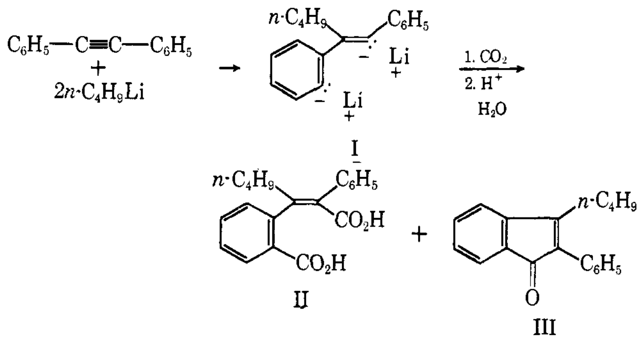


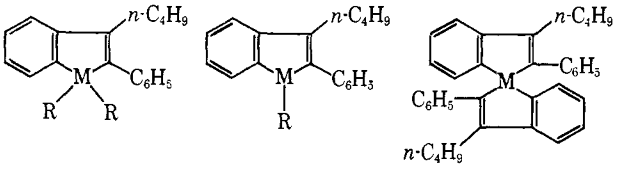
or with N,N,N′,N′-tetramethylethylenediamine (TMEDA) complexed *n*-butyllithium in hexane[13] produces I in yields higher than those obtained when the reaction is carried out in diethyl ether alone.[12] I was characterized by carbonation over Dry Ice, and the yield data are summarized in Table I.

Table I. Yield Data (%) for Formation of I as Determined by Carbonation

Product	1:1 Et_2O-THF system	TMEDA-hexane system	Et_2O system
II	27	30	14^a
III	11^b	17^b	$16^{a,c}$

[a] See ref 12. [b] Yield determined by isolation of 2,4-dinitrophenylhydrazone derivative from the neutral fraction of the reaction mixture. [c] Yield determined by vapor-phase chromatography of the neutral fraction.

Preparation of I in 1:1 ether–THF or in TMEDA–hexane and subsequent reaction with diphenyldichlorosilane in refluxing THF produces, after chromatography on alumina, 3-*n*-butyl-1,1,2-triphenyl-1-silaindene[14] (IV) in yields of 46 and 55%, respectively. After recrystallization from methylene chloride–methanol, IV was obtained in the form of colorless platelets, mp 84–84.5°. *Anal.* Calcd for $C_{30}H_{28}Si$: C, 86.48; H, 6.78; Si, 6.74; mol wt, 417. Found: C, 86.15; H, 7.14; Si, 6.63; mol wt,[15] 413. An nmr spectrum[16] of this compound exhibited resonances for aromatic protons at τ 2.56 (multiplet, 19 H's) and for aliphatic protons at τ 7.30, 8.55, and 9.12 (broadened multiplets, 9 H's).



IV, M = Si;
R = C_6H_5
VII, M = Sn;
R = $-CH{=}CH_2$

V, M = P;
R = C_6H_5
VI, M = P(O);
R = C_6H_5

VIII, M = Sn
IX, M = Ge
X, M = Si

Reaction of I with dichlorophenylphosphine afforded 3-*n*-butyl-1,2-diphenylbenzophosphole (V) as colorless plates, mp 90–91.2°, in 40% yield. *Anal.* Calcd for $C_{24}H_{23}P$: C, 84.18; H, 6.77; P, 9.05; mol wt, 342. Found: C, 83.85; H, 6.79; P, 9.08; mol wt,[15] 353. The corresponding phosphole oxide (VI) was prepared in 90% yield by the peroxide oxidation of V.

The product formed on reaction of I with divinyltin dichloride was not the expected divinyltin heterocycle (VII). The only insolable product, obtained in 9% yield, was shown to be pure by thin layer chromatography (tlc) experiments and had a melting point of 139.5–140.5°. Its nmr spectrum had an integrated aromatic to aliphatic proton ratio of 1.0, and a total analysis suggested a molecular formula of $C_{36}H_{36}Sn$. Evidence pointed toward the formation of the tin spirocycle VIII in this reaction, since nucleophilic displacements of vinyl groups from tin are known in the literature.[17] A compound assigned the spirocyclic structure VIII was subsequently prepared in 28% yield by the reaction of I with tin tetrachloride in ether solution. Its nmr and infrared spectra and tlc properties were in excellent agreement with those of the divinyltin dichloride reaction product. Recrystallization from methylene chloride–methanol afforded white crystals, mp 141.8–142.5°. *Anal.* Calcd for $C_{36}H_{36}Sn$: C, 73.61; H, 6.18; Sn, 20.21; mol wt, 587. Found: C, 73.85; H, 6.16; Sn, 20.02; mol wt,[15] 583.

Substitution of germanium tetrachloride or silicon tetrachloride for the source of the spiro atom has likewise given the crystalline spirocycles IX and X in yields of 28 and 22%, respectively. Analytical data together with molecular weight determinations and nmr spectra confirmed the structures of these compounds.

We are presently studying the reactions of I and related 1,4-dilithium intermediates with various transition metal halides. The details of this work and reactions of metallo–indenyl derivatives will be the subject of future publications.

Acknowledgment. The authors wish to thank the Metal and Thermit Co. and the Dow Corning Corp. for generous gifts of organotin and organosilicon intermediates used in this investigation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in partial support of this research.

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(13) M. D. Rausch and D. J. Ciappenelli, *J. Organometal. Chem.* (Amsterdam), **10**, 127 (1967).

(14) The guidance of Dr. Kurt L. Loening of the Chemical Abstracts Service for his suggestions on the nomenclature and numbering is gratefully acknowledged.

(15) Molecular weight determinations were run at 50° in benzene on a Mechrolab Model No. 302 osmometer.

(16) Recorded on a Varian A-60 nuclear magnetic resonance spectrometer in a saturated $CDCl_3$ solution.

(17) D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(18) National Science Foundation Graduate Trainee, 1965–1967.

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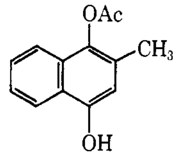
The Conservation of Oxidative Energy.
Formation of Acyl Anhydrides *via* the Oxidation of Hydroquinone Monocarboxylic Esters

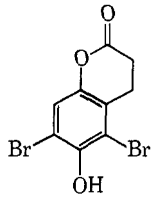
Sir:

The energy released in the course of oxidation of hydroquinone monoesters can be trapped and conserved in the form of highly reactive chemical species, such as acid anhydrides. The principle has been demonstrated by oxidation of the hydroquinone esters I and II in glacial acetic acid, whereupon acetic anhydride is formed from the hydroquinone monoacetate

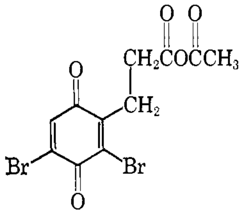
I, and the mixed anhydride III from the hydroquinone lactone II. Such observations may be of significance with respect to the mechanism of mitochondrial oxidative phosphorylation and the role of quinone cofactors therein.



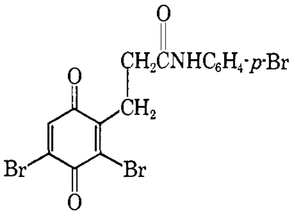
I



II



III



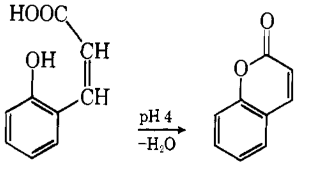
IV

Reaction of 2-methyl-1,4-naphthohydroquinone 1-acetate[1] with N-bromosuccinimide (2 equiv), in glacial acetic acid containing sodium acetate, leads rapidly to the formation of 2-bromo-3-methyl-1,4-naphthoquinone[2a] (74% recovery) and acetic anhydride (98% recovery as *p*-bromoacetanilide). In an analogous manner, by oxidation of the hydroquinone lactone II[3] with 1 equiv of N-bromosuccinimide the quinone carboxylic anhydride III is formed. Addition of *p*-bromoaniline to acetic acid solutions containing III results in nucleophilic attack at either carbonyl, *p*-bromoacetanilide being isolated in 62% yield. The quinone anilide IV, recovered in low yield, was identified by comparison with an authentic sample prepared by oxidation of the corresponding hydroquinone anilide. Control experiments show that, under the reaction conditions, *p*-bromoacetanilide formation does not occur in the absence of an oxidant.

Ultraviolet spectra of the reaction mixtures, following addition of oxidant and dilution with acetonitrile, correspond to those of quinones; thus, in the case of I, the spectrum is superimposable with that of authentic 2-bromo-3-methyl-1,4-naphthoquinone ($\lambda_{max}^{CH_3CN}$ 245, 251, and 280 mμ); in the case of II, the spectrum is very similar to that of 2,6-dibromoquinone ($\lambda_{max}^{CH_3CN}$ 288 mμ).[4] There is no evidence from the spectroscopic data for bromo or acetoxy dienone intermediates.

Although mechanistic experiments have not been completed, it seems likely that the reactions leading to anhydride formation proceed by nucleophilic or solvolytic attack of acetate on an oxidatively generated acylium ion, as a real or transition-state intermediate. Survival of the phenolic oxygen in such a pathway would be in accord with the results of recent isotope experiments.[5]

The possible formation of hydroquinone monoesters in biological systems is a matter of concern with respect to energy production and utilization. It is conceivable that a species such as the reduced form of ubiquinone might be bound tightly to an enzyme, bringing a phenolic group close to a *protein* carboxyl. That the normally difficult esterification of a phenol may be facilitated, under the unimolecular and sterically constrained conditions of enzyme–substrate interaction,[6] is exemplified by the formation of a lactone such as VI from the corresponding phenolic acid V. We have found that VI hydrolyzes at 25° in 0.0067 *M* potassium hydroxide (10% acetonitrile) with a half-life of 4.3 min; upon acidification of the solution to pH 4.0 with acetic acid, VI is regenerated with a half-life of 26.6 min. The rates of these transformations are readily determined from the ultraviolet spectral changes.



V VI

In the oxidation of hydroquinone monophosphates, energy conservation is achieved by cleavage of a phosphorus–oxygen bond and generation of the metaphosphate species.[2,4,7] Our experiments show that an analogous pathway is available for the oxidation of hydroquinone monocarboxylic esters, utilizing an acylium ion intermediate. Since acid anhydrides are isoenergetic with and convertible into acyl phosphates,[8] the coupling of oxidation and phosphorylation by discrete steps has been demonstrated. Furthermore, it is currently held that *nonphosphorylated* high-energy intermediates, $\sim$C, are critically important species in mitochondrial oxidative phosphorylation.[9]

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[1] B. R. Baker, T. H. Davies, L. McElroy, and G. H. Carlson, *J. Am. Chem. Soc.*, **64**, 1096 (1942); R. Hirschmann, R. Miller, and N. L. Wendler, *ibid.*, **76**, 4592 (1954).

[2] (a) V. M. Clark, D. W. Hutchinson, G. W. Kirby, and A. R. Todd, *J. Chem. Soc.*, 715 (1961); (b) T. Wieland and F. Pattermann, *Chem. Ber.*, **92**, 2917 (1959).

[3] G. L. Schmir, L. A. Cohen, and B. Witkop, *J. Am. Chem. Soc.*, **81**, 2228 (1959).

[4] W. Dürckheimer and L. A. Cohen, *Biochemistry*, **3**, 1948 (1964).

[5] C. D. Snyder and H. Rapoport, *J. Am. Chem. Soc.*, **89**, 1269 (1967).

[6] For a discussion of intramolecular processes as models of enzyme–substrate interaction, see T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. 1, W. A. Benjamin, Inc., New York, N. Y., 1966, p 119.

[7] A. Lapidot and D. Samuel, *Biochem. Biophys. Acta*, **65**, 164 (1962).

[8] A. W. D. Davison, *J. Chem. Soc.*, 732 (1955); T. Higuchi, G. L. Flynn, and A. C. Shah, *J. Am. Chem. Soc.*, **89**, 616 (1967).

[9] E. C. Slater, *Bull. Soc. Chim. Biol.*, **48**, 1151 (1966); E. C. Slater in "Comprehensive Biochemistry," Vol. 14, M. Florkin and E. H. Stotz, Ed., Elsevier Publishing Co., New York, N. Y., 1960, Chapter 7, pp 327–387.

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Tosylhydrazones. V.[1] Reaction of Tosylhydrazones with Alkyllithium Reagents. A New Olefin Synthesis

Sir:

We wish to report that aliphatic tosylhydrazones, containing an α-hydrogen, react with alkyllithium reagents to yield olefins, many of which may be difficult to prepare

[1] Tosylhydrazones. IV: R. H. Shapiro and J. H. Duncan, submitted for publication.