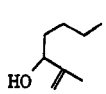
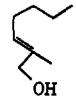
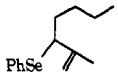
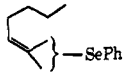
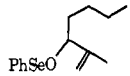
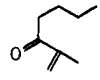
Table I

Reactant	Reagent[a]	Solvent[b]	Products (% yield)[c] Linalool (7)	Geraniol	Nerol	Limonene
1. Geranyl diselenide (5)	$3H_2O_2$	THF-H_2O	78			
2. Geranyl diselenide (5)	$3H_2O_2$	THF-$H_2{}^{18}O$	75 (100% $H_2{}^{18}O$ incorporation)			
3. Geranyl diselenide (5)	$3H_2O_2$	THF-CH_3OH	75 (no methyl ethers)			
4. Geranyl diselenide (5)	$3H_2O_2$	Et_2O	41	18	8	7
5. Geranylselenol (8)	$10H_2O_2$	THF-H_2O	80			
6. Geranyl monoselenide (9)	$3H_2O_2$	THF-H_2O	70			
7. Geranyl linalyl monoselenide (10)	$3H_2O_2$	THF-H_2O	36	22	14	
			 12	 4	 13	 14
8.  11[d]	$1H_2O_2$	THF-CH_3OH	14	71	<1	5
9.  15	$1H_2O_2$	THF-CH_3OH	100	<1		
10.  1[e]	SeO_2	95% EtOH	3	92	5	
11.  17		$CHCl_3$	 18			

[a] The oxidations were performed at 0–25° by addition of 98% H_2O_2. [b] The cosolvent systems consisted of THF with equal volumes of either H_2O or dry CH_3OH. [c] Yields were determined by glc using internal standards. [d] Contaminated with 6% of the *E* and *Z* isomers of **15**. [e] According to Büchi's procedure (ref 11).

Oxidation of these selenides (experiments 8 and 9) resulted in high yields of the rearranged alcohols. More importantly, selenide **11** gave only the (*E*)-alcohol **4**. Oxidation of olefin **1** with SeO_2 followed by borohydride reduction[11] (experiment 10) gave principally (*E*)-alcohol **4** but glpc analysis revealed some of the (*Z*)-alcohol **13** and the secondary isomer **12**. Thus, rearrangement of the selenoxide **16** derived from **11** leads even more selectively to the (*E*)-alcohol **4** than the selenium dioxide oxidation itself (experiment 10). Grieco has just reported[13] the same stereospecificity for the sigmatropic rearrangement of the sulfur analog of **16**.

Selenate ester **17**, formed by reaction of alcohol **12** with C_6H_5SeBr in the presence of AgOAc,[14] decomposed at room temperature to ketone **18** (experiment 11). By contrast, the analogous sulfonate esters rearrange rapidly to the sulfoxides.[6] This result suggests that the carbonyl products formed in SeO_2 oxidations may in part arise directly from the selenium(II) ester (path e, Scheme I).

With the exception of experiment 4, where involvement of path c seems likely,[15] most of the products in Table I appear to derive from hydrolysis of the Se–O bond in the selenium(II) ester (path d). The mild conditions employed for these oxidations (0–25°) are no doubt responsible for suppression of path c which would be favored at the higher temperatures (70–100°) usually required in SeO_2 oxidations. The ease with which phenyl allyl selenides undergo oxidation–rearrangement, in high yield, to allylic alcohols suggests synthetic applications which we are pursuing.

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(13) P. A. Grieco, *Chem. Commun.*, 702 (1972).
(14) According to the procedure of H. Rheinboldt, "Methoden der Organischen Chemie," H. Weyl, Ed., 4th ed, Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 1176.
(15) Actually small amounts (2–10%) of geraniol, nerol, and limonene were also observed in experiments 1, 2, 3, 5, and 6.

Reactions of π-Allylnickel Bromide Complexes with Conjugated Systems. I. Reaction with Quinones. The Synthesis of Coenzyme Q_1 and Plastoquinone-1

Sir:

We report here a new and unusual reaction, the alkylation of quinones by π-allylnickel bromide com-

Scheme I

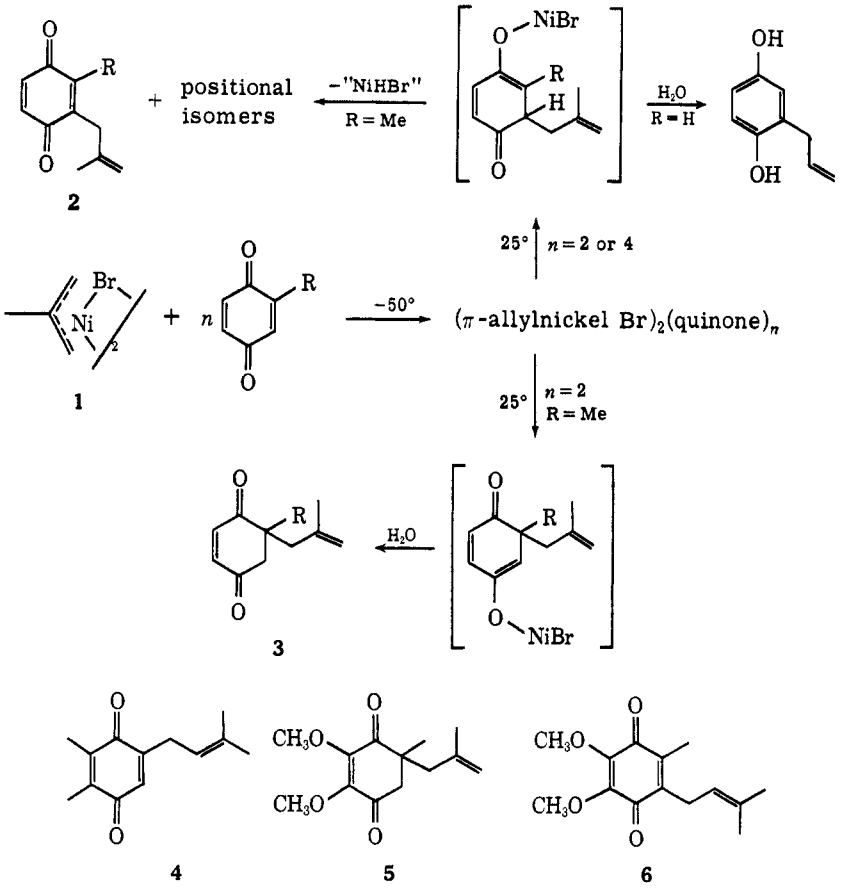

Table I. Alkylation of Quinones with π-Allylnickel Bromide Complexes[a]

π-Allylnickel bromide (1)	Quinone	Ratio quinone/Ni complex	Product[b]	Yield, %[c,d]
Allyl	*p*-Benzoquinone	2:1	Allylhydroquinone	58 (46)
2-Methallyl	*p*-Benzoquinone	2:1	(2-Methyl-2-propenyl)hydroquinone	86 (54)
1-Methallyl (crotyl)	*p*-Benzoquinone	2:1	(2-Butenyl)hydroquinone[e]	83 (42)
1,1-Dimethylallyl	*p*-Benzoquinone	2:1	(3-Methyl-2-butenyl)hydroquinone	54 (37)
2-Methallyl	1,4-Naphthoquinone	2:1	2-(2-Methyl-2-propenyl)-1,4-naphthoquinone	39 (39)
2-Methallyl	2-Methylbenzoquinone	2:1	2-Methyl-?-(2-methyl-2-propenyl)-benzoquinone (2)	38 (21)[f]
			5-Methyl-5-(2-methyl-2-propenyl)-cyclohex-2-ene-1,4-dione (3)	11 (6)
2-Methallyl	2-Methylbenzoquinone	4:1	2	45 (28)
			3	~0
2-Methallyl	2,3-Dimethylbenzoquinone	2:1	2,3-Dimethyl-5-(2-methyl-2-propenyl)benzoquinone	82 (40)
1,1-Dimethylallyl	2,3-Dimethylbenzoquinone	2:1	Plastoquinone-1 (4)	61 (30)
2-Methallyl	2,3-Dimethoxy-5-methylbenzoquinone	2:1	2,3-Dimethoxy-5-methyl-5-(2-methyl-2-propenyl)cyclohex-2-ene-1,4-dione (5)	48 (33)
1,1-Dimethylallyl	2,3-Dimethoxy-5-methylbenzoquinone	4:1	Coenzyme Q_1 (6)	30 (40)
2-Methallyl	Duroquinone	2:1	Duroquinone	~100

[a] Reaction conditions not optimized. [b] Characterized by infrared, nmr, and mass spectra, and elemental analysis. [c] Yields refer to purified product, isolated by preparative layer chromatography. [d] Varying amounts of hydroquinone, from reduction of substrate, are recovered. Yield is calculated from amount of quinone consumed [amount added − (amount recovered + amount hydroquinone recovered)]. Yields in parentheses are based on nickel complex. [e] Mixture of cis and trans isomers by nmr. [f] Mixture of positional isomers.

plexes, and its utilization in the synthesis of coenzyme Q_1 (6) and plastoquinone-1 (4). Thus, the reaction of π-allylnickel bromide complexes (1) with quinones in polar solvents (THF, DMF) produces *allyl-substituted* quinones in moderate to high yield (Scheme I).[1] The

(1) The reaction between π-allylnickel halides and benzoquinones in nonpolar solvents to form insoluble complexes which catalyze the polymerization of dienes has been reported. See, for example, A. G.

generality of this reaction is apparent from the results summarized in Table I.

The reactions were carried out by the dropwise addition of the π-allylnickel bromide complex (1 mmol) in THF (10 ml) to the quinone (2–4 mmol) in THF (10 ml) under argon at $-50°$. After addition was complete the reaction was stirred at $-50°$ for 2 hr, allowed to slowly warm to 25°, and stirred at this temperature for 4 hr. The crude product was isolated by partition between ether and water. The ether phase was dried over anhydrous magnesium sulfate and concentrated, and the crude product was purified by preparative layer chromatography on silica gel, developing with 1:1 pentane–ether mixtures.[2]

The type of product obtained is dependent upon substrate. *p*-Benzoquinone reacts to produce allyl-substituted *hydroquinones*, while all other quinones studied produce allyl-substituted *quinones*. A major side product in all reactions is the hydroquinone arising from simple reduction of the substrate. This reduction is most extensive with *p*-benzoquinone, but is observed to a lesser degree with the other substrates. Quinones having methyl groups adjacent to an unsubstituted position (*e.g.*, 2-methylbenzoquinone) suffer attack at the *methylated* position as well as the unsubstituted position (Scheme I). This can be eliminated, or at least greatly reduced, by using a twofold excess of quinone. No attack at the methylated position is observed when adjacent positions both bear methyl groups (*e.g.*, 2,3-dimethylbenzoquinone). Duroquinone (tetramethylbenzoquinone) is recovered unchanged from the reaction. Quinones with several unsubstituted positions are alkylated nonspecifically. However, *only monoalkylation* products are observed.

Although the mechanism of this substitution has not yet been clarified, the results can be rationalized by Scheme I. In this scheme initial π-allylnickel bromide–quinone complex formation occurs at low temperatures. Upon warming, 1,4 addition to the quinone results. The site of allyl attack depends upon the nature of the initial complex, which, in turn, depends upon reactant ratios.[3] The 1,4 adducts then decompose or hydrolyze to produce the observed products. However, other likely mechanisms cannot be dismissed at this time.

The synthetic utility of this procedure is demonstrated by the synthesis of coenzyme Q_1 (**6**) in one step from 2,3-dimethoxy-5-methylbenzoquinone in 40% yield.[4] Similarly, plastoquinone-1 (**4**) was prepared in 61% yield. This procedure avoids the disadvantages of polyalkylation, chromanol formation, side-chain cyclization, and difficult product isolation previously encountered in the synthesis of these compounds.[6] Since a major side product, the hydroquinone, is easily reoxidized in high yield to the starting quinone, little loss of that starting material is experienced. The requisite π-allylnickel bromide complexes are easily prepared in one operation in ~90% yield by the reaction of the allylic bromide with nickel carbonyl.[5] Complexes with polyisoprenoid allyl groups (π-geranyl, π-farnesyl) or allyl groups containing functionality (COOEt, OCH_3) can be prepared,[5] allowing in principle the synthesis of naturally occurring or unusually functionalized isoprenoid quinones not readily available by present methods.

Investigations are continuing into the scope, synthetic utility, and mechanism of this promising alkylation reaction.

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(2) The scale of this reaction can be increased without experimental difficulty.

(3) The recent isolation and preliminary characterization of complexes (π-allylnickel Cl)$_2$(quinone) and (π-allylnickel Cl)$_2$(quinone)$_3$ strengthen this hypothesis. See M. R. Gal'ding and N. A. Buzina, *Dokl. Akad. Nauk SSSR*, **197**, 586 (1971). We are presently investigating these complexes as intermediates in the above reaction.

(4) While this work was in progress K. Sato, S. Inoue, and R. Yamaguchi, *J. Org. Chem.*, **37**, 1889 (1972), reported the synthesis of coenzyme Q_1 in an overall yield of ~20% over eight steps from the quinone, using the well-known[5] reaction between π-allylnickel halides and aromatic halides as the key step.

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(6) D. E. Wolf, C. H. Hoffman, N. R. Trenner, B. H. Arison, C. H. Shunk, B. O. Lin, J. F. McPherson, and K. Folkers, *ibid.*, **80**, 4752 (1958); U. Gloor, O. Isler, R. A. Morton, R. Rüegg, and O. Wiss, *Helv. Chim. Acta*, **41**, 2357 (1958).

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Energy-Dependent Ring Opening of Cycloalkane Parent Ions[1]

Sir:

In recent communication[2] convincing evidence was presented for retention of the ring (cyclic) structure in the $C_3H_6^+$ ion produced by electron-impact ionization of cyclopropane. This evidence was based on the observation that $C_3H_6^+$ ions from cyclopropane reacted with NH_3 in the following manner

$$c\text{-}C_3H_6^+ + NH_3 \longrightarrow CH_2NH_2^+ + C_2H_5 \quad (1)$$
$$\Delta H = -27 \text{ kcal/mol}^3$$
$$\longrightarrow CH_2NH_3^+ + C_2H_4 \quad (2)$$
$$\Delta H = -16 \text{ kcal/mol}$$

These processes were not observed with $C_3H_6^+$ ions formed by ionization of propylene. Distinct variations both in the rate and modes of reaction of $C_3H_6^+$ ions formed by ionization of cyclopropane, when compared to propylene, were also noted in a previous mass spec-

(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) M. L. Gross and F. W. McLafferty, *J. Amer. Chem. Soc.*, **93**, 1267 (1971).

(3) Thermodynamic data given in this communication have been taken from (a) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **26** (1969); (b) H. E. O'Neal and S. W. Benson, "Thermochemistry of Free Radicals," to be published; (c) F. P. Lossing, private communication.