Reaction of Aminoquinones and Related Vinylogous Amides with Nitrous Acid. Synthesis and Chemistry of Cyclic Diazo Ketones

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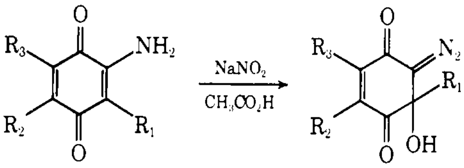
2-Amino-3-alkyl- (or aryl-) 1,4-quinones are shown to react with nitrous acid (sodium nitrite in glacial acetic acid) to give 5-diazo-6-alkyl- (or aryl-) 6-hydroxycyclohex-2-ene-1,4-diones **2**. Analogous reactions are observed for the related vinylogous amides, 4-amino-2,5-di-*tert*-butyl-2-cyano-4-cyclopentene-1,3-dione (**7**) and 2,5*H*-3-amino-4-methyl-6,7-benzoazepine-2,5-dione (**9**). The chemistry of the cyclic diazo compounds is discussed, and of particular interest are the thermal rearrangements of **2a**, **2b**, and **4** to the corresponding ring-contracted 4-cyclopentene-1,3-diones, **24**, **25**, and **27**, respectively. Also discussed is the thermal rearrangement of 4-acetyl-3-diazo-4-hydroxycarbostyril (**12**) to 3-acetyl-4-hydroxycarbostyril (**26**), the reductive cyclization of **12** to 3*H*,5*H*-1-methylpyrazolo[3,4-*c*]quinolin(4*H*)-one (**19**), and the acid-catalyzed conversion of **12** to 4*H*,6*H*(1*H*,5*H*)-dioxo-3,4-diazino[3,4-*c*]quinoline (**30**).

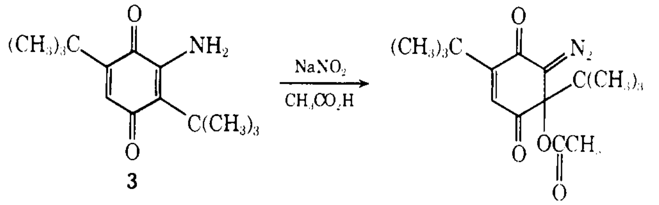
A vast methodology exists in the literature for the synthesis of aminoquinones. In fact, during the past 35 years alone well over 150 substituted primary amino-1,4-quinones have been reported. However, there is a paucity of information regarding the chemistry of these compounds. Our interest in the utility of quinones in organic synthesis[1] along with the plethora of such readily available starting materials[2] and the rich chemistry of the amino group[3] has stimulated an investigation of aminoquinones as potentially useful reagents. Reported here is a study of the reactions of selected 2-amino-1,4-quinones and certain related cyclic vinylogous amides with nitrous acid, a reaction resulting in the formation of cyclic α-diazo ketones. Also described is the pyrolytic ring contraction of such compounds. Of particular interest is the thermal rearrangement of the diazo ketones **2** to 2-acyl-4-cyclopentene-1,3-diones, a ring system found in a number of natural products.[4]

Synthetic Scope. Treatment of the aminoquinones **1a–d** with sodium nitrite in glacial acetic acid results in a rapid, exothermic reaction and gives fair to excellent yields of the corresponding diazo ketones **2a–d**. 2-Amino-3,6-di-*tert*-butyl-1,4-benzoquinone (**3**), having a bulky substituent adjacent to the amino group, behaves anomalously in that the acetoxy derivative **4** was obtained in 92% yield. The detailed scope of this reaction of aminoquinones has not been studied in detail. However, we have observed that 2-amino-1,4-quinones which are unsubstituted at the 3 position give complex reaction mixtures and that 2-amino-6-anilino-3-carbomethoxy-1,4-benzoquinone, a compound having a very nonnucleophilic amino group, fails to react. In addition, Mosby and Silva[5] found that 2-amino-3-chloro-1,4-naphthoquinone (**5a**) gave the diazo oxide **6** when treated with sodium nitrite in sulfuric acid. We have observed the same product when 2-amino-3-chloro- (**5a**), 2-amino-3-methoxy- (**5b**), 2-amino-3-azido- (**5c**), and 2-amino-3-thiophenyl-1,4-naphthoquinone (**5d**) are diazotized as described here.

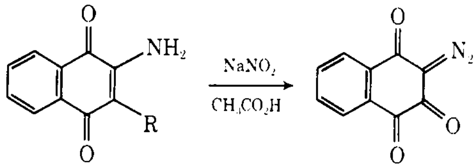


1 **2**

	R_1	R_2	R_3	Yield %
a	CH_3	-CH=CHCH=CH-		91
b	CH_3	H	CH_3	81
c	CH_3	N_3	CH_3	92
d	C_6H_5	H	C_6H_5	36



3 **4**



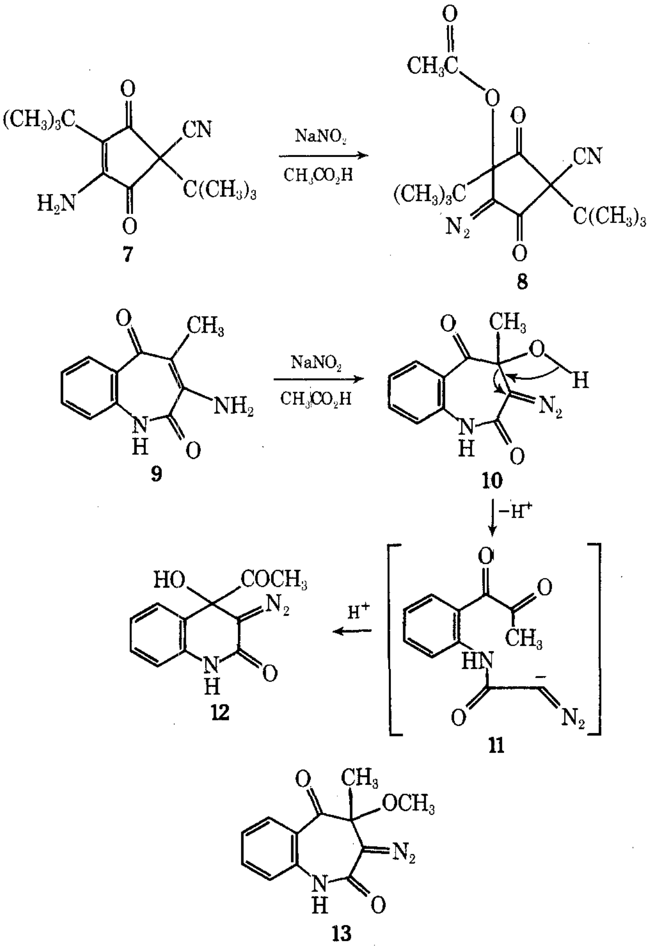
5 **6**

	R	Yield %
a	Cl	82
b	OCH_3	85
c	N_3	65
d	SC_6H_5	61

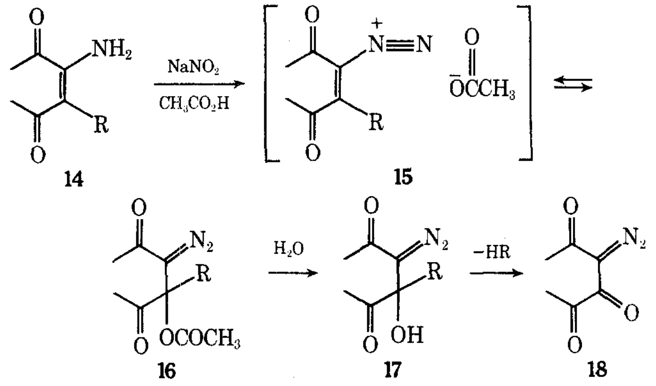
To further probe the utility of these diazotization reactions, the scope was widened to include some nonquinoid cyclic 2-aminoenediones. Treatment of 4-amino-2,5-di-*tert*-butyl-2-cyano-4-cyclopentene-1,3-dione (**7**) with sodium nitrite in glacial acetic acid gave a 62% yield of the acetoxydiazo derivative **8**. A more interesting transformation was observed when 3-amino-2,5*H*-4-methyl-6,7-benzoazepine-2,5-dione (**9**) was subjected to the above reaction conditions. Here, rather than the seven-membered cyclic diazo compound **10**, the ring-contracted quinoline **12** was isolated. However, a dichloromethane extract of the reaction mixture showed (^{1}H NMR) two products in a ratio of 3:2 as evidenced by methyl absorptions at δ 1.52 and δ 2.20, respectively, and the minor product was the quinoline **12**. The major product is assumed to be the azepine **10** which rearranges to **12** via the ring-opened intermediate **11**. Such a transformation was easily induced when the above dichloromethane solution was treated with 3% methanolic potassium hydroxide. This resulted in the disappearance of the δ 1.52 absorption and the δ 2.20 peak increased in intensity. It was possible to interrupt the diazotization of **9** at the azepine stage when the reaction was carried out in 1:1 acetic acid–methanol. Here, the methoxy adduct **13** was isolated in 90% yield. (See Scheme I).

Mechanism. The products observed from the diazotization reactions described here are consistent with a mechanism (Scheme II) in which the vinylogous amide is initially converted to a diazonium salt **15** which then suffers nucleo-

Scheme I

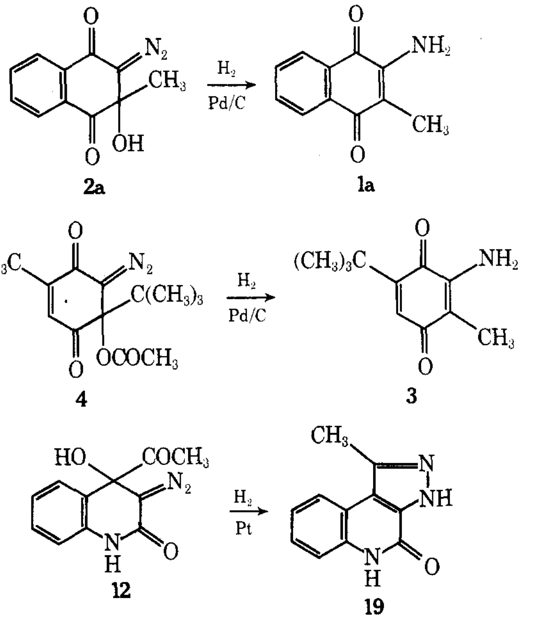


Scheme II

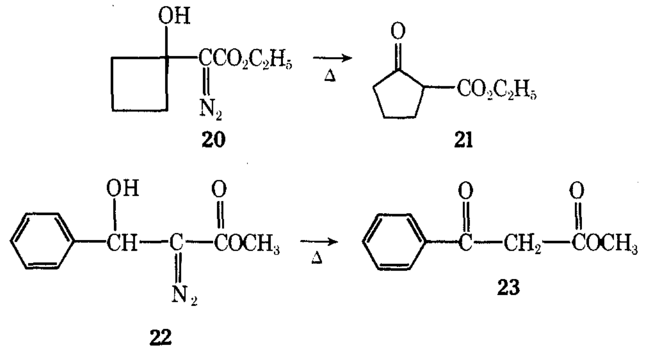


philic attack by solvent (CH_3CO_2H) to give the acetoxy derivative **16**. For those compounds having a relatively small substituent adjacent to the diazo linkage (**2a–d**, **9**), hydrolysis of the acetoxy group during the aqueous work-up would result in the observed β-hydroxydiazo compounds. Steric retardation of such hydrolysis by the bulky *tert*-butyl groups in **4** and **8** would account for the interception of these esters. For those compounds having a potential leaving group (R = Cl, OCH_3, N_3, SC_6H_5) adjacent to the diazo linkage, hydrolysis and subsequent elimination would give the diazo oxide **18**.

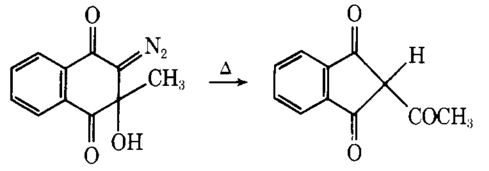
Chemistry. Wenkert and McPherson[6] have shown that catalytic hydrogenation (Pd/C) of acyclic α-diazo-β-hydroxycarbonyl compounds gives the corresponding β-hydroxycarbonyl compounds. Therefore, an analogous transformation was anticipated for **2a** and **4**. However, these compounds were converted to 2-amino-3-methyl-1,4-naphthoquinone (**1a**) and 2-amino-3,6-di-*tert*-butyl-1,4-benzoquinone (**3**), respectively, when subjected to hydrogenation conditions. This reductive cleavage of the diazo nitrogen–nitrogen bond appears to be rare but not unprecedented; Birkofer[7] reported that α-diazoacetophenone gives α-aminoacetophenone when subjected to hydrogenation under slightly acidic condition in the presence of Pd/C. Hydrogenation of the diazoquinoline derivative **12** also resulted in the reduction of the diazo nitrogen linkage. In this case, **19** was obtained in >90% yield and is envisaged as arising from an intermediate hydrazine derivative which suffers intramolecular condensation.



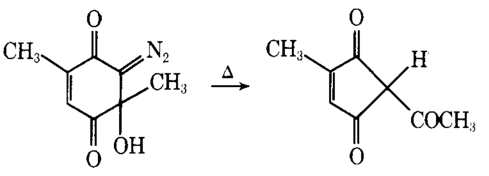
Wenkert and McPherson[6] have shown that acyclic α-diazo-β-hydroxy ketones and esters thermally rearrange with carbon or hydrogen migration as illustrated below. In analogy to these rearrangements it was found that **2a** and **2b** thermally rearranged in refluxing chlorobenzene with acyl migration to give 2-acetyl-1,3-indandione[8] (**24**, 97%) and 2-acetyl-4-methyl-4-cyclopentene-1,3-dione (**25**, 86%), respectively. Also, **12** gave a 28% yield of 3-acetyl-4-hydroxycarbostyril (**26**)[9] and **4** gave a 90% yield of **27** when subjected to the thermolysis conditions.



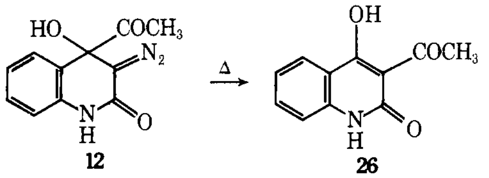
The acid-catalyzed decomposition of two of the diazo compounds described here was also studied. Decomposition of **2a** in cold (5°) concentrated sulfuric acid gave the same product, i.e., **24**, that resulted from its thermolysis. An entirely different transformation was observed for the acid-catalyzed decomposition of **12**. Here, a fascinating ring closure to **30** took place in nearly quantitative yield. This product is viewed as arising from the diazonium salt **28** which electrophilically attacks the enol double bond. Such a ring closure to a diazine is well documented in that one of



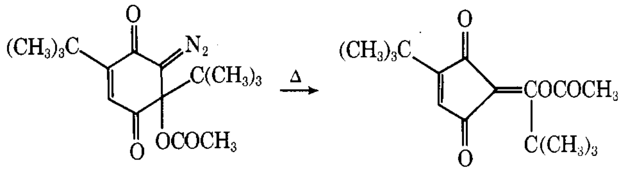
2a **24**



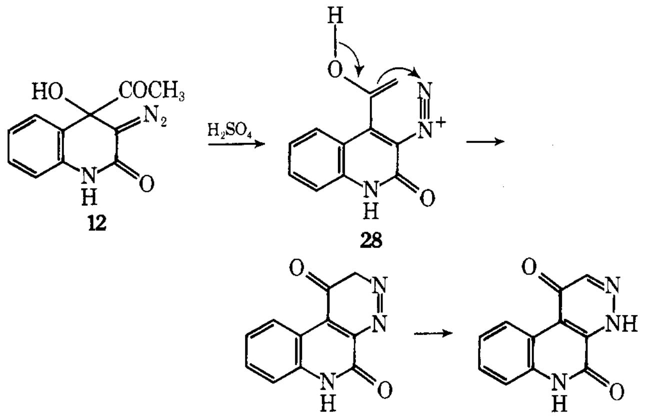
2b **25**



12 **26**



4 **27**



29 **30**

the standard synthetic routes to the cinnoline nucleus involves the intramolecular cyclization of an aryldiazonium salt which contains a reactive unsaturated ortho substituent.[10,11]

Experimental Section

2-Diazo-3-hydroxy-3-methylbenzocyclohexane-1,4-dione (2a). To a solution of 1.0 g (5 mmol) of 2-amino-3-methyl-1,4-naphthoquinone (**1a**) in 50 ml of glacial acetic acid was added 0.5 g (12 mmol) of sodium nitrite. After stirring for approximately 5 min at ambient temperature the solution turned yellow and was then diluted with 200 ml of water and extracted three times with dichloromethane. The combined organic extract was washed twice with 5% sodium bicarbonate and dried ($MgSO_4$). The solvent was removed in vacuo (25°) to give 1.0 g (91%) of the yellow, crystalline diazo compound **2a**: mp 106–107° (from pentane–ether); ir (Nujol) 3300, 2110, 1705, 1660, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 s (3), 4.32 br (1), 7.65–8.25 m (4).

Anal. Calcd for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.70; N, 12.96. Found: C, 60.99; H, 3.64; N, 12.89.

6-Diazo-5-hydroxy-2,5-dimethylcyclohex-2-ene-1,4-dione (2b). To a solution of 0.5 g (3.3 mmol) of 2-amino-3,6-dimethyl-1,4-benzoquinone (**1b**) in 20 ml of glacial acetic acid was added 0.3 g (4.3 mmol) of sodium nitrite. The initially purple solution turned yellow after approximately 5 min and was then diluted with 200 ml of an aqueous saturated sodium chloride solution and extracted four times with dichloromethane. The combined organic extract was washed twice with 5% sodium bicarbonate and dried ($MgSO_4$), and the solvent was removed in vacuo (25°) to give a yellow-orange oil. Trituration of this oil with cold pentane–ether gave 0.48 g (81%) of the yellow, crystalline diazo compound **2b**: mp 79–80° dec (pentane–ether); ir (Nujol) 3450, 2100, 1675, 1640, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) 1.62 s (3), 2.11 d (3) $J = 2$ Hz, 3.91 br (1), 6.60 q (1) $J = 2$ Hz.

Anal. Calcd for $C_8H_8N_2O_3$: C, 53.33; H, 4.44; N, 15.56. Found: C, 53.43; H, 4.41; N, 15.39.

3-Azido-6-diazo-5-hydroxy-2,5-dimethylcyclohex-2-ene-1,4-dione (2c). Treatment of 2-amino-5-azido-3,6-dimethyl-1,4-benzoquinone (**1c**, 0.5 g, 2.6 mmol) with sodium nitrite (0.24 g, 3 mmol) was carried out as described above for **1b** to give 0.54 g (92%) of the diazo compound **2c** as a golden, crystalline solid: mp 107–109° dec (pentane–ether); ir (Nujol) 3200, 2120, 1690, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) 1.68 s (3), 2.03 s (3), 3.52 br (1).

Anal. Calcd for $C_8H_7N_5O_3$: C, 43.44; H, 3.17; N, 31.67. Found: C, 43.55; H, 3.09; N, 31.57.

6-Diazo-5-hydroxy-2,5-diphenylcyclohex-2-ene-1,4-dione (2d). To a solution of 1.0 g (3.6 mmol) of 2-amino-3,6-diphenyl-1,4-benzoquinone (**1d**) in 50 ml of glacial acetic acid was added 0.48 g (7.2 mmol) of sodium nitrite. After stirring at ambient temperature for 15 min the initially purple solution turned yellow and the solution was diluted with 200 ml of water and extracted three times with diethyl ether. The combined organic extract was washed twice with 5% sodium bicarbonate and dried ($MgSO_4$) and the solvent was removed in vacuo (25°). The resulting orange oil was chromatographed on silica gel using 1:1 benzene–chloroform as the eluent to give 0.40 g (36%) of the diazo compound **2d**: mp 108–109° dec; ir (Nujol) 3400, 2100, 1700, 1625, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.65 br (1), 6.77 s (1), 7.25–7.70 m (10).

Anal. Calcd for $C_{18}H_{12}N_2O_3$: C, 71.05; H, 3.95; N, 9.21. Found: C, 71.07; H, 3.93; N, 9.25.

5-Acetoxy-6-diazo-2,5-di(1,1-dimethylethyl)cyclohex-2-ene-1,4-dione (4). A solution of 1.0 g (4.2 mmol) of 2-amino-3,6-di-*tert*-butyl-1,4-benzoquinone (**3**) in 75 ml of glacial acetic acid was treated with 0.44 g (6.3 mmol) of sodium nitrite at ambient temperature. After 15 min the reaction solution was diluted with 200 ml of water and extracted with three portions of dichloromethane. After drying ($MgSO_4$) the solvent was removed and the product recrystallized from methanol to give 1.3 g (92%) of the yellow diazo compound **4**: mp 83–84°; ir (Nujol) 2100, 1745, 1680, 1630, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 s (9), 1.32 s (9), 2.14 s (3), 6.59 s (1).

Anal. Calcd for $C_{16}H_{22}N_2O_4$: C, 62.72; H, 7.24, N, 9.15. Found: C, 62.55; H, 7.28; N, 8.93.

2-Diazobenzocyclohexane-1,3,4-trione (6). Treatment of acetic acid solutions of 2-amino-3-chloro- (**5a**),[5] 2-amino-3-methoxy- (**5b**),[5] 2-amino-3-azido- (**5c**),[5] and 2-amino-3-thiophenyl-1,4-naphthoquinone (**5d**) with a twofold molar excess of sodium nitrite gave the diazo oxide **6** in yields ranging from 61 to 85%. The product showed spectral and physical properties that were identical with those reported by Mosby and Silva.[5]

4-Diazo-5-acetoxy-2-cyano-2,5-di(1,1-dimethylethyl)cyclopentene-1,3-dione (8). A solution of 1.0 g (4.4 mmol) of 4-amino-2-cyano-2,5-di-*tert*-butyl-4-cyclopentene-1,3-dione (**7**) and 1.5 g of sodium nitrite in 70 ml of glacial acetic acid was stirred at ambient temperature for 12 hr. The solution was then diluted with 200 ml of water and extracted three times with dichloromethane. After drying, the solvent was removed in vacuo (25°) and the resulting yellow oil was crystallized from pentane–ether to give 0.87 g (62%) of the diazo compound **8**: mp 99–101°; ir (Nujol) 2220, 2120, 1760, 1725, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 s (9), 1.23 s (9), 2.15 s (3).

Anal. Calcd for $C_{16}H_{21}N_3O_4$: C, 60.19; H, 6.58; N, 13.17. Found: C, 60.25; H, 6.60, N, 13.36.

2,5-Di(1,1-dimethylethyl)-2-cyano-4-amino-4-cyclopentene-1,3-dione (7). A solution of 1 g (4.2 mmol) of 2,5-di-*tert*-butyl-3,6-diamino-1,4-benzoquinone and 3.72 g (8.4 mmol) of lead tetraacetate in 50 ml of chloroform was stirred at ambient temperatures for 5 min and then 5 ml of ethylene glycol was added. The reaction solution was then washed three times with water and dried ($MgSO_4$) and the solvent was removed in vacuo. The resulting residue was recrystallized from hexane to give 0.7 g (71%) of **7**: mp 82–84°; ir (Nujol) 3450, 3330, 2250, 1760, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 s (9), 1.40 s (9), 5.55 br (2).

Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.74; H, 8.06; N, 11.29. Found: C, 67.84; H, 8.12, N, 11.18.

2,5*H*-3-Azido-4-methyl-6,7-benzoazepine-2,5-dione. To a solution of 1.87 g (10 mmol) of 2,5*H*-4-methyl-6,7-benzoazepine-2,5-

dione[13] and 2.6 g (40 mmol) of sodium azide in 35 ml of dimethylformamide was added 5.08 g (20 mmol) of iodine and the resulting reaction mixture was stirred at ambient temperature. The course of the reaction was followed by ir spectroscopy and the mixture was worked up after all of the starting azepine had been consumed ($\sim$16 hr). Water was then added and the resulting white precipitate was collected and washed with methanol to give 1.67 g (73%) of 2,5*H*-3-azido-4-methyl-6,7-benzoazepine-2,5-dione, mp 161° dec. The analytical sample was obtained by recrystallization (30°) from dimethyl sulfoxide–methanol: ir (Nujol) 3125, 3005, 2130, 1650, 1585, 1315 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.05 s (3), 7.00–7.70 m (4), 11.32 br (1) exchanges with D_2O; mass spectrum (70 eV) *m/e* (rel abundance) 200 (40.9), 119 (100), 117 (27.8), 92 (53.6), 64 (39.0).

Anal. Calcd for $C_{11}H_8N_4O_2$: C, 57.89; H, 3.51; N, 24.56. Found: C, 57.86; H, 3.53; N, 24.56.

2,5*H*-3-Amino-4-methyl-6,7-benzoazepine-2,5-dione (9). A suspension of 2.28 g (10 mmol) of 2,5*H*-3-azido-4-methyl-6,7-benzoazepine-2,5-dione and 50 mg of platinum oxide in 100 ml of 95% ethanol was treated with hydrogen at 50 psi for 9 hr. The catalyst and solvent were then removed to give 2.0 g (99%) of the amine **9**: mp 241–243° (95% ethanol); ir (Nujol) 3380, 3270, 3060, 1680, 1595 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.17 s (3), 6.67 br (2), 7.67–7.10 m (3), 8.23–7.98 m (1), 11.50 br (1).

Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.95, N, 13.86. Found: C, 65.49; H, 4.97; N, 13.89.

4-Acetyl-3-diazo-4-hydroxycarbostyril (12). To a stirred solution of 1.04 g (15 mmol) of sodium nitrite in 20 ml of water was added a suspension of 2.02 g (10 mmol) of 2,5*H*-3-amino-4-methyl-6,7-benzoazepine-2,5-dione (**9**) in 60 ml of acetic acid. After 15 min the reaction solution was diluted with 200 ml of water and extracted with 200 ml of dichloromethane. The organic extract was washed with water and saturated sodium bicarbonate and then dried over anhydrous sodium sulfate. The dichloromethane extract was analyzed by ^1H NMR, which showed two methyl absorptions in a ratio of 3:2 coming at δ 1.52 and 2.20, respectively. The former absorption is assigned to the methyl group in the azepine **10** and the latter to the carbostyril **12**. The dichloromethane solution was then treated with 20 drops of 3% methanolic potassium hydroxide. The solvent was then removed by rotoevaporation at ambient temperature. The resulting residue (2.3 g) was analyzed by ^1H NMR (CH_2Cl_2) which showed only the δ 2.20 absorption in the methyl region of the spectrum. The crude product was recrystallized from benzene to give 1.02 g of pure **12**: mp 171° dec; ir (Nujol) 3380, 3100, 2105, 1720, 1675, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 s (3), 5.40 s (1), 7.78–6.90 m (4), 9.93 br (1).

Anal. Calcd for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.90; N, 18.18. Found: C, 57.16; H, 4.02; N, 18.07.

2,3,4,5*H*-3-Diazo-4-methoxy-4-methyl-6,7-benzoazepine-2,5-dione (13). A solution of 0.57 g (2.5 mmol) of 2,5*H*-3-amino-4-methyl-6,7-benzazepine-2,5-dione (**9**) in 40 ml of anhydrous methanol and 40 ml of glacial acetic acid (35°) was treated with 3.5 g of sodium nitrite in 0.5-g portions over a period of 4 hr. The reaction mixture was then diluted with 100 ml of water and extracted four times with 15-ml portions of dichloromethane. The combined organic extract was then washed twice with saturated aqueous sodium bicarbonate and dried (Na_2SO_4) and the solvent was removed in vacuo (40°). The resulting residue (0.70 g) was shown by ^1H NMR analysis to be composed of approximately 90% of **13**, 3% of the starting amine, and several unidentified minor products. It was then subjected to column chromatography on silica gel using ethyl acetate–petroleum ether (1:1) to give **13** as a yellow, crystalline solid: mp 133° dec; ir (Nujol) 3250, 3150, 2990, 2090, 1690, 1640, 1610, 1580 cm^{-1}; ^1H NMR ($CDCl_3$), 1.67 s (3), 3.17 s (3), 6.93–7.87 m 4), 9.40 br (1) exchanges with D_2O.

Anal. Calcd for $C_{12}H_{11}N_3O_3$: C, 58.78; H, 4.49; N, 17.14. Found: C, 58.84; H, 4.55; N, 16.70.

Catalytic Reduction of 2-Diazo-3-hydroxy-3-methylbenzocyclohexane-1,4-dione (2a). A suspension of 1.0 g (4.8 mmol) of **2a** and 0.5 g of 10% palladium on charcoal was subjected to 40 psi of hydrogen for 1.5 hr. After removal of the catalyst and solvent the residue was chromatographed on silica gel using chloroform as the eluent to give 0.4 g (47%) of 2-amino-3-methyl-1,4-naphthoquinone (**1a**) which was identical with an authentic sample.

Catalytic Reduction of 5-Acetoxy-6-diazo-2,5-di-*tert*-butylcyclohex-2-ene-1,4-dione (4). Catalytic reduction of **4** (0.5 g, 1.6 mmol) using 10% palladium on charcoal (0.2 g) in 30 ml of methanol for 1 hr gave a quantitative yield of 2-amino-3,6-di-*tert*-butyl-1,4-benzoquinone (**3**) which was identical with an authentic sample.

3*H*,5*H*-1-Methylpyrazolo[3,4-*c*]quinolin-(4*H*)-one (19). A suspension of 1.25 g (5.4 mmol) of 4-acetoxy-3-diazo-4-hydroxycarbostyril (**12**) and approximately 10 mg of platinum oxide in 25 ml of 95% ethanol was treated with hydrogen at 35 psi for 5 hr. Filtration and removal of the solvent in vacuo gave 1.0 g (93%) of **19**, mp 330–340°. This product was recrystallized from 95% ethanol to give the analytical sample: mp 356–358, sinter 345°; ir (Nujol) 3080, 1690, 1630 cm^{-1}; ^1H NMR (Me_2SO-d_6) 2.68 s (3), 7.58–7.15 m (3), 8.10–7.80 m (1), 11.73 br (1) exchanges with D_2O, 14.05 br (1) exchanges with D_2O; mass spectrum (70 eV) *m/e* (rel abundance) 200 (15.4), 199 (100), 170 (14.6), 130 (12.8), 115 (12.2), 103 (25.2), 76 (11.3).

Anal. Calcd for $C_{11}H_9N_3O$: C, 66.33; H, 4.52; N, 21.11. Found: C, 66.61; H, 4.72; N, 21.00.

2-Acetyl-1,3-indandione (24). A solution of 0.50 g (2.5 mmol) of 2-diazo-3-hydroxy-3-methylbenzocyclohexane-1,4-dione (**2a**) in 50 ml of dioxane was refluxed for 2 hr. Evaporation of the solvent in vacuo and recrystallization of the residue from methanol gave 0.42 g (97%) of **24**: mp 109–110 (lit.[8] mp 110–112°); ir (Nujol) 1720, 1700, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.52 s (3), 7.75 m (4), 10.92 br (1).

2-Acetyl-4-methyl-4-cyclopentene-1,3-dione (25). The title compound was prepared as described above for **24** except benzene was used as the solvent, i.e., 0.270 g (1.54 mmol) of **2b** give 0.20 g (86%) of **25**: mp 53–55° (methanol); ir (Nujol) 1710, 1670, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 d (3), $J = 1.5$ Hz, 2.35 s (3), 6.51 q (1), $J = 1.5$ Hz, 11.51 br (1).

Anal. Calcd for $C_8H_8O_3$: C, 63.16; H, 5.26. Found: C, 63.05; H, 5.32.

Acid-Catalyzed Rearrangement of 2-Diazo-3-hydroxy-3-methylbenzocyclohexane-1,4-dione (2a). To vigorously stirred, cold (5°) concentrated sulfuric acid was slowly added (20 min) 0.25 g (1.2 mmol) of **2a**. After gas evolution had ceased, the reaction mixture was diluted with ice water and the resulting precipitate was collected and dried to give 80 mg (38%) of 2-acetyl-1,3-indandione which was shown to be identical with an authentic sample.[8]

3-Acetyl-4-hydroxycarbostyril (26). A solution of 13.5 mg (0.05 mmol) of **12** in 5 ml of anhydrous benzene was refluxed for 72 hr. Upon cooling 3.5 mg of **26**, mp 254–257° (lit.[9] mp 258–259°), precipitated. This product was shown to be identical with an authentic sample of 3-acetyl-4-hydroxycarbostyril which was kindly supplied by Calvin M. Foltz.[9] This same compound was obtained in 74% yield when 50 mg of 2,3,4,5-tetrahydro-3-diazo-4-methyl-4-methoxy-6,7-benzoazepine-2,5-dione (**13**) was decomposed in 5 ml of refluxing chlorobenzene. After 10 min at the reflux temperature the solution was cooled to 80–100° and a few drops of water were added. The solvent was then removed and the residue was subjected to dry column chromatography over silica gel using methanol as the eluent to give 31 mg (74%) of **26**.

2-(1-Acetoxy-2,2-dimethylpropylidine)-4-(2,2-dimethylethyl)-4-cyclopentene-1,3-dione (27). A solution of 1 g (3.75 mmol) of 5-acetoxy-6-diazo-2,5-di(1,1-dimethylethyl)cyclohex-2-ene-1,4-dione (**4**) in 25 ml of chlorobenzene was refluxed for 2 hr and the solvent was removed in vacuo. The resulting yellow solid was recrystallized from heptane to give 0.83 g (90%) of **27**: mp 61–62°; ir (Nujol) 1815, 1750, 1710, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 s (18), 2.46 s (3), 5.16 s (1).

Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.16; H, 8.09.

4*H*,6*H*(1*H*,5*H*)-Dioxo-3,4-diazino[3,4-*c*]quinoline (30). Concentrated sulfuric acid (5 ml, 0.5°) was vigorously stirred while 0.231 g (1.0 mmol) of 1,2,3,4-tetrahydro-4-acetyl-3-diazo-4-hydroxy-2-oxoquinoline (**12**) was added over a period of 20 min. During the course of this addition, the temperature of the reaction solution raised to 30°. Thirty minutes after the addition was complete, the reaction solution was poured onto 20 ml of crushed ice. The resulting precipitate was collected to give 0.22 g of **29** as a light yellow solid, mp 430° dec, which was recrystallized from dimethylformamide to give the pure product as white microcrystals: mp 430° dec; ir (Nujol) 3160, 1675, 1580, 1570, 1545 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.57–7.17 m (3), 8.00 s (1), 9.60–9.37 m (1), 12.77 br (1), 14.20 br (1); mass spectrum *m/e* (rel abundance) 213 (100), 186 (14.6) 158 (12.5), 103 (15.6).

Anal. Calcd for $C_{11}H_7N_3O_2$: C, 61.97; H, 3.31; N, 19.71. Found: C, 61.91; H, 3.33; N, 19.63.

2-Amino-3-thiophenyl-1,4-naphthoquinone (5d). To a stirred solution of 1.0 g (5.0 mmol) of 2-azido-1,4-naphthoquinone[14] in 70 ml of absolute ethanol was added 0.83 g (7.5 mmol) of thiophenol in one portion; gas evolution was observed and the reaction solution gradually turned from yellow-orange to red. After 12 hr the resulting precipitate was collected to give 1.15 g (82%) of the quinone **5d**: mp 164–166° (lit.[15] mp 172°); ir (Nujol) 3475, 3275, 1685, 1590 cm^{-1}; ^{1}H NMR (CDCl$_3$) 6.05 br (2), 7.25 br (5), 7.62–8.33 m (4).

2-Amino-5-azido-3,6-dimethyl-1,4-benzoquinone (1c). A solution of 1.1 g (5.0 mmol) of 2,5-diazido-3,6-dimethyl-1,4-benzoquinone[14] in 200 ml of ether was treated with 100 ml of a saturated aqueous solution of sodium dithionite, and the mixture was vigorously stirred for 60 min under an atmosphere of nitrogen. The organic layer was washed several times with water and dried and the solvent was then removed in vacuo (25°). The resulting 2,5-diazido-3,6-dimethylhydroquinone was dissolved in 75 ml of acetone and small amount of sodium azide was added. This caused the rapid disproportionation[16] of the hydroquinone and gave the crude product, **1c**, after approximately 1 hr. Chromotography of this crude product on 100 g of silica gel using chloroform as the eluent gave 0.72 g (74%) of **1c**, which turns from purple to white at 132–134° with gas evolution and the white solid then melts at 150–151°: ir (Nujol) 3310, 3220, 2100, 1630, 1590 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.84 s (3), 1.89 s (3), 5.00 br (2).

Anal. Calcd for $C_8H_8N_4O_2$: C, 50.00; H, 4.17; N, 29.17. Found: C, 49.83; H, 4.29; N, 28.93.

2-Amino-3-methyl-1,4-naphthoquinone (2a), 2-Amino-3,6-dimethyl- (2b), 2-Amino-3,6-diphenyl- (2d), 2-Amino-3,6-di(1,1-dimethylethyl)- (3) and 2,5-Diamino-3,6-di(1,1-dimethylethyl)-1,4-benzoquinone. The above aminoquinones were prepared in good yields (>75%) by catalytic reduction (PtO$_2$, 30–40 psi) of ethanolic solutions of the respective azidoquinones.[12,14,17]

2-Amino-3-methyl-1,4-naphthoquinone (**1a**), mp 164–165° (lit.[18] mp 162–163°).

2-Amino-3,6-dimethyl-1,4-benzoquinone (**1b**): mp 194–196°; ir (Nujol) 3420, 3300, 1640, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.82 s (3), 1.98 d (3), J = 2 Hz, 4.79 br (2), 6.42 q (1), J = 2 Hz.

Anal. Calcd for $C_8H_9NO_2$: C, 63.57; H, 5.96; N, 9.27. Found: C, 63.71; H, 6.17; N, 9.12.

2-Amino-3,6-diphenyl-1,4-benzoquinone (**1d**): mp 244–246°; ir (Nujol) 3410, 3250, 1630, 1560 cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 6.14 br (2), 6.65 s (1), 7.15–7.52 m (10).

Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.54; H, 4.72; N, 5.09. Found: C, 78.39; H, 4.71; N, 4.92.

2-Amino-3,6-di(1,1-dimethylethyl)-1,4-benzoquinone (**3**): mp 111–113°; ir (Nujol) 3450, 3320, 1675, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.22 s (9), 1.38 s (9), 5.49 br (2), 6.44 s (1).

Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.49; H, 8.94; N, 5.96. Found: C, 71.37; H, 9.10; N, 5.73.

2,5-Diamino-3,6-di(1,1-dimethylethyl)-1,4-benzoquinone: mp 192–193°; ir (Nujol) 3440, 3320, 1540 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.34 .

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.20; H, 8.80; N, 11.20. Found: C, 67.15; H, 8.94; N, 11.12.

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Registry No.—**1a**, 7427-09-0; **1b**, 31679-93-3; **1c**, 26351-46-2; **1d**, 56908-60-2; **2a**, 56908-61-3; **2b**, 56908-62-4; **2c**, 56908-63-5; **2d**, 56908-64-6; **3**, 35612-59-0; **4**, 56908-65-7; **5d**, 56908-66-8; **7**, 56908-67-9; **8**, 56908-68-0; **9**, 56908-69-1; **12**, 56908-70-4; **13**, 56908-71-5; **19**, 56908-72-6; **24**, 1133-72-8; **25**, 4056-72-8; **26**, 26138-64-7; **27**, 56908-73-7; **30**, 56908-74-8; 2,5-di-*tert*-butyl-3,6-diamino-1,4-benzoquinone, 56908-75-9; 2,5*H*-3-azido-4-methyl-6,7-benzoazepine-2,5-dione, 56908-76-0; 2,5*H*-4-methyl-6,7-benzoazepine-2,5-dione, 10315-37-4; sodium azide, 26628-22-8; 2-azido-1,4-naphthoquinone, 15707-29-6; 2,5-diazido-3,6-dimethyl-1,4-benzoquinone, 27977-29-3.

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Asymmetric Synthesis of Oxaziridines

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Oxidation of Schiff bases formed by the reaction of chiral (R)-(+)-α-phenylethylamine and carbonyl compound using *m*-chloroperbenzoic acid gives rise to the formation of nonracemic diastereomeric 3,3-disubstituted oxaziridines in a high optical yield. Oxidation of (E)-(R)-(−)-N-benzylidene-α-phenylethylamine yields a mixture of all four possible nonracemic diastereomers with predominance of E products.

The relatively small group of oxaziridines, containing the stable chiral N atom, is characterized by a high energy barrier for inversion, thus permitting the separation of enantiomers.[1-6]

Until now, optically active oxaziridines have been obtained by the oxidation of imines, using optically active peroxy acids.[2,3] Depending upon the substrate used, mixtures of compounds obtained represented nonracemic diastereomers or enantiomers with the presence of a small excess of one of them.[2,3] Such mixtures were usually separated by physical methods; in the case of a mixture of enantiomers, multiple recrystallizations afforded compounds which did not show a marked change of optical rotation after further recrystallizations.[4,6]

Two alternative mechanisms of imine oxidation have been postulated: (a) olefin type epoxidation (one step) involving nucleophilic reaction of π electrons of the C=N bond,[7,8] (b) Baeyer–Villiger (two step) type, through cleavage of π bonding followed by the elimination of one molecule of carboxylic acid used as peroxy acid.[9]