followed by aqueous acid completed the synthetic sequence, affording the aldehydes 8 (E = Me, CH_2=$CHCH_2$, and MeS, respectively) in generally good to very good overall yields (Table I).[14]

An important variant of the above method entails the use of homologous *N*-benzylideneaminoalkylphosphonates such as **5**.[15] For example, treatment of cyclohexanecarboxaldehyde (**1a**) with the anion obtained by metalation of **5**, followed by the sequential addition of *n*-butyllithium, methyl iodide, and then aqueous acid cleanly produced the methylated ketone **9a**. Since the methyl ketone **9a** appeared to be formed exclusively, the generation and trapping of the metallo enamines **7** (R^3 = Me) occurred with a high degree of regioselectivity. The attainment of a similar degree of regiocontrol in the production of metallo enamines such as **7** (R^3 = alkyl) by the simple deprotonation of the corresponding ketimines is not generally feasible. Thus, by appropriately varying the carbonyl precursor and the alkyl substituent on the phosphonates **4** (R^3 = alkyl), it should now be possible to effect the regioselective generation and trapping of *either* of the two possible metallo enamines of an unsymmetrical, acyclic ketone.

The efficiency and particular ease with which the entire reaction sequence may be executed in one pot is illustrated by the following general procedure. A solution of diethyl *N*-benzylideneaminomethylphosphonate (**4**)[12] (12.0 mmol) in anhydrous THF (5 mL) was added to a stirred solution of *n*-butyllithium (12.0 mmol, 3.3 N hexane) in anhydrous THF (50 mL) at −78 °C. After 1 h, a solution of the carbonyl compound **1** (10.0 mmol) in anhydrous THF (5 mL) was added, and the reaction mixture was allowed to warm to room temperature. After heating the reaction at reflux for 3 h, the solution of 2-aza diene was cooled to −78 °C, whereupon *n*-butyllithium (20.0 mmol, 3.3 N hexane) was added. The reaction mixture was stirred at −78 °C for 1 h, the resulting metallo enamine was treated with the appropriate electrophilic reagent (50.0 mmol), and the mixture was then allowed to warm to room temperature. Following the hydrolysis of the intermediate imine with 1 N hydrochloric acid (2 h at room temperature), extractive workup afforded the crude product **8** or **9**, which was purified by vacuum distillation.

As clearly evidenced by the entries in Table I, this new synthetic strategy for the efficient homologation–alkylation of the carbonyl function via metallo enamines, some of which were heretofore inaccessible, is applicable to a variety of carbonyl compounds and alkylating agents. Furthermore, these intermediate metallo enamines may also be sulfenylated to give β-oxo sulfides, which are known precursors of, inter alia, α,β-unsaturated carbonyl compounds[16] and 1,2-dicarbonyl compounds.[17] The applications of this procedure for geminal substitution to other synthetic transformations, including annelation operations and directed aldol processes, are under active investigation and will be reported independently. The feasibility of extending this methodology to the enantioselective construction of quaternary carbon centers is also being examined.

Acknowledgement. We wish to thank the Robert A. Welch Foundation, the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University Research Institute of the University of Texas at Austin for their generous financial support.

Supplementary Material Available: Characterization of all new compounds together with representative experimental details (3 pages). Ordering information is given on any current masthead page.

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(2) For a survey of the reactions of enolates, see in H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, Chapters 8, 9, 10.
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(7) S. F. Martin, *J. Org. Chem.*, **41**, 3337 (1976).
(8) S. F. Martin, T. S. Chou, and C. W. Payne, *J. Org. Chem.*, **42**, 2520 (1977).
(9) For examples of other approaches to the conversion of ketones to quaternary carbon centers, see (a) B. M. Trost, M. J. Bogdanowicz, and J. Kern, *J. Am. Chem. Soc.*, **97**, 2218 (1975); (b) B. M. Trost, M. Preckel, and L. M. Leichter, *ibid.*, **97**, 2224 (1975); (c) E. Nakamura and I. Kuwajima, *ibid.*, **99**, 961 (1977); (d) B. M. Trost, D. E. Keeley, H. C. Arndt, and M. J. Bogdanowicz, *ibid.*, **99**, 3088 (1977); (e) D. A. Evans, C. L. Sims, and G. C. Andrews, *ibid.*, **99**, 5453 (1977); (f) E. J. Corey and D. L. Boger, *Tetrahedron Lett.*, 5, 9, 13 (1978); (g) ref 6 and references cited therein.
(10) For a review of homologations of carbonyl compounds, see S. F. Martin, *Synthesis*, in press.
(11) Subsequent to the completion of this work another application of this strategy to the synthesis and regioselective trapping of metallo enamines was reported.[4k]
(12) R. W. Ratcliffe and B. G. Christensen, *Tetrahedron Lett.*, 4645 (1973).
(13) During the course of this investigation several other syntheses of 2-aza dienes appeared: (a) A. Dehnel, J. P. Finet, and G. Lavielle, *Synthesis*, 474 (1977); (b) T. Kauffmann, U. Koch, F. Steinseifer, and A. Vahrenhorst, *Tetrahedron Lett.*, 3341 (1977); (c) T. Kauffmann, H. Berg, E. Köppelmann, and D. Kuhlmann, *Chem. Ber.*, **110**, 2659 (1977).
(14) All compounds were adequately characterized by spectral methods (IR, NMR, MS) and all new compounds gave satisfactory high-resolution mass spectral and/or combustion analytical data.
(15) Prepared in 75% yield from **4** by the sequence of metalation–methylation.
(16) C.f., B. M. Trost, T. N. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, **98**, 4887 (1976).
(17) B. M. Trost and G. S. Massiot, *J. Am. Chem. Soc.*, **99**, 4405 (1977).

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Deprotonations with Potassium Diisopropylamide–Lithium *tert*-Butoxide. Alkylation of 1-(Phenylseleno)alkenes and Bis(phenylseleno) Acetals[1]

Summary: A readily prepared, nonnucleophilic, strongly basic mixture of potassium diisopropylamide–lithium *tert*-butoxide (KDA) rapidly deprotonates both 1-(phenylseleno)alkenes (**1**) and bis(phenylseleno) acetals (**3**); in contrast, neither lithium diisopropylamide nor potassium bis(trimethylsilyl)-amide were able to deprotonate these compounds at a perceptible rate. The deprotonation–alkylation of both **1** and **3** is described.

Sir: Nonnucleophilic, strong bases such as lithium diisopropylamide (LDA) have been of invaluable utility in organic chemistry.[2] Although the *rate* of deprotonation of weakly acidic compounds may be changed by several orders of magnitude simply by altering the cation accompanying the amide

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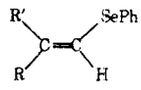
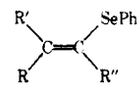
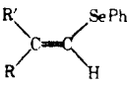
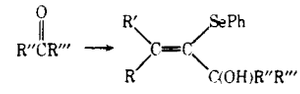
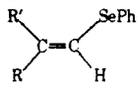
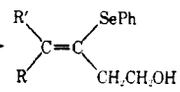
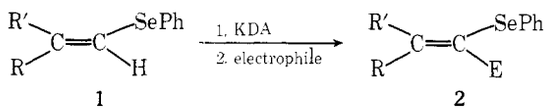
Table I. Products and Yields for the α-Deprotonation–Alkylation of 1-(Phenylseleno)alkenes

entry	R	R′	electrophile[a]	% yield 2[b]
			R″X → 	
a	H	H	CH_3I	98
b	H	H	n-$C_{10}H_{21}Br$	94
c	n-C_4H_9[c]	H	CH_3I	85
d	H	n-C_4H_9	CH_3I	85
e	$(CH_3)_2CH$	H	CH_3I	80
f	$(CH_3)_2CH$	H	n-$C_{10}H_{21}Br$	88
				
g	H	H	$(CH_3)_2CHCHO$	92
h	H	H	2-cyclohexenone	80[d]
i	$(CH_3)_2CH$	H	$(CH_3)_2CHCHO$	95
			epoxide → 	
j	H	H	ethylene oxide	92

[a] 1.05–1.2 equiv of electrophile/equiv of 1. [b] Isolated yields, see ref 14. [c] Starting material contained <10% of (Z)-1-(phenylseleno)hexene. [d] 1,2 addition product.

Scheme I



base,[3] the majority of synthetic applications have involved lithium salts.[4]

We now wish to report that a readily prepared mixture of potassium diisopropylamide–lithium *tert*-butoxide (KDA) rapidly α-deprotonates[5] 1-(phenylseleno)alkenes (1);[6,7] in contrast, neither lithium diisopropylamide nor potassium bis(trimethylsilyl)amide were able to deprotonate 1 at a perceptible rate.[9]

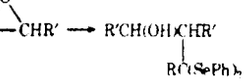
KDA may be prepared by the addition of diisopropylamine to a mixture of n-butylpotassium–lithium *tert*-butoxide[10] in hexane at 0 °C. Although it is possible to prepare n-butylpotassium free of lithium alkoxides,[11] their presence has no detrimental effect on the deprotonation of 1. Alternatively, KDA may be prepared with comparable results by the addition of n-butyllithium to a solution of potassium *tert*-butoxide and diisopropylamine in THF at −78 °C.[12]

The selenium-stabilized carbanions derived by KDA α deprotonation of 1-(phenylseleno)alkenes (1) react rapidly[13] with a variety of electrophiles including primary alkyl halides, epoxides, aldehydes, and ketones (Table I).[14] The deprotonation–alkylation occurs with retention of stereochemistry about the double bond (entries c–f, i). Carbonyl compounds which contain α hydrogens undergo nucleophilic addition rather than enolate formation (entries g–i); 2-cyclohexenone undergoes 1,2 addition (entry h).

The readily available 1-(phenylseleno)alkenes 1[6] may be utilized as acyl carbanion equivalents by conversion to 2 followed by hydrolysis[15] to the corresponding carbonyl compounds (Scheme I).

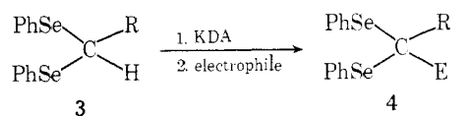
Although LDA is unable to deprotonate bis(phenylseleno) acetals 3 (R = alkyl) at a perceptible rate,[16,17] KDA rapidly deprotonates 3 at −78 °C. The resulting selenium-stabilized carbanions react smoothly with primary and secondary alkyl halides, aldehydes, ketones, enones, and epoxides to give 4 in high overall yield (Scheme II, Table II).[18] It is noteworthy that carbonyl compounds which contain α-hydrogens undergo

Table II. Products and Yields for Alkylations of $RCH(SePh)_2$

entry	R	electrophile[a]	% yield 4[b]
	$RCH(SePh)_2$	R′X →	$RR'C(SePh)_2$
a	CH_3	CH_3I	98
b	CH_3	n-C_4H_9I	95
c	CH_3	$(CH_3)_2CHI$	70[c]
d	CH_3	n-$C_{10}H_{21}Br$	95
e	CH_3	$PhCH_2Br$	88
f	$(CH_3)_2CH$	$PhCH_2Br$	71
g	n-$C_{10}H_{21}$	$PhCH_2Br$	98
	$RCH(SePh)_2$	R′CR″ → 	
h	CH_3	CH_3COCH_3	77
i	CH_3	2-cyclohexenone	76[d]
j	CH_3	$(CH_3)_2CHCHO$	90
k	$(CH_3)_2CH$	$(CH_3)_3CHCHO$	63
l	n-$C_{10}H_{21}$	$(CH_3)_2CHCHO$	84
	$RCH(SePh)_2$	 → 	
m	CH_3	ethylene oxide	82
n	n-$C_{10}H_{21}$	cyclohexene oxide	91

[a] 1.05–1.2 equiv of electrophile/equiv of bis(phenylseleno) acetal. [b] Isolated yields, see ref 18. [c] ~20% 1,1-bis(phenylseleno)-ethane recovered. [d] 1,2-Addition product.

Scheme II



nucleophilic addition rather than enolate formation (entries h–l). Not surprisingly, 2-cyclohexenone undergoes 1,2 addition (entry i).

Bis(phenylseleno) ketals (4) may be utilized in a number of valuable synthetic transformations.[19] In addition, hydrolysis of 4 to the corresponding carbonyl compounds occurs readily under extremely mild conditions (2 equiv of $CuCl_2$, 4 equiv of CuO, 99% acetone, 0 °C, 30 min).[20] For example, **4e** gave phenylacetone (86%), **4g** gave 1-phenyl-2-dodecanone (90%), and the benzoate ester of **4m** gave 4-benzoyloxy-2-butanone (85%).

We believe that KDA will prove to be extremely useful as a nonnucleophilic, strong base for the rapid deprotonation of weakly acidic compounds,[9] and we are currently investigating the use of KDA for the formation of other selenium-stabilized carbanions.[21]

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

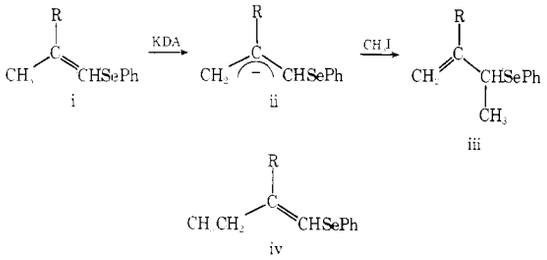
Supplementary Material Available: Full NMR data for compounds 2 and 4 (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Organoselenium Chemistry. 4. For previous paper in this series, see: S. Raucher, *Tetrahedron Lett.*, 2261 (1978).
(2) For leading references concerning the use of lithium diisopropylamide, lithium isopropylcyclohexylamide, lithium dicyclohexylamide, lithium 2,2,6,6-tetramethylpiperidide, and lithium bis(trimethylsilyl)amide, see the appropriate entries in: L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1–6, Wiley-Interscience, New York, N.Y., (1967–1977).
(3) For example, see A. Streitwieser, Jr., and R. A. Caldwell, *J. Am. Chem. Soc.*, **87**, 5394 (1965).
(4) We have found no examples for the preparation of *hindered* potassium *dialkyl*amides; preparation of the less basic potassium bis(trimethylsilyl)-amide and potassium *N*-isopropylanilide has been reported: (a) U. Wannagat

and H. Niederprum, *Chem. Ber.*, **94**, 1540 (1961); (b) G. Stork, J. O. Gardner, R. K. Boeckman, Jr., and K. A. Parker, *J. Am. Chem. Soc.*, **95**, 2014 (1973); (c) C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974); (d) C. A. Brown, *Synthesis*, 427 (1974).

(5) (a) Reaction of 2-methyl-1-(phenylseleno)alkenes (i, R = H or CH_3) with KDA leads to allylic deprotonation rather than α-deprotonation; the resulting selenium-stabilized allyl carbanions (ii) react with methyl iodide to give mixtures (4:1) of α and γ alkylation products, iii and iv, respectively.



(b) For the formation and alkylation of selenium-stabilized allyl carbanions from the corresponding allyl phenylselenides, see: H. J. Reich, *J. Org. Chem.*, **40**, 2570 (1975).

(6) 1-(Phenylseleno)alkenes are easily prepared from the corresponding alkenes: S. Raucher, *J. Org. Chem.*, **42**, 2950 (1977).

(7) Attempts to deprotonate **1** with alkyllithiums led to other reactions,[8] including carbon–selenium bond cleavage: H. Gilman and F. J. Webb, *J. Am. Chem. Soc.*, **71**, 4062 (1949).

(8) S. Raucher and G. A. Koolpe, submitted for publication.

(9) The ability of KDA to deprotonate weakly acidic compounds that are uneffected by LDA is undoubtedly a *kinetic* rather than a *thermodynamic* effect; thus, quantitative deprotonation of compounds which are intrinsically less acidic than diisopropylamine under equilibrium conditions should not be expected. Attempts to deprotonate 1-butyl phenyl selenide with KDA (THF, −78 °C, 30 min; or hexane, 0 °C, 4 h) were unsuccessful.

(10) (a) L. Lochmann, J. Pospisil, and D. Lim, *Tetrahedron Lett.*, 257 (1966); (b) M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 508 (1973); (c) M. Schlosser, *J. Organomet. Chem.*, **8**, 9 (1967). See also: (d) E. Weiss and G. Sauerman, *Chem. Ber.*, **103**, 265 (1970); (e) G. Thirase and E. Weiss, *J. Organomet. Chem.*, **81**, C1 (1974).

(11) L. Lochmann and D. Lim, *J. Organomet. Chem.*, **28**, 153 (1971).

(12) (a) Potassium diisopropylamide–lithium *tert*-butoxide is stable in hexane at 0 °C for at least 1 h; KDA decomposes rapidly at 0 °C in THF. (b) After the initial portion of this research was completed, Professor D. Seebach informed us that he has utilized potassium diisopropylamide–lithium *tert*-butoxide, prepared in a similar manner, for the deprotonation of nitrosamines.

(13) Formation of $PhSe^-$, presumably by α-elimination, occurs to some extent at −78 °C if the carbanions are not utilized immediately.

(14) (a) A typical experimental procedure for the synthesis of **2a** follows. To a solution of potassium *tert*-butoxide (168 mg, 1.50 mmol) and diisopropylamine (152 mg, 1.50 mmol) in THF (4 mL) cooled to −78 °C under an atmosphere of argon was added *n*-butyllithium in hexane (2.4 M, 0.50 mL, 1.2 mmol) over 30 s. The mixture was stirred for 10 min at −78 °C, and a solution of (phenylseleno)ethene (183 mg, 1.00 mmol) in THF (1.5 mL) was added over 1 min. The reaction mixture was stirred at −78 °C for 1 min,[13] a solution of methyl iodide (213 mg, 1.50 mmol) in THF (0.5 mL) was added over 5 s, and stirring at −78 °C was continued for 10 min. The reaction was quenched with methanol (0.5 mL) and poured into saturated aqueous NH_4Cl (4 mL), the THF was removed in vacuo, and the residue was extracted with hexane. Evaporation of the hexane, and purification by evaporative distillation (85 °C, 0.5 mm) gave 2-(phenylseleno)propene (194 mg, 98%): ^1H NMR (CCl_4) δ 2.07 (d, J = 1 Hz, 3 H), 5.08 (s, 1 H), 5.43 (q, J = 1 Hz, 1 H), 7.2–7.7 (m, 5 H). (b) All new compounds were fully characterized by spectroscopic methods. Yields are given for isolated, purified compounds. (c) Additional data: Anal. $C_9H_{10}Se$ (**2a**) *m/e* calcd 197.9948, found 197.9940; $C_{15}H_{22}OSe$ (**2l**) *m/e* calcd 298.0836, found 298.0824; $C_{10}H_{12}OSe$ (**2j**) *m/e* calcd 228.0053, found 228.0066.

(15) (a) Hydrolyzed with $HgCl_2$ in CH_3CN/H_2O: E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970); (b) N. Petragnani, R. Rodrigues, and J. V. Comasseto, *J. Organomet. Chem.*, **114**, 281 (1976).

(16) (a) It is possible to deprotonate the more acidic $(PhSe)_2CH_2$ with LDA in THF at −30 °C. We have successfully alkylated the resulting carbanion with methyl iodide (98% yield), *n*-decyl bromide (95% yield), and benzyl bromide (92%) yield). It is noteworthy that $(PhSe)_2CH_2$ undergoes no detectable dialkylation even in the presence of excess LDA and alkylating agent. (b) Deprotonation of $(PhSe)_2CH_2$ with lithium diisobutylamide in THF at −78 °C, and subsequent reaction with benzophenone, methyl iodide, and D_2O has been reported: D. Seebach and N. Peleties, *Angew. Chem., Int. Ed. Engl.*, **8**, 450 (1969); D. Seebach and N. Peleties, *Chem. Ber.*, **105**, 511 (1972).

(17) Bis(phenylseleno) acetals are available either from the corresponding aldehydes and selenophenol–zinc chloride, or by the alkylation of bis(phenylseleno)methane: (a) W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **16**, 540 (1977), and references cited therein; (b) ref 16.

(18) (a) A typical experimental procedure for the synthesis of **4e** follows. To a suspension of KDA prepared as above[14a] was added a solution of 1,1-bis(phenylseleno)ethane (340 mg, 1.00 mmol) in THF (1.5 mL) over 2 min. After 10 min at −78 °C, a solution of benzyl bromide (180 mg, 1.05 mmol) in THF (1.5 mL) was added over 15 s, and stirring at −78 °C was continued for 15 min. The reaction was quenched with methanol (0.5 mL) and poured into saturated aqueous NH_4Cl (4 mL), the THF was removed in vacuo, and the residue was extracted with hexane. Evaporation of the hexane gave a white solid which was crystallized from methanol to yield 1-phenyl-2,2-bis(phenylseleno)propane (**4e**): 380 mg (88%); mp 109–110 °C; ^1H NMR ($CDCl_3$) δ 1.48 (s, 3 H), 3.27 (s, 2 H), 7.0–7.8 (m, 15 H). (b) All new compounds were fully characterized by spectroscopic methods. Yields are given for chromatographically pure, isolated products. (c) Additional data: Anal. $C_{21}H_{20}Se_2$ (**4e**) *m/e* calcd 429.9903, found 429.9896; $C_{17}H_{20}OSe_2$ (**4h**) *m/e* calcd 397.9852, found 397.9902.

(19) For example, see: (a) ref 16; (b) D. Seebach and A. K. Beck, *Angew. Chem., Int. Ed. Engl.*, **13**, 806 (1974); (c) W. Dumont, P. Bayet, and A. Krief, *ibid.*, **13**, 804 (1974); (d) W. Dumont and A. Krief, *ibid.*, **14**, 350 (1975); (e) W. Dumont and A. Krief, *ibid.*, **15**, 161 (1976); (f) A. Anciaux, A. Eman, W. Dumont, D. Van Ende, and A. Krief, *Tetrahedron Lett.*, 1613 (1975); (g) A. Anciaux, A. Eman, W. Dumont, and A. Krief, *ibid.*, 1617 (1975); (h) J. N. Denis, W. Dumont, and A. Krief, *ibid.*, 453 (1976); (i) J. Remion, W. Dumont, and A. Krief, *ibid.*, 1385 (1976); (j) M. Sevrin, D. Van Ende, and A. Krief, *ibid.*, 2643 (1976).

(20) (a) T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, **94**, 8641 (1972); (b) T. Mukaiyama, K. Narasaka, K. Maekawa, and M. Furusato, *Bull. Chem. Soc. Jpn.*, **44**, 2285 (1971).

(21) **Note Added in Proof:** Professor Seebach's research involving KDA has now been published: B. Renger, H. Hugel, W. Wykypiel, and D. Seebach, *Chem. Ber.*, **111**, 2630 (1978).

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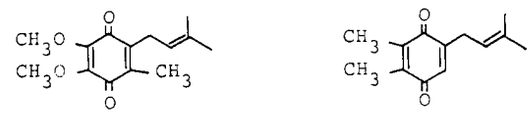
Allylation of Quinones with Allyltin Reagents. New Synthesis of Coenzyme Q_1 and Plastquinone-1[1]

Summary: Lewis-acid catalyzed allylation of *p*-benzoquinone with allyltributyltins is examined; coenzyme Q_1 and plastquinone-1 are prepared in good yields.

Sir: Prenylated quinones, which are widely distributed in nature, play an important role in the life of living things, e.g., in electron transport, oxidative phosphorylation, and blood clotting.[2] Regiospecific and direct introduction of the prenyl group into a quinone ring has been a challenging subject for organic chemists. So far, the direct introduction of an allyl or prenyl group into the quinone ring has met limited success,[4] though the successful allylation of protected quinones has been attained.[3]

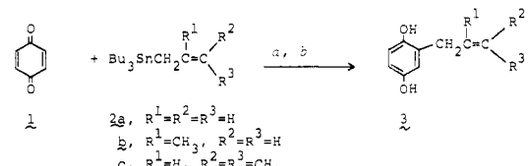
In this communication, we wish to report on the successful direct introduction of the prenyl group into the quinone ring using allyltributyltin reagent. With our procedure regiospecific synthesis of coenzyme Q_1 (**4**) and plastquinone-1 (**5**) was



4 5

successfully accomplished. Typically the reaction was carried out by dropwise addition of an allyltributyltin (**2**) (2 mmol) to a dichloromethane solution (10 mL) of quinone (**1**) (1 mmol) and $BF_3{\cdot}OEt_2$ (1 mmol) under N_2 at −78 °C. After addition was completed, the temperature of the reaction mixture was

Scheme I



1 3

2a, $R^1=R^2=R^3=H$
b, $R^1=CH_3$, $R^2=R^3=H$
c, $R^1=H$, $R^2=R^3=CH_3$
d, $R^1=H$, $R^2=cis$-CH_3 a, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78°C
$R^3=trans$-$CH_2CH_2CH{=}CMe_2$ b, 2N-HCl