teraction,[9] and the evidence is persuasive that Förster's transfer applies. If this point is accepted, our results also serve as a strict test of the Yokota–Tanimoto treatment for transfer in diffusing systems. On the basis of these limited data, their result from the Padé approximant method seems accurate for $\bar{r}/R_0^*$ values near 2 or 3 and probably for lower values as well. For ratios above 7, the limiting result for $\bar{r} \gg R_0^*$, as obtained from the scattering length method, is a much better choice. However, more data in the region of $\bar{r}/R_0^* \geq 5$ are needed to clarify the validity of (6) in view of Swenberg and Stacy's criticism of it.[53]

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Reactions of π-Allylnickel Bromide Complexes with Quinones. Synthesis of Isoprenoid Quinones

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Abstract: The reaction of π-allylnickel bromide complexes with quinones under a standard set of conditions results in a 1:1 mixture of allylhydroquinone and hydroquinone (eq 1). By varying reaction conditions, production of allylhydroquinones can be favored in some cases. This method was used to synthesize coenzyme Q_1 (**6**) and plastoquinone-1 (**9**). With various dimethylbenzoquinones, the allyl group is introduced exclusively at the noncarbonyl ring site of highest spin density in the corresponding radical anion, leading either to allylhydroquinones or enediones. Electron transfer processes are thought to be involved.

Introduction

Isoprenoid quinones play a pivotal role in the electron transport chain in both photosynthetic and respiratory processes.[2] The usual method of synthesis of these compounds involves a Lewis acid-catalyzed reaction between the appropriate allylic alcohol and hydroquinone, followed by oxidation to the quinone.[3] This method suffers from side reactions such as cyclization of the unsaturated side chain, cyclization of the isoprenoid hydroquinone to the chromanol, and polyalkylation of the aromatic ring. Recently vitamin K,[4] coenzyme Q_1,[5] and vitamin E[6] analogues have been synthesized in moderate yields by a multistep procedure involving as a key step the well-known[7] reaction of π-allylnickel halide complexes with the appropriate aryl halide of the protected hydroquinone. A preliminary communication from this laboratory reported a direct reaction of π-allylnickel bromide complexes with quinones to produce allylhydroquinones (eq 1). We report herein the full details of this study.

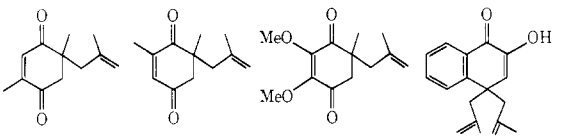
Results and Discussion

Synthetic Studies. The course of the reaction between π-allylnickel bromides and quinones was quite sensitive to reaction conditions, small changes in conditions often resulting in significantly altered yields and product distributions. The results of a series of reactions between a variety of nickel complexes and quinones under similar conditions (1 mol of

Table I. Reaction of π-Allylnickel Bromide Complexes with Quinones[a]

π-Allylnickel bromide (1)	Quinone	Products	% yield[b,c]
Allyl	*p*-Benzoquinone[d]	Allylhydroquinone	46 (77)
		Hydroquinone	40
2-Methallyl	*p*-Benzoquinone[d]	(2-Methyl-2-propenyl)hydroquinone	54 (86)
		Hydroquinone	36
1-Methallyl	*p*-Benzoquinone[d]	(2-Butenyl)hydroquinone	42 (83)
		Hydroquinone	46
1,1-Dimethylallyl	*p*-Benzoquinone[d]	(3-Methyl-2-butenyl)hydroquinone	37 (54)
		Hydroquinone	34
2-Methallyl	Methylbenzoquinone	2-(2-Methyl-2-propenyl)-*n*-methylhydroquinone[e]	40 (71)
		Methylhydroquinone	44
2-Methallyl	2,3-Dimethylbenzoquinone	2,3-Dimethyl-5-(2-methyl-2-propenyl)-hydroquinone	48 (99)
		2,3-Dimethylhydroquinone	50
2-Methallyl	2,5-Dimethylbenzoquinone	**2**	47 (94)
		2,5-Dimethylhydroquinone	42
2-Methallyl	2,6-Dimethylbenzoquinone	**3**	46 (87)
		2,6-Dimethyldroquinone	47
2-Methallyl	2,3-Dimethoxy-5-methyl-benzoquinone	**4**	33 (54)
		2,3-Dimethoxy-5-methylhydroquinone	39
2-Methallyl	1,4-Naphthoquinone	2-(2-Methyl-2-propenyl)1,4-naphthoquinone	39
2-Methallyl	1,2-Naphthoquinone	4-(2-Methyl-2-propenyl)-1,2-naphthoquinone	49
		5	26
2-Methallyl	4-*tert*-Butyl-1,2-benzoquinone	5-(2-Methyl-2-propenyl)-4-*tert*-butylcatechol	54
2-Methallyl	Trimethylbenzoquinone	No reaction	
2-Methallyl	Duroquinone	No reaction	

[a] All reactions were run under the conditions described in eq 1. [b] Yields refer to purified product, isolated by preparative chromatography. [c] Yields in parentheses are based on quinone consumed. [d] These reactions were run in THF solvent at −78°. [e] This product consists of a mixture of 2,3 (5%), 2,5 (20%), and 2,6 (15%) disubstituted isomers by NMR.



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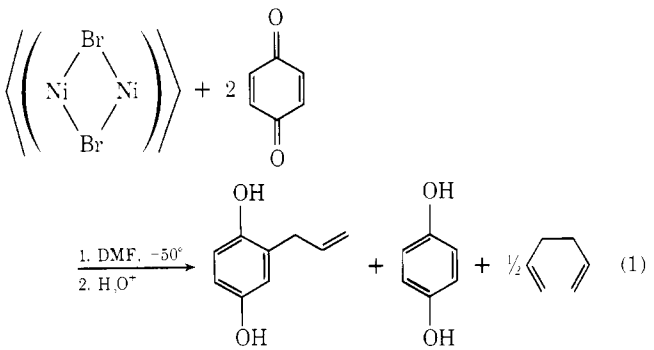


(1)

complex/2 mol of quinone, THF or DMF solvent, −50°) are summarized in Table I. Under these conditions the reactions have the stoichiometry expressed in eq 1, wherein 1 equiv of quinone is reduced and alkylated, while 1 equiv is simply reduced. This 1:1 ratio of reduced to reduced-and-alkylated quinone is obtained regardless of the initial ratio of reactants. Since the hydroquinone is easily reoxidized in high yield to the starting quinone, little loss of that starting material is experienced. However, 1 equiv of allyl group is sacrificed in this procedure, a disadvantage if the particular π-allylnickel bromide complex used is difficult to prepare.

Particularly striking is the site specificity of the reaction under these conditions. In all but one case, only monoalkylated hydroquinones were obtained. Benzoquinone, methylbenzoquinone, and 2,3-dimethylbenzoquinone all reacted exclusively at an unsubstituted ring site, producing the corresponding allylhydroquinone in good yield. In contrast, 2,5- and 2,6-dimethylbenzoquinone, and 2,3-dimethoxy-5-methylbenzoquinone underwent reaction exclusively at the *methyl substituted* ring site to produce enediones **2, 3,** and **4** in fair to good yield. Few synthetic approaches to enediones of this type are available. This site specificity for the 5 position of 2,3-dimethoxy-5-methylbenzoquinone precluded the synthesis of coenzyme Q_1 (**6**) by this method, and alternative conditions were required (vide infra).

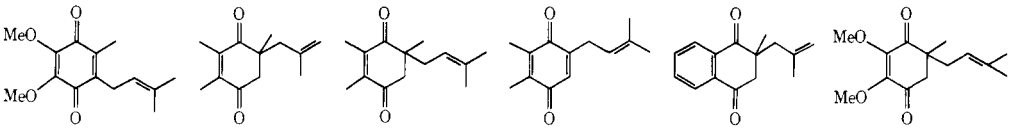
Ortho quinones also react with π-allylnickel bromide complexes. Thus 4-*tert*-butyl-1,2-benzoquinone reacted at the 5 position to produce the corresponding methallylcatechol, while 1,2-naphthoquinone produced in a 2:1 mixture the mono- and dialkylated products. The monoallyl compound was quite unstable and resisted attempts to obtain analytically pure samples, while the diallyl product **5** was a stable, white crystalline solid. Trimethylbenzoquinone and duroquinone were unreactive under the conditions used in Table I, and were recovered unchanged from reaction mixtures.

Several variations in reaction conditions were made in attempts to suppress the simple reduction of the quinone starting material, to extend the range of quinones that would undergo reaction, and to change the site specificity of the reaction to allow the synthesis of isoprenoid quinones such as coenzyme Q_1. The results of these variations are collected in Table II. With benzo- and methylbenzoquinone simple reduction was suppressed by the addition of CO or excess triphenylphosphine, thereby increasing the overall alkylation of the quinone from 50 to 80%. However, excess π-allylnickel bromide complex was still required, resulting again in the loss of 1 equiv of allyl group. With more highly substituted quinones such as di-

Table II. Effect of Conditions on the Product Distribution in the Reaction of π-Allylnickel Bromides with Quinones

π-Allylnickel complex	Quinone	Solvent	Additive	Products	% yield[a]
2-Methallyl (2 equiv)	*p*-Benzoquinone	DMF	CO	(2-Methyl-2-propenyl)-hydroquinone	78
2-Methallyl (2 equiv)	Methylbenzoquinone	DMF	CO	2-(2-Methyl-2-propenyl)-*n*-methylhydroquinone[b]	79
2-Methallyl	2,6-Dimethylbenzoquinone	DMF	Δ[c]	**3**	63 (93)
				2,6-Dimethylhydroquinone	35
2-Methallyl (0.5 equiv)	2-Methyl-1,4-naphthoquinone	DMF	Δ[c]	**10**	72[d]
2-Methallyl	Trimethylbenzoquinone	DMF	$C_{10}H_8^{\cdot-}$	2-(2-Methyl-2-propenyl)-3,5,6-trimethylbenzoquinone[e]	16
				7	45
2-Methallyl	Trimethylbenzoquinone	Formamide		2-(2-Methyl-2-propenyl)-3,5,6-trimethylbenzoquinone[e]	22 (73)
				Trimethylbenzoquinone[e]	70
1,1-Dimethylallyl	Trimethylbenzoquinone	Formamide		2-(3-Methyl-2-butenyl)-3,5,6-trimethylbenzoquinone[e]	34 (38)
				8	32 (36)
				Trimethylbenzoquinone[e]	11
1,1-Dimethylallyl	2,3-Dimethoxy-5-methylbenzoquinone	Formamide		**6**[e]	26 (34)
				11	9 (12)
				2,3-Dimethoxy-5-methylbenzoquinone[e]	23
2-Methallyl	2,5-Dimethylbenzoquinone	DMF	$NiBr_2$ (1 equiv)[f]	3-(2-Methyl-2-propenyl)-2,5-dimethylbenzoquinone[e]	11 (14)
				3	37 (46)
				2,5-Dimethylbenzoquinone[e]	19
2-Methallyl	2,6-Dimethylbenzoquinone	DMF	$NiBr_2$ (0.5 equiv)	3-(2-Methyl-2-propenyl)-2,6-dimethylbenzoquinone[e]	41 (56)
				2	16 (22)
				2,6-Dimethylbenzoquinone[e]	28
1,1-Dimethylallyl	2,3-Dimethylbenzoquinone	THF	$NiBr_2$ (4 equiv)	**9**[e]	31

[a] Yields refer to purified products, isolated by preparative chromatography. Yields in parentheses are based on quinone consumed. [b] Mixture of isomers. [c] The mixture was heated at 60° for 15 h. [d] Based on limiting reagent, the nickel complex. [e] Crude reaction mixtures were oxidized with $FeCl_3$ prior to purification. [f] Added as $NiBr_2 \cdot 3DMF$, which is soluble in a range of solvents.



6 7 8 9 10 11

methyl- and dimethoxymethylbenzoquinone *no* increase in alkylation resulted from added ligands. Conversion of 2,6-dimethylbenzoquinone to **3** was substantially enhanced (from 46 to 63%) by simply carrying out the reaction at a higher temperature. Similar results were obtained with 2-methylnaphthoquinone. However, other quinones would not tolerate higher temperatures, with yields of the desired products dropping substantially as the temperature was increased.

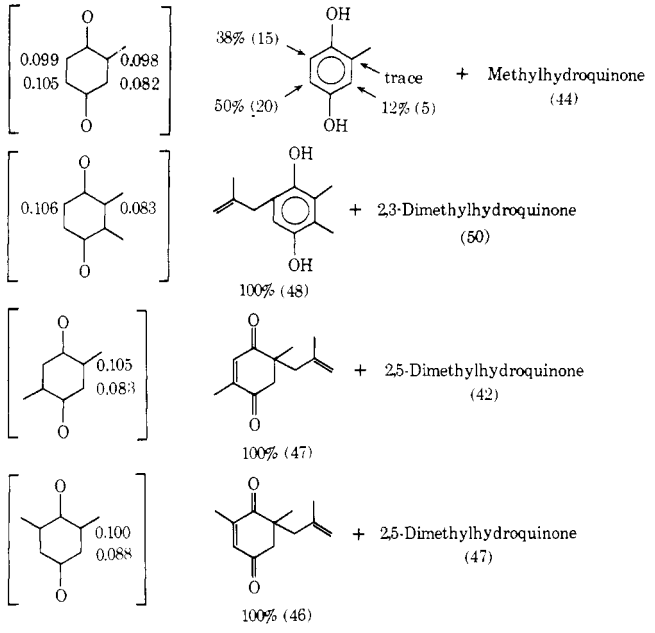
Trimethylbenzoquinone, which was unreactive in DMF, was made to react by the use of an initiator (sodium naphthalenide) in DMF, or by the use of the much more polar solvent, formamide. Addition of 10 mol % of sodium naphthalenide to a mixture of trimethylbenzoquinone and π-2-methallylnickel bromide in DMF led to production of endione **7** in 45% yield, as well as a small amount of methallyltrimethylbenzoquinone resulting from alkylation at the unsubstituted position of the quinone ring. When the reaction was run in formamide without initiator, this quinone was the sole product. However, under identical conditions using 1,1-dimethylallylnickel bromide as the complex, a 1:1 mixture of enedione **8** from alkylation at the methyl-substituted position and 1,1-dimethylallyltrimethylbenzoquinone from alkylation at the unsubstituted site was obtained. Duroquinone remained unreactive under all conditions attempted. Finally, reaction of π-1,1-dimethylallylnickel bromide with 2,3-dimethoxy-5-methylbenzoquinone in formamide produced an acceptable yield of coenzyme Q_1 (**6**), while in DMF enedione **11** was the exclusive product. Thus, formamide not only increased the range of reactive quinones, but also somewhat altered the site specificity of the reactions. However, no general trend was obvious.

The site of alkylation could also be somewhat altered by the addition of various amounts of nickel bromide to the reaction mixture. Thus both 2,5- and 2,6-dimethylbenzoquinone produced appreciable quantities of product resulting from alkylation at the unsubstituted quinone ring site in the presence of nickel bromide, while enedione products **2** and **3** were exclusive products in the absence of nickel bromide (Table I). Nickel bromide was also required to produce an acceptable yield of plastoquinone-1 (**9**).

In summary, the reaction between π-allylnickel bromides and quinones provides a one-step procedure for the direct introduction of allyl groups into quinones in moderate to high yields. In several instances, enediones of unusual structure are obtained. This method was used to prepare coenzyme Q_1 and plastoquinone-1 in one step in moderate yield. The reaction is sensitive to both substrate and conditions, but general trends were difficult to discern. Instead each specific substrate required individual optimization. The ready availability of a variety of π-allylnickel halide complexes, the ease in carrying out the reaction, the regioselectivity, and the lack of production of polyalkylated and/or cyclized side products make this procedure an attractive synthetic route to isoprenoid quinones or enediones. However, the loss of 1 equiv of allyl group observed in many of these reactions is a definite disadvantage in some cases.

The Course of the Reaction. Transition metals interact with quinones in a variety of ways, and several types of quinone–metal complexes have been reported.[9] Duroquinone reacts with

Table III. Spin Densities of Quinone Radical Anions and Products from Eq 1[a]



[a] The percent figures refer to the amount of a particular allyl product relative to the total amount of allyl product obtained. The numbers in parentheses refer to the *isolated* yield of each product based on the starting quinone as limiting reagent.

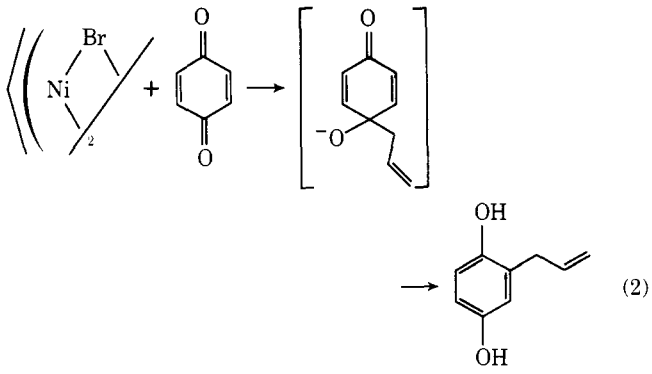
nickel carbonyl to produce the stable bis(duroquinone)nickel complex.[10] This is a π complex with extensive electron back donation from the metal to the quinone, as evidenced by the appearance of the quinone C=O stretching frequency at 1577 cm^{-1} in the complex vs. 1629 cm^{-1} for free duroquinone. In contrast, benzoquinone and methylbenzoquinone react with nickel carbonyl to produce black insoluble paramagnetic complexes best characterized as $Ni^{2+}(quinone)_2^{2-}$ complexes resulting from complete electron transfer from nickel to the easily reduced quinone.[11] Bis(benzene)chromium reacts with benzoquinone to form $Ph_2Cr^+(BQ\cdot^-)$ by complete electron transfer.[12] This complex has an intense absorption at 1500 cm^{-1} in the infrared attributed to the benzoquinone radical anion. Finally a variety of electron donor-acceptor complexes (charge transfer complexes) between metals and quinones are known.[13] The type of complex formed depends both on the electron affinity (reduction potential) of the quinone and the donor ability of the complex. Clear-cut distinction among complex types is not always possible. The following features of the reaction between π-allylnickel bromide complexes and quinones under the conditions of Table I suggest that intermediates involving significant electron transfer from metal to quinone are involved.

All products are obtained in the reduced state as hydroquinones, with the nickel complex being the only reducing agent present. The reactivity of the various quinones studied parallels their reduction potentials, the more easily reduced quinones being the most reactive. Specifically, quinones which will accept an electron at potentials less negative than −0.7 V vs. SCE will react with π-allylnickel bromides, while quinones with reduction potentials more negative than −0.7 V are recovered unchanged. Thus, benzoquinone ($E_{1/2}$ = −0.58 V), methylbenzoquinone ($E_{1/2}$ = −0.62 V), and dimethylbenzoquinones ($E_{1/2}$ = −0.70 V) react while trimethylbenzoquinone ($E_{1/2}$ = −0.80 V) and tetramethylbenzoquinone ($E_{1/2}$ = −0.88 V) are unreactive. The site of alkylation of the various methylbenzoquinones studied corresponds to the *noncarbonyl ring site of highest spin density* in the corresponding quinone radical anion, as measured from ESR hyperfine splitting constants and as calculated by Hückel LCAO-MO methods.[14-16] Table III shows this correlation by listing the calculated spin densities for the various quinone radical anions followed by the allyl products obtained from the reactions summarized in Table I. With the minor exception of the small amount of 2-attack with methylbenzoquinone, there is a striking correlation. It is unlikely that the free quinone radical anion is the reactive intermediate since the site of highest spin density in this species is the oxygen, which does not undergo attack in these reactions.[17] Instead it is likely that the reduced quinone species is coordinated to the nickel complex, and allyl transfer occurs in this complexed intermediate in a fashion similar to that proposed in the alkylation of conjugated enones by lithium dimethylcuprate.[18] Low-temperature NMR spectra of reaction mixtures exhibited extensive line broadening and shifting due to the presence of paramagnetic species, although low-temperature ESR studies produced no observable signals.

The reaction between π-allylnickel chloride and benzoquinone in benzene was reported to give black insoluble paramagnetic complexes which were considered to be donor-acceptor complexes in which the π-allylnickel was the donor and the quinone was the acceptor. The benzoquinone was reported to be present as the semiquinone, although these complexes were only poorly characterized.[19] Since complexes of this type are possible intermediates in the above reactions, we prepared these black complexes from benzoquinone and methylbenzoquinone by adding 2 equiv of the quinone to 1 equiv of π-2-methallylnickel bromide in benzene solution. After filtration, washing, and drying under vacuum, the resulting air-sensitive, amorphous black solids had an intense ir absorption at 1490 cm^{-1}, similar to that of $Ph_2Cr^+(BQ\cdot^-)$ (vide supra) assigned to the bound benzoquinone radical anion.[12] Dissolution of these black solids in DMF at −46° followed by warming to 25° and isolation led to the *same products in the same ratios* as the corresponding reaction of π-2-methallylnickel bromide with benzo- and methylbenzoquinone under the conditions used in the examples in Table I. Treatment of trimethylbenzoquinone with π-2-methallylnickel bromide in benzene resulted in no reaction, and no precipitate was formed. Thus, complexes similar to these black solids could be intermediates in the reaction between π-allylnickel bromides and quinones in DMF. However, they themselves are so poorly characterized that they afford little insight into the specific details of the reaction.

All of the above experimental results are consistent with the reaction involving electron transfer from the nickel to the quinone, followed by allyl group transfer. Other substitutions on the quinone ring have been shown to involve both charge transfer and electron transfer interactions.[20] An example is the amination of quinones by primary or secondary organic amines, in which the amine is the donor, the quinone is the acceptor, and both charge transfer complexes and quinone radical anions from complete electron transfer were detected.[21] The alkylation of quinones by alkylboranes[22] or other sources of alkyl radicals[23] has also been shown to proceed via semiquinone radicals. Finally, π-allylpalladium chloride has been shown to reduce benzoquinone to hydroquinone,[24] while a variety of Ni(0) complexes reacted with chloranil and dichlorodicyanobenzoquinone to produce the corresponding quinone radical anions.[25]

The site of *initial* allyl group transfer in the reactions in Tables I and II is not known. It is possible that alkylation initially occurs at the *carbonyl* carbon[26] to give a quinol intermediate, which undergoes a Cope (1,3) rearrangement to the allylhydroquinone observed (eq 2).[27] The site to which the allyl group migrated in unsymmetrically substituted quinone may be governed by the specific reaction conditions employed. However, quinol intermediates were never detected in the re-



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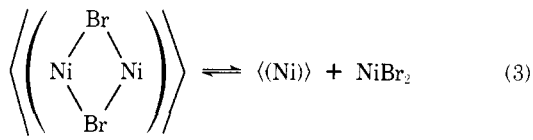
actions reported in Tables I and II.

A final consideration is the nature of the reactive allylnickel species. In DMF, π-allylnickel halides are in equilibrium with bis-π-allylnickel complexes (eq 3).[28] To test if bis-π-allylnickel



(3)

complexes were the reactive nickel species, bis-π-2-methallylnickel was treated with 1,4-naphthoquinone under conditions identical with those used in Table I. After product isolation, only 1,4-dihydroxynaphthalene was obtained. Thus bis-π-2-methallylnickel did not alkylate the quinone and, in this case at least, was not the reactive species in the reactions discussed above.

Experimental Section

General. All melting points are uncorrected. Infrared (ir) spectra were measured with either Perkin-Elmer Models 137 or 127 spectrophotometers, and are reported in μ. Nuclear magnetic resonance (NMR) spectra were measured with either Varian Associates Model A-60-A or T-60, or Jeol MH100 spectrophotometers using Me_4Si as the internal standard and are reported in δ. Mass spectra were measured on an Associate Electronics Industries MS-12 mass spectrometer. Analytical vapor phase chromatography was performed on a Bendix Model 2300 gas chromatograph. Liquid chromatography was performed using moderate (40–60 psi) pressures with a 25 × 1000 mm column packed with Woelm Type 206 silica gel. Column chromatography was performed using Baker reagent grade silica gel (60–200 mesh). Analytical thin layer chromatography was performed using Brinkmann precoated silica gel F-254 plates (0.25 mm). Preparative thin layer chromatography was performed using Brinkman 20 × 20 cm plates (2.0 mm). Products were visualized by uv light or iodine vapor. Microanalyses were performed by Midwest Microanalytical Laboratory, Indianapolis, Ind.

Materials. All solvents were freshly distilled and stored under an argon atmosphere. Immediately before use they were degassed and saturated with argon. DMF (Mallinkrodt, reagent grade) was distilled from calcium hydride at 15–20 mmHg. Formamide (Eastman, practical grade) was distilled from calcium hydride at 15–20 mmHg, redistilled at 1 mmHg, and stored over type 4A molecular sieves in the refrigerator. HMPA was distilled from calcium hydride at 1 mmHg and stored over Type 4A molecular sieves. THF (Fisher, reagent) was refluxed over lithium aluminum hydride and distilled at atmospheric pressure. Benzene (Fisher, reagent grade, thiophene-free) used in the preparation of the nickel complexes was distilled and stored over Type 4A sieves prior to its use. Nickel carbonyl was purchased from Matheson in 1-lb lecture bottles. 2-Methyl-3-bromopropene and 2-methyl-4-bromobut-2-ene were prepared by the method of Osbond.[29] Allyl bromide and crotyl bromide are commercially available and were used without further purification. 2,3-, 2,5-, and 2,6-dimethylbenzoquinone were prepared from the appropriate phenol by the method of Nilsson et al.[30] 2,3-Dimethoxy-5-methylbenzoquinone was prepared by the method of Weinstock.[31] 1,2-Naphthoquinone was prepared by the method of Vogel[32] from Orange II. Trimethylbenzoquinone was prepared by the oxidation of trimethylhydroquinone following the procedure described by Brewster et al.[33] 4-*tert*-Butyl-1,2-benzoquinone was prepared via the oxidation of 4-*tert*-butylcatechol according to the method of Durst and Mack.[34] All the other quinones studied are commercially available and were sublimed prior to use. The π-allylnickel bromide complexes were prepared by the method of Semmelhack and Helquist.[35] All manipulations of the nickel complexes were carried out under an argon atmosphere.

General Reaction Procedure (Table I). The reactions between quinones and π-allylnickel bromides were all carried out in the same general way. The nickel complex was transferred to a 50-ml two-neck flask fitted with a stopcock and a rubber serum cap in a nitrogen-filled glove bag. The quinone was placed in a 100-ml two-neck flask fitted with a stopcock and a 50-ml pressure equalizing addition funnel fitted with a rubber serum cap. The system was alternately evacuated and filled with argon on a vacuum line. The quinone (2 mmol) was dissolved in 20 ml of solvent and cooled to −50° with constant stirring. The nickel complex (1.0 mmol) was dissolved in 10 ml of solvent and transferred by syringe to the addition funnel. After waiting approximately 15 min for the quinone solution to cool, the π-allylnickel bromide solution was added drop by drop over a period of 1 h. The solution was allowed to stir at low temperature for 2 h and was slowly warmed to room temperature over another 2 h. Finally, the reaction mixture was allowed to stir at room temperature for an additional 2–3 h. It was then quenched with 50 ml of 1.2 M aqueous HCl and extracted with 3 × 50 ml ethyl ether or until the ether extract remained colorless. If DMF or HMPA were used, the ether phase was washed with three 50-ml portions of 1.2 M HCl. If THF was used, this wash was unnecessary. The ether phase was dried over $MgSO_4$ and concentrated on a rotary evaporator. The products were isolated by preparative chromatography on silica gel by eluting with ether–petroleum ether mixtures. Allyl-substituted products were further purified by preparative chromatography, distillation, or sublimation.

Reactions of π-Allylnickel Bromides with Benzoquinones. a. Allylhydroquinone. The nickel complex (0.519 g, 1.44 mmol) in 15 ml of THF was added to 0.216 g (2.65 mmol) of benzoquinone in 10 ml of THF at −78°, following the general reaction procedure. After routine isolation the products were separated by preparative TLC, developing three times with 1:1 petroleum ether–ether. The R_f 0.66 band contained 0.184 g (46%) of allylhydroquinone, mp 92–93 °C: NMR (acetone-d_6) δ 3.38 (d, J = 7 Hz, 2, $-CH_2-$), 4.94 (m, 1, C=CH), 5.16 (m, 1, C=CH), 6.04 (m, 1, CCH=C), 6.73 (s, 3, ArH), 7.60 (s, 1, OH); ir ($CHCl_3$) 2.76 (s, OH), 2.97 (br, OH), 3.25 (w, gem disubstituted alkene), 3.30 (w), 3.42 (w), 5.65 (w), 5.77 (w), 5.88 (w), 6.02 (w, C=C), 6.10 (w), 6.65 (s, aromatic), 6.90 (m), 8.15 (m), 8.25 (m), 8.82 (m), 8.95 (w), 9.57 (w), 10.05 (w), 10.40 (w), 10.90 (m), 11.50 (m), 12.30 μ (m, aromatic, 2 adjacent H); MS *m/e* 150 (P, base), 135 (52%), 123 (27%), 107 (53%), 91 (21%), 77 (30%). Anal. ($C_8H_{10}O_2$) C, H. The R_f 0.46 band gave 0.116 g (40%) of hydroquinone.

b. (2-Methyl-2-propenyl)hydroquinone. The nickel complex (0.316 g, 0.82 mmol) in 8 ml of THF was added to 0.162 g (1.50 mmol) of the quinone in 8 ml of THF at −78° in the usual manner. After routine isolation the products were separated by preparative TLC, developing twice with 3:2 petroleum ether–ether. The R_f 0.68 band contained 0.132 g (54%) of (2-methyl-2-propenyl)hydroquinone, mp 86–87 °C: NMR (acetone-d_6) δ 1.72 (s, 3, $-CH_3$), 3.33 (s, 2, $-CH_2-$), 4.77 (m, 2, C=CH_2), 6.69 (m, 3, ArH), 7.51 (broad s, 2, OH); ir ($CHCl_3$) 2.77 (s, free OH), 2.94 (broad s, H-bonded OH), 3.24 (m, gem disubstituted alkene), 3.32 (m), 3.34 (m), 3.41 (m), 3.44 (m), 5.80 (w), 5.91 (m), 6.07 (m, gem-disubstituted alkene), 6.19 (w), 6.23 (m), 6.67 (s, aromatic C=C), 6.87 (s, aromatic C=C), 7.24 (m), 7.46 (s), 7.81 (s), 8.06 (s), 8.47 (s, aromatic CO), 8.68 (s), 9.09 (m), 9.60 (w), 9.77 (w), 10.20 (w), 10.40 (m), 11.00 (s), 11.17 μ (m, gem-disubstituted alkene); MS *m/e* 164 (P, base), 149 (50%, P − CH_3), 123 (23%), 121 (20%), 107 (8%), 94 (6%), 77 (10%). Anal. ($C_{10}H_{12}O_2$) C, H. The R_f 0.50 band contained 0.060 g (37%) of hydroquinone.

c. (2-Butenyl)hydroquinone. The nickel complex (0.337 g, 0.865 mmol) in 10 ml of THF was added to 0.178 g (1.65 mmol) of the quinone in 10 ml of THF at −78° as above. After routine isolation the products were separated by preparative TLC developing twice with 1:1 petroleum ether–ether. The R_f 0.84 band contained 0.115 g (42%) of a mixture of cis and trans isomers of 2-butenylhydroquinone, mp 114 °C: NMR (acetone-d_6) δ 1.55 (m, 3, C=CCH_3), 3.20 (m, 2, $-CH_2-$), 5.60 (m, 2, HC=CH), 6.60 (m, 3, ArH), 7.37 (s, 1, OH), 7.50 (s, 1, OH); ir ($CHCl_3$) 2.77 (s, free OH), 2.98 (br s, H bonded OH), 3.32 (w), 3.35 (w), 3.43 (w), 6.67 (s, aromatic C=C), 6.90 (m), 7.25 (w), 7.60 (m), 8.10 (m), 8.50 (s), 8.80 (m), 9.02 (w), 9.62 (w), 10.35

(m), 10.45 (w), 11.48 (w), 12.35 μ (w); MS *m/e* 164 (P, base), 149 (32%, P − CH_3), 124 (64%), 108 (36%), 95 (45%), 78 (36%). Anal. ($C_{10}H_{12}O_2$) C, H. The R_f 0.42 band contained 0.089 g (46%) of hydroquinone.

d. (3-Methyl-2-butenyl)hydroquinone. The nickel complex (0.568 g, 1.38 mmol) in 12 ml of THF was added to 0.302 g (2.80 mmol) of the quinone in 20 ml of THF at −78° as above. The products were separated by preparative TLC, developing twice with 1:1 petroleum ether–ether. The R_f 0.62 band contained 0.155 g (37%) of (3-methyl-2-butenylhydroquinone, mp 150 °C: NMR (acetone-d_6) δ 1.72 (s, CH_3), 3.32 (d, J = 8 Hz, 2, $-CH_2-$), 5.35 (t, J = 8 Hz, 1, C=CH), 6.64 (m, 3, ArH), 7.52 (br s, 2, OH); ir ($CHCl_3$) 2.77 (s, free OH), 2.99 (br m, H-bonded OH), 3.28 (w, trisubstituted alkene), 3.32 (w), 3.35 (m), 3.42 (w), 6.67 (s, aromatic C=C), 6.90 (s), 7.24 (w), 7.60 (w), 8.12 (m), 8.48 (m), 8.70 (w), 9.00 (w), 9.61 (w), 10.40 (w), 10.75 (w), 11.40 (w), 11.70 (w), 12.35 μ (w); MS *m/e* 178 (P, base), 163 (21%, P − CH_3), 161 (20%), 149 (8%), 123 (100%), 110 (8%), 97 (8%), 94 (9%), 77 (8%). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.47; H, 7.78. The R_f 0.45 band contained 0.102 g (34%) of hydroquinone.

e. 2-(2-Methyl-2-propenyl)-*n*-methylbenzoquinone. The nickel complex (0.210 g, 0.543 mmol) in 10 ml of DMF was added to 2-methylbenzoquinone (0.133 g, 1.08 mmol) in 10 ml of DMF at −46° as above. The products were separated by preparative layer chromatography, developing twice with 1:1 petroleum ether–ether. The R_f 0.70 band contained 0.081 g (40%) of 2-(2-methyl-2-propenyl)-*n*-methylbenzoquinone (after oxidation). This product was obtained as a mixture of three geometrical isomers where n = 3, 5, or 6. These isomers were not separated: NMR ($CDCl_3$) δ 1.78 (s, 3, C=CCH_3), 2.06 (m, 3, ring $-CH_3$), 3.12 (s, 2, $-CH_2-$), 4.82 (m, 1, C=CH), 4.93 (m, 1, C=CH), 6.60 (m, 2, ArH). A 100-MHz NMR spectrum resolved the multiplet at 6.60 into three absorptions due to the three different geometrical isomers: 6.75 (s, 11%, 2,3-disubstituted quinone); 6.61 (q, 39%, 2,5-disubstituted quinone); 6.56 (m, 50%, 2,6-disubstituted quinone). Ir (neat) 3.25 (w, gem disubstituted alkene), 3.38 (m), 3.45 (m), 6.05 (s, 1,4-quinone), 6.21 (m, C=C interaction with quinone carbonyls), 6.95 (m), 7.28 (m), 7.42 (w), 7.69 (m), 8.01 (m), 8.30 (w), 8.80 (w), 9.05 (m), 9.43 (m), 9.89 (w), 10.98 (m), 11.70 (w), 12.30 μ (m); MS *m/e* 176 (P, 57%), 161 (base, P − CH_3), 148 (27%, P −CO), 133 (70%, base − CO), 121 (37%, P − methallyl), 105 (70%, base − 2CO), 91 (30%), 79 (52%), 77 (43%), 68 (37%), 57 (58%). Anal. ($C_{11}H_{12}O_2$) C, H. The R_f 0.44 band contained 0.058 g (44%) of 2-methylhydroquinone.

f. 2,3-Dimethyl-5-(2-methyl-2-propenyl)hydroquinone. The nickel complex (0.31 g, 0.80 mmol) was added to 2,3-dimethylbenzoquinone (0.19 g, 1.40 mmol) in DMF as above. The products were isolated by preparative layer chromatography, developing twice with 1:1 petroleum ether–ether. The R_f 0.68 band contained 0.13 g (48%) of 2,3-dimethyl-5-(2-methyl-2-propenyl)hydroquinone as white crystals: NMR (acetone-d_6) δ 1.70 (s, 3, C=CCH_3), 2.10 (s, 3, ring CH_3), 2.12 (s, 3, ring $-CH_3$), 3.28 (s, 2, $-CH_2-$), 4.75 (m, 2, C=CH_2), 6.13 (br s, 1, OH), 6.47 (s, 1, ArH), 7.30 (s, 1, OH); ir (KBr) 3.01 (vs, OH), 3.25 (w, gem-disubstituted alkene), 3.37 (w), 3.42 (m), 3.51 (w), 6.06 (m, gem-disubstituted alkene), 6.16 (w), 6.28 (w), 6.70 (m), 6.92 (s), 7.05 (s), 7.27 (m), 7.40 (s), 7.84 (w), 8.08 (m), 8.21 (s, ArOH), 8.80 (w), 9.20 (s), 9.75 (w), 10.50 (w), 11.10 (m), 11.75 (w), 11.90 (w), 13.30 (w), 14.20 μ (w); MS *m/e* 192 (P, base), 177 (95%, P − CH_3), 162 (17%), 159 (19%), 149 (57%), 107 (36%), 91 (47%), 79 (40%), 77 (51%), 53 (36%). This material was oxidized ($FeCl_3$) to the quinone and analyzed. Anal. ($C_{12}H_{16}O_2$) C, H. The R_f 0.40 band contained 2,3-dimethylhydroquinone (0.10 g, 50%).

g. 2,5-Dimethyl-2-(2-methyl-2-propenyl)cyclohex-2-ene-1,4-dione (2). The reaction was run in the usual fashion using 0.31 g (0.80 mmol) of the nickel complex and 0.19 g (1.4 mmol) of 2,5-dimethylbenzoquinone in DMF. The products were purified by preparative layer chromatography developing twice with 1:1 petroleum ether–ether. The R_f 0.70 band contained 0.13 g (47%) of the product, a yellow liquid: 100-MHz NMR ($CDCl_3$) δ 1.24 (s, 3, ring $CCCH_3$), 1.66 (d, J = 1 Hz, 3, C=CCH_3), 2.02 (d, J = 2 Hz, 3, ring C=CCH_3), 2.17 (d, J = 14 Hz, 1, diastereotopic C=CCH_2-), 2.62 (d, J = 14 Hz, 1 diastereotopic C=CCH_2-), 2.63 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 2.97 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 4.71 (m, 1, C=CH), 4.92 (m, 1, C=CH), 6.59 (m, 1, ring C=CH); ir (neat) 3.23 (m, gem-disubstituted alkene), 3.36 (s), 3.40 (s), 5.77 (s), 5.92 (vs, cyclic six-membered α,β-unsaturated ketone), 6.08 (m, gem-disubstituted alkene), 6.15 (m, nonconjugated alkene), 6.85 (m), 6.95 (m), 7.25 (m), 7.38 (m), 7.48 (w), 7.72 (w), 7.91 (w), 8.06 (w), 8.35 (w), 8.80 (m), 9.25 (w), 9.60 (w), 9.90 (w), 11.10 (m), 12.80 (w), 13.35 μ (w); MS *m/e* 192 (P, 4%), 177 (20%, P − CH_3), 164 (48%, P − CO), 149 (24%, P − CH_3CO), 137 (16%, P − methallyl), 122 (14%), 109 (45%), 96 (42%), 68 (100%), 56 (52%), 55 (30%, methallyl$^+$). Anal. ($C_{12}H_{16}O_2$) C, H. The R_f 0.42 band contained 2,5-dimethylhydroquinone (0.09 g, 47%).

h. 2,6-Dimethyl-6-(2-methyl-2-propenyl)cyclohex-2-ene-1,4-dione (3). The reaction was run in the usual manner with 0.31 g (0.80 mmol) of the nickel complex and 0.19 g (1.40 mmol) of 2,6-dimethylbenzoquinone. The products were separated as in (g). The R_f 0.75 band contained compound **3** (0.12 g, 46%), a yellow oil: 100 MHz NMR ($CDCl_3$) δ 1.29 (s, 3, ring $CCCH_3$), 1.68 (s, 3, C=CCH_3), 2.06 (d, J = 2 Hz, 3, ring C=CCH_3), 2.28 (d, J = 14 Hz, 1, diastereotopic C=CCH_2), 2.60 (d, J = 14 Hz, 1, diastereotopic C=CCH_2), 2.65 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 2.95 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 4.71 (m, 1, C=CH), 4.95 (m, 1, C=CH), 6.62 (m, 1, ring C=CH); ir (neat) 3.23 (m, gem disubstituted alkene), 3.35 (s), 3.40 (s), 5.94 (vs, cyclic six-membered α,β-unsaturated ketone), 6.07 (m, gem disubstituted alkene), 6.18 (m, nonconjugated alkene), 6.89 (s), 7.22 (s), 7.81 (s), 7.95 (m), 8.22 (m), 8.90 (w), 9.30 (w), 9.70 (m), 10.10 (m), 10.80 (sh), 11.15 (s), 11.75 (w), 13.20 μ (w); MS *m/e* 192 (P, 62%), 177 (25%, P − CH_3), 164 (9%, P − CO), 159 (5%), 149 (11%), 137 (base, P − methallyl), 123 (10%), 119 (6%), 55 (9%, methallyl$^+$). Anal. ($C_{12}H_{16}O_2$) C, H. The R_f 0.40 band contained the 2,6-dimethylhydroquinone (0.09 g, 47%). When this same reaction was run at 60° for 6 h, a 65% yield of **3** was obtained, along with 35% of 2,6-dimethylhydroquinone.

i. 2,3-Dimethoxy-5-methyl-5-(2-methyl-2-propenyl)cyclohex-2-ene-1,4-dione (4). The reaction was run in the usual manner using 0.21 g (0.57 mmol) of the nickel complex and 0.19 g (1.04 mmol) of 2,3-dimethoxy-5-methylbenzoquinone in DMF. The products were separated as in (g). The R_f 0.54 band contained compound **4** (0.083 g, 33%), an orange oil: NMR ($CDCl_3$) δ 1.24 (s 3, ring CH_3), 1.66 (s, 3, C=CCH_3), 2.17 (d, J = 14 Hz, 1, diastereotopic CH_2C=C), 2.60 (d, J = 14 Hz, 1, diastereotopic CH_2C=C), 2.25 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 2.78 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 4.00 (s, 6, $-OCH_3$), 4.70 (m, 1, H_2C=C), 4.90 (m, 1, H_2C=C); ir (neat) 3.25 (w), 3.35 (s), 3.40 (s), 3.60 (m), 6.00 (vs, C=O), 6.25 (vs), 6.68 (s), 6.88 (s), 7.22 (m), 7.50 (m), 7.60 (m), 7.80 (m), 8.30 (s), 8.85 (s), 9.20 (s), 9.90 (m), 10.41 (m), 11.00 μ (m); MS parent *m/e* 238. The R_f 0.49 band contained 0.045 g (30%) of 2,3-dimethoxy-5-methylhydroquinone.

j. 2-(2-Methyl-2-propenyl)-1,4-naphthoquinone. The reaction was carried out in the usual fashion using 0.28 g (0.71 mmol) of the nickel complex and 0.22 g (1.40 mmol) of 1,4-naphthoquinone in DMF. Prior to separation as in (g) the mixture was oxidized with a dilute solution of I_2 in acetone. The R_f 0.85 band contained 0.12 g (39%) of 2-(2-methyl-2-propenyl)-1,4-naphthoquinone: NMR (acetone-d_6) δ 1.78 (d, J = 2 Hz, 3, C=CCH_3), 3.27 (s, 2, $-CH_2-$), 4.90 br m, 2, C=CH_2), 6.80 (m, 1, C=CH), 7.85 (br m, 4, Ar − H); ir (neat) 3.25 (w), 3.38 (m), 3.52 (m) 3.58 (m), 6.00 (vs), 6.13 (m), 6.27 (s), 6.90 (m), 7.20 (w), 7.38 (m), 7.53 (m), 7.68 (s, aromatic CH), 7.88 (m), 7.98 (m, C–C vibrated by adjacent quinone carbonyl), 8.70 (m), 8.95 (m), 9.40 (m), 11.00 (m), 11.60 μ (w). MS *m/e* 212 (P, 79%), 197 (base, P − CH_3), 183 (8%), 169 (22%, base − CO), 141 (40%, base − 2CO), 115 (51%), 105 (60%), 76 (66%), 63 (15%), 50 (34%). Anal. ($C_{14}H_{12}O_2$) C, H.

Reaction of π-2-Methallylnickel Bromide with 1,2-Naphthoquinone. The nickel complex (0.53 g, 1.36 mmol) in 15 ml of DMF was added to 1,2-naphthoquinone (0.43 g, 2.72 mmol) in 10 ml of DMF at −50°. The resulting mixture was stirred for 24 h, slowly warming to 25° in the process. After routine isolation and purification by preparative layer chromatography, (silica gel, 4:1 pentane–ether, three developments) two major products were obtained.

Compound 1: R_f 0.72; 187 mg (26%) of white crystals; ir (paraffin oil) 2.94 (sh, OH), 3.25 (w, gem-disubstituted alkene); 3.29 (m), 3.41 (s), 3.50 (s), 6.00 (m, nonconjugated alkene C=C), 6.10 (s, α,β-unsaturated ketone), 6.17 (m), 6.25 (m, arom C=C), 6.83 (m), 7.04 (m), 7.25 (m), 7.69 (w), 7.87 (m), 8.26 (m), 9.01 (m), 10.20 (s), 11.24 (m), 11.36 (m), 13.70 μ; NMR ($CDCl_3$–Me_4Si) δ 1.30 (s, 6, C=CCH_3), 2.12 (d, 2, J = 14 Hz, C=CCH_2-), 2.88 (d, J = 14 Hz, 2, C=CCH_2), 4.41 (m, 2, C=CH_2), 4.65 (m, 2, C=CH_2), 6.20 (s, 1, vinyl H of ring), 6.64 (s, 1, OH), 7.68 (m, 4, arom H); MS *m/e* 268 (P, 14%), 269 (P + 1, 4%), 214 (15%), 213 (base, P − methallyl), 212 (11%), 195 (15%), 185 (16%), 167 (16%), 158 (5%), 153 (9%), 146

(6%), 144 (5%), 143 (6%), 142 (9%), 130 (6%), 129 (6%), 128 (10%), 116 (15%), 92 (5%), 84 (5%), 78 (9%), 56 (9%), 42 (5%), 40 (8%), 38 (10%). This compound is **5**. Anal. ($C_{18}H_{20}O_2$) C, H.

Compound 2: R_f 0.59; 281 mg (49%) of red crystals; ir (paraffin oil) 3.24 (w, gem-disubstituted alkene), 5.68 (w, α-diketone), 5.88, 6.02 (s, quinone C=O), 6.21, 6.29 (m, arom C=C), 6.39, 6.83, 7.09, 7.25, 7.30, 7.75, 8.03, 10.99, 13.16 μ; NMR ($CDCl_3$-Me_4Si) δ 1.84 (s, 3, C=CCH$_3$), 3.40 (s, 2, C=CCH$_2$), 4.92 (m, 2, C=CH$_2$), 6.40 (s, 1, vinyl H of ring), 7.60 (m, 4, arom H); MS *m/e* 212 (P, 14%), 184 (P − CO, 36%), 169 (P − CO − CH_3, 36%), 156 (55%), 155 (P − CO − C_2H_5, 45%), 141 (P − CO − C_3H_7, 86%), 128 (27%), 115 (base), 102 (18%), 101 (23%), 91 (18%), 89 (27%), 76 (23%), 75 (18%), 65 (18%), 63 (27%), 51 (27%), 50 (18%), 41 (18%), 39 (41%). All attempts at purification led to decomposition, and acceptable elemental analysis was not obtained. This compound is 4-(2-methyl-2-propenyl)-1,2-naphthoquinone.

Reaction of π-2-Methallylnickel Bromide with 4-*tert*-Butyl-1,2-benzoquinone. Following the procedure of Durst and Mack,[34] 0.33 g (1.98 mmol) of the *o*-quinone was prepared by oxidizing 4-*tert*-butylcatechol (0.33 g, 1.98 mmol) with *N*-chlorosuccinimide (0.40 g, 3.0 mmol), and triethylamine (0.3 cm^3, 2.2 mmol) in 15 ml of CH_2Cl_2 at −18° for 10 min. The resulting red solution was filtered and 15 ml of DMF was added. The CH_2Cl_2 was removed by rotary evaporator at 1-mm pressure and the resulting *o*-quinone/DMF solution was cooled to −20° overnight. Subsequent filtration yielded a clear red solution to which was added at −50° the nickel complex (0.44 g, 1.14 mmol) in 10 ml of DMF. The resulting mixture was stirred for 12 h, slowly warming to 25° in the process. After routine isolation and purification by preparative layer chromatography (silica gel, 23:3 benzene-*p*-dioxane), 236 mg (54%) of white crystals (mp 109–110.5 °C) was obtained: R_f 0.56; ir (paraffin oil) 2.92 (br, H-bonded OH), 3.09 (br, H-bonded OH), 3.25 (w, gem-disubstituted alkene), 6.06, 6.18, 6.60 (str, arom C=C), 6.83 (str, arom C=C), 6.94, 7.14, 7.25, 7.30 (str, in-plane OH bend), 7.41, 7.63, 7.78, 8.05, 8.30, 8.66, 9.62, 9.73, 10.75, 11.25, 11.43, 11.63, 12.27, 12.99, 13.85 μ; NMR ($CDCl_3$-Me_4Si) δ 1.34 (s, 9, $(CH_3)_3C$-), 1.72 (s, 3, vinyl -CH_3), 3.46 (m, 2, vinyl -CH_2-), 4.68 (m, 2, vinyl H), 5.20 (br, s, 2, OH), 6.76 (s, 1, arom H), 7.04 (s, 1, arom H), the two downfield singlets are characteristic[35] of 1,2,4,5-tetrasubstituted aromatics; MS *m/e* 220 (P, 69%), 221 (P + 1, 14%), 206 (17%), 205 (base, P − CH_3), 177 (P − CO, 7%), 176 (29%), 175 (24%), 164 (14%), 163 (P − C_4H_9, 65%), 162 (14%), 161 (14%), 145 (38%), 137 (10%), 117 (12%), 115 (12%), 91 (7%), 77 (5%), 57 (14%). A portion was recrystallized from hot pentane and submitted for analysis. Anal. ($C_{14}H_{20}O_2$) C, H. This material is 1,2-dihydroxy-4-*tert*-butyl-5-(2-methyl-2-propenyl)-benzene.

Reactions in the Presence of Carbon Monoxide. (a) π-2-Methallylnickel bromide (0.520 g, 1.34 mmol) in 15 ml of DMF was added to benzoquinone (0.145 g, 1.30 mmol) in 13 ml of DMF at −46° over a period of 1 h. The reaction vessel was opened to a balloon filled with carbon monoxide and the mixture was allowed to stir and warm up as usual. After 9 h the reaction was quenched and the products were isolated and purified in the usual way be developing twice with 1:1 petroleum ether–ether on silica gel. The R_f 0.53 band contained 0.167 g (78%) of (2-methyl-2-propenyl)hydroquinone, the only product.

(b) π-2-Methallylnickel bromide (0.387 g, 1.00 mmol) in 11 ml of DMF was added to 2-methylbenzoquinone (0.122 g, 1.00 mmol) in 11 ml of DMF at −46° over a period of 1 h. The reaction vessel was opened to a balloon filled with carbon monoxide and the mixture was allowed to stir and warm up as usual. After 7 h the reaction was quenched and the only product was isolated and purified in the usual manner, developing twice with 1:1 petroleum ether–ether on silica gel. The R_f 0.50 band contained 0.107 g (79%) of 2-(2-methyl-2-propenyl)-*n*-methylhydroquinone as the only product.

2,3-Benzo-6-methyl-6-(2-methyl-2-propenyl)cyclohexane-1,4-dione (10). The nickel complex (0.378 g, 2.20 mmol) in 11 ml of DMF was added to 2-methyl-1,4-naphthoquinone (0.213 g, 0.550 mmol) in 11 ml of DMF at 25°. The reaction was stirred for 7.5 h and quenched. The products were isolated and purified in the usual manner. The R_f 0.82 band contained 0.170 g (72%) of **10**: 100-MHz NMR ($CDCl_3$) δ 1.34 (s, 3, ring -CH_3), 1.66 (d, J = 2 Hz, 3, C=CCH$_3$), 2.27 (d, J = 18 Hz, 1, diastereotopic C=CCH-), 2.69 (d, J = 18 Hz, 1, diastereotopic C=CCH-), 2.87 (d, J = 17 Hz, 1, diastereotopic ring -CH-), 3.13 (d, J = 17 Hz, 1, diastereotopic ring -CH-); 4.69 (m, 1, C=CH), 4.92 (m, 1, C=CH), 7.82 (m, 2, ArH), 8.10 (m, 2, ArH); ir (neat) 3.23 (m, gem disubstituted alkene), 3.36 (s), 3.40 (s), 5.90 (vs, cyclic ketone), 5.98 (m, nonconjugated alkene), 6.25 (s, aromatic C=C), 6.86 (m), 7.05 (w), 7.24 (m), 7.39 (w), 7.54 (sh), 7.74 (s), 7.89 (s), 7.99 (s), 8.22 (m), 8.63 (w), 8.96 (w), 9.42 (w), 9.84 (w, 10.08 (m), 10.12 (m), 10.80 (m), 11.10 (m), 12.45 (m), 12.80 (m), 13.10 (s), 13.60 (m), 14.10 (w), 14.80 μ (w); MS *m/e* 228 (P, 17%), 213 (33%, P − CH_3), 173 (16%, P − methallyl), 145 (29%, P − methallyl − CO), 115 (32%, P − methallyl − 2CO), 104 (56%), 91 (27%), 76 (base), 55 (30%, methallyl$^+$). Anal. ($C_{15}H_{16}O_2$) C, H. The R_f 0.72 band contained 0.189 g (50%) of 2-methyl-1,4-naphthoquinone.

Preparation of Sodium Naphthalenide. Following a previously described procedure,[37] naphthalene (1.44 g, 11.3 mmol) was dissolved in 36 ml of THF and added to freshly cut sodium metal (0.27 g, 11.7 mmol) in a 50-ml three-necked flask containing a magnetic stir bar and fitted with a serum cap, stopper, and stopcock. The entire operation was conducted under an argon atmosphere. The reaction mixture was stirred at 0° for 2 h, resulting in a dark green homogeneous mixture. Assuming quantitative conversion of naphthalene, the resulting solution is 0.31 M in radical anion. Solutions of sodium naphthalenide were stored under argon in the refrigerator and thus kept were stable for several weeks.

Initiation of π-Allylnickel Bromide Reactions by Sodium Naphthalenide. (a) Reaction of Trimethylbenzoquinone with π-2-Methallylnickel Bromide. The nickel complex (0.24 g, 0.61 mmol) in 10 ml of DMF and sodium naphthalenide (0.4 cm^3 of the above solution, 0.12 mmol) were added over a period of 15 min to a solution of trimethylbenzoquinone[33] (0.19 g, 1.2 mmol) in 10 ml of DMF at −50°. The resulting mixture was stirred for 16 h, slowly warming to 25° in the process. After routine isolation and purification by preparative layer chromatography (silica gel, 4:1 pentane–ether, two developments), two major products were obtained.

Compound 1: R_f 0.68; 38 mg (16%) of yellow oil; ir (neat) 3.05, 3.24 (w, gem-disubstituted alkene), 3.36, 3.41, 3.49 (CH), 5.75, 6.02, 6.10, (s, 1,4-quinone), 6.17 (m), 6.94 (m), 7.27 (m), 7.69 (m), 7.91 (m), 8.20 (w), 8.85 (w), 9.00 (w), 9.35 (w), 9.60 (w), 9.75 (w), 10.60 (w), 11.24 (m), 13.89 μ (m); 100 MHz NMR (acetone-d_6/Me_4Si) δ 1.72 (s, 3, vinyl CH_3 of allyl), 1.98 (s, 9, ring -CH_3), 3.20 (s, 2, vinyl -CH_2-), 4.50 (m, 1, vinyl H), 4.70 (m, 1, vinyl H); MS *m/e* 204 (P, 91%) 189 (base, P − CH_3), 175 (6%), 161 (59%, P − C_3H_7), 133 (27%, P − C_3H_7CO), 91 (27%), 77 (27%), 53 (35%).

Anal. ($C_{13}H_{16}O_2$) C, H. This material is 2-(2-methyl-2-propenyl)3,5,6-trimethylbenzoquinone.

Compound 2: R_f 0.46; 68 mg (45%) of pale yellow oil; 100-MHz NMR ($CDCl_3$) δ 1.22 (s, 3, C-C-CH_3), 1.63 (s, 3, C=CCH$_3$), 2.00 (s, 6, ring C=CCH$_3$), 2.20 (d, J = 14 Hz, 1, diastereotopic C=CCH-), 2.55 (d, J = 14 Hz, 1, diastereotopic C=CCH-), 2.50 (d, J = 16 Hz, 1, diastereotopic ring -CH-), 2.91 (d, J = 16 Hz, 1, diastereotopic ring -CH-), 4.67 (m, 1, C=CH), 4.89 (m, 1, C=CH); ir (neat) 3.23 (m, gem-disubstituted alkene), 3.34 (s), 3.40 (s), 5.96 (vs, cyclic six-membered α,β-unsaturated ketone), 6.08 (s), 6.18 (m), 6.88 (m), 7.22 (s), 7.43 (w), 7.63 (m), 7.87 (m), 7.98 (m), 8.10 (m), 8.29 (w), 9.05 (sh), 9.22 (m), 9.70 (m), 11.05 (s), 11.70 (w), 12.20 (w), 12.50 (w), 12.85 (w), 13.20 μ (w). MS *m/e* 206 (P, 8%), 191 (18%), 178 (37%, P − CO), 164 (23%), 151 (45%, P − methallyl), 137 (13%), 123 (50%), 105 (22%), 95 (75%), 43 (base). Anal. ($C_{13}H_{18}O_2$) C, H. This compound is 2,3,5-trimethyl-5-(2-methyl-2-propenyl)-cyclohex-2-ene-1,4-dione (**7**).

Reactions of π-Allylnickel Halide Complexes with Quinones in Formamide. a. Reaction of π-2-Methallylnickel Bromide with Trimethylbenzoquinone. The nickel complex (0.54 g, 1.38 mmol) in 15 ml of formamide was added to trimethylbenzoquinone (0.42 g, 2.77 mmol) in 10 ml of formamide and the resulting mixture was stirred at 25° for 12 h. After routine isolation, oxidation with aqueous $FeCl_3$, and purification by preparative layer chromatography (silica gel, 4:1 pentane–ether), 0.12 g (22% R_f 0.83) of a yellow oil was obtained which exhibited spectral data identical with those of the 2-(2-methyl-2-propenyl)-3,5,6-trimethylbenzoquinone obtained by this reaction in DMF. A portion was distilled at reduced pressure and submitted for analysis. Anal. ($C_{13}H_{16}O_2$) C, H. Trimethylbenzoquinone (0.29 g, 70%) was also recovered.

b. Reaction of π-1,1-Dimethallylnickel Bromide with Trimethylbenzoquinone. The nickel complex (0.46 g, 1.11 mmol) in 10 ml of formamide was added to trimethylbenzoquinone (0.33 g, 2.22 mmol) in 10 ml of formamide and the resulting mixture was stirred at 25° for 22 h. After routine isolation, oxidation with aqueous $FeCl_3$ and purification by column chromatography (silica gel, 15:1 pentane–ether), two products were obtained.

Compound 1: 0.16 g (34%) of yellow oil; ir (neat) 3.07 (w), 3.35 (m), 3.40 (m), 3.49 (m), 6.09 (s, 1,4-quinone), 6.17 (m), 6.93 (m), 7.29 (m), 7.68 (m), 7.77 (m), 7.92 (m), 8.12 (w), 8.49 (w), 8.83 (w), 9.11 (w), 9.36 (w), 9.78 (w), 10.60 (w), 11.47 (w), 11.95 (w), 12.95 (w), 13.90 μ (m); 100 MHz NMR ($CDCl_3$-Me_4Si) δ 1.64 (s, 3, vinyl $-CH_3$), 1.70 (s, 3, vinyl $-CH_3$), 1.99 (s, 9 H, ring $-CH_3$), 3.10 (m, 1, C=CH), 3.20 (m, 1, C=CH); MS *m/e* 218 (P, 91%), 203 (P − CH_3, 77%), 190 (14%), 189 (14%), 188 (14%), 176 (32%), 175 (P − CH_3 − CO, 100%), 161 (14%), 157 (14%), 147 (14%), 119 (14%), 105 (14%), 91 (23%), 79 (14%), 77 (18%), 67 (18%), 65 (14%), 55 (14%), 54 (14%), 53 (27%), 43 (18%), 41 (32%), 40 (27%), 39 (27%). Anal. ($C_{14}H_{18}O_2$) C, H. This compound is 2-(3-methyl-2-butenyl)-3,5,6-trimethylbenzoquinone.

Compound 2: 0.15 g (32%) of pale yellow oil; ir (neat) 3.00 (w), 3.25 (w), 3.35 (m), 3.42 (m), 3.48 (m), 5.98 (vs, cyclic six-membered α,β-unsaturated ketone), 6.18 (m), 6.89 (m), 7.26 (s), 7.51 (w), 7.65 (m), 7.99 (m), 8.25 (w), 9.07 (w), 9.33 (w), 9.69 (w), 10.95 (w), 11.60 (w), 12.09 (w), 12.63 (w), 12.95 (w), 13.30 μ (w); 100-MHz NMR ($CDCl_3$-Me_4Si) δ 1.18 (s, 3, $-CH_3$ of ring), 1.54 (s, 3, vinyl $-CH_3$), 1.65 (s, 3, vinyl $-CH_3$), 1.99 (s, 6, ring vinyl $-CH_3$), 2.09 (d, J = 14 Hz, 1, diastereotopic C=CCH), 2.30 (d, J = 14 Hz, 1, diastereotopic C=CCH), 2.56 (d, J = 16 Hz, 1, diastereotopic ring -CH); 2.82 (d, J = 16 Hz, 1, diastereotopic ring -CH-), 5.00 (m, 1, vinyl H); MS *m/e* 220 (P, 44%), 192 (P − CO, 15%), 178 (P − C_3H_6, 29%), 177 (10%), 152 (P − C_5H_8, 39%), 137 (7%), 124 (24%), 110 (5%), 69 (100%), 55 (10%), 54 (12%), 53 (12%), 44 (63%), 43 (10%), 41 (76%). Anal. ($C_{14}H_{20}O_2$) C, H. This compound is 2,3,5-trimethyl-5-(3-methyl-2-butenyl)cyclohex-2-ene-1,4-dione (**8**). Trimethylbenzoquinone (0.05 g, 11%) was also recovered.

Synthesis of Coenzyme Q_1 (6). 1,1-Dimethylallylnickel bromide (1.32 g, 3.18 mmol) in 85 ml of formamide was added dropwise over a 32-min period to a solution of 2,3-dimethoxy-5-methylbenzoquinone (1.15 g, 6.30 mmol) in 60 ml of formamide. The substrate in formamide was cooled to 1 °C before addition was completed and remained there during addition. After addition was complete the reaction mixture was allowed to slowly warm up overnight, then quenched at 20 °C. Isolation as usual gave a red-brown oil. This crude reaction mixture was dissolved in 20 ml of diethyl ether and stirred overnight with $FeCl_3 \cdot 6H_2O$ (47 g) in 80 ml of H_2O. Routine isolation gave a bright red oil which was placed on a medium-pressure liquid chromatography column and eluted with 6:1 hexane-ether. Band 1, coenzyme Q_1, (0.4 g, 1.6 mmol, 26% yield): NMR ($CDCl_3$) δ 1.66 (s, 3, C=CCH_3), 1.74 (s, 3, C=CCH_3), 1.98 (s, 3, ring $-CH_3$), 3.15 (d, J = 7 Hz, 2, $-CH_2-$), 3.98 (s, 6, OCH_3), 4.91 (m, 1, C=CH); ir (neat) 3.40 (m), 3.51 (sh), 6.08 (vs, 1,4-quinone), 6.20 (vs, C=C interaction with quinone carbonyls), 6.70 (m), 6.89 (s), 7.26 (m), 7.70 (m), 7.90 (s, C=C vibration activated by adjacent quinone carbonyl), 8.30 (m), 8.52 (m), 8.95 (m), 9.10 (m), 9.60 (m), 9.90 (w), 10.50 (w), 10.85 (w), 11.30 (w), 11.80 (w), 13.40 (w), 14.05 μ (w); MS *m/e* 250 (P, 65%), 235 (base, P − CH_3), 203 (25%, base − CO), 197 (16%, benzylium ion), 184 (65%), 169 (19%), 146 (12%), 119 (9%), 91 (18%), 77 (16%), 53 (15%). Anal. ($C_{14}H_{18}O_4$) C, H.

The coenzyme Q_1 band was followed by the red band of starting material (0.26 g, 1.43 mmol, 23%) and the light yellow band of 2,3-dimethoxy-5-methyl-5-(3-methyl-2-butenyl)cyclohex-2-ene-1,4-dione (**11**) (0.14 g, 0.55 mmol, 9%): 100-MHz NMR ($CDCl_3$) δ 1.21 (s, 3, ring $-CH_3$), 1.59 (s, 3, C=CCH_3), 1.70 (s, 3, C=CCH_3), 2.26 (m, 2, diastereotopic $-CH_2C$=C); 2.52 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 2.78 (d, J = 16 Hz, 1, diastereotopic ring $-CH_2-$), 3.96 (s, 3, OCH_3), 4.00 (s, 3, OCH_3), 5.08 (m, 1, C=CH); ir (neat) 3.36 (m), 3.39 (m), 3.48 (w), 5.96 (s, cyclic six-membered α,β-unsaturated ketone), 6.25 (s), 6.86 (m), 7.21 (w), 7.44 (w), 7.60 (w), 7.79 (w), 8.23 (m), 8.72 (w), 8.88 (m), 9.28 (m), 10.02 (m), 10.80 (w), 11.60 (w), 12.80 (w), 13.50 μ (w). MS *m/e* 252 (P, base), 235 (15%, P − CH_3), 224 (39%, P − CO), 209 (30%), 196 (33%, P − 2CO), 183 (64%, P − C_5H_9 side chain), 169 (28%), 156 (19%), 141 (13%), 129 (10%), 111 (10%), 95 (13%), 83 (69%), 69 (54%). Anal. ($C_{14}H_{20}O_2$) C, H.

Synthesis of 3-(2-Methyl-2-propenyl)-2,5-dimethylbenzoquinone. A solution of π-2-methallylnickel bromide (0.28 g, 0.73 mmol) in 8 ml of DMF was added over a 30-min period to a mixture of 2,5-dimethylbenzoquinone (0.20 g, 1.46 mmol) and $NiBr_2 \cdot 3DMF$ (0.63 g, 1.44 mmol) in 12 ml of DMF. The substrate in DMF was cooled to −65 °C before addition and was allowed to slowly warm up after completion of addition. After 16 h, the clear green reaction mixture was quenched at room temperature (20 °C). The crude reaction mixture was extracted with ether and the ether extracts were combined and washed with aqueous HCl as usual. The ether extract was then evaporated to 5–10 ml and 5 ml of H_2O was added. $FeCl_3 \cdot 6H_2O$ (excess) was added to this mixture and the two-phase system was stirred gently for 5.5 h. The oxidized product was isolated as usual, giving a brown-yellow oil (0.258 g).

A 0.201-g portion of this crude reaction mixture was transferred to a preparative layer plate and developed three times with 10:1 petroleum ether–ether. Three compounds were isolated.

Compound 1: yellow crystals, R_f 0.68, 0.03 g; this compound is starting material (0.22 mmol, 19% yield).

Compound 2: a light yellow oil, R_f 0.5, 0.024 g; NMR ($CDCl_3$-Me_4Si) δ 1.80 (s, 3, vinyl CH_3), 2.10 (m, 6, ring CH_3), 3.20 (s, 2, C=CCH_2), 4.60 (m, 1, C=CH), 4.80 (m, 1, C=CH), 6.62 (m, 1, ring H); ir (neat) 3.05 (w), 3.25 (m, gem-disubstituted alkene), 3.37 (s, CH), 3.50 (s), 6.06 (vs, C=O), 6.18 (vs), 6.95 (s), 7.30 (s), 7.62 (s), 7.90 (s), 8.30 (m), 8.44 (s), 8.95 (w), 9.40 (w), 9.70 (m), 9.95 (w), 10.35 (w), 10.50 (m), 11.30 (s), 12.70 (m), 14.80 μ (m). This compound is 3-(2-methyl-2-propenyl)-2,5-dimethylbenzoquinone (0.13 mmol, 11% yield). Anal. ($C_{12}H_{14}O_2$) C, H.

Compound 3: light yellow crystals, R_f 0.44, 0.081 g; this compound is 2,5-dimethyl-2-(2-methyl-2-propenyl)cyclohex-5-ene-1,4-dione (**2**) (0.42 mmol, 36.9% yield).

Synthesis of 3-(2-Methyl-2-propenyl)-2-6-dimethylbenzoquinone. A solution of π-2-methallylnickel bromide (0.28 g, 0.73 mmol) in 8 ml of DMF was added over a 60-min period to a mixture of 2,6-dimethylbenzoquinone (0.20 g, 1.46 mmol) and $NiBr_2 \cdot 3DMF$ (2.6 g, 5.9 mmol) in 12 ml of DMF. The substrate in DMF was cooled to −65 °C before addition and was allowed to slowly warm up after completion of addition. After 16 h, the clear green reaction mixture was quenched at room temperature (20 °C). The crude reaction mixture was extracted with ether and the ether extracts were combined and washed with aqueous HCl as usual. The ether extract was then evaporated to 5–10 ml and 5 ml of H_2O was added. $FeCl_3 \cdot 6H_2O$ (excess) was added to this mixture and the two-phase system was stirred gently for 5.5 h. The oxidized product was isolated as usual, giving a light brown oil (0.279 g).

A 0.178-g portion of this crude reaction mixture was transferred to a preparative layer plate and developed three times with 6:1 petroleum ether–ether. Three compounds were isolated.

Compound 1: a light yellow oil, R_f 0.71, 0.072 g; NMR ($CDCl_3$/Me_4Si) δ 1.75 (s, 3, vinyl CH_3), 2.05 (m, 6, ring CH_3), 3.20 (s, 2, C=CCH_2), 4.55 (m, 1, C=CH), 4.75 (m, 1, C=CH), 6.55 (m, 1, ring H); ir (neat) 3.09 (w), 3.27 (w, gem-disubstituted alkene), 3.40 (m, CH), 3.50 (w), 6.08 (s, C=O), 6.22 (m), 6.95 (m), 7.25 (m), 7.45 (m), 7.60 (m), 7.65 (m), 7.95 (m), 8.20 (w), 8.49 (m), 9.19 (m), 9.45 (w), 9.73 (m), 10.00 (w), 10.50 (m), 11.39 (m), 12.30 (w), 12.60 μ (w); MS, parent *m/e* 190, 175 (P − CH_3), 147, 119, 91, 77, 44, 40. This compound is 3-(2-methyl-2-propenyl)-2,6-dimethylbenzoquinone (0.38 mmol, 40.6% yield). Anal. ($C_{12}H_{14}O_2$) C, H.

Compound 2: yellow crystals, R_f 0.47, 0.034 g; this compound is starting material (0.25 mmol, 27.1% yield).

Compound 3: light yellow crystals, R_f 0.38, 0.027 g; this compound is 2,6-dimethyl-2-(2-methyl-2-propenyl)cyclohex-5-ene-1,4-dione (0.14 mmol, 15.3% yield).

Plastoquinone (9). 1,1-Dimethylallylnickel bromide (0.22 g, 0.51 mmol) in 12 ml of THF was added over a 45-min period to a solution of 2,3-dimethylbenzoquinone (0.14 g, 1.02 mmol) and $NiBr_2 \cdot 3DMF$ (0.86 g, 5 mmol) in 10 ml of THF at −78 °C. After the addition, the reaction mixture was stirred for 16 h and allowed to reach room temperature. Quench at room temperature and workup as usual produced an orange-yellow oily solid. This crude reaction mixture was oxidized by stirring overnight with $FeCl_3 \cdot 6H_2O$. Workup as usual gave a brown oil. A 0.20-g portion of oxidized material was separated by preparative layer chromatography, developing three times with 20:1 petroleum ether–ether. Plastoquinone (0.06 g, 31%) was contained in the R_f 0.59 band: NMR ($CDCl_3$) δ 1.65 (s, 3, C=CCH_3), 1.75 (s, 3, C=CCH_3), 2.01 (s, 6, ring $-CH_3$), 3.10 (d, J = 7 Hz, 2, $-CH_2-$), 5.15 (m, 1, C=CH), 6.44 (m, 1, ring H); ir (neat) 3.36 (m), 3.43 (m), 3.50 (sh), 6.06 (vs, 1,4-quinone), 6.18 (m, C=C), 6.90 (m), 7.25 (m), 7.57 (m), 7.70 (w), 7.88 (w, C=C), 8.02 (w), 8.50 (w), 9.00 (w), 10.05 (w), 10.50 (w), 11.25 (w), 12.20 (w), 12.90 μ (w). MS *m/e* 204 (P, base), 189 (94%, P − CH_3), 174 (10%), 163 (30%), 161 (32%, pyrylium ion − CO), 151 (12%, benzylium ion), 143 (6%), 133 (10%, pyrylium ion − 2CO), 111 (11%), 105 (10%), 91 (17%), 77 (22%), 65 (6%), 53 (6%). Anal. ($C_{13}H_{16}O_2$) C, H.

Reaction of π-2-Methallylnickel Bromide with Quinones in Benzene. a. With Benzoquinone. The quinone (0.084 g, 0.78 mmol) was placed in a Schlenk filtration apparatus, flushed with argon, and dissolved in 8 ml of air-free benzene. The nickel complex (0.30 g, 0.78 mmol) in 7 ml of benzene was added and the mixture was stirred for 2 h at 25°, during which time a black precipitate formed. This precipitate was filtered, washed thoroughly with benzene, and dried under vacuum. The KBr pellet for ir was prepared in an argon-filled glove bag; ir (KBr) 2.95 (s, br), 3.41 (m), 6.07 (m), 6.71 (s), 6.83 (s), 8.34 (s), 9.13 (w), 9.80 (w), 11.15 (w), 12.02 (m), 12.50 (m), 13.24 μ (m).

This black precipitate was dissolved in DMF at −46°, and the reaction was allowed to proceed in the normal fashion. After isolation a 1:1 mixture of hydroquinone and (2-methyl-2-propenyl)hydroquinone was obtained, identified by comparison with authentic material.

b. With Methylbenzoquinone. The above procedure was followed using 0.11 g (0.87 mmol) of benzoquinone and 0.26 g (0.87 mmol) of the nickel complex: ir (KBr) 2.93 (s, br), 3.43 (w), 6.09 (m), 6.23 (m), 7.09 (w), 7.27 (w), 7.81 (m), 8.37 (s), 8.69 (w), 9.14 (m), 10.00 (w), 10.58 (w), 11.42 (w), 12.41 (w), 12.90 (w), 13.00 (w), 14.80 μ (w).

After reaction in DMF and isolation of products as usual, a 1:1 mixture of methylhydroquinone and 2-(2-methyl-2-propenyl)-*n*-methylhydroquinone was obtained, identified by comparison with authentic material.

Reaction of Bis(π-2-methallyl)nickel with 1,4-Naphthoquinone. The requisite nickel complex was obtained by the reduction of π-2-methallylnickel bromide (0.30 g, 0.78 mmol) with Zn/Cu couple in DMF, followed by distillation.[28] This distillate was added to naphthoquinone (0.20 g, 1.3 mmol) in DMF at −50°. After routine reaction and isolation, only 1,4-dihydroxynaphthalene was obtained. No alkylation had resulted.

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