oxolane, 3308-98-3; potassium phthalimide, 1074-82-4; 2-(3-phthalimidopropyl)-2-phenyldioxolane, 3308-99-4; 2-hydroxy-2-phenylpyrrolidine, 73434-11-4; 2-phenyl-1-pyrroline, 700-91-4; 2-phenylpyrrolidine, 1006-64-0; pivalyl chloride, 3282-30-2; phenyllithium, 591-51-5; 1,3,3-trimethylazetidine-2,2-d_2, 73453-13-1; β-chloropivalyl chloride, 4300-97-4; methylamine, 74-89-5; *N*-methyl-3-chloropivalamide, 73434-12-5; ethyl benzoate, 93-89-0; benzyl-α,α-d_2 alcohol, 21175-64-4; benzyl-α,α-d_2 bromide, 51271-29-5; dibenzyl-α,α-d_2-dimethylammonium bromide, 73434-13-6; benzyldimethylamine, 103-83-3; pentylbenzene, 538-68-1; *trans*-stilbene, 103-30-0; pentylbenzene-α,α-d_2, 68639-74-7; benzyldimethylamine-α-*d*, 3535-98-6; benzyldimethylamine-α,α-d_2, 38161-07-8; 2,2-dimethyl-3-(*N*-methylbenzamido)propanal, 15451-21-5; 3,3-dimethyl-4-(*N*-methylbenzamido)-2-butanol, 73434-14-7; 4-(methylamino)-3,3-dimethyl-2-butanol, 73434-15-8; 1-(methylamino)-2,2-dimethyl-3-sulfatobutane, 73434-16-9.

Catalytic Asymmetric Induction in Oxidation Reactions. Synthesis of Optically Active Epoxynaphthoquinones

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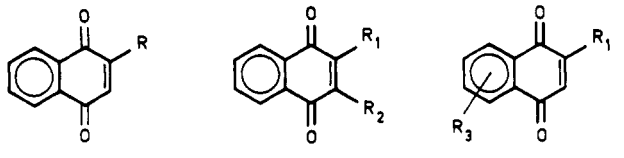
Optically active 2,3-epoxides of a variety of substituted 1,4-naphthoquinones have been prepared in an asymmetric synthesis. Enantiomeric excesses of up to 45% were realized. Some data could be obtained concerning the influence of substituents on the enantiomeric excess. Furthermore, the absolute configurations could be deduced from the CD spectra.

The roles of vitamin K[1,2] and its epoxide[3,4] are of considerable current interest. Since many quinones and a few quinone epoxides have been shown to possess antimicrobial and antitumor activity and since the quinone epoxides seem to play an important role in metabolic processes, the synthesis of *optically active*[5] quinone epoxides seemed to us to be an important goal.

The preparation of chiral epoxides in good optical yields is difficult and often tedious. Epoxides do not lend themselves to the classical method of diastereomeric resolution unless the compounds contain an additional functional group. Consequently, asymmetric synthesis using chiral peracids or metal catalyzed epoxidations using peroxides have been the subject of much activity.[6a-c] Recently electron-deficient olefins (e.g., chalcones, quinones) have been epoxidized with H_2O_2 or *t*-BuOOH in an asymmetric synthesis, using quinine salts as chiral catalysts, in optical yields of up to 55%.[7a-c]

The reactions have been carried out under phase-transfer conditions. The great versatility of phase-transfer catalysts has provided a stimulus for extensions into the area of catalytic asymmetric synthesis.

Chiral catalysts based on alkaloids or amino acid salts have produced modest but encouraging results.[8] That this reaction is a true counterion effect rather than a solvent effect is shown by the zero optical yields achieved under non-phase-transfer conditions in the presence of quinine. In the present study the above-described phase-transfer epoxidation method has been applied to a great variety of naphthoquinones. To obtain a better insight into the influence of substituents on the enantiomeric excess by the epoxidation reaction, we synthesized naphthoquinones with different substituents at carbon two (see Tables I and II).



Additionally, 2,3-disubstituted and 2,5-, 2,6-, and 2,7-disubstituted 1,4-naphthoquinones were prepared. In order to correlate the reaction mechanism, the structure of substrate, and the extent of asymmetric induction, i.e., enantiomeric excess, one must determine a number of parameters. In addition to the knowledge of the absolute configuration of the product, the influence of minor structural variations on the enantiomeric excess needs to be cleared up.

Synthesis of Starting Materials

For the synthesis of substituted 1,4-naphthoquinones several protocols are possible. The classical method is the oxidation of substituted naphthalenes by means of chromic anhydride in acetic acid.[9a] Other oxidants such as H_5IO_6[9b] and H_2O_2[9c] have also been used. A disadvantage of this method is the low yield (normally lower than 30%) as well

(1) R. W. McKee, S. B. Binkley, D. W. MacCorquodale, S. A. Thayer, and E. A. Doisy, *J. Am. Chem. Soc.*, **61**, 1295 (1939).
(2) J. W. Suttie, A. E. Lawson, L. M. Canfield, and T. L. Carlisle, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **37**, 2605 (1978).
(3) J. T. Matschiner, R. G. Bell, J. M. Amelotti, and T. E. Knauer, *Biochim. Biophys. Acta*, **201**, 309 (1970).
(4) A. K. Willingham and J. T. Matschiner, *Biochem. J.*, **140**, 435 (1974).
(5) Although the synthesis and study of 2,3-epoxy-1,4-naphthoquinones parallels that of vitamin K_1, no one appears to have considered the possible chirality of the vitamin K 2,3-epoxides. Since successful resolution attempts with racemic 1,4-naphthoquinone 2,3-epoxides have not been reported, the asymmetrically catalyzed epoxidation appears to be the only in vitro route to the chiral epoxides.
(6) (a) A. O. Chong and K. B. Sharpless, *J. Org. Chem.*, **42**, 1587 (1977); (b) S. Yamada, T. Mashiko, and S. Terashima, *J. Am. Chem. Soc.*, **99**, 1988 (1977); (c) R. C. Michaelson, R. E. Palermo, and K. B. Sharpless, *ibid.*, **99**, 1990 (1977).
(7) (a) R. Helder, J. C. Hummelen, R. W. P. M. Laane, J. S. Wiering, and H. Wynberg, *Tetrahedron Lett.*, 1831 (1976); (b) H. Wynberg, *Chimia*, **30**, 445 (1976); (c) H. Wynberg and B. Greydanus, *J. Chem. Soc., Chem. Commun.*, 427 (1978).
(8) J.-C. Fiaud, *Tetrahedron Lett.*, 3495 (1975).
(9) (a) P. P. T. Sah, *Recl. Trav. Chim. Pays-Bas*, **59**, 461 (1940); (b) A. J. Fatiadi, *Chem. Commun.*, 1978 (1967); (c) T. Arnold and R. Lawson, *J. Org. Chem.*, **5**, 250 (1940).

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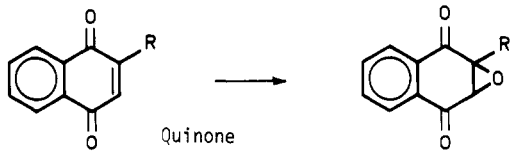
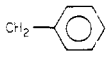
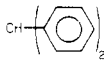
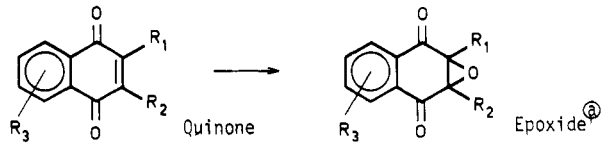
Table I



	R	method[a]	quinone yield,[d] %	quinone mp,[d] °C	epoxide yield,[d] %	epoxide mp,[d] °C	$[\alpha]^{21}_{436}$	ee[b]
a	CH_3	A[c]	40	105.5	60-70	96-97	-6.8	~5
			40[24]	105-106.5[24]		96-96.5[25]		
b	C_2H_5	A	40	87-88	50-60	49-50	-12.3	10
			37[26]	87-88[26]		50.5-51[25]		
		C	65	86-88	76	34-35	-12.8	14
c	C_3H_7	D	60	37-38.5		34-35[25]		
				38-39[27]				
d	i-C_3H_7	D	50	44.5-46	74	30-31	-12.1	31
				45.5-46.5[28]		30-31[29]		
e	C_4H_9	D	77	45-46	67	39-40	-10.6	18
				46-47[30]				
f	i-C_4H_9	D	76	50.5-52	60	oil	-6.5	16
g	t-C_4H_9	D	55	75-76,	60	65-66	+7.3	23
				76-77[31]		65-66[25]		
h	C_5H_{11}	A	30	32.5-33.5	64	22-23	-13.7	19
				33.5-35[30]				
		D	60	33-34				
i	C_6H_{13}	D	60	50-52	60	49-49.5	-15.4	24
				51-52[32]				
j		C	57	87-89	85	78-79	+2.8	39
			60[33]	87-88[33]				
		D	70	86-88				
k	$CH_2CH=C(CH_3)_2$	D	53	63-64	53	oil	+7.5	27
			58[34]	62[34]				
l		D	60	83-84	66	109-110	-4.9	23
				82[35]		110-111[25]		
m		D	40	188.5-189	100	134-135	-39.1	30
				189[36]				
n		A	69	110-111	92	62-63	-55.1	45
				109-110[37]		63[38]		

[a] The methods used are described in the Experimental Section. [b] The enantiomeric excess was determined by using $Eu(CDM)_3$ as shift reagent; ee ± 5%. [c] 2-Methyl-1,4-naphthoquinone can be obtained commercially from Aldrich. [d] Literature yield and melting points are indicated by footnotes.

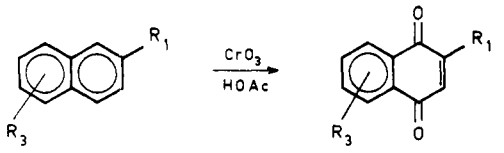
Table II



	R_1	R_2	R_3	method[a]	quinone yield, %	quinone mp,[e] °C	epoxide yield, %	epoxide mp,[e] °C	$[\alpha]^{21}_{436}$	ee[b]
a	CH_3	H	5-CH_3	A	41	93-94	40	125-126	-10.3	18
						94[39]				
b	CH_3	H	6-CH_3	A	35	136.5-137.5	70	97.5-98.5	-6	5
						136-137[40]		97-98[26]		
c	CH_3	H	7-CH_3	B	55	114-115	65	91.5-92	-4.8	5
						114-115[40]		91-92[26]		
d	CH_3	H	5-OCH_3	c	90	97.5-98.5	35	107-108	+10.6	12
						94[42]				
e	CH_3	C_2H_5	H	D	56	69-70.5	65	45-46	~0	d
						72-73[43]				
f	CH_3	C_4H_9	H	D	63	68-69	35	oil	-2.8	d

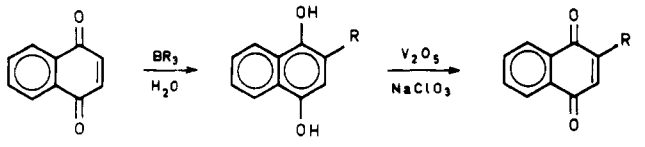
[a,b] See Table I. [c] 5-Hydroxy-2-methyl-1,4-naphthoquinone was methylated in 90% yield by Ag_2O/CH_3I.[41] [d] The enantiomeric excess was not determined, but is most probably low. [e] Literature melting points are indicated with a footnote.

as the difficult accessibility of substituted naphthalenes.



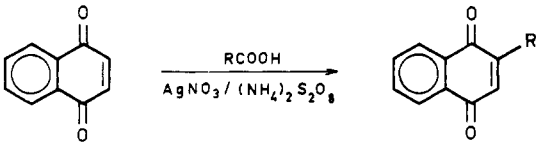
Method A + B

The method of Kabalka[10] is based on the facile addition of a wide variety of trialkylboranes to 1,4-naphthoquinone, producing high yields of the corresponding 2-alkylhydroquinones after hydrolysis. The hydroquinones thus obtained can readily be oxidized[11] to the quinones.



Method C

Finally, the method of Jacobsen and Torssell[12] can be used. This method involves the decarboxylation of carboxylic acids with ammonium persulfate. The alkyl radicals formed are scavenged by quinones, thus producing alkylated quinones in reasonable yields.



Method D

The latter two methods have the unfavorable condition that 2,3-disubstituted naphthoquinones are formed as byproducts. However, these side products can usually be suppressed by careful regulation of the reaction conditions. We have found the method of Jacobsen to be the method of choice (Tables I and II list the quinones prepared).

Results

In the present study the original chirally catalyzed epoxidation method[7] (e.g., 30% hydrogen peroxide, aqueous sodium hydroxide, and benzylquininium chloride) was used. In spite of the possibility of degradation reactions, the epoxides normally could be obtained in good yields. Increased bulkiness of the alkyl substituents seemed to diminish the ease of cleavage (e.g., the yield of the 2-(diphenylmethyl)-1,4-naphthoquinone 2,3-epoxide was almost quantitative after 24 h of reaction). Only when labile epoxides were formed (i.e., from naphthoquinones containing hydroxy or methoxy groups) were no epoxides isolated.

Optical yields of up to 45% could be obtained. The enantiomeric excess of the asymmetric synthesis was determined by ^{1}H NMR with Eu(DCM)$_3$[19] as shift reagent, which gave distinct signals for the two enantiomers. The commercially available Eu(TFC)$_3$ gave hardly any shift and no splitting of the signals. The proton adjacent to the epoxide ring at C-3 gives a sharp singlet, which gives two distinct signals for the two enantiomers when complexation with the shift reagent takes place (Figure 1). The results are summarized in Tables I and II.

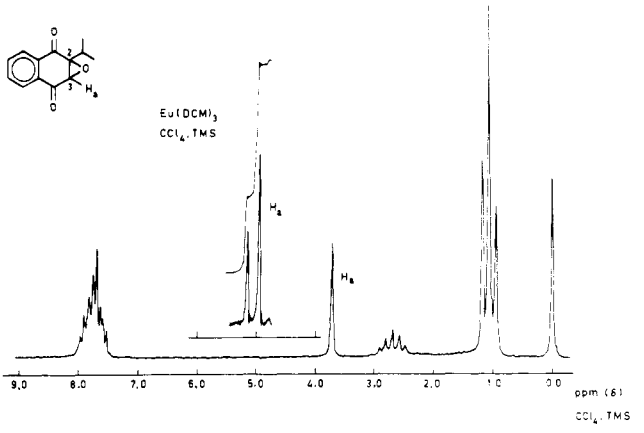


Figure 1. ^{1}H NMR spectrum.

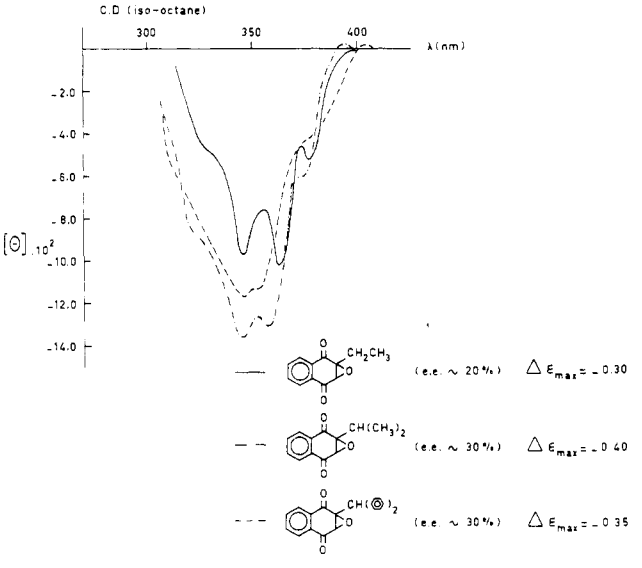


Figure 2. CD spectra.

The UV absorption spectra exhibited three absorption bands in isooctane at about 305, 265, and 235 nm. A very weak absorption band at about 340 nm ($\epsilon \sim 200$) can be attributed to the n $\rightarrow$ π^* transition.

For the 2,3-epoxide of vitamin K$_3$ the absolute configuration has been deduced from the CD spectrum.[20] The largest CD band is found at about 350 nm and is associated with an n $\rightarrow$ π^* transition. The compound with the negative Cotton effect between 340 and 400 nm has a 2*R*,3*S* configuration. Determination of the absolute configuration for very similar compounds may be carried out by comparison of the CD spectra. It could be concluded that the absolute configuration of the predominantly formed enantiomers was identical (see Figure 2). It was very fortunate that it proved to be possible to obtain enantiomeric enrichment by crystallization either of the crystals (2-alkyl-1,4-naphthoquinone 2,3-epoxides) or of the mother liquid (for instance for 2-phenyl-, 2-(diphenylmethyl)-, and 2-cyclohexyl-1,4-naphthoquinone 2,3-epoxides).

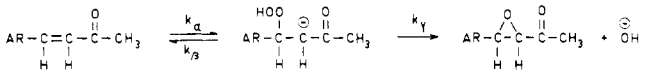
Possible Mechanism of the Epoxidation Reaction

The mechanism of the epoxidation reaction of 1,4-naphthoquinones should show some resemblance to the conversion of α,β-unsaturated ketones into α,β-epoxy ketones by alkaline hydrogen peroxide. The classical stud-

(10) G. W. Kabalka, *J. Organomet. Chem.*, **33**, C25-8 (1971).
(11) H. W. Underwood and W. L. Walsh, "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, p 553.
(12) (a) N. Jacobsen and K. Torssell, *Justus Liebigs Ann. Chem.*, **736**, 135 (1972); (b) N. Jacobsen and K. Torssell, *Acta Chem. Scand.*, **27**, 3211, (1973); (c) N. Jacobsen, *Org. Synth.*, **56**, 68-71 (1976).

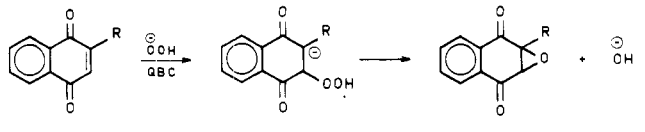
ies[13-17] for the epoxidation of α,β-unsaturated ketones are probably applicable to the corresponding reaction with 1,4-naphthoquinones.

Bunton and Minkoff[17] observed second-order kinetics for the epoxidation of α,β-unsaturated ketones (e.g., mesityl oxide and ethylideneacetone). A rate-decreasing effect of methyl substituents at the double bond suggested that the rate-determining step is the Michael addition of the hydroperoxide anion to the carbon–carbon double bond. Stereochemical studies supported this mechanism.[14] The epoxidation reaction can be represented by the following equation:



The first step in the epoxidation, the conjugate addition of the hydroperoxide anion to the unsaturated ketone, will be impeded by the presence of an α-alkyl substituent which will destabilize the intermediate carbanion.[15] On the other hand, an alkyl substituent at the β-carbon also has a rate-decreasing effect on the addition of the hydroperoxide anion caused by both the electron-donating property and the bulkiness of the alkyl group.

Although the mechanistic comparison between epoxidation of α,β-unsaturated ketones and quinones is useful, a crucial difference exists. In the case of bulky β substituents on α,β-unsaturated ketones, epoxidation becomes difficult, and rates are slow. In the case of *one* bulky substituent on the double bond of the 1,4-naphthoquinone system, addition still can take place since the initial, chirality-inducing step may proceed at the unsubstituted carbon. It is of considerable interest that no easy answer can be given to the question of at which carbon attack will occur. An indication that the addition will take place at the sterically least hindered carbon atom is found in the rate decrease of epoxidation with increasing bulkiness of the alkyl group and the great increase of reaction rate when the naphthoquinone is substituted at C-2 by a transition-state-stabilizing phenyl substituent. Furthermore, the epoxidation of 2,3-disubstituted 1,4-naphthoquinones is extremely difficult and slow.



In the system at hand, four reactions may occur.[18] Epoxidation, oxidative cleavage of the epoxide by the hydroperoxide (i.e., a bond cleavage by a possible base-catalyzed counterpart of the Baeyer–Villiger reaction[16]), and cleavage of the quinone as well as the epoxide by hydroxide. The degradation reactions all lead to phthalic acid derivatives.

Normally the epoxidation and epoxidation cleavage by the hydroperoxy anion are orders of magnitude faster than the hydroxide-catalyzed degradation.[18]

Conclusions

Two facts stand out. (a) In a family of compounds such as the one studied here, a prediction about the absolute configuration of the products can be made with some assurance. Thus the chirally catalyzed epoxidation reaction becomes a trustworthy route to hitherto inaccessible optically active 2,3-epoxy-1,4-naphthoquinones. (b) Systematic variations in the structure of the substituents of the quinones furnish some insight into the factors which influence the extent of enantiomeric excess.

Experimental Section

The melting points were measured with a Reichert melting point apparatus and are uncorrected. Microanalyses were performed by the microanalytical laboratory of the university. IR spectra were recorded on a Varian spectrophotometer, NMR spectra were taken with a Hitachi Perkin-Elmer spectrometer with the use of tetramethylsilane as an internal standard and chemical shifts are expressed as δ values. UV spectra were recorded on a Beckman 200 spectrophotometer. The rotational values were determined with a Perkin-Elmer 241 polarimeter, and CD spectra were taken with a Cary 60 spectrometer.

Preparation of 2-Substituted 1,4-Naphthoquinones. In the case where the 2-substituted naphthalenes were easily acquired, the classical oxidation method (CrO_3/HOAc) was used.

Method A. A typical example is as follows. A solution of 40 g (0.4 mol) of chromic anhydride in 75 mL of 80% acetic acid was added dropwise to a solution of 6.0 g (0.038 mol) of 2-ethylnaphthalene in 100 mL of glacial acetic acid while the reaction mixture was cooled to maintain a temperature of 20–30 °C during the addition. The resulting mixture was poured on 500 mL of crushed ice with continuous stirring. After 1 h, the crystals were separated by filtration and recrystallized from 96% ethanol to give 2.8 g (40%) of yellow needles: mp 87–88 °C (lit.[9a] mp 86–87 °C); IR (Nujol) 1665 cm^{-1} (C=O); NMR (CCl_4) δ 1.20 (3 H, t, J = 7.5 Hz), 2.60 (2 H, q, J = 7 Hz), 6.74 (1 H, br s), 7.50–7.80 (2 H, m), 7.80–8.20 (2 H, m). In certain cases a slightly modified procedure gave better yields.[21]

Method B. 2,5-Dimethylnaphthalene (4 g, 0.056 mol) was dissolved in glacial acetic acid. Chromium trioxide (25 g, dried under vacuum at 100 °C) was added, and the mixture was slowly warmed to 20–30 °C. After a few minutes a highly exothermic reaction started (cooling was necessary in order to prevent the temperature of the reaction from rising above 40 °C) which subsided after a few minutes. The reaction mixture was subsequently stirred for 0.5 h at 30–40 °C and then poured onto water (200 mL), and the products were extracted with chloroform (3 × 50 mL). The combined chloroform layers were washed with water, saturated sodium bicarbonate solution, and water, respectively, and then dried over Na_2SO_4. Evaporation of the solvent gave 2 g (41%) of the product, and after crystallization from a mixture of petroleum ether and ethanol (10:1) the 2,5-dimethyl-1,4-naphthoquinone could be obtained: mp 93–94 °C (lit.[30] mp 94 °C). IR (Nujol) 1655 cm^{-1} (C=O); NMR (CCl_4) δ 2.15 (3 H, s), 2.72 (3 H, s), 6.69 (1 H, br s), 7.38–7.58 (1 H, m), 7.70–8.10 (2 H, m).

The procedure with organoboranes as described by Kabalka[10] was only used in a few cases, and a general procedure is as follows.

Method C. A 200-mL three-necked flask fitted with an inlet carrying a rubber septum cap, a magnetic stirring bar, and a condenser was flushed with nitrogen. In the flask was placed a solution of 50 mmol of borane in 25 mL of tetrahydrofuran. Then 15.2 g (150 mmol) of cyclohexene in 25 mL of tetrahydrofuran was added to form tricyclohexylborane. The mixture was stirred at 50 °C for 3 h to complete the hydroboration. Then 1.08 mL of water was added, followed by a solution of 7.8 g (50 mmol, purified by steam distillation) of 1,4-naphthoquinone in 50 mL of tetrahydrofuran. Air was passed through the solution at a rate of 1 mL/min through a syringe needle placed through the rubber septum cap. The reaction was completed in 20 min (GLC). The solvent and the boronic and borinic acids were removed by steam distillation. After that, the product was oxidized by the method

(13) G. B. Payne and P. M. Williams, *J. Org. Chem.*, **26**, 651 (1961).
(14) H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 2428 (1958).
(15) H. O. House and D. J. Reif, *J. Am. Chem. Soc.*, **79**, 6491 (1957).
(16) H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **79**, 1157 (1957).
(17) C. A. Bunton and G. J. Minkoff, *J. Chem. Soc., Chem. Commun.*, 665 (1979).
(18) R. D. Temple, *J. Org. Chem.*, **35**, 1275 (1970).
(19) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 1038 (1974).
(20) G. Snatzke, H. Wynberg, B. Feringa, B. Greydanus, B. Marsman, and H. Pluim, to be submitted for publication.
(21) Wolter ten Hoeve, Thesis, Groningen University, 1979, p 112.

of Underwood and Walsh.[11] The 2-cyclohexyl-1,4-naphthalenediol was dissolved in an equal amount of glacial acetic acid and acetone[22] (50 mL of each). To this mixture were added 50 mg of vanadium pentoxide, 7.6 g of sodium chlorate, and 20 mL of 2% sulfuric acid. The reaction mixture was warmed until a vigorous reaction ensued. After about 20 min this exothermic reaction abated whereupon the mixture was refluxed for 1 h more and then cooled in ice. The solution was extracted with ether (2 × 100 mL) after saturation with sodium chloride. The combined organic layers were dried over Na_2SO_4 and concentrated. The yellow oil (7.6 g, 60%) was recrystallized from 96% ethanol, giving yellow crystals: mp 86–88 °C (lit.[33] mp 87–88 °C); IR (Nujol) 1608 cm^{-1} (C=O); NMR (CCl_4) δ 0.90–2.20 (10 H, m), 2.9 (1 H, t, J = 9 Hz), 6.73 (1 H, br s), 7.50–7.82 (2 H, m), 7.82–8.20 (2 H, m).

The best way of preparing 2-substituted naphthoquinones was by the method described by Jacobsen and Torssell. The following procedure was employed.

Method D. A solution of 7.9 g (50 mmol) of naphthoquinone, 4.4 g (50 mmol) of propionic acid, and 1.5 g (9 mmol) of silver nitrate in a solvent mixture of acetonitrile, sulfolane, and water (1:3:7, 125 mL) was heated to 60–65 °C until dissolution was complete. With vigorous stirring a solution of 13.7 g (60 mmol) of ammonium persulfate in 25 mL of water was added at a rate of 0.5 mL/min. Throughout the addition the temperature was maintained at 60–65 °C as well as for 10 min after the addition was complete. The mixture was then cooled in an ice bath. The reaction mixture was extracted with ether (3 × 70 mL), and the combined ethereal layers were washed with a 10% sodium bicarbonate solution (2 × 100 mL), several times with water, and ultimately with brine, dried on Na_2SO_4, and concentrated. The product was purified by Kugelrohr distillation [6.1 g (60%); bp 123–127 °C (0.008 mmHg)] followed by recrystallization from ethanol, furnishing yellow needles: mp 37–38.5 °C (lit.[27] mp 38–39 °C); IR (Nujol) 1660 cm^{-1} (C=O); NMR (CCl_4) δ 1.08 (3 H, t, J = 8 Hz), 1.60 (2 H, m), 2.60 (2 H, t, J = 8 Hz), 6.73 (1 H, br s), 7.48–7.82 (2 H, m), 7.84–8.20 (m, 2 H).

The quinones have all been transformed to the epoxyquinones by the following procedure. To a vigorously stirred solution of 0.5 g (2.9 mmol) of 2-methyl-1,4-naphthoquinone in 4 mL of toluene was slowly added a solution of 285 mg of sodium hydroxide in 2 mL of water and 2 mL of 30% hydrogen peroxide. To this two-phase system was added 25 mg of benzylquininium chloride ($[\alpha]^{21}_{578}$ −231° (c 1, H_2O) [lit.[23] $[\alpha]^{22}_{D}$ −230.5° (c 1.479, H_2O)]). The temperature of the reaction mixture was kept at 35–40 °C. An indication for the completion of the reaction is the disappearance of the color of 2-methyl-1,4-naphthoquinone after 1.5–2 h.

The reaction mixture was worked up by diluting the toluene layer with ether (50 mL), washing the organic phase with water and brine, and drying the organic phase over $MgSO_4$. The organic layer was passed through a silica gel column (1 × 10 cm, ϕ = 1.5 cm, CH_2Cl_2) in order to remove the catalyst completely. Evaporation of the eluate furnished 385 mg (70%) of crystalline epoxyquinone: $[\alpha]^{21}_{578}$ 0; $[\alpha]^{21}_{436}$ −6.8 (c = 0.4, $CHCl_3$). Recrystallization from alcohol furnished colorless needles of somewhat higher enantiomeric purity: mp 95.5–96.5 °C (lit.[24] mp 96–96.5 °C); NMR (CCl_4) δ 1.72 (3 H, s), 3.82 (1 H, s), 7.64–8.12 (4 H, m); UV (hexane) λ_{max} 304 (log ϵ 3.23), 269 (3.66), 227 (4.48).

Registry No. 2-Methyl-1,4-naphthoquinone, 58-27-5; 2-ethyl-1,4-naphthoquinone, 5409-32-5; 2-propyl-1,4-naphthoquinone, 34491-84-4; 2-isopropyl-1,4-naphthoquinone, 20175-89-7; 2-butyl-1,4-naphthoquinone, 34491-88-8; 2-isobutyl-1,4-naphthoquinone, 73377-70-5; 2-*tert*-butyl-1,4-naphthoquinone, 51595-06-3; 2-pentyl-1,4-naphthoquinone, 41245-43-6; 2-hexyl-1,4-naphthoquinone, 31489-49-3; 2-cyclohexyl-1,4-naphthoquinone, 34987-31-0; 2-(3-methyl-2-butenyl)-1,4-naphthoquinone, 3568-90-9; 2-benzyl-1,4-naphthoquinone, 33440-68-5; 2-(diphenylmethyl)-1,4-naphthoquinone, 14039-65-7; 2-phenyl-1,4-naphthoquinone, 2348-77-8; 2,5-dimethyl-1,4-naphthoquinone, 46255-71-4; 2,6-dimethyl-1,4-naphthoquinone, 6290-94-4; 2,7-dimethyl-1,4-naphthoquinone, 482-70-2; 2-methyl-5-methoxy-1,4-naphthoquinone, 22266-99-5; 2-methyl-3-ethyl-1,4-naphthoquinone, 2589-56-2; 2-methyl-3-butyl-1,4-naphthoquinone, 2397-62-8; (−)-2-methyl-1,4-naphthoquinone 2,3-epoxide, 61840-91-3; (−)-2-ethyl-1,4-naphthoquinone 2,3-epoxide, 73377-71-6; 2-propyl-1,4-naphthoquinone 2,3-epoxide, 63534-40-7; (−)-2-isopropyl-1,4-naphthoquinone 2,3-epoxide, 73377-72-7; (−)-2-butyl-1,4-naphthoquinone 2,3-epoxide, 73377-73-8; (−)-2-isobutyl-1,4-naphthoquinone 2,3-epoxide, 73377-74-9; (+)-2-*tert*-butyl-1,4-naphthoquinone 2,3-epoxide, 73377-75-0; (−)-2-pentyl-1,4-naphthoquinone 2,3-epoxide, 73377-76-1; (−)-2-hexyl-1,4-naphthoquinone 2,3-epoxide, 73377-77-2; (+)-cyclohexyl-1,4-naphthoquinone 2,3-epoxide, 73377-78-3; (+)-2-(3-methyl-2-butenyl)-1,4-naphthoquinone 2,3-epoxide, 73377-79-4; (−)-2-benzyl-1,4-naphthoquinone 2,3-epoxide, 73377-80-7; (−)-2-(diphenylmethyl)-1,4-naphthoquinone 2,3-epoxide, 73377-81-8; (−)-2-phenyl-1,4-naphthoquinone 2,3-epoxide, 73377-82-9; (−)-2,5-dimethyl-1,4-naphthoquinone 2,3-epoxide, 73377-83-0; (−)-2,6-dimethyl-1,4-naphthoquinone 2,3-epoxide, 73377-84-1; (−)-2,7-dimethyl-1,4-naphthoquinone 2,3-epoxide, 73377-85-2; (+)-2-methyl-5-methoxy-1,4-naphthoquinone 2,3-epoxide, 73377-86-3; 2-methyl-3-ethyl-1,4-naphthoquinone 2,3-epoxide, 73377-87-4; (−)-2-methyl-3-butyl-1,4-naphthoquinone 2,3-epoxide, 73377-88-5; 2-ethylnaphthalene, 939-27-5; 2,5-dimethylnaphthalene, 571-61-9; 1,4-naphthoquinone, 130-15-4.

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