Table III. Relative Enthalpies for the Perhydrophenanthrenes from Equilibrium Studies and Calculations (kcal/mol)

isomer	Johnson,[2] 1953, est	Dauben,[3] 1956, est	Grant,[4] 1974, est	Sandorfy,[5] 1966, est	Aref'ev,[6] 1972, est	MM,[1] 1971	MM1,[17] 1973	MM2, 1979	this work, exptl
tat	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
cat	2.4	2.4	2.7	2.67	2.7	2.57	2.34	2.63	2.66 ± 0.22
cst	2.4	2.4	2.7	2.66	2.7	2.44	2.10	2.53	2.25 ± 0.18
cac di-e							5.09	5.54	
	4.0	4.0	4.5	4.47	5.4	4.01	3.70	4.27	4.60 ± 0.36
di-a							3.59	4.14	
tst twist							7.17	7.49	
	4.8	6.4	4.5	9.74	5.6	7.03	7.32	7.85	8.98 ± 0.70
boat							8.28	8.04	
csc	6.4	7.2-8.2	9.2	7.29	7.5	9.01	8.22	8.46	7.43 ± 0.56

Table IV. Perhydrophenanthrene Isomer Percentage Compositions at Equilibrium[a]

isomer	temp, °C (time, h) 278 (600)	305 (158)	323 (68)	348 (46)
tat	82.1	77.0	72.8	62.9
cat	9.0	10.9	12.2	14.5
dcst	7.9	10.8	13.5	20.3
cac	1.0	1.2	1.4	1.9
tst	0.01	0.03	0.05	0.08
csc	0.04	0.07	0.1	0.3

[a] Gc conditions: Perkin-Elmer F11 chromatograph, support coated capillary column, Carbowax 20 M, 50 ft × 0.02 in. (Perkin-Elmer); carrier gas, N_2; detector, FID. The retention times of the perhydrophenanthrenes were all found to be in the range of 3–5 min, whereas the side products needed over 10 min to elute.

with the values for ΔS_{rel} in Table II, to calculate the values for ΔH. These values, together with estimated and calculated values which appeared in the earlier literature are summarized in Table III. The errors listed correspond to twice the average deviations in the experimental values. The agreement is good except for the two least stable isomers, where the discrepancy between experimental and the MM2 values is about 1 kcal/mol in each case.

The tst compound should have its energy calculated rather accurately. The conformational enthalpy of the twist form of cyclohexane has been directly measured[11] and indirectly measured in substituted compounds,[12,13,14] to yield values of 5.5, 5.9 ± 0.6, 5.5 ± 0.4, and 4.8 ± 0.9, respectively. These values are all in good agreement with each other, and the MM2 value of 5.36 kcal/mol is also in agreement with them. The X-ray structure of a derivative of this ring system has been reported recently,[15] and the geometry found for ring B is almost exactly as calculated by MM2. The reliability of the calculated energy for the csc isomer is hard to assess, since no good value for an analogue is experimentally known. We would take the "best value" for the energy of this compound to be the average of the experimental and MM2 values (7.95 kcal/mol).

Experimental Section

Perhydrophenanthrene (a mixture containing 0.4% tat, 3.2% cat, 38.6% cst, 7.2% cac, and 50.6% csc) was obtained by hydrogenation of phenanthrene in acetic acid with the aid of reduced platinum oxide catalyst. The reaction was carried out at 40–60 psi of pressure at 70 °C, one replacement of the catalyst being necessary to bring the reaction to completion. Equilibration was then carried out on the neat material at 270–350 °C in sealed glass tubes in the presence of 10% Pd/C catalyst. The equilibrated liquid was filtered, diluted with pentane, and analyzed by gas chromatography. The individual isomers were identified by comparison with already known physical constants and behavior on GC or by their relative peak areas before and after equilibration.[9] The assumption was made that equilibrium was reached in each case, which was shown to be correct earlier with the perhydroanthracenes.[9] Some side products, probably from dehydrogenation, were noted, but none of them interfered with the analysis. These higher boiling side products seemed to increase in amount approximately in proportion to the less stable perhydrophenanthrene isomers at higher temperatures, and thus they are very likely at equilibrium too.

The percentage of each isomer in the equilibrium mixture at each temperature was recorded as an average of at least five determinations. The product ratios of the less stable isomers were always checked against the next higher peak in attenuated chromatograms. The numbers are summarized in Table IV.

Acknowledgment. We are grateful to the National Science Foundation (Grant CH 8315543) for support of this work.

Registry No. Pd, 7440-05-3; *tat*-perhydrophenanthrene, 2108-89-6; *cat*-perhydrophenanthrene, 27389-73-7; *cst*-perhydrophenanthrene, 27425-35-0; *cac*-perhydrophenanthrene, 27389-74-8; *tst*-perhydrophenanthrene, 27389-76-0; *csc*-perhydrophenanthrene, 26634-41-3; phenanthrene, 85-01-8.

(11) Squillacote, M.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1975**, *97*, 3244.
(12) Allinger, N. L.; Freiberg, L. A. *J. Am. Chem. Soc.* **1960**, *82*, 2393.
(13) Johnson, W. S.; Bauer, V. J.; Margrave, J. L.; Frisch, M. A.; Dreger, L. H.; Hubbard, W. N. *J. Am. Chem. Soc.* **1961**, *83*, 606.
(14) Margrave, J. L.; Frisch, M. A.; Bautista, R. G.; Clarke, R. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1963**, *85*, 546.
(15) Allinger, N. L.; Hönig, H.; Burkert, U.; Zsolnai, L.; Huttner, G. *Tetrahedron* **1984**, *40*, 3449.
(16) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1982; p 175.
(17) Unpublished calculations with the MM1 force field.[18]
(18) The MM1 and MM2 force field programs are available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405.

Baeyer–Villiger Oxidation of Naphthaldehydes: Easy Access to Naphthoquinones

Richard W. Franck* and Ram B. Gupta

Department of Chemistry, Hunter College/CUNY, New York, New York 10021

Received February 19, 1985

Recently, we[1,2] reported that various 1-naphthaldehydes could be easily obtained by the cycloaddition of an isoquinolinium salt with vinyl ethers. The method was an extension of that first developed by Bradsher[3] and later modified by Falck.[4] We were primarily interested in using this reaction for the synthesis of quinone antibiotics via the naphthaldehydes.

Two possible routes were considered to determine the feasibility of converting 1-naphthaldehydes to 1,4-naphthoquinones. One scheme was the conversion of 1-

(1) Franck, R. W.; Gupta, R. B. *J. Chem. Soc., Chem. Commun.* **1984**, 761.
(2) Franck, R. W.; Gupta, R. B. *Tetrahedron Lett.* **1985**, *26*, 293.
(3) Chen, T. K.; Bradsher, C. K. *J. Org. Chem.* **1979**, *44*, 4680 and earlier references cited therein.

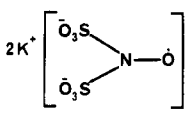
0022-3263/85/1950-4632$01.50/0

naphthaldehydes to 1-naphthylamines, as demonstrated by Falck,[4a] followed by the oxidation to quinones. The second scheme was the conversion of 1-naphthaldehydes to 1-naphthols by the Baeyer–Villiger reaction and then carrying out the oxidation to the quinones. We preferred the latter approach, as more oxidizing reagents are available for the oxidation of 1-naphthols than for 1-naphthylamines, and the yields of quinones are, generally, better.

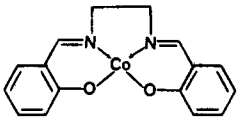
Studies of the Baeyer–Villiger reaction with aromatic aldehydes are mostly limited to benzaldehydes.[5-8] The Baeyer–Villiger reaction of benzaldehydes with electron-donating substituent(s) at ortho and/or para positions by peracids yields mainly the arylformates which are then hydrolyzed by using aqueous base to give the phenols, whereas benzaldehydes lacking electron-donating substituent(s) at the said positions and/or possessing electron-withdrawing group(s) in the aromatic ring give predominantly benzoic acids. Recently, Matsumoto et al.[8] have shown that by using hydrogen peroxide in acidic methanol, phenols could be directly obtained from benzaldehydes without going through the formates. To the best of our knowledge, however, the Baeyer–Villiger reaction has never been applied to naphthaldehydes. This prompted us to carry out the study on naphthaldehydes which we wish to report in this paper.

We have observed that the treatment of naphthaldehydes with *m*-chloroperbenzoic acid in anhydrous dichloromethane at room temperature, followed by nonaqueous workup using anhydrous potassium fluoride according to Camp's procedure,[9] smoothly converts them to naphthylformates (Table I). Initially, we employed conventional aqueous basic treatment of formates to get the naphthols. Interestingly, we observed that the treatment of formates with alumina, activity 1, in dichloromethane cleaved the formates. Thus aqueous conditions (acidification, extraction, etc.) are avoided, and the reaction is very clean. The formate obtained by the Baeyer–Villiger reaction of *p*-anisaldehyde[7] was also cleanly cleaved by alumina to give *p*-methoxyphenol demonstrating the generality of the reaction for arylformates. Apart from nonaqueous reaction conditions, alumina has the additional advantage of selectively cleaving the formates in the presence of acetates (see Table I, entry iv).

Finally, some of the naphthols thus obtained were oxidized to quinones (Table I). The oxidizing reagents, Fremy's salt[10,11] and salcomine,[12,13] gave comparable yields of the quinones. Oxidation with salcomine, however, can be carried out in nonaqueous medium and is thus the method of choice.



Fremy's salt



salcomine

To summarize the cycloaddition of isoquinolinium salts with vinyl ethers followed by the Baeyer–Villiger reaction and oxidation constitutes a new route to naphthoquinones including pyranonaphthoquinones (Table I, entry viii). We are currently applying this method to the synthesis of quinone antibiotics.

Experimental Section

Melting points were determined on a Fisher–Johns melting point apparatus and were uncorrected. Nuclear magnetic resonance spectra were obtained on a JEOL GX400 MHz instrument using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Elemental analyses were performed by the Spang Microanalytical Laboratory, Eagle Harbor, MI. The high resolution mass spectrum was obtained at Mass Spec Facility, The Pennsylvania State University, University Park, PA.

Fremy's salt and salcomine were purchased from Aldrich and *m*-chloroperbenzoic acid was bought from Fluka. All the solvents used were dry and distilled. Thin-layer chromatograms were done on precoated TLC sheets of silica gel 60 F_{254} (E. Merck) by using (2,4-dinitrophenyl)hydrazine spray (for aldehydes and quinones), phosphomolybdic acid spray (for formates and naphthols), or short-wave ultraviolet light to visualize the spots. Alumina, Brockman activity 1, 80–200 mesh, and Florisil, F-100, 60–100 mesh, were obtained from Fisher Scientific. Chromatotron (radial chromatography) plates were prepared by using Kieselgel 60 PF_{254} gipshalting (E. Merck), and all separations using the chromatotron were done under N_2 atmosphere.

General Procedure. (a) Baeyer–Villiger Reaction. To a solution of the naphthaldehyde (0.1 mmol) in anhydrous dichloromethane (5 mL) was added *m*-chloroperbenzoic acid (0.2 mmol). The solution was stirred at room temperature under N_2 atmosphere until TLC showed the disappearance of the aldehyde (4–48 h). Anhydrous potassium fluoride (0.4 mmol) was then added to the reaction mixture, and the stirring was continued for another 4–5 h. It was then filtered, the residue was washed with anhydrous dichloromethane, and the solvent was removed from the filtrate under reduced pressure. The formate so obtained showed a single spot on TLC, and the NMR was recorded without further purification.

(b) Cleavage of the Formate. (i) Using Aqueous Basic Conditions. To a solution of the formate (0.1 mmol) in methanol (2 mL) at 0 °C was added dropwise with stirring a 10% aqueous methanolic solution of Na_2CO_3 (1 mL), and the stirring was continued at 0 °C for 1 h under N_2 atmosphere. The solution was then acidified with cold dilute hydrochloric acid at 0 °C and was extracted with dichloromethane (3 × 10 mL). The organic layer was washed with water and then with saturated sodium chloride and dried (anhydrous $MgSO_4$), and the solvent was removed under reduced pressure. The residue so obtained was purified by use of the Chromatotron to give the naphthol.

(ii) Using Alumina. The formate (0.1 mmol) was dissolved in anhydrous dichloromethane (2 mL), and alumina (250 mg) was added to it. It was stirred under an N_2 atmosphere for 4–6 h. To the solution was then added methanol (1 mL), and it was stirred for additional 0.5 h. It was filtered, the residue was washed with dichloromethane–methanol (1:1), and the combined filtrate was concentrated under reduced pressure. The residue on purification by use of the chromatotron gave the naphthol.

(c) Oxidation of Naphthols to Quinones. (i) Using Fremy's Salt. To a solution of Fremy's salt (0.25 mmol) in 4 mL of water and 1.25 mL of aqueous KH_2PO_4 (0.167 M) at 0 °C was

(4) (a) Manna, S.; Falck, J. R.; Mioskowski, C. *J. Org. Chem.* **1982**, *47*, 5021. (b) Falck, J. R.; Manna, S.; Mioskowski, C. *J. Am. Chem. Soc.* **1983**, *105*, 631.

(5) For reviews see: (a) Hassal, C. H., "Organic Reactions"; Wiley: New York, 1967; Vol. 9, pp 73–106. (b) "Methoden der Organischen Chemie", Houben-Weyl, George Thieme Verlag: Stuttgart, 1976; Vol. VI-1C Part I, pp 286–308. (c) Trahanovsky, W. S.; "Oxidation in Organic Chemistry"; Academic Press: New York, 1978; Part C, pp 254–267.

(6) Hue, R.; Jubier, A.; Andrieux, J.; Resplandy, A. *Bull. Soc. Chim. Fr.* **1970**, 3617.

(7) Godfrey, I. M.; Sargent, M. V.; Elix, J. A. *J. Chem. Soc. Perkins Trans. I*, **1974**, 1353.

(8) Matsumoto, M.; Kobayashi, H.; Hotta, Y. *J. Org. Chem.* **1984**, *49*, 4740.

(9) Camp, F.; Coll, J.; Messeguer, A.; Pericas, M. A. *Tetrahedron Lett.* **1981**, *22*, 3895.

(10) Teuber, H. J.; Gotz, N. *Chem. Ber.* **1954**, *87*, 1236.

(11) For a review see: Zimmer, H.; Lankin, D. C.; Horgan, S. W. *Chem. Rev.* **1971**, *71*, 229.

(12) Van Dort, H. M.; Geursen, H. J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 520.

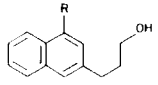
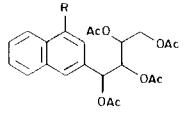
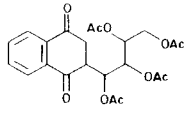
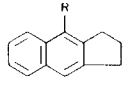
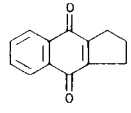
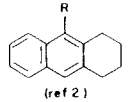
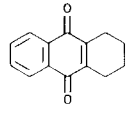
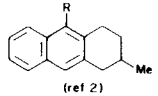
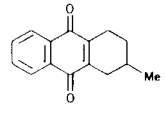
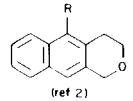
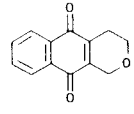
(13) Wakamatsu, T.; Nishi, T.; Ohnuma, T.; Ban, Y. *Synth. Commun.* **1984**, *14*, 1167.

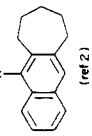
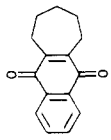
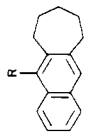
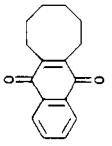
(14) "Dictionary of Organic Compounds", 5th ed.; Chapman and Hall: New York, 1982; Vol. IV, p 4157.

(15) Braun, J. V.; Bayer, O. *Chem. Ber.* **1925**, *58*, 2667.

(16) Rieke, R. D.; Rich, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 7349.

Table I.[a] Yields and Spectral Data for Compounds Prepared

no.	aldehydes	*b*	yield (%)	mp (°C)	naphthols (R = OH) NMR, δ	naphthoquinones	yield (%)	mp (°C)	NMR, δ	analysis/mass
i	1-naphthaldehyde	8.49	92[a]/88[b]	94–95 (Lit.[14] 94)						
ii	2-naphthaldehyde	8.39	80[a]	121–23 (lit.[14] 123)						
iii	 (ref 1)	8.51	80[a]	85–86	1.76 (br s, 1 H, CH_2OH), 1.92–1.99 (m, 2 H, CH_2CH_2OH), 2.78 (t, 2 H, J = 7.63, Ar CH_2CH_2), 3.71 (t, 2 H, J = 6.41, CH_2CH_2OH), 6.21 (br s, 1 H, Ar OH), 6.68 (s, 1 H, Ar H), 7.21 (s, 1 H, Ar H), 7.39–7.46 (m, 2 H, Ar H), 7.70–7.72 (d, 1 H, J = 7.33, Ar H), 8.11–8.13 (d, 1 H, J = 7.93, Ar H)					
iv	 (ref 1)	8.51	59[a]		1.95, 1.99, 2.01, 2.10 (4 s, 3 H each, 4× $OCOCH_3$), 4.13 (dd, 1 H, J = 6.10, 12.27), 4.29 (dd, 1 H, J = 2.75, 12.48), 5.14–5.18 (m, 1 H), 5.64 (m, 1 H), 6.01 (br s, 1 H, Ar OH), 6.06 (d, 1 H, J = 4.88), 6.83 (d, 1 H, J = 1.22, Ar H), 7.39 (s, 1 H, Ar H), 7.44–7.55 (m, 2 H, Ar H), 7.75–7.77 (m, 1 H, Ar H), 8.11–8.13 (m, 1 H, Ar H)		60[f]/63[s]		1.94, 2.04, 2.12, 2.17, (4s, 3 H each, 4 × $OCOCH_3$), 4.19 (dd, 1 H, J = 4.24, 12.81), 4.28 (dd, 1 H, J = 2.12, 12.51), 5.31–5.35 (m, 1 H), 5.48 (dd, 1 H, J = 1.84, 9.74), 6.22 (d, 1 H, J = 1.84), 6.74 (d, 1 H, J = 1.22), 7.73–7.76 (m, 2 H, Ar H), 8.02–8.04 (m, 1 H, Ar H), 8.09–8.11 (m, 1 H, Ar H)	high-resolution electron impact MS, *m/e* 446.1233; $C_{22}H_{22}O_{10}$ requires 446.1213
v	 (ref 2)	8.47	88[a]	92–99	2.18 (quintet, 2 H, J = 7.33), 2.96 (t, 2 H, J = 7.32), 3.06 (t, 2 H, J = 7.12), 4.91 (s, 1 H, Ar OH), 7.30 (s, 1 H, Ar H), 7.37–7.41 (m, 2 H, Ar H), 7.70–7.74 (m, 1 H, Ar H), 8.08–8.10 (m, 1 H, Ar H)		81[f]/85[s]	163–65 (lit.[16] 164–65)	2.11 (quintet, 2 H, J = 7.63), 2.96 (t, 4 H, J = 7.60), 7.69–7.71 (m, 2 H, Ar H), 8.06–8.10 (m, 2 H, Ar H)	
vi	 (ref 2)	8.49	88[a]	106–07 (lit.[15] 108)	1.82–1.89 (m, 2 H), 1.92–1.97 (m, 2 H), 2.80–2.83 (t, 2 H, J = 6.4), 2.74–2.97 (t, 2 H, J = 6.1), 5.09 (s, 1 H, Ar OH), 7.21 (s, 1 H, Ar H), 7.37–7.39 (m, 2 H, Ar H), 7.67–7.69 (m, 1 H, Ar H), 8.05–8.08 (m, 1 H, Ar H)		82[f]	154–55 (lit.[15] 154)	1.74–1.77 (m, 4 H), 2.59–2.62 (m, 4 H), 7.68–7.70 (m, 2 H, Ar H), 8.06–8.08 (m, 2 H, Ar H)	
vii	 (ref 2)	8.46	81[a]/76[b]	89–90	1.09 (d, 3 H, J = 6.1, $CH_3CH<$), 1.43–1.52 (1 H, m), 1.86–1.89 (m, 1 H), 2.04–2.07 (m, 1 H), 2.52–2.59 (m, 1 H), 2.69–2.77 (m, 1 H), 2.90–3.00 (m, 2 H), 5.08 (s, 1 H, Ar OH), 7.18 (s, 1 H, Ar H), 7.29–7.38 (m, 2 H, Ar H), 7.66–7.68 (m, 1 H, Ar H), 8.04–8.06 (m, 1 H, Ar H)		76[f]	103–04	1.08 (d, 3 H, J = 6.71, $CH_3CH<$), 1.20–1.31 (m, 1 H), 1.73–1.75 (m, 1 H), 1.86–1.91 (m, 1 H), 1.99–2.08 (m, 1 H), 2.41–2.49 (m, 1 H), 2.78–2.85 (m, 2 H), 7.64–7.68 (m, 2 H, Ar H), 8.03–8.08 (m, Ar H)	Calcd for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19. Found: C, 79.55; H, 6.15.
viii	 (ref 2)	8.50	90[a]		2.90 (t, 2 H, J = 6.10), 4.10 (t, 2 H, J = 6.10), 4.92 (s, 2 H), 5.26 (s, 1 H, Ar OH), 7.11 (s, 1 H, Ar H), 7.40–7.43 (m, 2 H, Ar H), 7.69–7.72 (m, 1 H, Ar H), 8.04–8.07 (m, 1 H, Ar H)		84[s]	123–25	2.67–2.71 (m, 2 H), 3.93 (t, 2 H, J = 5.50), 4.64 (t, 2 H, J = 2.74), 7.72–7.76 (m, 2 H, Ar H), 8.07–8.12 (m, 2 H, Ar H)	Calcd. for $C_{13}H_{10}O_3$: C, 72.90; H, 4.67. Found: C, 72.40; H, 4.84.

ix		8.49	85[a]	109–10	1.69–1.73 (m, 4 H), 1.82–1.88 (m, 2 H), 2.92–2.96 (m, 4 H), 5.17 (s, 1 H, Ar OH), 7.23 (s, 1 H, Ar H), 7.38–7.44 (m, 2 H, Ar H), 7.67–7.71 (m, 1 H, Ar H), 7.99–8.01 (m, 1 H, Ar H)		75[f]	100–02	1.56–1.61 (m, 4 H), 1.84–1.90 (m, 2 H), 2.85–2.88 (m, 4 H), 7.66–7.71 (m, 2 H, Ar H), 8.05–8.08 (m, 2 H, Ar H)	Calcd. for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19. Found: C, 79.45; H, 6.26.
x		8.51	84[a]	99–100	1.32–1.47 (m, 4 H), 1.72–1.76 (m, 4 H), 2.90–2.97 (m, 4 H), 5.17 (s, 1 H, Ar OH), 7.26 (s, 1 H, Ar H), 7.39–7.44 (m, 2 H, Ar H), 7.69–7.72 (m, 1 H, Ar H), 8.04–8.06 (m, 1 H, Ar H)		84[f]	79–80	1.48–1.50 (m, 4 H), 1.55–1.74 (m, 4 H), 2.80–2.83 (m, 4 H), 7.69–7.71 (m, 2 H, Ar H), 8.08–8.10 (m, 2 H, Ar H)	Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.67. Found: C, 79.90; H, 6.71.

[a] a = formate hydrolysis with Al_2O_3. [b] b = formate hydrolysis with aq. Na_2CO_3. [f] f = oxidation with Fremy's salt. [s] s = oxidation with salcomine. [b] Chemical shift of formate proton (δ) (R = OCHO).

added a methanolic solution of the naphthol (0.1 mmol). The solution was stirred at 0 °C for 2–4 h and then extracted with dichloromethane (3 × 10 mL). The organic layer was washed with water, dried (ahydrous $MgSO_4$), and concentrated under reduced pressure. The residue was purified with use of the chromatotron to give the quinone.

(ii) Using Salcomine. The naphthol (0.1 mmol) was dissolved in anhydrous tetrahydrofuran (4 mL), and salcomine (0.05 mmol) was added to it. It was stirred under oxygen atmosphere for 3–4 h at room temperature. It was then concentrated under reduced pressure and passed through a small bed of Florisil using dichloromethane or dichloromethane–methanol (95:5) (for polar quinones) as the solvent. The eluted solvent was concentrated, and the residue was finally purified by chromatotron to give the pure quinone.

Acknowledgment. The research was supported by Grants CA-37359 from the National Cancer Institute, DHHS, and CH-272 from the American Cancer Society. The JEOL GX 400 NMR spectrometer used in this work was purchased with funds awarded by NSF-PCM 111745.

Registry No. i (R = CHO), 66-77-3; i (R = OCHO), 1988-19-8; i (R = OH), 90-15-3; ii (R = CHO), 66-99-9; ii (R = OCHO), 1988-18-7; ii (R = OH), 135-19-3; iii (R = CHO), 93831-85-7; iii (R = OCHO), 98170-01-5; iii (R = OH), 98170-09-3; iv (R = CHO), 98243-95-9; iv (R = OCHO), 98170-02-6; iv (R = OH), 98170-10-6; iv (naphthoquinone), 98170-14-0; v (R = CHO), 96301-83-6; v (R = OCHO), 98170-03-7; v (R = OH), 27532-59-8; v (naphthoquinone), 26386-96-9; vi (R = CHO), 82584-15-4; vi (R = OCHO), 98170-04-8; vi (R = OH), 50703-94-1; vi (naphthoquinone), 4923-66-4; vii (R = CHO), 96301-88-1; vii (R = OCHO), 98170-05-9; vii (R = OH), 98170-11-7; vii (naphthoquinone), 52651-48-6; viii (R = CHO), 96301-86-9; viii (R = OCHO), 98170-06-0; viii (R = OH), 98170-12-8; viii (naphtoquinone), 98170-15-1; ix (R = CHO), 96301-84-7; ix (R = OCHO), 98170-07-1; ix (R = OH), 98170-13-9; ix (naphthoquinone), 98170-16-2; x (R = CHO), 96301-85-8; x (R = OCHO), 98170-08-2; x (R = OH), 50703-96-3; x (naphthoquinone), 98170-17-3.

Phosphate Ester Cleavage by Functionalized Quaternary Phosphonium Surfactants

David A. Jaeger* and Durgadas Bolikal

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071

Received February 5, 1985

There have been numerous studies of micellar catalysis of phosphate ester hydrolysis involving functionalized quaternary ammonium surfactants.[1] Herein, we report such a study with the first examples of functionalized quaternary phosphonium analogues.

Hydroxyl-functionalized surfactants **1** were evaluated as potential turnover catalysts for the basic hydrolysis of phosphate ester **4** according to eq 1–4. If eq 3 and 4 are faster than the formation of **5**, **1** would indeed function as turnover catalysts. The catalytic abilities of **1a** and

$$\underset{\mathbf{1}}{RPh_2P^+CH_2CH_2OH,Br^-} \qquad \underset{\mathbf{2}}{RPh_2P^+C_3H_7\text{-}n,Br^-}$$

$$\underset{\mathbf{3}}{RPh_2P^+CH{=}CH_2,Br^-}$$

a, R = 4-n-$C_{12}H_{25}C_6H_4$ **b**, R = n-$C_{12}H_{25}$

analogues **2a** and **3a** were studied first in 0.01 M NaOH; pseudo-first-order rate constant (k_ψ) vs. concentration profiles (not shown) are summarized in Table I. With **1a**

(1) For a summary and examples, see: Moss, R. A.; Ihara, Y. *J. Org. Chem.* **1983**, *48*, 588 and references therein.

0022-3263/85/1950-4635$01.50/0