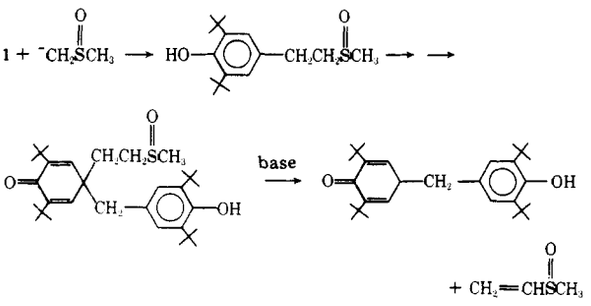
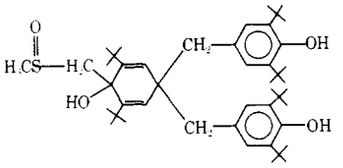


Attempts to trap methyl vinyl sulfoxide using anthracene, a Michael receptor, failed.

(10) We thank referee 1 for his fruitful comments and suggestions concerning the mechanism.

(11) This compound could not be unequivocally identified. Owing to its very low solubility, a satisfactory NMR spectrum could not be obtained, although it appeared to possess two different *tert*-butyl groups and a methyl group. The infrared spectrum (KBr) showed absorptions at 3618 and 3400 cm^{-1}, indicating both hindered and bound hydroxyl groups; a single peak at 1638 cm^{-1}, unlike the doublet characteristic of cyclohexadienones,[3] suggesting a nonconjugated double bond; and an absorption at 1020 cm^{-1} possibly due to a sulfoxide absorption. The mass spectrum gave an apparent parent ion at *m/e* 728 ± 4. A spray reagent used to detect sulfoxides on TLC plates[12] gave a positive test. Based upon these data, a possible structure would be an adduct between the dimsyl anion and **5**, e.g.



(12) J. S. Grossert and R. F. Langler, *J. Chromatogr.*, **97**, 83 (1974).

A Dramatic Solvent Effect in the Diels–Alder Reactions of Ortho Benzoquinones

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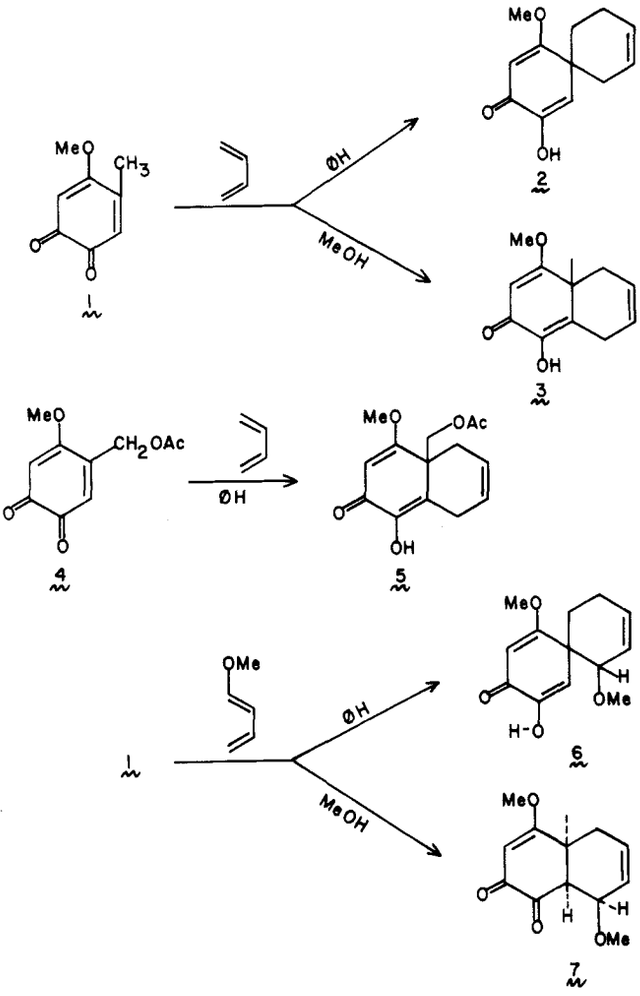
Conventional wisdom has it that solvent effects are of relatively nominal importance in determining the course of Diels–Alder reactions.[1] This might be expected in the light of the concerted nature perceived for the [2 + 4] cycloaddition process.[2]

Recently we have investigated the efficacy of 5-substituted 4-methoxy-1,2-benzoquinones as dienophiles.[3,4] Compound **1** reacts with 1,3-butadiene in benzene quite slowly. Upon heating at 105 °C (sealed tube) for 5 h, a 60% yield of "abnormal" adduct **2** was obtained.[3] Under these conditions we did not isolate any of the expected "normal" product **3**, though the absence of an authentic sample precluded a definitive statement as to whether small amounts of **3** might have been produced. Curiously, this "abnormal" process, involving enolization of the 5-alkyl group followed by cycloaddition to the tautomeric quinone methide,[5] is quite structure dependent since, under the same conditions, ortho quinone **4** gives only the expected product **5**.[4] In studying Diels–Alder reactions of compound **4**, we found that cycloaddition occurred more rapidly and efficiently when the reactions were conducted in methanol. Accordingly, it was of interest to examine the cycloaddition of **1** with 1,3-butadiene in this solvent.

Reaction of **1** with 1,3-butadiene in methanol at 100 °C (sealed tube) for 20 h gave, upon rapid chromatography on Florisil, a 63% yield of a crystalline 1:1 adduct, mp 103.5–104 °C, whose spectral properties clearly define it to be the "expected" product, **3**.[6] Examination of the NMR spectrum of the crude reaction mixture indicated the presence of ca. 12% of abnormal adduct **2**.[7] Thus a pronounced solvent effect is observed in promoting the course of the two modes of Diels–Alder reaction of **1** with 1,3-butadiene.[8]



A similar trend was observed in studying the cycloaddition of **1** with *trans*-1-methoxybutadiene. In benzene, upon heating under reflux for 6 h, a 37% yield of spiro adduct **6**, mp 110–111 °C, is obtained.[9] Since the compound is rather unstable to chromatography, a clearer definition of the competing processes was provided by examination of the NMR spectrum of the crude reaction mixture. This indicated a 5:1 ratio of **6**:**7** (vide infra). Conversely, when the reaction was conducted in methanol under reflux, a 67% yield of normal adduct **7**, mp 118.5–119.5 °C, was obtained after chromatography on Florisil. NMR analysis prior to chromatography indicated the ratio of **6**:**7** to be ca. 1:10.[7]

We have studied the effect of mixed solvents on the course of these cycloadditions. Using a 1:1 molar mixture of methanol–benzene (100 °C, sealed tube) reaction of **1** with butadiene gave essentially the same product distribution (**7** ≫ **6**) as with pure methanol. However, reaction of **1** with 1-methoxybutadiene in 1:1 molar methanol–benzene gave ca. a 1:1 mixture of **7**:**6**.

Clearly, these data do not allow for a precise definition of the role of solvents in determining the course of Diels–Alder products. However, they suggest that solvent manipulation may be of more useful consequence in producing desired results than has been hitherto supposed.

Experimental Section[10]

Diels–Alder Reaction of Quinone (1) with 1,3-Butadiene in Absolute Methanol. Formation of *dl*-1-Hydroxy-4-methoxy-

4a-methyl-4a,5-dihydronaphthalen-2(8*H*)-one (3). A solution of 0.250 g (1.65 mmol) of quinone 1 in 5 mL of absolute methanol and 3.5 mL of 1,3-butadiene was heated in a sealed glass tube at 100 °C for 20 h. The color changed from red-orange to light yellow during this time. Evaporation of the volatiles left a residue which was *rapidly* chromatographed on 30 g of Florisil. Elution with 3:1 hexane–ethyl acetate afforded 0.214 g (63%) of adduct **3.** Washing with pentane gave analytically pure material: mp 103.5–104 °C; λ_{max} ($CHCl_3$) 2.86, 6.20 μ; δ ($CDCl_3$, 250 MHz) 1.38 (s, 3), 2.11 (d, J = 17.5 Hz, 1), 2.56 (dd, J = 17.5, 4 Hz, 1), 2.86 (d, J = 20 Hz, 1), 3.45 (d, J = 20 Hz, 1), 3.78 (s, 3), 5.66 (s, 1), 5.67–5.75 (m, 2), 6.70 (s, 1 exchanges with D_2O).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.62; H, 6.74.

Diels–Alder Reaction of Quinone (1) with 1-Methoxy-1, 3-butadiene in Absolute Methanol. Preparation of *dl*-4aα-Methyl-8aα-4,8β-dimethoxy-1,2,4a,5,8,8a-hexahydronaphthalene-1,2-dione (7). To a solution of 0.200 g (1.32 mmol) of quinone 1 in 5 mL of absolute methanol was added 0.331 g (3.95 mmol] of 1-methoxy-1,3-butadiene (Aldrich). The orange solution was heated under reflux under a nitrogen atmosphere for 6 h. During this time the color became yellow. The solution was cooled and the volatiles removed in vacuo to afford a brown solid which upon trituration with pentane containing a small amount of ether gave 0.206 g (67%) of adduct (7), as an off-white crystalline solid: mp 118.5–119.5 °C; λ_{max} ($CHCl_3$) 5.80, 6.06, 6.23 μ; δ ($CDCl_3$, 250 MHz) 1.34 (s, 3), 1.71 (d, J = 15 Hz, 1), 2.85 (d,d J = 15, 6 Hz, 1), 3.09 (d, J = 9 Hz, 1), 3.23 (s, 3), 3.81 (s, 3), 4.00 (d, J = 9 Hz, 1), 5.78 (s, 1), 5.80–5.99 (m, 2).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.07; H, 6.78.

Diels–Alder Reaction of Quinone (1) with 1-Methoxy-1,3-butadiene in Benzene. Formation of Spiro Adduct (6). To a solution of 0.150 g (0.99 mmol) of quinone (1) in 6 mL of benzene was added 0.250 g (2.96 mmol) of 1-methoxy-1,3-butadiene. The solution was heated under reflux for 6 h. The reaction mixture was cooled and the volatiles evaporated in vacuo to give an oil. This was *rapidly* chromatographed on 20 g of Florisil. Elution with 3:1 hexane–ethyl acetate afforded 0.087 g (37%) of spiro adduct (6): mp 110–111 °C; λ_{max} ($CHCl_3$) 6.11, 6.38 μ; δ ($CDCl_3$, 60 MHz) 1.8–3.0 (m, 5), 3.4 (s, 3), 3.9 (s, 3), 5.1 (m, 1) 5.6 (s, 1), 5.9–6.1 (m, 2), 6.8 (q, 1).

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.96; H, 6.81.

Diels–Alder Reaction of Quinone (1) with 1,3-Butadiene in 1:1 Molar Ratio Benzene–Absolute Methanol. A solution of 0.100 g (0.66 mmol) of quinone (1), 2 mL of 1,3-butadiene, and 2 mL of a 1:1 molar ratio solution of benzene–absolute methanol was heated at 100 °C in a sealed glass tube for 20 h. The color changed from red-orange to a light yellow during this time. Evaporation of the volatiles gave an oil which was *rapidly* chromatographed on 12 g of Florisil. Elution with 3:1 hexane–ethyl acetate afforded 0.075 g (56%) of adduct **3.**

Diels–Alder Reaction of Quinone (1) with 1-Methoxy-1,3-butadiene in 1:1 Molar Ratio Benzene–Absolute Methanol. To a solution of 0.100 g (0.66 mmol) of quinone (1) in 2 mL of 1:1 molar ratio solution of benzene–methanol was added 0.175 g (3.16 equiv, 2.08 mmol) of 1-methoxy-1,3-butadiene. The solution was heated under reflux under N_2 for 6 h. The volatiles were removed completely in vacuo to give an oil which could not be crystallized. The crude NMR spectra of this material showed it to be a mixture of adduct **7** and spiro adduct 6 in a ratio of approximately 1:1.

Acknowledgments. These studies were supported by PHS Grant CA-12107-10-12 and by a grant from the Merck Corp. NMR spectra were obtained on facilities supported by PHS Grant RR-00292-08. The assistance of Mr. Vance Bell and Mr. Glen Herman in obtaining mass spectra is gratefully acknowledged.

Registry No.—1, 13523-09-6; **3**, 62006-21-7; **6**, 62006-22-8; **7**, 62006-23-9; 1,3-butadiene, 106-99-0; methanol, 67-56-1; 1-methoxy-1,3-butadiene, 3036-66-6; benzene, 71-43-2.

References and Notes

(1) For the effect of solvent polarity on endo–exo ratios in Diels–Alder reactions see J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962); K. Nakagawa, Y. Ishii, and M. Ogawa, *Chem. Lett.*, 511 (1976).
(2) See S. Seltzer, *Adv. Alicyclic Chem.* **2**, 1 (1960).
(3) S. Mazza, S. Danishefsky, and P. M. McCurry, *J. Org. Chem.*, **39**, 3610 (1974).
(4) S. Danishefsky, P. F. Schuda, S. Mazza, and K. Kato, *J. Org. Chem.*, **41**, 3468 (1976).
(5) Cf. inter alia (a) L. F. Fieser and C. K. Bradsher, *J. Am. Chem. Soc.*, **61**, 417 (1939); (b) L. F. Fieser and M. Fieser, *ibid.*, **61**, 596 (1939); (c) W. Brown, J. W. A. Findlay, and A. B. Turner, *Chem. Commun.*, 10 (1968); (d) S. M. Ali and A. B. Turner, *J. Chem. Soc., Perkin Trans. 1*, 2225 (1974).
(6) As previously observed[4] the normal adducts of orthoquinones with 1,3-butadiene exist as the diosphenols while those derived from *trans*-1-methoxy-1,3-butadiene exist in the α-diketone form.
(7) Unfortunately, in our hands, these products are unstable to column or gas chromatography. Only the major components are isolated after substantial loss by rapid chromatography on Florisil. Product ratios are thus approximate and are based on integration of the angular methyl signal of the normal adducts relative to the methoxy signals of both compounds.
(8) For a report indicating that Diels–Alder cycloaddition to quinones (though not acid catalyzed) occurs faster in ethanol than in benzene see A. Wasserman, *J. Chem. Soc.*, 828 (1935).
(9) The stereochemistry of the secondary methoxyl group is unassigned. Apparently only a single isomer is produced in the "normal" mode.
(10) Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded in chloroform solution using sodium chloride optics on either a Perkin-Elmer 137 infrared spectrophotometer or a Perkin-Elmer 247 infrared spectrophotometer. The polystyrene absorption at 6.238 μ was used as a reference. Only selected high intensity absorptions are reported. The NMR spectra were measured in $CDCl_3$ with tetramethylsilane as an internal reference. Chemical shifts are reported in parts per million (δ) relative to Me_4Si. Elemental analyses were conducted by Galbraith Laboratories, Inc., Knoxville, Tenn.

Studies on *N*-Alkyl-2(1*H*)-pyridothione. 1. A New Synthetic Method for Thiols

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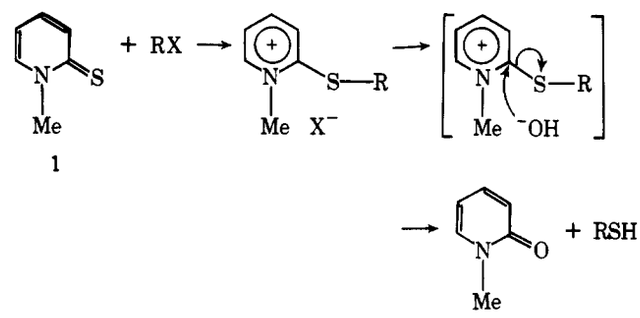
Widely used laboratory methods for the preparation of thiols are the reaction of alkyl halides with sodium hydrosulfide[1] or thiourea with subsequent alkaline hydrolysis,[2] and the direct alkylation of free sulfur with aryllithium[3] or Grignard reagents.[4] Although the thiourea method has been generally employed in preparative scale, α-mercaptocarbonyl compounds cannot be obtained because of thiazole formation.[5]

In this laboratory, the chemistry of *N*-methyl-2-alkylthiopyridinium salts has been investigated as an extension of studies on *N*-(ω-haloalkyl)pyridinium salts.[6] It was found in preliminary experiments that *N*-methyl-2(1*H*)-pyridothione



(1) reacted readily with alkyl halides to give the corresponding 2-alkylthiopyridinium salts, which were very labile under alkaline conditions.

We now wish to describe briefly a new preparative method for various kinds of thiol by alkaline hydrolysis of these salts, which are activated intermediates similar to *S*-thiouronium salts.[2] Primary and secondary halide, α-halo ketone, α- and β-halocarboxylic ester, and halo sugar were employed as alkyl halide for quaternization.

A series of the key intermediates, *N*-methyl-2-alkylthiopyridinium salts, was synthesized in refluxing ethanol in yields of 81–84% (see Table I). A little higher temperature (in