydrochloric acid with stirring whereupon a yellow precipitate and a sticky red-brown material formed. The precipitate was removed by filtration and the red-brown mass was redissolved in 1 N sodium hydroxide, washed with chloroform, and reprecipitated as above. This procedure was repeated until all the material had been converted into yellow 2-nitrodiphenylamine-6,2′-dicarboxylic acid: yield 5.0 g (80%); after recrystallization from glacial acetic acid mp 285–290 °C; TLC (silica gel), ethyl acetate/methanol (1:1), R_f 0.2; λ_{max} (EtOH) 260, 340, 415 nm. Anal. Calcd for $C_{14}H_{10}N_2O_6$: C, 55.64; H, 3.33; N, 9.27. Found: C, 55.65; H, 3.43; N, 9.17. In a manner analogous to the preparation of phenazine-1,6-dicarboxylic acid[15] 2-nitrodiphenylamine-6,2′-dicarboxylic acid (19.4 g) was added with stirring to 494 ml of absolute ethanol containing 17.8 g of dissolved sodium and 12.6 g of sodium borohydride whereupon a red solution was obtained. It was refluxed for 23 h turning into a greenish-brown suspension. After addition of water, ethanol was evaporated off. The residue was taken up in 1500 ml of water to obtain a brown solution which was acidified at 0 °C with concentrated hydrochloric acid. Filtration of the greenish-brown microcrystalline precipitate yielded 16.1 g (87%) of crude phenazine-1,9-dicarboxylic acid, mp 290–310 °C, λ_{max} (MeOH) 249, 359 nm. Crude phenazine-1,9-dicarboxylic acid (240 mg) was suspended in 20 ml of methanol and treated with an excess of ethereal diazomethane at 0 °C. The evaporation residue was taken up in chloroform and washed with sodium bicarbonate solution. Drying and evaporation of the chloroform yielded 276 mg of a half-crystalline 1,9-dicarbomethoxyphenazine which was sublimed at 140 °C (0.1 mm): mp 156–157 °C; TLC (silica gel), methanol, R_f 0.6; NMR 7.5–8.3, m, 6 H; 4.0 ppm, s, 6 H; λ_{max} (MeOH) 245, 365 nm. Anal. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45. Found: C, 64.85; H, 4.21; N, 9.72.

1,9- and 1,6-Dinitrophenazine. According to the literature[7] phenazine (Aldrich) (18 g) was dissolved in 360 ml of sulfuric acid monohydrate. At 75 °C 90 ml of nitric acid, *d* 1.49, was added with stirring during 30 min and the mixture was kept at 75 °C for 8 h. The solution was poured on 10 kg of crushed ice and basified with concentrated ammonium hydroxide giving an orange suspension which was filtered and dried. The material was chromatographed on a 50 × 900 mm column SilicAR CE-7 (Mallinckrodt) in benzene. A first small yellow band was discarded. The second yellow band contained

2.5 g of 1,6-dinitrophenazine which was recrystallized from glacial acetic acid, mp 348–349 °C (lit.[7] 343 °C). The third yellow band contained a mixture of 1,6- and 1,9-dinitrophenazine. It was rechromatographed yielding 0.5 g of 1,6-dinitrophenazine and 1.5 g of 1,9-dinitrophenazine which was recrystallized from 50% aqueous acetic acid, mp 267–270 °C (lit.[7] 273 °C). 1,6-Dinitrophenazine, λ_{max} (EtOH) 246, 365 nm.

1,6-Diaminophenazine. 1,6-Dinitrophenazine (816 mg) was suspended in 230 ml of 90% aqueous acetic acid, according to the literature.[7] At the boiling temperature 1.8 g of zinc powder was added with stirring in small portions over a period of 1.5 h. At the end of this period the dark red solution turned brown. Another 300 mg of Zn powder was added over 5 min. The solution was filtered and diluted with 230 ml of water. Concentrated ammonium hydroxide was added to pH 8 and the red precipitate was allowed to form during 24 h at 0 °C. It was taken up in 100 ml of 2% hydrochloric acid, boiled for 2 h, treated with a little Norit, and filtered. Neutralization with concentrated ammonium hydroxide gave 632 mg of a red precipitate which was recrystallized twice from ethanol: yield 473 mg (75%) of 1,6-diaminophenazine; mp 250 °C (lit.[7] 245 °C), TLC (silica gel), chloroform/methanol (9:1), R_f 0.55; λ_{max} (EtOH) 242, 290, 357, 377, 512 nm. The electronic spectrum did not change upon addition of sodium sulfite or sodium borohydride. Also in warm Me_2SO the spectrum remained the same.

Registry No.—2-Nitrodiphenylamine-6,2′-dicarboxylic acid, 58718-49-3; iodinin, 68-81-5; 2-chloro-3-nitrobenzoic acid, 3970-35-2; anthranilic acid, 118-92-3.

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Studies on 4-Quinazolinones. 8.[1] Mechanism of Chromic Acid Oxidation of Arborine[2]

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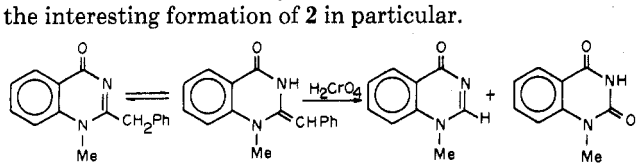
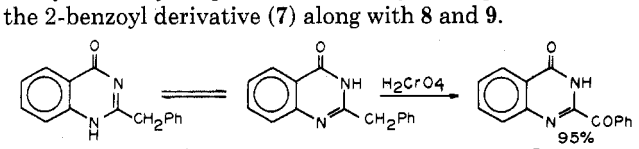
Plausible mechanisms of formation of **2** and **3** from **1** by chromic acid oxidation have been advanced. A novel hydride shift from the side chain to the nucleus, or protonation across C=C in the alkene form, has been envisaged in the conversion of **1** to **2**. Oxidation of a number of 1,2- and 2,3-disubstituted and 2-monosubstituted alkyl/aryl derivatives of 4-quinazolinone has also been studied and the formation of various products explained.

It was earlier reported[4] that arborine (**1**),[5] the major 4-quinazolinone alkaloid of *G. arborea* (Roxb.) DC. (Rutaceae), underwent facile oxidation on brief heating with chromic acid in glacial acetic acid to glycorine (**2**) and glycosmicine (**3**), the co-occurring[6] minor bases in 78 and 14% yields, respectively. In view of the biogenetic implications,[7] we have studied this reaction in more detail to gain insight into the mechanism of the interesting formation of **2** in particular.

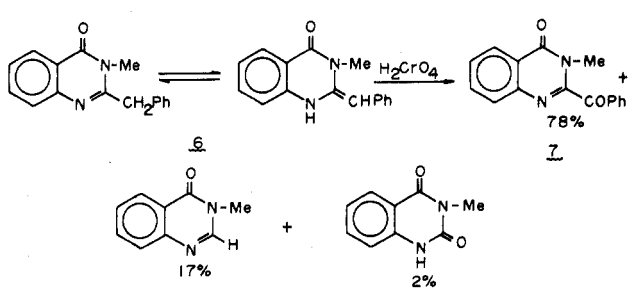


1a **1b** **2** **3**

The same reaction could also be brought about to the extent of 50% by heating with aqueous chromic acid, while chromic oxide in pyridine at room temperature afforded **3** and benzaldehyde. On the other hand, glycosminine (**4**) upon heating with chromic acid in glacial acetic acid furnished the expected 2-benzoyl-4-quinazolinone (**5**) as the sole product while 2-benzyl-3-methyl-4-quinazolinone (**6**) yielded predominantly the 2-benzoyl derivative (**7**) along with **8** and **9**.



4 **5**



6 **7** **8** **9**

Conceivably, the oxidation of **1** to **2** with chromic acid involves the benzylidene form of arborine (**1b**), which almost certainly[5,8] takes part in all the oxidative processes studied so far,[4,5,9,10] and the inductive effect of the N-1 alkyl group. Should the benzylic form **1a** be involved, glycosminine, definitely shown[8] to exist in this form (**4**) only, would have furnished benzoyleneurea (**13**) as one of the products, contrary to the observation. Furthermore, oxidative debenzylation of **6**, though less favored, also indicated the participation of the lone pair of electrons on nitrogen. A plausible mechanism put forward in Scheme I involves an initial electrophilic addition of H_2CrO_4 to the benzylidene double bond of **1b**, analogous to that suggested[11,12] for the oxidation of alkenes. Attachment of the reagent at the benzylic carbon (path a) followed successively by a hydride shift[13] (path a_1), further attack by the oxidant, and cleavage of C–C bond could then form **2**. On the