Table I. Carbon Chemical Shifts of Algal Sesquiterpenes[a]

carbon	compound 1	2	4	5	6
1	49.1	45.8	48.6	n.o.	50.1
2	48.2	44.8	29.5	44.2	48.9
3	157.7	85.1	18.7	86.2	143.6
4	28.0	36.7	25.3	35.1	124.5
5	34.6	41.4	35.4	41.8	41.9
6	135.4	129.4	135.4	129.9	137.5
7	150.7	151.8	151.9	n.o.	147.4
8	133.1	117.5	133.2	117.7	125.4
9	134.9	136.6	134.9	136.9	136.5
10	121.8	115.8	121.8	115.2	121.4
11	116.5	128.2	115.9	128.6	132.4
12	106.7	11.2	16.2	34.6	62.3
13	19.8	7.1	24.2	7.2	15.0
14	25.4	20.5	22.3	20.4	28.4
15	20.0	22.4	19.7	22.5	22.4
					168.7
					170.9
					21.6
					20.9

[a] n.o. = not observed. Chemical shifts are in parts per million from Me_4Si in $CDCl_3$.

to those of bromo ether A. The 90-MHz ^1H NMR spectrum of this compound displayed signals due to three methyl groups at 0.74 (3 H, d, $J = 7$ Hz), 1.37 (3 H, s), and 2.27 ppm (3 H, s), two protons on a carbon bearing halogen at 3.24 and 3.42 ppm (1 H each, AB quartet, $J = 11$ Hz), and two aromatic protons at 6.60 (1 H, s) and 7.10 ppm (1 H, s). The mass spectrum of this compound showed a molecular formula of $C_{15}H_{18}BrIO$. After loss of iodine, the mass spectrum was superimposable on the mass spectrum of bromo ether A (**5**) after loss of bromine. The ^{13}C NMR spectra of the two compounds were essentially identical except for the resonance of carbon 12. A shift in this resonance of −23.4 ppm can only be ascribed to replacement of a bromine with an iodine.[5,6] Consideration of these data[13] led assignment of the structure as that of iodo ether A (**2**). Iodination of 10-bromo-7-hydroxylaurene using iodine/silver trifluoroacetate in chloroform[8] gave a product in 23% yield identical in all respects with the natural product.

To facilitate separation, the later column chromatographic fractions were acetylated using acetic anhydride/pyridine. LC of the resulting oil gave filiforminyl acetate[4] and a slow-forming solid. Examination of the 90-MHz ^1H NMR spectrum of the latter compound showed the presence of four quaternary methyls, a secondary methyl, two protons α to an acetate, an olefinic proton, and two aromatic protons. The IR spectrum indicated two acetate carbonyls typical of a phenolic acetate and a primary acetate. Analysis of the mass spectrum gave a molecular formula of $C_{19}H_{23}BrO_4$. The ^{13}C NMR spectrum displayed resonances for two acetates, an aromatic ring, an aromatic methyl, and an endocyclic olefin (trisubstituted). These data[14] established the structure as that of 10-bromo-7,12-diacetoxy-$\Delta^{2,3}$-laurene (**6**). Hydrolysis of the acetates using 2% KOH/EtOH gave the unaltered diol. The IR spectrum showed hydroxyl and olefinic absorbance. Mass spectral analysis gave a molecular formula of $C_{15}H_{19}BrO_2$. The 90-MHz ^1H NMR spectrum displayed resonances for a secondary methyl, two quaternary methyls, a methine, an allylic methylene, a methylene α to a hydroxyl, a vinyl proton, two aromatic protons, and two exchangeable protons. These data[15] also supported the structure as that of 10-bromo-7,12-dihydroxy-$\Delta^{2,3}$-laurene (**3**).

The relative stereochemistry of methyls 13 and 14 in compounds **1–3** is based on ^1H NMR and ^{13}C NMR[7] analogies to related compounds.

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(9) Both 11-iodo- and 8-iodolaurinterol were formed in the reaction, with the latter predominating.

(10) Data: mp 147–153 °C dec; $[\alpha]_D$ +225° (c 0.24, $CHCl_3$); mass spectrum *m/e* (rel intensity) 420 (1), 422 (1), 295 (1), 293 (1), 281 (1), 279 (1), 199 (10), 149 (43), 85 (50), 83 (50), 73 (40), 71 (50), 69 (69), 67 (35), 60 (31), 57 (88), 55 (89), 43 (base), and 41 (55); UV (EtOH) 287 nm (log ϵ 3.68) and 292 (3.33); IR ($CHCl_3$) 2.84, 3.38, 6.04, 7.32, 8.29, 8.67, and 11.26 μm; ^1H NMR (CCl_4) 0.71 (3 H, d, $J = 7.0$ Hz), 1.24 (3 H, s), 2.07 (3 H, s), 3.00 (1 H, q, $J = 7.0$ Hz), 4.73 (1 H, s, D_2O), 4.90 (1 H, s), 5.00 (1 H, s), 7.53 (1 H, s), and 0.7–2.6 ppm (4 H, m).

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(13) Data: mp 99–102 °C dec; $[\alpha]_D$ +29° (c 0.94, $CHCl_3$); high resolution mass spectrum (70 eV) *m/e* 419.9594 (calcd for $C_{15}H_{18}{}^{79}BrIO$, 419.9588); mass spectrum *m/e* (rel intensity) 422 and 420 (base), 295 (36), 293 (36), 239 (30), 237 (30), 214 (78), 201 (47), 199 (82), 169 (31), 145 (47), 128 (41), 11, (41), 107 (87), 94 (31), and 91 (32); UV (EtOH) 237 nm (log ϵ 3.89), 288 (3.34), and 298 nm (3.36); IR (CCl_4) 3.38, 6.18, 6.41, 6.76, 7.20, 8.06, 9.22, 10.73, and 11.34 μm; ^1H NMR (CCl_4) 0.74 (3 H, d, $J = 7.0$ Hz), 1.37 (3 H, s), 2.27 (3 H, s), 3.24 and 3.42 (2 H, AB quartet, $J = 11$ Hz), 6.60 (1 H, s), 7.10 (1 H, s), and 1.0–2.1 ppm (5 H, m).

(14) Data: mp 104–105 °C; $[\alpha]_D$ +74° (c 1.82, $CHCl_3$); high resolution mass spectrum (70 eV) *m/e* 396.0765 (calcd for $C_{19}H_{23}{}^{81}BrO_4$, 396.0760); mass spectrum *m/e* (rel intensity) 396 (4), 336 (11), 334 (11), 213 (40), 198 (73), 105 (30), 91 (38), 77 (27), and 43 (base); UV (EtOH) 231 nm (log ϵ 4.16, sh), 274 (3.20), 283 (3.16), and 290 (2.95); IR (neat) 3.14, 5.66, 5.72, 6.72, 6.88, 6.92, 7.34, 8.03, 8.14, 8.86, 9.32, 9.77, 11.02, 12.69, and 13.10 μm; ^1H NMR (CCl_4) 0.68 (3 H, d, $J = 7.0$ Hz), 1.27 (3 H, s), 2.04 (3 H, s), 2.28 (3 H, s), 2.39 (3 H, s), 2.56 (1 H, q, $J = 7.0$ Hz), 2.92 (1 H, br d, $J = 5.0$ Hz), 4.53 (2 H, s), 5.54 (1 H, br s), 6.90 (1 H, s), 7.26 (1 H, s), and 2.2 ppm (1 H, m).

(15) Data: mp 141–145 °C; $[\alpha]_D$ + 100° (c 1.18, $CHCl_3$); mass spectrum *m/e* (rel intensity) 312 (2), 310 (2) 294 (4), 292 (4), 279 (4), 277 (4), 231 (4), 198 (11), 168 (20), 141 (40), 128 (30), 115 (63), 77 (base), and 51 (38); UV (EtOH) 233 nm (log ϵ 3.87), 286 (3.44), and 293 (3.42); IR (film) 2.96, 3.22, 3.40, 3.45, 6.04, 6.22, 6.71, 6.86, 7.18, 7.39, 7.99, 8.54, 9.36, 9.82, 9.09, 10.09, 10.36, 10.47, 11.40, 11.83, 12.13, and 12.48 μm; ^1H NMR (acetone-d_6) 0.72 (3 H, d, $J = 7.0$ Hz), 1.37 (3 H, s), 2.03 (3 H, s), 2.27 (3 H, s), 2.93 (2 H, m), 3.73 (1 H, t, $J = 5.0$ Hz, D_2O), 4.13 (2 H, br s, $w_{1/2} = 9.0$ Hz), 5.51 (1 H, m), 6.77 (1 H, s), 7.19 (1 H, s), and 8.43 ppm (1 H, s, D_2O).

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Evidence Further Substantiating the $S_{RN}1$ Mechanism of Aromatic Substitution[1]

Sir:

Despite the common opinion that unsubstituted phenyl halides are unreactive with nucleophiles, several have in recent years been found to react readily with simple halobenzenes and like substrates, at room temperature or below, to form substitution products in high yield.[2] Representative reactions are those of eq 1 and 2. A few reactions of this class occur spon-

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Table I. Competitive Reactions with Monosubstituted Benzenes of Diethyl Phosphite Ion vs. Pinacolone Enolate Ion[a]

expt	PhX	[PhX], M	$[(EtO)_2PO^-K^+]$, M	$[t\text{-}BuCOCH_2^-K^+]$, M	no. of lamps[b]	k_P/k_C[c]	$t_{1/2}$, s (approx)
1	PhI	0.05	0.13	0.16	1	1.35 ± 0.09	110
2	PhI	0.05	0.11	0.10	16	1.37 ± 0.02	12
3	PhBr	0.05	0.12	0.15	1	1.30 ± 0.13	720
4	PhBr	0.05	0.11	0.14	16	1.37 ± 0.10	59
5	PhBr	0.06	0.12	0.14	16[d]	1.31 ± 0.10	145
6	$PhNMe_3^+I^-$	0.05	0.12	0.15	16	1.25 ± 0.03	61
7	PhSPh	0.05	0.12	0.14	16	1.37 ± 0.14	140
8	PhCl	0.05	0.12	0.14	1	1.33 ± 0.03	1380
9	PhCl	0.07	0.12	0.14	16	1.57 ± 0.14	225
10	PhF	0.05	0.12	0.14	16	1.4[e]	18900

[a] In ammonia at reflux, in Pyrex flasks under irradiation in a Rayonet RPR-100 photochemical reactor. [b] Number of "350-nm" lamps in the photochemical reactor. [c] Reckoned as $k_P/k_C = \ln\{[\mathbf{1}]_0/([\mathbf{1}]_0 - [\mathbf{2}]_t)\}/\ln\{[\mathbf{3}]_0/([\mathbf{3}]_0 - [\mathbf{4}]_t)\}$ from observations at several times in each run. [d] "300-nm" lamps. [e] The observed product ratio, [**2**]/[**3**], declined with time owing to slow destruction of **2** in this system; the ratio extrapolated to time zero is listed.

$$PhX + \underset{\mathbf{1}}{(EtO)_2PO^-K^+} \xrightarrow{h\nu} \underset{\mathbf{2}}{PhPO(OEt)_2} + KX \qquad (1)$$

$$PhX + \underset{\mathbf{3}}{Me_3CC(O)CH_2^-K^+} \xrightarrow{h\nu} \underset{\mathbf{4}}{PhCH_2C(O)CMe_3} + KX \qquad (2)$$

taneously in the dark, but most require provocation by photons or solvated electrons.

These reactions are believed, on the basis of evidence of several sorts, to occur by the radical-chain, $S_{RN}1$ mechanism[2] originally proposed[3] (without symbol[4]) in 1966. The propagation cycle is sketched in Scheme I.

An alternative radical-chain mechanism that warrants consideration has the propagation cycle presented in Scheme II. We suggest the symbol $S_{RN}2$. In this mechanism, substrate radical anion $[PhX]^{-}\cdot$ undergoes replacement reaction with nucleophile Y^-, in single step M4 without intermediate, to form product radical anion $[PhY]^{-}\cdot$, whereas the $S_{RN}1$ mechanism utilizes two steps, M1 and M2, and has the phenyl radical as an intermediate.

As a probe of the $S_{RN}2$ possibility, we conducted reactions 1 and 2 in competition with each other, for six substrates, measuring yields of products **2** and **4** by GLC on samples withdrawn at various times. In steps of type M4, nucleofugal group X would be expected to have some effect on discrimination between the two rather different nucleophiles, and therefore the relative reactivities of the two nucleophiles would be expected to depend on the nucleofugal group.[5] On the other hand, in the $S_{RN}1$ mechanism the same intermediate, phenyl radical, reacts with the two nucleophiles in steps of type M2, and relative nucleophile reactivities should not depend on the nucleofugal group.

Our results are displayed in Table I. They show that, with the four phenyl halides, diphenyl sulfide, and phenyltrimethylammonium ion, virtually the same relative reactivity, k_P/k_C, of diethyl phosphite ion with respect to pinacolone enolate ion is observed. k_P/k_C is 1.36 ± 0.08, and all the observations, plus or minus their standard deviations, fall within one standard deviation of this value.[8] The greatest deviation, for chlorobenzene in experiment 9, is countered by the superbly conforming result for the same substrate in experiment 8.

Scheme I. The $S_{RN}1$ Mechanism (Propagation Cycle)

$$[PhX]\cdot^- \longrightarrow Ph\cdot + X^- \qquad (M1)$$

$$Ph\cdot + Y^- \longrightarrow [PhY]\cdot^- \qquad (M2)$$

$$[PhY]\cdot^- + PhX \longrightarrow PhY + [PhX]\cdot^- \qquad (M3)$$

Scheme II. The $S_{RN}2$ Mechanism (Propagation Cycle)

$$[PhX]\cdot^- + Y^- \longrightarrow [PhY]\cdot^- + X^- \qquad (M4)$$

$$[PhY]\cdot^- + PhX \longrightarrow PhY + [PhX]\cdot^- \qquad (M3)$$

The observed uniformity of competition ratio is in excellent accord with the $S_{RN}1$ mechanism but inconsistent with the $S_{RN}2$. We call attention particularly to the difference in steric requirements between the -F and $-NMe_3^+$ nucleofugal groups. Had reaction occurred by the $S_{RN}2$ mechanism with its necessarily close approach of nucleophile to nucleofugal group, significant discrimination between nucleophiles of quite different steric characteristics ought to have been manifested in the reactions of these two substrates. Discrimination between the two nucleophiles would have been expected even if step M4 occurred at encounter-controlled rate.[9]

The fact that k_P/k_C is so near to unity is noteworthy. Previous work has indicated the reactivity of phenyl radical with diethyl phosphite ion to be very high, perhaps similar to that with $(MeO)_3P$,[10] for which a rate constant of 3.5×10^8 M^{-1} s^{-1} has been estimated.[11] It is conceivable that the rates of reactions of both nucleophiles of the present study are close to or at the encounter-controlled limit. In that case, low discrimination between the two would be a natural consequence.

Substrates are listed in Table I in order of diminishing reactivity according to the approximate half-lives with 16 lamps in the reactor. The substantial differences in substrate reactivity doubtless stem largely from differences in initiation rates.

Division of ln $[t_{1/2}(1\ \text{lamp})/t_{1/2}(16\ \text{lamps})]$ by ln 16 gives roughly the kinetic order in light intensity. It is 0.80 for PhI, 0.90 for PhBr and 0.65 for PhCl, all in the vicinity of the kinetic order 0.84 previously estimated for reaction of iodobenzene with $(EtO)_2PO^-K^+$ in Me_2SO solution.[10] In principle these kinetic orders depend on the nature and prevalence of the termination steps involved. It will be of interest to see whether the apparent differences among substrates are upheld by further measurements.

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Spectral Sensitization of the Heterogeneous Photocatalytic Oxidation of Hydroquinone in Aqueous Solutions at Phthalocyanine-Coated TiO_2 Powders

Sir:

Recent investigations have described the application of the principles of semiconductor electrodes to the design of large surface area powders that serve as photocatalysts for reactions of fundamental and practical interest.[1] These photocatalysts were generally materials with wide band gaps and thus they only absorb a small fraction of the available sunlight. However photoactive dyes can be either adsorbed or covalently attached to semiconductor electrode surfaces to sensitize the electrode to visible wavelength light and thus produce photocurrents or photovoltages at longer wavelengths.[2-14] We were intrigued by the possibility that dye-coated semiconductor powders could be employed as useful sensitized heterogeneous photocatalysts with an improved response to visible light. The phthalocyanines appear most appropriate for this study because (1) they are chemically very stable, (2) they have highly absorbing chromophores within the solar spectrum, (3) they have moderately high electrical conductivity so that reasonably thick films with good optical absorption can be prepared, and (4) their redox potentials can be varied by changes in the central metal. To our knowledge, spectral sensitization of semiconductor powders has not yet been demonstrated, although Uchida et al.[15] have shown that the photocatalytic activities for the oxidation of 2-propanol on phthalocyanine-covered ZnO correlated with the oxidation potentials of the phthalocyanine.

We report here the photocatalyzed oxidation of hydroquinone by oxygen in the presence of phthalocyanine-coated TiO_2 powder in the anatase form. The phthalocyanine-coated TiO_2 catalysts were prepared as follows. The phthalocyanines, either metal free (H_2Pc) or magnesium phthalocyanine (MgPc), were dissolved in *N,N'*-dimethylacetamide, TiO_2 (MCB reagent grade, particle size 125–250 μm) was added, the mixture was stirred thoroughly, and the solvent was then removed by evaporation. The reaction was studied with illumination from a 1.6-kW xenon lamp with appropriate optical filters. The general procedure involved irradiation of 20-mL solution samples of 0.20 M Na_2SO_4 containing 2.0 mM hydroquinone and 0.200 g of photocatalyst in Pyrex tubes with continuous bubbling of oxygen. The amount of hydroquinone oxidized was determined by cyclic voltammetric analysis before and after irradiation. Typical results are given in Table I. In control experiments 3 and 4 involving uncoated TiO_2 or H_2Pc-containing solutions irradiated with light of wavelength longer than 460 nm where TiO_2 shows no absorption but H_2Pc has strong absorption, very little oxidation of hydroquinone occurred. The photooxidation efficiency at long wavelengths (>460 nm) was, however, substantially enhanced by coating the phthalocyanines on TiO_2 powder (experiments 5 and 6). Accordingly, the photocatalytic activity at long wavelengths (>460 nm) is associated with the excitation of phthalocyanines and charge transfer at the interface between the phthalocyanine and TiO_2; i.e., it is spectrally sensitized.

Table I. Sensitized Photocatalytic Oxidation of Hydroquinone in Oxygen-Saturated Solutions[a]

expt	catalyst[b]	time of illumination, h	illumination wavelengths	hydroquinone oxidized, %
1	TiO_2 (anatase)	4.0[c]	white light	<1
2	TiO_2 (anatase)	4.0	white light	52
3	H_2Pc	23.0	>460 nm	1
4	TiO_2 (anatase)	22.0	>460 nm	3
5	TiO_2 (anatase)/ H_2Pc[d]	22.5	>460 nm	25
6	TiO_2 (anatase)/ MgPc[d]	23.0	>460 nm	17

[a] 20 mL of 0.20 M Na_2SO_4 containing 2.0 mM hydroquinone. [b] 200 mg of TiO_2 taken. [c] Solution was deoxygenated thoroughly with N_2. [d] TiO_2 was partially coated with ~2 mg of the phthalocyanine from *N,N'*-dimethylacetamide solution.

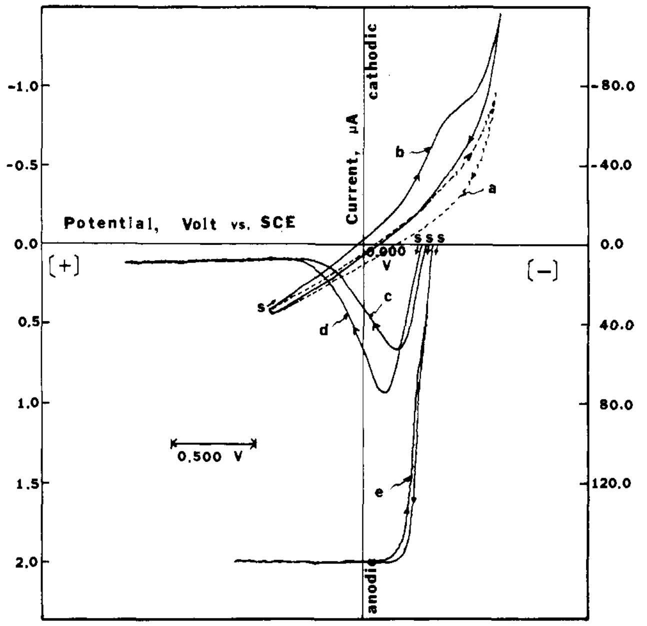

Figure 1. Current-potential curves for n-type TiO_2 (rutile, single crystal) and metal-free phthalocyanine-coated n-type TiO_2 electrodes in the dark and under chopped illumination with 450-W Xe lamp fitted with a 590-nm cut-on filter. Curves a and b use the right-hand scale and curves c–e use the left-hand scale. The photocurrent was measured by phase-sensitive detection techniques. Cyclic voltammetry in the dark at TiO_2 in (a) deoxygenated and (b) oxygen-saturated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH ≃6.9) (scan rate, 100 mV/s; initial potential, +0.60 V vs. SCE). (c) Current-potential curve under illumination at H_2Pc-coated TiO_2 electrodes in deoxygenated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH ≃6.9) or 0.50 M KCl, 0.025 M phosphate buffer (pH ≃6.9) (H_2Pc film thickness, ~500 Å; scan rate, 5 mV/s; initial potential, −0.37 V vs. SCE). (d) Current-potential curve under illumination at TiO_2 in deoxygenated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH ≃6.9) with or without 0.50 mM hydroquinone (scan rate, 5 mV/s; initial potential, −0.28 V vs. SCE). (e) Current-potential curve under illumination at H_2Pc-coated TiO_2 electrodes in deoxygenated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH ≃6.9) containing 0.50 mM hydroquinone (H_2Pc film thickness, ~500 Å; scan rate, 5 mV/s; initial potential, −0.45 V vs. SCE). s denotes the potential at which the scan was initiated.

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