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Nitrodienamines: An Easy Synthesis and [4+2] Cycloaddition Reactions with α,β-Unsaturated Carbonyl Compounds and Quinones

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The nitrodienamine **6** was synthesized through the vinamidinium salt **7**. The reactivity of **6** was investigated with the α,β-unsaturated carbonyls and styrene **8**—**14**, and the quinones **15**, **16**, **25**, **29**, **31**, **33**, **37**, and **41**.

Keywords——nitrodienamine; synthesis; cycloaddition; α,β-unsaturated carbonyl; quinone; vinamidinium salt

Considerable interest has been focused on the reactivities of nitroenamines because they may turn out to be useful intermediates in organic synthesis.[1] The center of interest in nitroenamine chemistry may lie in the enaminic character and the electronic "push-pull" nature. Reactions of nitrodienamines are also of interest from the viewpoint of the diene character, and also the analogy with nitroenamines. Nevertheless, only a few reports on the reactions of nitrodienamines have been published to date.[2,3] One reason may be the difficulty of preparation of nitrodienamines. This paper describes a new and easy synthesis of nitrodienamine and some reactions with α,β-unsaturated carbonyl compounds and quinones.

Two methods are available for the synthesis of nitrodienamines, namely, by the reaction of acetaldehydes with 1-dimethylamino-2-nitroethylene (**1**) and followed by treatment of the resulting 4-*aci*-nitrocrotonaldehyde (**2**) with pyrrolidinium acetate to give 1-nitro-4-pyrrolidino-1,3-butadiene (**3**),[2] and by treatment of the methylsulfate salt **5** of **4** with nitromethane to afford 1-(*N*,*N*-dimethylamino)-4-nitro-1,3-butadiene (**6**).[3] These syntheses present difficulties in terms of yields and purification procedures, because nitrodienamines are supposed to be unstable under chromatographic conditions. The present synthesis of the nitrodienamine **6** was performed as follows. Reaction of the aminoacrolein **4**, prepared from dimethylformamide in 72% yield, with dimethylamine gave the vinamidinium salt **7** in 85% yield,[4] and subsequent treatment of **7** with nitromethane in the presence of NaH and trimethylamine afforded the nitrodienamine **6**, in 81% yield. Overall yield from dimethylformamide to **6** was 50%, and purifications at all steps were performed by distillation and recrystallization.

Reactivities of the nitrodienamine **6** with α,β-unsaturated carbonyl compounds, quinones, and styrene **8**—**16** were investigated. Reactions were generally carried out under reflux in xylene until disappearance of the nitrodienamine. The results are shown in Chart 2 and Table I. Among the cycloadducts, the structures of **17**—**21** were identified by direct comparison with authentic samples,[5,6a] and the structures of **22** and **23** were postulated on the basis of spectroscopic analyses. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **22** shows the presence of three aromatic proton signals, that is, δ 7.48 (1H, dd, J=8.1 and 7.8 Hz), δ 8.09 (1H, dd, J=8.1 and 1.5 Hz), and δ 8.36 (1H, dd, J=7.8 and 1.5 Hz). The presence of two protons at lower field than δ 8.00 compared to α-tetralone suggests the structure of **22**. The structure of **23** was also similarly assigned from a comparison of the ^{1}H-

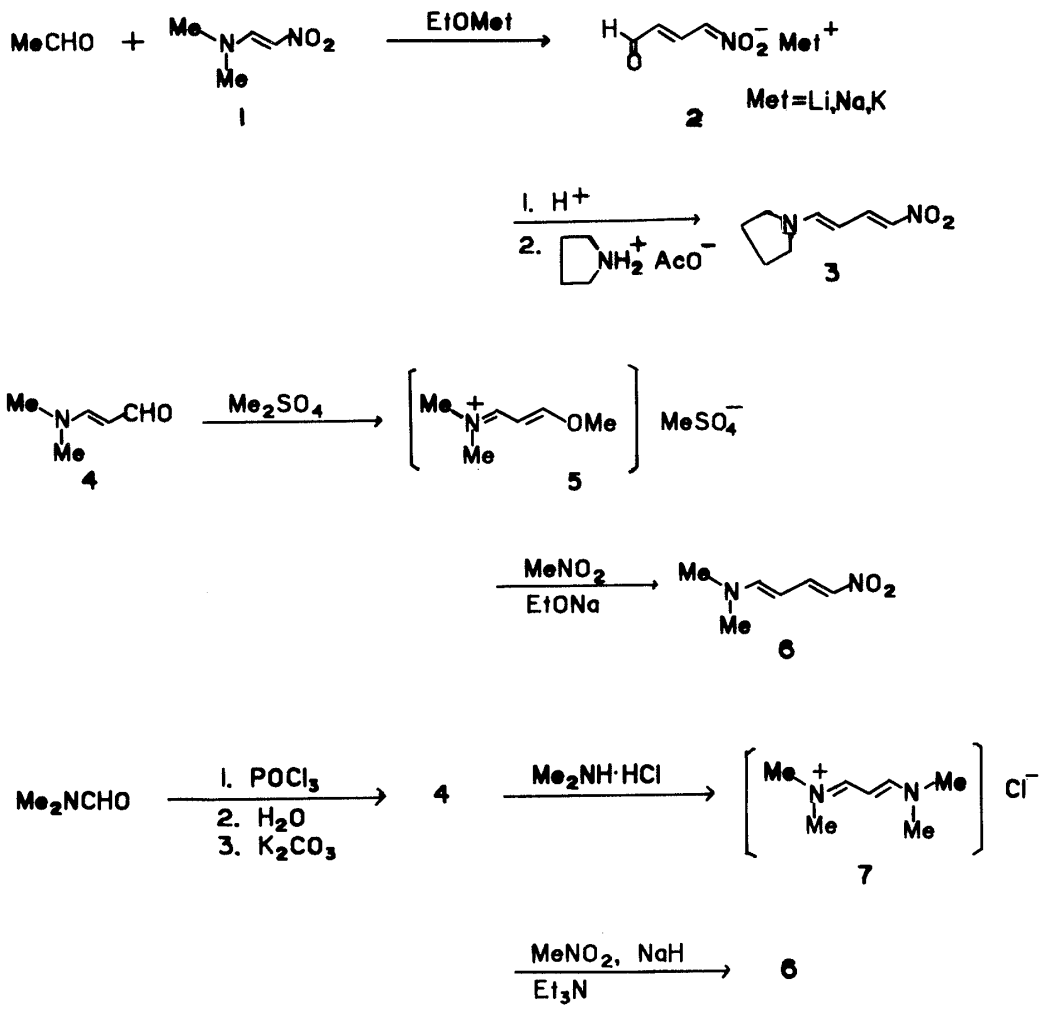

Chart 1

NMR signals with those of phthalide. These results also suggest the presence of site selectivity in this annelation reaction as shown in Chart 3.

Although reaction of **6** with *p*-benzoquinone in refluxing xylene gave a complex mixture, reaction of **6** with 1,4-naphthoquinone (**16**) in xylene at room temperature for 24 h afforded the cycloadduct **24** in 47.8% yield. This result is of interest in connection with synthesis of 9,10-anthraquinones. Thus, further investigations of **6** with several 1,4-naphthoquinones were performed. Reaction of **6** with juglone (**25**) at room temperature for 6 h gave the anthraquinone **26**, and the nitroanthraquinone **27**, in yields of 4.4% and 37.1%, respectively. Treatment of **27** with methyl iodide in the presence of silver oxide afforded the methylether **28**. Reaction of **6** with the methylether of jugulone (**29**) gave the annelation product **30** (46.3% yield) as a sole product. Regioselective formations of the nitroanthraquinones **28** and **30** are consistent with the common Diels–Alder reactions of jugulones where the regioselectivity of the annelation reaction may be controlled by the presence or absence of hydrogen bonding between the hydroxyl group and the ketone (Chart 3).[7] On the other hand, reaction of **6** with juglone acetate (**31**) afforded **26** and the mixed crystals A (mixture of **32** and **27**) in yields of 6.7% and 67.5%. Treatment of the mixed crystals A with methyl iodide in the presence of silver oxide yielded the methylethers of the 5-nitro derivative **28** and the 8-nitro derivative **30** in the ratio of 1 : 1. That is, formation of **27** in this reaction may be a result of the reaction of **25** produced by hydrolysis of **31** during the reaction.

Reactions of **6** with naphthazarins **33**, **37**, and **41** were also investigated. Reaction of

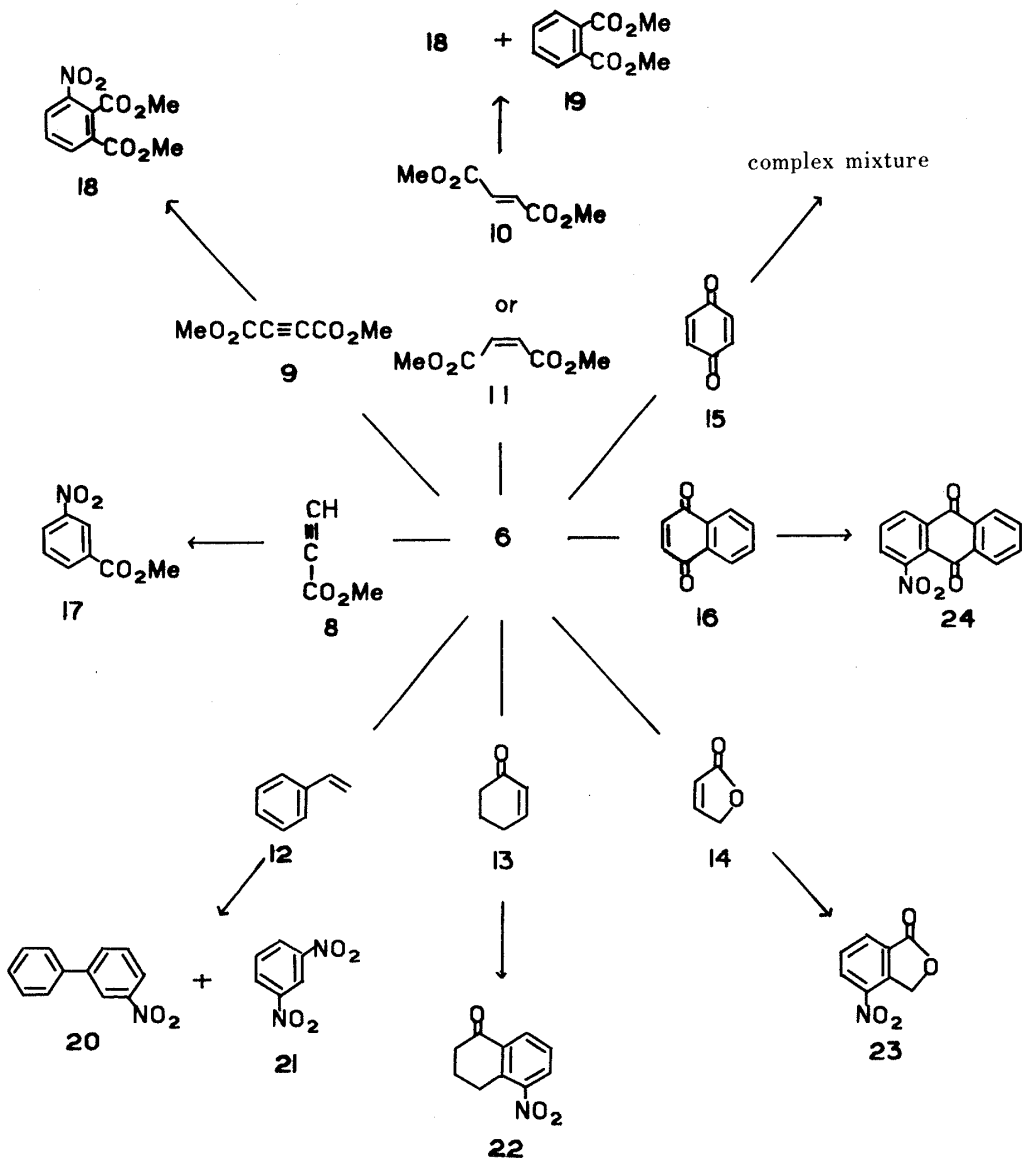

Chart 2

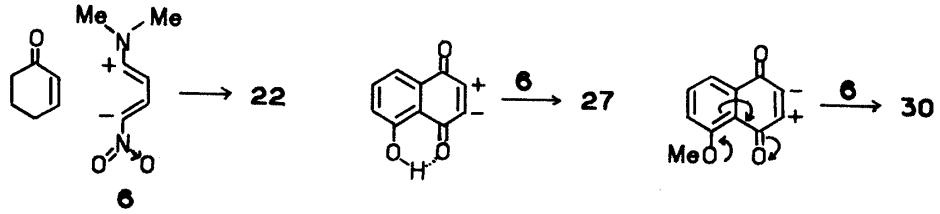

Chart 3

6 with naphthazarin (**33**) gave quinizarin (**34**), 5-nitroquinizarin (**35**), and 2-(*N*,*N*-dimethylamino)naphthazarin (**36**) in yields of 9.2%, 14.1%, and 24.9%, respectively. Treatment of **6** with naphthazarin dimethylether (**37**) afforded quinizarin dimethylether (**38**), 5-nitroquinizarin dimethylether (**39**), and dihydroxydimethoxynaphthalene **40**, in yields of 8.2%, 40.6%, and 24.6%, respectively. Finally, reaction of **6** with naphthazarin diacetate (**41**) gave quinizarin (**34**), 5-nitroquinizarin (**35**), and the mixed crystals B of monoacetates **42** and **43** in yields of 4.2%, 30.2%, and 53.2%, respectively. The mixed crystals B could be transformed to **35** by hydrolysis with diluted hydrochloric acid. Thus, the total yield of 5-nitroquinizarin from **6** and **41** was 80%.

TABLE I. The [4+2] Cycloaddition Reactions of Nitrodienamine, **6** with α,β-Unsaturated Carbonyl Compounds, Styrene, and Quinones

Initial compounds	Reaction products	Yield (%)	mp or bp (mmHg)
8	**17**	74.8	mp 74—75 °C
9	**18**	61.9	mp 67—68 °C
10	**18**	24.0	mp 67—68 °C
	19	66.3	bp 130—138 °C (20 mmHg)
11	**18**	9.6	mp 67—68 °C
	19	44.3	bp 130—138 °C (20 mmHg)
12	**20**	21.5	mp 57—58 °C
	21	39.2	mp 86—88 °C
13	**22**	36.4	mp 102—103 °C
14	**23**	12.3	mp 137—139 °C
15	Complex mixture		
16	**24**	47.8	mp 235—237 °C

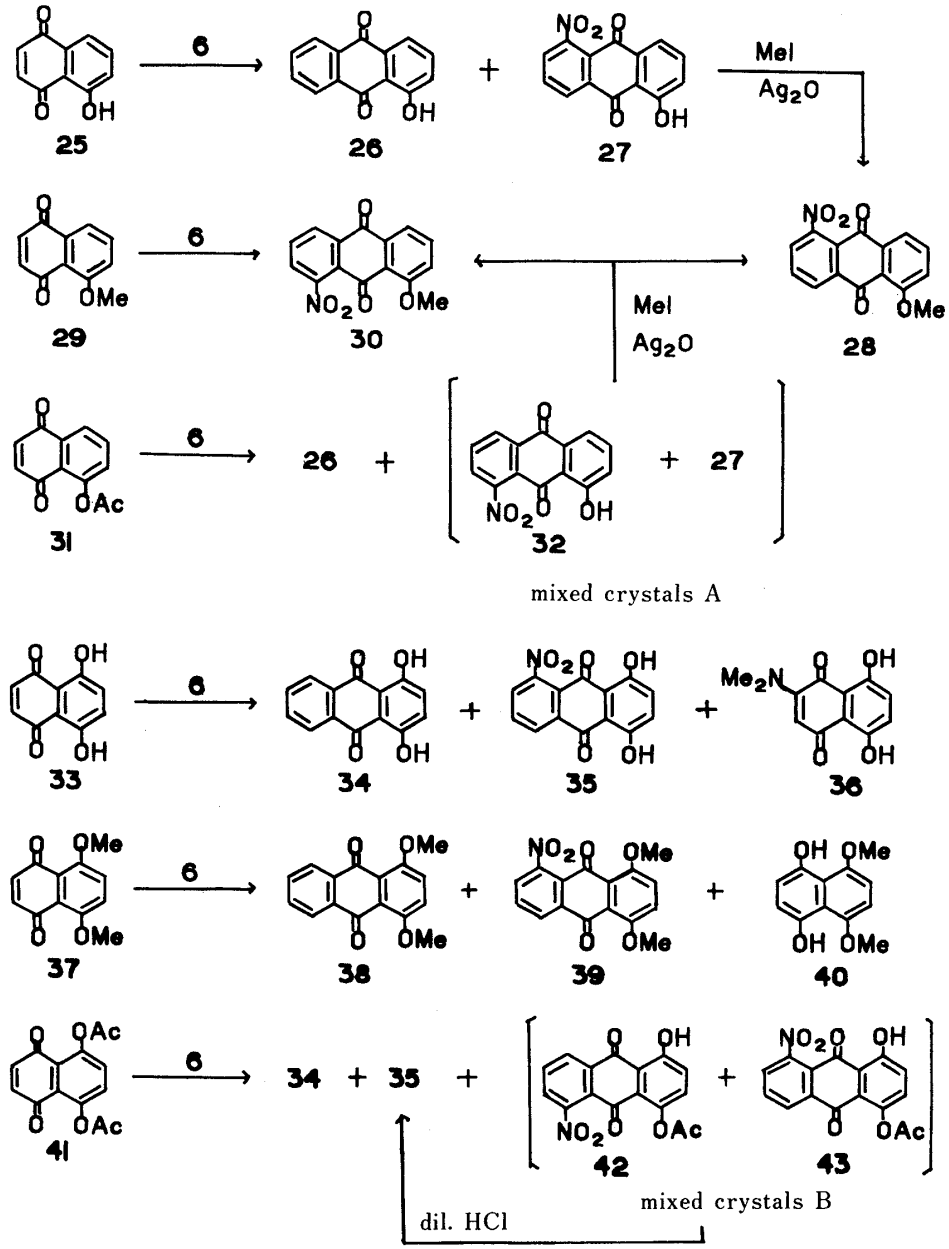

Chart 4

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded with a Hitachi 260-10 spectrometer, NMR spectra with a Varian T-60 or JEOL JNM-FX 100 spectrometer with tetramethylsilane as an internal standard, and mass spectra (MS) with a JEOL JMS-D 300 spectrometer. Elemental analyses were done by Ms. M. Takeda, Kissei Pharmaceutical Company, Ltd., Matsumoto, Japan. Mallinckrodt silica gel (100 mesh) and Merck Kieselgel G nach Stahl were used for column chromatography and thin layer chromatography (TLC), respectively.

1-(*N*,*N*-Dimethylamino)-4-nitro-1,3-butadiene (6)——A mixture of NaH (3.5 g) and triethylamine (200 ml) and then a solution of nitromethane (6.6 g) in tetrahydrofuran (THF, 300 ml) were added dropwise to a mixture of 1,1,5,5-tetramethyl-1,5-diazapentadienium chloride[4] (**7**, 16.3 g) and triethylamine (400 ml) with stirring at −15 °C under a nitrogen atmosphere. The whole was stirred at −15 °C for 30 min, and then heated at 60 °C for 48 h under the same conditions. The reaction mixture was cooled at room temperature and the resulting solids were removed by filtration. The filtrate was concentrated at 60 °C under a vacuum. The residue was recrystallized from hexane–ethyl acetate to yield 11.5 g (81.0%) of **6** as yellow-brown flaky crystals, mp 92—93 °C (lit.[3] mp 87 °C). IR (KBr) cm^{-1}: 1630, 1590. NMR ($CDCl_3$) δ: 3.02 (6H, s, $-NMe_2$), 5.17 (1H, t, J=12.4 Hz, olefinic H), 6.95 (1H, d, J=12.4 Hz, olefinic H), 7.00 (1H, d, J=12.4 Hz, olefinic H), 7.80 (1H, t, J=12.4 Hz, olefinic H). MS m/z: Calcd for $C_6H_{10}N_2O_2$ (M^+): 142.0742. Found: 142.0752.

General Procedure for Reactions of 6 with 8—14——A solution of **6** (1 mmol) and one of **8**—**14** (1.5 mmol) in dry xylene was refluxed for an appropriate period until the disappearance of **6** (checked by TLC). The reaction mixtures were concentrated under a vacuum, and then the residues were subjected to silica gel column chromatography with appropriate solvents.

Reaction with Methyl Propiolate (8)[2]——Reaction period: 8 h. Solvent for chromatography: 25% ethyl acetate in benzene. Product: 143 mg (74.8%) of methyl *m*-nitrobenzoate (**17**), light yellow prisms (hexane–ether), mp 74—75 °C (lit.[5] mp 78—80 °C).

Reaction with Dimethyl Acetylenedicarboxylate (9)——Reaction period: 2 h. Solvent for chromatography: 25% ethyl acetate in benzene. Product: 149 mg (61.9%) of dimethyl 3-nitrophthalate (**18**), yellow prisms (hexane–ether), mp 67—68 °C (lit.[6a] mp 68—69 °C).

Reaction with Dimethyl Fumarate (10)——Reaction period: 24 h. Solvent for chromatography: chloroform. Products: 129 mg (66.3%) of dimethyl phthalate (**19**), liquid, and 57 mg (24.0%) of **18**.

Reaction with Dimethyl Maleate (11)——Reaction period: 24 h. Solvent for chromatography: chloroform. Products: 86 mg (44.3%) of **19** and 23 mg (9.6%) of **18**.

Reaction with Styrene (12)——Reaction period: 72 h. Solvent for chromatography: 30% chloroform in benzene. Products: 33 mg (39.2%) of *m*-dinitrobenzene (**21**), yellow flaky crystals, mp 88—90 °C (lit.[5] mp 88—90 °C) and 43 mg (21.5%) of 3-nitrobiphenyl (**20**), yellow-brown needles (hexane–ether), mp 57—58 °C (lit.[5] mp 58—60 °C).

Reaction with 2-Cyclohexanone (13)——Reaction period: 24 h. Solvent for chromatography: benzene. Product: 70 mg (36.4%) of 5-nitro-α-tetralone (**22**), light yellow needles (hexane–ether), mp 102—103 °C. IR (KBr) cm^{-1}: 1680, 1605, 1530. NMR ($CDCl_3$) δ: 2.17 (2H, m, $-CH_2-$), 2.73 (2H, t, J=6.5 Hz, $-CH_2-$), 3.23 (2H, t, J=6.1 Hz, $-CH_2-$), 7.48 (1H, dd, J=8.1, 7.8 Hz, aromatic H), 8.09 (1H, dd, J=8.1, 1.5 Hz, aromatic H), 8.36 (1H, dd, J=7.8, 1.5 Hz, aromatic H). MS m/z: Calcd for $C_{10}H_9NO_3$ (M^+): 191.0582. Found: 191.0582. *Anal.* Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.94; H, 4.93; N, 7.27.

Reaction with γ-Butenolactone (14)——Reaction period: 60 h. Solvent for chromatography: chloroform. Product: 22 mg (12.3%) of 4-nitrophthalide (**23**), light yellow needles (hexane–ether), mp 137—139 °C. IR (KBr) cm^{-1}: 1755, 1630, 1600, 1525. NMR ($CDCl_3$) δ: 5.76 (2H, s, $-CH_2-$), 7.81 (1H, dd, J=8.1, 7.6 Hz, aromatic H), 8.30 (1H, dd, J=7.6, 1.0 Hz, aromatic H), 8.54 (1H, dd, J=8.1, 1.0 Hz, aromatic H). MS m/z: Calcd for $C_8H_5NO_4$ (M^+): 179.0218. Found: 179.0228. *Anal.* Calcd for $C_8H_5NO_4$: C, 53.64; H, 2.81; N, 7.82. Found: C, 53.77; H, 2.85; N, 7.73.

Reaction of 6 with 1,4-Naphthoquinone (16)——**16** (237 mg, 1.5 mmol) was added to a solution of **6** (142 mg, 1 mmol) in dry xylene (5 ml) and the whole was stirred at room temperature for 24 h. The reaction mixture was concentrated under a vacuum. The residue was subjected to silica gel chromatography. The benzene eluate gave 122 mg (47.8%) of 1-nitro-9,10-anthraquinone (**24**) as yellow needles (chloroform), mp 235—237 °C (lit.[6b] mp 230 °C).

Reaction of 6 with Juglone (25)——**25** (261 mg) was added to a solution of **6** (142 mg) in dry xylene (5 ml) and the whole was stirred at room temperature for 6 h. The reaction mixture was concentrated under a vacuum. The residue was subjected to silica gel chromatography. The first eluate with 50% chloroform in benzene gave 7 mg (4.4%) of 1-hydroxy-9,10-anthraquinone (**26**) as yellow needles (*N*,*N*-dimethylformamide (DMF)), mp 195—196 °C (dec.) (lit.[5] mp 196—198 °C (dec.)). The second eluate with 50% chloroform in benzene gave 70 mg (37.1%) of 1-hydroxy-5-nitro-9,10-anthraquinone (**27**) as yellow flaky crystals (DMF), mp 237—238 °C. IR (KBr) cm^{-1}: 1675, 1630, 1596, 1538. NMR ($CDCl_3$) δ: 7.35 (1H, dd, J=7.1, 2.2 Hz, aromatic H), 7.63—8.01 (4H, m, 4 × aromatic H), 8.53 (1H, dd, J=7.8, 1.5 Hz, aromatic H), 12.25 (1H, s, –OH). MS m/z: Calcd for $C_{14}H_7NO_5$ (M^+): 269.0322. Found: 269.0296. *Anal.* Calcd for $C_{14}H_7NO_5$: C, 62.46; H, 2.62; N, 5.20. Found: C, 62.56; H, 2.54; N, 5.18.

1-Methoxy-5-nitro-9,10-anthraquinone (28)——Ag_2O (30 mg) and methyl iodide (100 mg) were added to a solution of **27** (27 mg) in methylene chloride (2 ml) and the whole was stirred at room temperature for 24 h. The resulting solids were removed by filtration and the filtrate was concentrated. The residue was recrystallized from DMF to yield 27 mg (95%) of **28** as yellow needles, mp 265—267 °C. IR (KBr) cm^{-1}: 1680, 1590, 1530. NMR ($CDCl_3$) δ: 4.08 (3H, s, –OMe), 7.41 (1H, dd, J=8.4, 1.2 Hz, aromatic H), 7.72 (1H, dd, J=7.9, 1.3 Hz, aromatic H), 7.78 (1H, dd, J=8.4, 7.7 Hz, aromatic H), 7.89 (1H, t, J=7.9 Hz, aromatic H), 7.92 (1H, dd, J=7.7, 1.2 Hz, aromatic H), 8.48 (1H, dd, J=7.9, 1.3 Hz, aromatic H). MS m/z: Calcd for $C_{15}H_9NO_5$ (M^+): 283.0479. Found: 283.0464. *Anal.* Calcd for $C_{15}H_9NO_5$: C, 63.61; H, 3.20; N, 4.95. Found: C, 63.50; H, 3.14; N, 4.82.

Reaction of 6 with 5-Methoxy-1,4-naphthoquinone (29)——**29** (282 mg) was added to a solution of **6** (142 mg) in dry xylene (5 ml) and the whole was stirred at room temperature for 48 h. The reaction mixture was concentrated under a vacuum. The residue was subjected to silica gel chromatography. The eluate with 30% ethyl acetate in benzene gave 132 mg (46.3%) of 1-methoxy-8-nitro-9,10-anthraquinone (**30**) as yellow needles (DMF), mp 253—254 °C. IR (KBr) cm^{-1}: 1680, 1595, 1540. NMR ($CDCl_3$) δ: 4.03 (3H, s, –OMe), 7.38 (1H, dd, J=8.7, 1.1 Hz, aromatic H), 7.76 (1H, dd, J=8.7, 7.8 Hz, aromatic H), 7.78 (1H, dd, J=7.7, 1.7 Hz, aroamtic H), 7.85 (1H, t, J=7.7 Hz, aromatic H), 7.92 (1H, dd, J=7.8, 1.1 Hz, aromatic H), 8.43 (1H, dd, J=7.7, 1.7 Hz, aromatic H). MS m/z: Calcd for $C_{15}H_9NO_5$ (M^+): 283.0482. Found: 283.0489. *Anal.* Calcd for $C_{15}H_9NO_5$: C, 63.61; H, 3.20; N, 4.95. Found: C, 63.79; H, 3.08; N, 4.84.

Reaction of 6 with 5-Acetoxy-1,4-naphthoquinone (31)——**31** (324 mg) was added to a solution of **6** (142 mg) in dry xylene (5 ml) and the whole was stirred at room temperature for 48 h. The reaction mixture was worked up and then subjected to silica gel chromatography. The first eluate with 50% chloroform in benzene gave 15 mg (6.7%) of **26** as yellow needles (DMF). The second eluate with the same solvent afforded 182 mg (67.5%) of mixed crystals A (mixture of **32** and **27**), as yellowish orange flaky crystals (DMF), mp 240—245 °C.

Preparation of 28 and 30 from Mixed Crystals A——Ag_2O (300 mg) and methyl iodide (1 g) were added to a solution of mixed crystals A (182 mg) in methylene chloride (20 ml) and the whole was stirred at room temperature for 24 h. The resulting solids were removed by filtration and the filtrate was concentrated. The residue was subjected to silica gel chromatography. The first eluate with 30% ethyl acetate in benzene gave 89 mg (46%) of **30** as yellow needles (DMF). The second eluate with the same solvent afforded 96 mg (50%) of **28** as yellow needles (DMF).

Reaction of 6 with Naphthazarin (33)——**33** (285 mg) was added to a solution of **6** (142 mg) in dry xylene (5 ml) and the whole was stirred at room temperature for 12 h. The reaction mixture was concentrated under a vacuum. The residue was subjected to silica gel chromatography. The first chloroform eluate gave 22 mg (9.2%) of quinizarin (**34**) as orange needles (chloroform), mp 188—190 °C (dec.) (lit.[5] mp 191—193 °C (dec.)). The second chloroform eluate afforded 40 mg (14.1%) of 5-nitroquinizarin (**35**) as dark violet needles (DMF), mp 240—242 °C. IR (KBr) cm^{-1}: 1630, 1590, 1560, 1540. NMR ($CDCl_3$) δ: 7.38 (2H, s, 2 × aromatic H), 7.77 (1H, dd, J=8.0, 1.2 Hz, aromatic H), 8.00 (1H, t, J=8.0 Hz, aromatic H), 8.58 (1H, dd, J=8.0, 1.2 Hz, aromatic H), 12.36 (1H, s, –OH), 12.75 (1H, s, –OH). MS m/z: Calcd for $C_{14}H_7NO_6$ (M^+): 285.0273. Found: 285.0288. *Anal.* Calcd for $C_{14}H_7NO_6$: C, 58.96; H, 2.47; N, 4.91. Found: C, 59.11; H, 2.38; N, 4.83. The third chloroform eluate yielded 58 mg (24.9%) of 2-(*N*,*N*-dimethylamino)naphthazarin (**36**) as dark red needles (hexane–ethyl acetate), mp 158—160 °C. IR (KBr) cm^{-1}: 1610, 1560. NMR ($CDCl_3$) δ: 3.27 (6H, s, $-NMe_2$), 5.81 (1H, s, olefinic H), 7.08 (1H, d, J=9.0 Hz, aromatic H), 7.32 (1H, d, J=9.0 Hz, aromatic H), 12.11 (1H, s, –OH), 13.20 (1H, s, –OH). MS m/z: Calcd for $C_{12}H_{11}NO_4$ (M^+): 233.0644. Found: 233.0647. *Anal.* Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.57; H, 5.00; N, 6.24.

Reaction of 6 with 5,8-Dimethoxy-1,4-naphthoquinone (37)——**37** (327 mg) was added to a solution of **6** (142 mg) in dry xylene (5 ml) and the whole was stirred at room temperature for 12 h. The reaction mixture was concentrated under a vacuum. The residue was subjected to silica gel chromatography. The first chloroform eluate gave 58 mg (24.6%) of 1,4-dihydroxy-5,8-dimethoxynaphthalene (**40**) as light red needles (ethanol), mp 168—170 °C (lit.[8] mp 165.5—166.5 °C). The second chloroform eluate afforded 22 mg (8.2%) of 1,4-dimethoxy-9,10-anthraquinone (**38**) as orange needles (chloroform), mp 167—168 °C (lit.[6c] mp 170—171 °C). The third chloroform eluate gave 127 mg (40.6%) of 1,4-dimethoxy-5-nitro-9,10-anthraquinone (**39**) as red needles (chloroform), mp 197—198 °C. IR (KBr) cm^{-1}: 1675, 1600, 1575, 1540. NMR ($CDCl_3$) δ: 3.97 (3H, s, –OMe), 4.01 (3H, s, –OMe), 7.37 (2H, s, 2 × aromatic H), 7.77—7.83 (2H, m, 2 × aromatic H), 8.33—8.40 (1H, m, aromatic H). MS m/z: Calcd for $C_{16}H_{11}NO_6$ (M^+): 313.0587. Found: 313.0603. *Anal.* Calcd for $C_{16}H_{11}NO_6$: C, 61.35; H, 3.54; N, 4.47. Found: C, 61.27; H, 3.46; N, 4.38.

Reaction of 6 with 5,8-Diacetoxy-1,4-naphthoquinone (41)——**41** (411 mg) was added to a solution of **6** (142 mg) in dry xylene (5 ml) and the whole was stirred at room temperature for 24 h. The reaction mixture was concentrated under a vacuum. The residue was subjected to silica gel chromatography. The first eluate with 50% chloroform in benzene gave 10 mg (4.2%) of quinizarin (**34**) as orange needles (chloroform). The second eluate with the same solvent afforded 86 mg (30.2%) of **35** as dark violet needles (DMF). The third eluate with the same solvent provided 174 mg (53.2%) of mixed crystals B (mixture of the acetates **42** and **43**) as red flaky crystals (DMF), mp 195—198 °C.

Preparation of 35 from Mixed Crystals B——A mixture of mixed crystals B (174 mg) and 10% HCl (20 ml) was refluxed for 7 h. The reaction mixture was allowed to stand at room temperature. The separated crystals were collected and recrystallized from DMF to yield 150 mg (98.9%) of **35** as dark violet needles.

References

1) S. Rajappa, *Tetrahedron*, **37**, 1453 (1981).
2) Th. Severin and I. Ipack, *Chem. Ber.*, **109**, 3541 (1976).
3) Th. Severin and I. Ipack, *Chem. Ber.*, **111**, 692 (1978).
4) V. Nair and T. S. Jahnke, *Tetrahedron Lett.*, **25**, 3547 (1984).
5) This product was identified by comparison with an authentic sample obtained from a commercial supplier.
6) *a*) J. Buckingham, "Dictionary of Organic Compounds," Vol. 4, Chapman and Hall, New York, 1982, p. 4225; *b*) *Idem*, *ibid.*, Vol. 4, p. 4223; *c*) *Idem*, *ibid.*, Vol. 2, p. 1907.
7) V. H. Powell, *Tetrahedron Lett.*, **1970**, 3463; A. J. Birch and V. H. Powell, *ibid.*, **1970**, 3467; T. R. Kelly, L. Ananthasubramanian, K. Borah, J. W. Gillard, R. N. Goerner, Jr., P. F. King, J. M. Lyding, W. G. Tsang, and J. Vaya, *Tetrahedron*, **40**, 4569 (1984).
8) M. S. Pearson, B. J. Jensky, F. X. Greer, J. P. Hagstrom, and N. M. Wells, *J. Org. Chem.*, **43**, 4617 (1978).