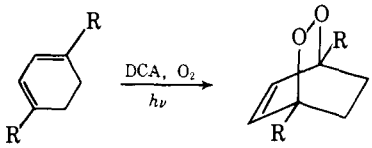
suggested by Bartlett and Landis.[17]

Similarly, DCA sensitized irradiation of **2** gave 2 equiv of benzaldehyde (**4**) and ~2% of *cis*-stilbene (**5**), identified by comparison with authentic samples. Again, rose bengal or methylene blue sensitized photooxygenation of **2** did not lead to **4**[20] (0.5% would have been detected) or **5** (detection limit not established). Formation of **4** or **5** was not a result of direct light absorption by **2** under the reaction conditions; **5** could have been formed either by sensitization by triplet **4** (from decomposition of the corresponding dioxetane) or by bond rotation in the radical cation of **2** followed by back-transfer of the electron. Triplet sensitization by **4** to form **5** from **2** is a very facile reaction, as determined in a separate irradiation at 350 nm in oxygen-saturated CH_3CN.

Sulfides. DCA sensitized photooxygenation of diphenyl sulfide (**6**) gave diphenyl sulfoxide, while diethyl sulfide (**7**) gave a mixture of diethyl sulfoxide and diethyl sulfone. Addition of β-carotene at concentrations up to 10^{-4} M did not quench the formation of the photoproducts.[19] It was found that **6** was three times as reactive as **7**, whereas **6** is 2800 times *less* reactive than **7** toward singlet oxygen (in CH_3OH[4a]). It appears, therefore, that singlet oxygen is not involved (at least in the major pathway) in the DCA sensitized photooxygenation of **6**.

1,3-Cyclohexadienes. DCA sensitized photooxygenation of 1,3-cyclohexadiene (**8**) and 1,4-dimethyl-1,3-cyclohexadiene (**9**) gave the endoperoxides **10** and **11**, respectively. Since **8** and **9** react with singlet oxygen to give the same products, a careful kinetic study is necessary to establish whether the DCA sensitization involved singlet oxygen or not. Preliminary quenching studies indicate that a non-singlet-oxygen pathway is involved at least to some extent.



8, R = H; **9**, R = Me — **10**, R = H; **11**, R = Me

It is noteworthy that this reaction permits oxidation of substrates such as **1** and **2** which are too electron poor to react with singlet oxygen, and we expect that the oxidation will be limited by the oxidation potential of the substrate as described above.

Two very recent papers have discussed a similar mechanism in different systems.[21]

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One-Step Preparation of Vitamin K_1 or K_2 Analogues by Cyclodextrin Inclusion Catalysis

Sir:

One of the most important and interesting, although uninvestigated, aspects of the rapidly developing field of cyclodextrin chemistry is application to the highly selective synthesis of bioactive compounds[1] by inclusion catalysis. Reactions modeling enzymatic processes by the use of cyclodextrins have been extensively studied mostly from the mechanistic viewpoint, particularly once cyclodextrins were found to behave as hydrolytic enzyme models toward their own pyrophosphate[2] or carboxylate ester substrates.[3]

In this communication, we wish to report the first successful application of cyclodextrin to the one-step synthesis of a bioactive compound, i.e., the highly selective preparation of vitamin K_1 (or K_2) analogues in dilute aqueous alkaline solution.

Vitamin K_1 was first synthesized from 2-methylhydronaphthoquinone-1,4 and phytol via the Friedel–Crafts reaction by Fieser,[4] and thereafter many modifications of the original preparation have been reported.[5] However, these Friedel–Crafts-type preparations seem to have the serious and inevitable disadvantage that they are accompanied by the formation of undesirable products from alkylation on the C_2 position and further cyclization to naphthotocopherol.

In the present communication, we wish to report a novel preparation of vitamin K_1 (or K_2) analogues by use of β-cyclodextrin. Thus, a solution of 8.505 g (7.5 mmol) of β-cyclodextrin, 3.630 g (30 mmol) of allyl bromide, and 261 mg (1.5 mmol) of 2-methylhydronaphthoquinone-1,4 in a mixture of 105 mL of borate buffer solution (pH 9.0) and 45 mL of

Table I. 3-Allylation of 2-Methylhydronaphthoquinone-1,4

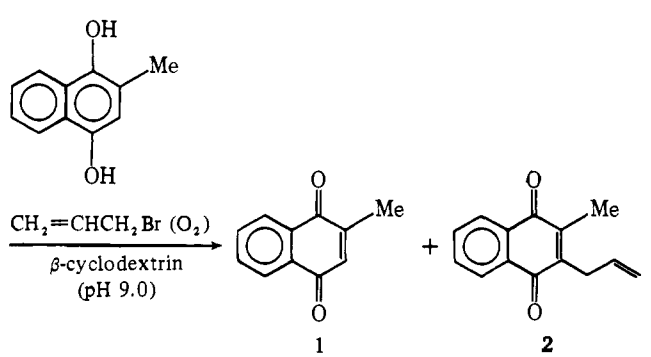
β-Cyclodextrin	M: R–CH=CH–CH2–Br	M: 2-Methylhydronaphthoquinone-1,4	Reaction period, h	Yield, % 1	Yield, % 2
5.0×10^{-2}	R = H, 2.0×10^{-1}	1.0×10^{-2}	9	54	40 (86)[a,b]
None	R = H, 2.0×10^{-1}	1.0×10^{-2}	9	14	16 (19)[a,c]
5.0×10^{-2}	R = Me, 2.0×10^{-1}	1.0×10^{-2}	9	22	60 (77)[a,b]
None	R = Me, 2.0×10^{-1}	1.0×10^{-2}	9	9	20 (22)[a,c]

[a] The yield based on a consideration of the amount of 1 recovered is shown in parenthesis. [b] The yield was very sensitive to the presence of a trace amount of oxygen. The values listed in the last two columns are the averages of several experiments. [c] Contaminated with considerable amounts of undefined by-products.

methanol was stirred at room temperature for 9 h under nitrogen atmosphere (nitrogen was carefully deoxygenated through a cupper column) in the dark. After the addition of 600 mL of water, 30 mL of concentrated HCl, and 24 mL of cyclohexylamine with cooling by ice, the mixture was extracted with eight portions of 45 mL of chloroform. The chloroform extracts were combined, washed with two portions of 60 mL of 1 N HCl, and dried over anhydrous sodium sulfate. Evaporation of chloroform, followed by column chromatography (silica gel, petroleum ether–ethyl acetate, 10:1), gave 216 mg (68% based on 2-methylhydronaphthoquinone-1,4 and 96% based on the consumed starting material) of 2-methyl-3-allylnaphthoquinone-1,4, **2**, and 75.6 mg (29% of the starting material used) of 2-methylnaphthoquinone, **1**. The allylation was also carried out in the absence of β-cyclodextrin under similar conditions, as a standard experiment.

Since the yield of the product was still sensitive to the presence of the trace amount of oxygen present in the "purified" nitrogen employed, the average yields for several independent runs were calculated based on the NMR analysis and are listed in the Table I. Thus, chloroform solutions of the crude products obtained as described above were dried over anhydrous sodium sulfate, and chloroform was carefully replaced by carbon tetrachloride. The NMR determination was made on the peaks for the vinyl proton (δ 4.93–5.20) and 3 proton of methylnaphthoquinone (6.80)[6] by using 1,2-dichlorethane (4.7) as a standard. The results of the NMR determination were in a good agreement with the preparative determination. The yields of **2** in repeated experiments are 92, 82, 86, and 84% with β-cyclodextrin and 18, 19, 15, and 13% without β-cyclodextrin.

That the yield of the vitamin K_1 or K_2 analogue formed through the inclusion complex was considerably higher than under the usual conditions indicates that β-cyclodextrin plays a significant role in the present allylation, as if it were a "vitamin K_1 (or K_2) synthetase". The crotyl group was similarly introduced into the 3 position by the "vitamin K-synthetase model" (see Table I).



1 2

Vitamin K_1 was also prepared from methylnaphthohydroquinone by treatment with potassium hydride or potassium methoxide and alkenyl bromide in toluene followed by silver oxide oxidation,[7] but the yield was rather low. The marked catalytic effect of the cyclodextrin shown here seems to have its origin in the increase in nucleophilicity of the carbon atom on naphthohydroquinone monoanion[8] included in the cyclodextrin cavity ("base effect"),[9] which was also shown to be significant for the accelerated dehydrobromination (as well as the hydrolysis) of β-bromomethylnaphthalene in aqueous alkaline solution in the presence of β-cyclodextrin,[10] and in the protection[11] against oxidative cleavage of the included naphthoquinone derivatives. Detailed quantitative analysis of these two possible contributing factors are now under way.

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Trans → Cis Photoisomerization of *all-trans*-Retinal

Sir:

During their pioneering studies of the visual protein rhodopsin Wald, Hubbard, and coworkers[1-3] first examined the photochemical properties of the isomeric retinals in solution. A number of quantitative studies on the cis-trans photoisomerization of the retinals have since been reported,[4-7] in-