added to 10 ml of acetic anhydride and 5 ml of acetic acid and then gently heated in a water bath. Ten minutes after the acetyl nitrate was added, the reaction was allowed to warm to room temperature. Water was then added and the reaction was worked up in a conventional manner. Preparative TLC of the product on silica gel eluting with hexane afforded 22 mg of nitronaphthalene (2) whose NMR was essentially identical with that of the analytical sample obtained by recrystallization from methanol (18.5 mg, 54% yield), mp 124.5–125.5°.

Anal. Calcd for $C_{26}H_{39}NO_2$: C, 78.98; H, 9.80; N, 3.40. Found: C, 78.89; H, 9.90; N, 3.43.

4-Bromo-1,3,6,8-tetra-*tert*-butylnaphthalene (3). A solution of 50 mg (0.14 mmol) of naphthalene 1[2] in 4 ml of anhydrous ether was cooled in an ice–salt bath (−3°) and treated with a solution of 110 mg (0.41 mmol) of dioxane dibromide in 4 ml of ether. The reaction was complete in 45 min. The solution was allowed to warm to room temperature, diluted with ether, washed with sodium thiosulfate solution, and worked up in the usual manner. Preparative TLC of the product on silica gel eluting with hexane afforded 41 mg of crude bromo product whose NMR was essentially identical with that of the analytical sample prepared by recrystallization from 80:20 ethanol–ethyl acetate (27 mg, 39%), mp 142.5–144.0°.

Anal. Calcd for $C_{26}H_{39}Br$: C, 72.72; H, 9.01; Br, 18.65. Found: C, 72.46; H, 9.14; Br, 18.68.

Debromination of Bromonaphthalene 3. A solution of 18 mg (0.04 mmol) of bromonaphthalene 3 in 2 ml of anhydrous ether was prepared in an oven-dried flask equipped with a serum cap. Excess butyllithium in hexane was then injected into the solution. After the resulting solution was stirred for 1.5 hr, 10 ml of water was added. The solution was then worked up in the normal way to afford 13 mg of naphthalene 1 identical with an authentic sample by TLC and NMR comparison.

5-Bromo-1,3,8-tri-*tert*-butylnaphthalene (6). To an anhydrous ether solution of 60 mg (0.2 mmol) of 1,3,8-tri-*tert*-butylnaphthalene (5)[2] was added an ether solution of 100 mg (0.4 mmol) of dioxane dibromide. The reaction was cooled in an ice–salt bath initially and then allowed to warm to room temperature over a 2-hr period. Work-up included washing the ether with 15% sodium thiosulfate. The crude product was an oil which was distilled in a Kugelrohr, oven temperature 120° (0.1 Torr), to afford 60 mg (90%) of bromonaphthalene 6 as a clear oil.

Anal. Calcd for $C_{22}H_{31}Br$: C, 70.57; H, 8.35; Br, 21.34. Found: C, 70.40; H, 8.36; Br, 21.32.

5-Iodo-1,3,8-tri-*tert*-butylnaphthalene (7). To a solution of 131 mg (1 mmol) of iodine and 50 mg (0.5 mmol) of naphthalene 5[2] in 3 ml of benzene was added 110 mg (0.5 mmol) of mercuric oxide (yellow). The mixture was stirred overnight after which time it became orange colored. Work-up afforded a mixture of product 7 (28 mg) and starting material which was separated by preparative TLC on silica gel. Crude 7 was rechromatographed on silica and then distilled at 65° and 1 Torr to yield 18 mg of a clear oil which was used as the analytical sample.

Anal. Calcd for $C_{22}H_{31}I$: C, 62.57; H, 7.35; I, 30.08. Found: C, 62.89; H, 7.60; I, 29.70.

Registry No.—**1**, 22495-86-9; **2**, 55669-70-0; **3**, 55669-71-1; **5**, 22495-89-2; **6**, 53535-11-8; **7**, 55669-72-2; acetyl nitrate, 591-09-3; dioxane dibromide, 21992-70-1.

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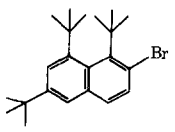

i

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Synthesis of Benzoquinone-1,4-aldehyde Diacetate

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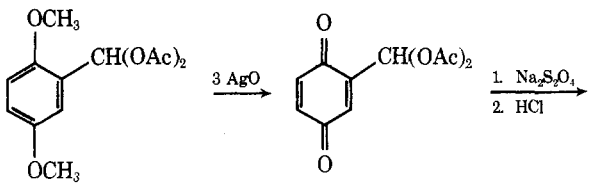
The oxidative demethylation of unsubstituted and several substituted hydroquinone and naphthohydroquinone ethers to give the corresponding quinones with argentic oxide (AgO) in excellent yields was reported by Rapoport and coworkers.[1] In our efforts related to the demethylation of 2,5-dimethoxybenzaldehyde,[2] we examined this method in order to see if benzoquinone-1,4-aldehyde could be readily obtained. Aldehydic groups are reported to remain intact under the specified mild reaction conditions.[1]

Treatment of 2,5-dimethoxybenzaldehyde with argentic oxide in the presence of nitric acid produced only small amounts of benzoquinone-1,4-aldehyde, as evidenced by the detection of traces of gentisaldehyde (by TLC) after reduction of the reaction products with sodium dithionite. In contrast, reaction of 2,5-dimethoxybenzaldehyde diacetate (1)[3] with 3 equiv of argentic oxide in the presence of 6 *N* HNO_3 produced the previously unreported benzoquinone-1,4-aldehyde diacetate (2) in 96% yield. The spectral data



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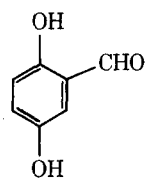

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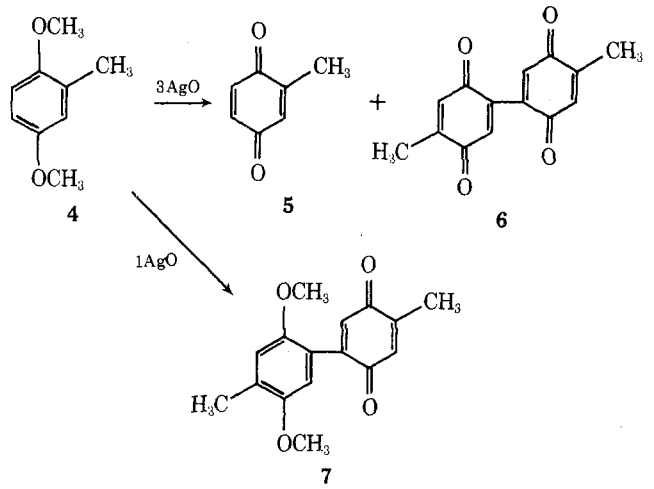
and elemental analysis agree with structure 2, and further proof was provided by the reduction of 2 with sodium dithionite, followed by hydrolysis to give gentisaldehyde (3) in 69% yield. In our attempts to further extend this method to monosubstituted alkylhydroquinone ethers, difficulties were encountered. For example, oxidation of 2,5-dimethoxytoluene (4) with argentic oxide gave a mixture of the expected methyl-1,4-benzoquinone (5) and 4,4′-dimethylbiphenyl-2,5,2′,5′-diquinone (6) in approximately equal amounts with an overall yield of 83%. The formation of 6 was due to the arylation of 5 by the starting ether 4, as evidenced by the isolation of 7, when only 1 equiv of argentic oxide was used. The formation of diquinones was also re-

ported in the oxidation of 1,4-dimethoxybenzene and 2,5-dimethoxytoluene with ceric sulfate and a threefold increase in diquinone was observed with the latter,[4] suggesting that with electron-donating substituents arylation becomes a competing pathway.

The reduction of the electron-donating ability of the methyl group by introducing two acetoxy groups in 1 changed the reaction to cause exclusive demethylation. However, the fact that arylation occurs with 1,4-dimethoxybenzene if ceric sulfate is being used as oxidizing agent, while argentic oxide produced exclusively 1,4-benzoquinone, indicates that the oxidative demethylation reaction is sensitive to both the substituent and the oxidizing agent used.



Experimental Section

Oxidative Demethylation of 2,5-Dimethoxybenzaldehyde Diacetate (1).[3] To a suspension of 3.4 g (27.4 mmol) of AgO (supplied by Alfa Inorganics) in a solution of 2.1 g (7.8 mmol) of 1 in 80 ml of THF (freshly distilled over CaH_2) under stirring was added 8 ml of 6 *N* HNO_3, and after 3 min (by this time all AgO was dissolved) the reaction mixture was diluted with 160 ml of chloroform and 40 ml of water and stirred. The organic layer was separated, washed with water, dried (anhydrous $MgSO_4$), and evaporated to give 1.8 g of 2 (96%), mp 88–90°. By TLC examination (8:2 benzene–ether, silica gel plate) it was found to be pure. A recrystallized (2-propanol) sample had mp 90–92°; NMR ($CDCl_3$) δ 2.13 (s, 6, $OCOCH_3$), 6.83 (s, 3, 1,4-benzoquinone), 7.61 [s, 1, $CH(OAc)_2$]; ir ($CHCl_3$) 1666 (1,4-benzoquinone C=O), 1765 cm^{-1} (acetate C=O).

Anal. Calcd for $C_{11}H_{10}O_6$: C, 55.46; H, 4.23. Found: C, 55.37; H, 4.20.

Formation of Gentisaldehyde (3) from 2. A solution of 1.0 g (42 mmol) of 2 in 200 ml of ether was shaken with aqueous sodium dithionite in a separatory funnel until the ether layer turned colorless. The ether layer was separated, washed with water, and stirred with 50 ml of 1 *N* HCl for 2 hr (the reaction was followed by TLC, silica gel plates, 8:2 benzene–methanol). From the ether layer 0.4 g (69%) of gentisaldehyde was isolated, mp 90–92°. It was found to be identical with an authentic sample of 3.

Oxidation of 2,5-Dimethoxytoluene (4). A. The oxidation was carried out with 0.3 g (2 mmol) of 4 using 0.86 g (6 mmol) of AgO and 3 ml of 6 *N* HNO_3 following the procedure given for 1, which yielded 0.2 g of solid from which were separated by trituration with ether, followed by recrystallization (2-propanol), 0.1 g (42%) of 6, mp 189–190° (lit.[4] mp 178.5–179.5°), as an ether-insoluble component and 0.1 g (41%) of 5, mp 64–65°, as an ether-soluble component. 5 was compared with an authentic sample. 6 was confirmed based on its NMR spectrum ($CDCl_3$): δ 2.08 (d, 6, CH_3), 6.70 (m, 2, 1,4-benzoquinone, H adjacent to methyl group), 6.78 (s, 2, 1,4-benzoquinone, H adjacent to carbonyl group).

Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.17; H, 4.10.

B. When 0.3 g of 4 was oxidized with 0.3 g (2 mmol) of AgO and 2 ml of 6 *N* HNO_3 in the manner described above, besides the unconverted 4 (separated by *n*-hexane trituration), 0.1 g (37%) of 7, mp 150–152°, was isolated, which melted at 154–155° after recrystallization from 2-propanol (lit.[5] mp 153°), NMR ($CDCl_3$) δ 2.03 (d, 3, CH_3 on quinone), 2.21 (s, 3, CH_3 on aromatic), 3.70 (s, 3, OCH_3), 3.73 (d, 3, OCH_3), 6.58 (m, 2, aromatic), 6.71 (m, 2, *p*-benzoquinone).

Registry No.—1, 55669-73-3; 2, 55669-74-4; 3, 1194-98-5; 4, 24599-58-4; 5, 553-97-9; 6, 4388-07-2; 7, 19965-46-9; silver oxide, 1301-96-8; sodium dithionite, 7775-14-6.

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Phenylcarbene from 3,5-Diphenyl-1-pyrazoline

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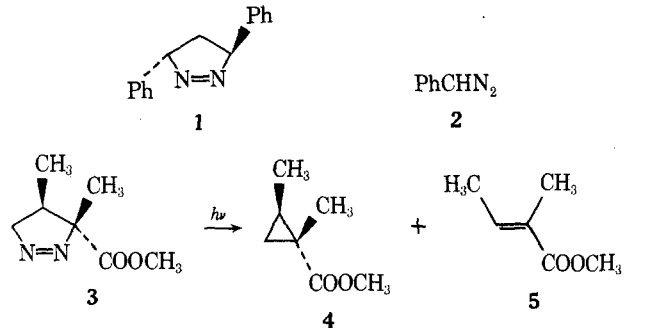
Thermal and photochemical extrusion of nitrogen from 1-pyrazolines has often been studied as a means of generating 1,3-diradicals.[1] In work directed toward observing such species,[2] we have recently noted an interesting alternate mode of decomposition in the case of *trans*-3,5-diphenyl-1-pyrazoline (1).

Previous workers[3–7] have suggested that retro-1,3-dipolar addition to give diazomethane (or a derivative) and an olefin may be a competing pathway of decomposition of some 1-pyrazolines. Thus, Rinehart and Van Auken[3] reported that irradiation of 3 gave methyl tiglate (5) as a side product in the formation of the cyclopropane (4). Their



conclusion was that a reversal of the formation of 3 from 5 and diazomethane had occurred, although direct fragmentation to methylene, nitrogen, and olefin could not be ruled out. Similarly, it has been suggested, based on product analysis, that several bicyclic pyrazolines decompose by retro-1,3-dipolar addition.[4,5]

In the present case, direct evidence is adduced for a carbene-generating pathway in the photolysis of 1. A triplet ESR spectrum was observed when 1 was irradiated for short periods with ultraviolet light at 5.5 K either neat or in dilute toluene solution (see Table I). The spectrum from the neat sample was identical with the phenylcarbene spectrum obtained by irradiating phenyldiazomethane under the same conditions.[8] In addition to the carbene spectrum, the samples of 1 and 2 in toluene also gave weak spectra at-