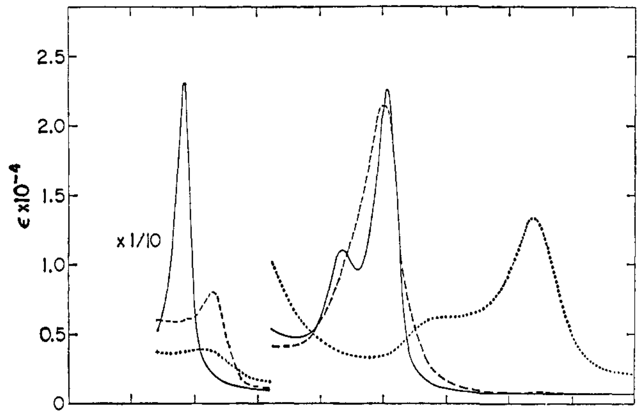

Figure 3. Absorption spectra of CoOEP (————), [Co^{III}OEP]$^+$Br$^-$ (— — —), and [Co^{III}OEP]$^{2+}$2Br$^-$ (- - - - - - - - -) in CHCl$_3$.

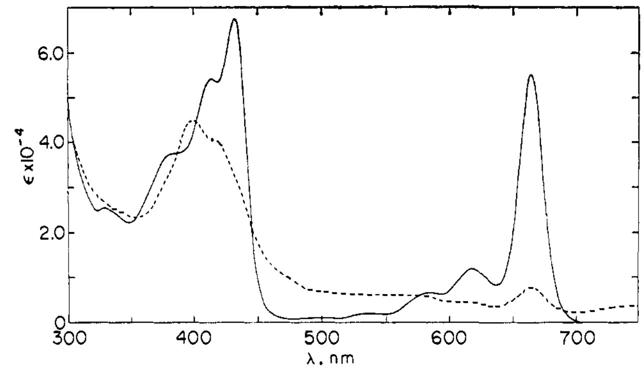

Figure 4. Absorption spectra of ethylchlorophyllide *a* (————) and its cation radical (- - - - - -) in CH$_2$Cl$_2$.

phylls prompted us to study the electrochemical oxidation of ethyl chlorophyllide *a*. One-electron oxidation at 0.6 V *vs.* sce yielded a yellow solution whose optical spectrum is shown in Figure 4. The product exhibited a singlet esr signal 9 G wide (g = 2.0028). Attempted chemical oxidation by bromine led to allomerized material.

Stable oxidized products of CdTPP, CoTPP, H$_2$TPP, zinc tetraphenylchlorin, free base and zinc etioporphyrin I, and ZnOEP have also been prepared by the above techniques. These results will be discussed fully in a later publication.

Acknowledgments. We are indebted to Dr. S. W. Feldberg for his assistance with the electrochemical work and to Dr. G. M. Sherman for a sample of ethyl chlorophyllide *a*. This work was supported in part by the U. S. Atomic Energy Commission, in part by the Petroleum Research Fund of the American Chemical Society (PRF-849-Gl), and in part by National Science Foundation Grant GP-6628.

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A Large Deuterium Solvent Isotope Effect on a Photochemical Reaction[1]

Sir:

We wish to draw attention to a large acceleration, measured in methanol-O-*d*, of the photochemically induced double bond migration in α,β-unsaturated esters.

In a previous publication[2] we reported that isomerization of ester **1** in methanol proceeded overwhelmingly with the abstraction of the tertiary allylic hydrogen leading to **2**, rather than to esters **3** or **4** which would result from the relocation of primary allylic and homoallylic hydrogens, respectively. We have now observed that irradiation in methanol-O-*d* brings about a remarkable change in the reaction course;[3] esters **2** and **3** are generated at comparable rates in this medium.

The results of the photolysis of **1a** in methanol-O-*d* and ordinary methanol are plotted in Figure 1.[3,4] The rate of formation of **3** is much faster than that of **2** during the period over which the photostationary state is being approached, consonant with previous conclusions[5,6] that the photochemical deconjugation reactions occur stereospecifically from the geometrically isomeric states of the starting ester. The solvent isotope effect ($k_{\mathrm{CH_3OD}}/k_{\mathrm{CH_3OH}}$) on the formation of ester **3**, while impossible to evaluate precisely,[4] is in the order of 15–50.

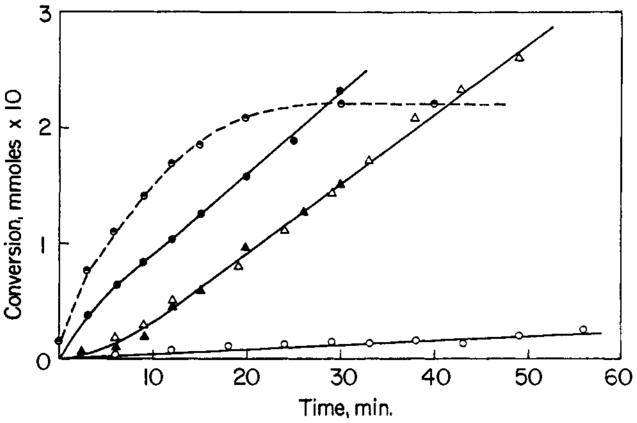

Figure 1. Irradiation of **1a** (0.4 mmol, 4% of **1b** present) in methanol and methanol-O-*d* (5.0 ml): photoequilibration of **1a**, depicted as mmol of total starting ester present as the *cis* isomer (**1b**) (broken line, ◐); formation of ester **3**, in methanol (○), in methanol-O-*d* (●); formation of ester **2**, in methanol (△), in methanol-O-*d* (▲).

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[1] Photochemistry of α,β-Unsaturated Esters. VI.

[2] M. J. Jorgenson, *Chem. Commun.*, 137 (1965).

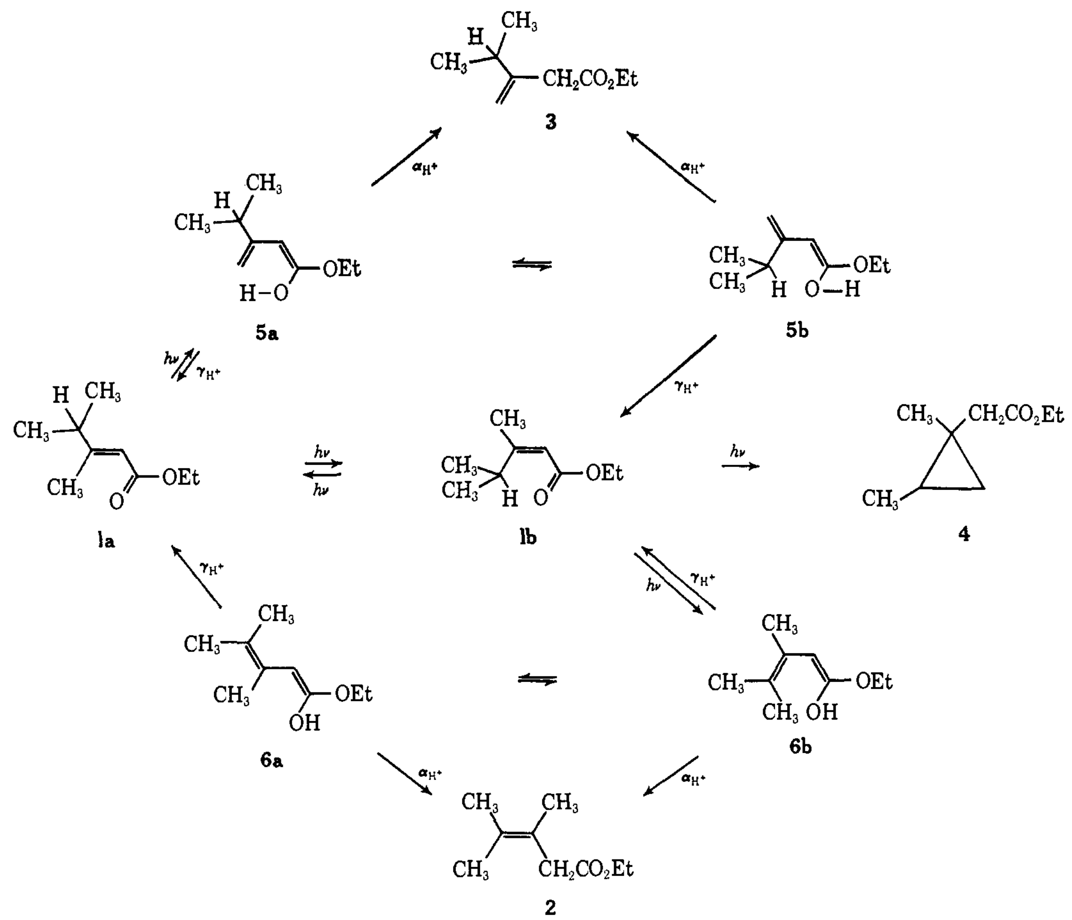
[3] Irradiations were conducted consecutively and on identical scales and concentrations, keeping the geometry of the irradiation set-up constant. A Hanovia 450-W lamp and Vycor filter were employed. Control experiments were carried out to exclude the possibility that the solvent effect of methanol-O-*d* was caused by the presence of impurities. Methanol-O-*d* prepared by three different routes gave identical results, and ordinary methanol prepared by one of these procedures did not differ in behavior from commercial samples. Added amounts of acid did not affect the reaction.

[4] Total yields of β,γ isomers in methanol-O-*d* was better than 95%; in the slower runs conducted in methanol the material balance remained not lower than 90% throughout the reaction course. Repeated runs in methanol-O-*d* gave similar results, **3** varying between 52 and 60%. Irradiations in ordinary methanol were more erratic; in a total of ten runs conducted under identical conditions the amount of **3** formed varied between 3 and 8%. Irradiation of **1a** in hexane gave results which were similar to those obtained in methanol, but the amount of **3** formed never exceeded 5%.

[5] M. J. Jorgenson and L. Gundel, *Tetrahedron Letters*, 4991 (1968).

[6] J. A. Barltrop and J. Wills, *ibid.*, 4987 (1968).

Scheme I



Mass spectroscopic determinations of the deuterium content in **2** and **3**, at completion of photolysis in media of varying deuterium content (Table I), indicate that the isotope effect on the protonation of the dienol intermediates **5** and **6** is normal[7] and therefore cannot account for the observed acceleration. The low deuterium content of **2** and **3** argues for a negligible rate of γ deuteration of dienols **5** and **6** (**5a** and **6a** to **1a** and **5b** and **6b** to **1b**). Since the rate of formation of **2** is unaffected by the medium, γ protonation in ordinary methanol of **5a** and **5b** must also be very slow in comparison to α protonation. The conclusion can be drawn from these data and the observation that the rate at which the photostationary state is reached is not appreciably affected by the isotopic medium, that it is the fate of the dienol **5** which is strongly affected by the isotopic content of the methanol medium. In ordinary methanol the photochemistry of **1a** is unproductive, since the dienol **5a** is partitioned *via* γ protonation overwhelmingly into the return pathway (to **1a** and possibly to **1b** *via* **5b**). In the presence of methanol-O-*d*, however, α protonation becomes the dominant course. We are unable to account for this difference in protonation behavior and for the magnitude of the isotope effect, particularly since the presence of a completely deuterated methanol medium (Table I) is not a condition for the manifestation of this effect. One possible interpretation is that the photochemical fate[8] of the dienol **5** is altered upon exchange with deuterium of the hydroxyl proton, in an over-all two-photon sequence **1a** → **5a** → **3** (Scheme I).[9,10]

Table I. Deuterium Content (Per cent) of Photoproducts

	2			3		
CH_3OD	d_0	d_1	d_2	d_0	d_1	d_2
99[a]	9	88	3	12	86	2
40[b]	88.5	11.5	0	89.5	10.5	0
20[c]	94.5	5.5	0	95.5	4.5	0
10[d]	97.2	2.8	0	97.5	2.5	0
50[e] (ether)	12.5	84.5	3	26	73	1

[a] Nmr analyses of **2** and **3** indicate that approximately 90% of one α-methylene proton has been exchanged. Control experiments established that about 1–2% deuterium in **2** and **3** is lost during isolation. [b] Esters **2** and **3** formed in a 48:52 ratio. [c] Esters **2** and **3** formed in a 56:44 ratio in this run, but results were erratic in other runs. [d] Esters **2** and **3** formed in a 60:40 ratio, but results in other runs afforded lower percentages of **3**. [e] Medium is 50:50 methanol-O-*d*-ether; product ratio (**2**:**3**) was 1:1, results were reproducible. Reference photolysis carried out in a 50:50 methanol–ether medium gave product ratios similar to those found in methanol.

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(7) For a discussion of deuterium solvent isotope effects in rate-determining proton transfers, see C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3214 (1961).

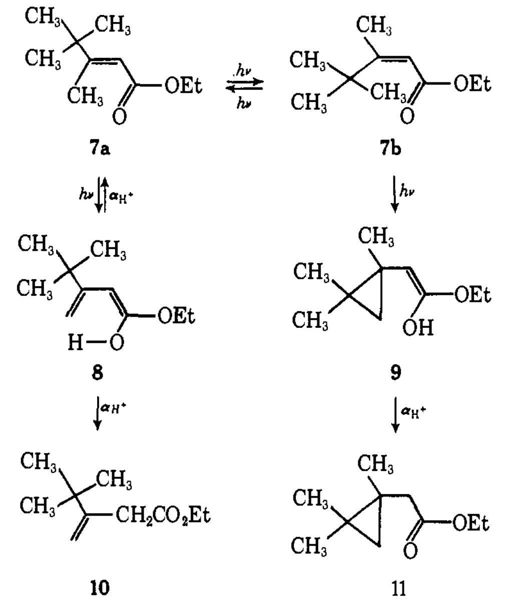
(8) The dienols absorb strongly under the conditions of their formation and might, therefore, be protonated in the excited state. The direction of protonation of dienol ethers in the excited state has been shown to differ from that in the ground state [T. N. Huckerby, N. A. J. Rogers, and A. Attar, *Tetrahedron Letters*, 1113 (1967)].

(9) Organic molecules upon deuteration can exhibit distinct changes in their excited-state behavior [D. R. Coulson and N. C. Yang, *J. Am. Chem. Soc.*, **88**, 4511 (1966), and references therein].

(10) The major conformers of the dienols may not be *s-cis* (**5a**, **6b**) or *s-trans* (**5b**, **6a**) as is assumed in Scheme I. Being 1,1,3-trisubstituted dienes, they might exist predominantly or competitively as skew conformers [*cf.* A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968); A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968)]. The con-

Irradiation of ester **7** (Scheme II) in nonhydroxylic solvents leads to the formation of the cyclopropane ester **11** only. Formation of **10** is a competitive but erratic process in methanol; in more than 50 runs which we have carried out on **7a** ester **11** was always found to be the major product. The preference for the abstraction of a nonallylic primary hydrogen over that of an allylic primary hydrogen has remained an intriguing anomaly.[5] It is now found that in methanol-O-*d* the behavior of **7a** becomes normal; ester **10** is produced at a reproducibly fast rate in this medium, approximately 13 times faster than **11**, so that ester **10** comprises 90–95% of photoproduct. The rate at which **11** is formed remains unaffected, in accord with Scheme II where, in contrast to the dienol **8**, only one ketonization pathway is available to the cyclopropyl enol **9**. Acceleration in methanol-O-*d* of the deconjugation reaction of the double bond into a terminal location is also observed for ethyl 3,5-dimethyl-2-heptenoate.[2]

Scheme II



From the rates of isomerization of esters **1** and **7** approximate values, corrected for statistical factor, for the ease of abstraction of various hydrogens in methanol-O-*d* can be derived; these are primary allylic:primary homoallylic 40:1, primary allylic:tertiary allylic 1:3. On this basis it can be estimated that, in competition with the removal of allylic hydrogens in **1**, the δ hydrogen will be abstracted to give ester **4** at a rate which is at least 40 times[11] slower than the rates at which **2** and **3** are formed; the formation of cyclopropane **11** from ethyl 3,5-dimethyl-2-heptenoate will occur about 360 times[11] more slowly than the formation of the β,γ isomers. Cyclopropane products are, in fact, not formed in the photolyses of these esters.

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formation of the dienols may play a significant role in the deconjugation reaction, if a concerted 1,5 proton transfer contributes to γ protonation. The geometry of the photochemically formed dienols (*e.g.*, as depicted for **5a**) is well suited for such a protonation pathway.

(11) This calculation does not take into account an unfavorable conformational factor which would raise these values. The preferred conformation of ester **1b** is as shown in Scheme I, so that the nonallylic δ hydrogens are located at too far a distance from the carbonyl to be abstracted by it in the singlet[5,6] excited state of the ester.

Internal Insertion of an Olefin into a Palladium σ Bond

Sir:

Recent investigations[1,2] have given a firm assignment to the stereochemistry of the methoxy complex I obtained from the reaction of sodium methoxide with dichloro(norbornadiene)palladium. In view of the availability of this well-defined complex, a study of ligand displacements of the olefinic bond was undertaken.

Although the reaction of I with various ligands has been reported to give simple bridge-cleavage products,[1] no apparent attempt was made to critically examine the products. In our hands, the reaction of I with various phosphines gave profoundly different products. For example, mixing methylene chloride solutions of 1,2-bis(diphenylphosphino)ethane (DPPE) and 0.5 molar equiv of I gave, on dilution with hexane, a 90% weight recovery of tan platelets, mp 195° dec (under N_2). The structure of this product[3] was deduced from physical and chemical evidence to be II, containing ~0.3 molar equiv of methylene chloride of crystallization.

Elemental analysis[4] and an ebullioscopic molecular weight determination (found, 665 in CH_2Cl_2; calcd, 663) were in agreement with II. Infrared analysis revealed new absorptions (see Table I) characteristic[5] of a nortricyclene ring system. The nmr spectrum revealed an absence of olefinic protons. Additional nmr data are summarized in Table I.

Reduction of II with excess $LiAlH_4$ in ether yielded a single product which was shown to be 3-*exo*-methoxynortricyclene (III) by comparison with an authentic sample.[6] This reaction thus established both the position and the stereochemistry of the methoxy substituent.

The reaction of II with 0.9 molar equiv of Cl_2 and Br_2 in methylene chloride gave the corresponding 3-halo-5-methoxynortricyclenes and (DPPE)PdX_2. Physical data pertinent to these nortricyclenes, IV and V, may be found in Table I.

The problem of the stereochemistry at the 3 position of compounds II, IV, and V was resolved by an analysis of the nmr chemical shifts. Sufficient information[7-9] exists concerning chemical shift data of 3,5-substituted nortricyclenes from which correlations may be made

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(1) M. Green and R. I. Hancock, *J. Chem. Soc., A.*, 2054 (1967).

(2) J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.*, **88**, 5153 (1966).

(3) It was also noted that only 2 molar equiv of triphenylphosphine was necessary to effect a complete reaction on the olefinic bond to give a product whose nmr spectrum resembled that of II. However, we were unable to obtain the product in pure form.

(4) All new compounds described here gave satisfactory elemental analyses (within 0.5% unit of the calculated value). The nmr spectra were recorded at 60 Mcps in deuteriochloroform. The infrared spectra were recorded in neat form for the liquids and in KBr for the solids.

(5) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(6) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurak, *ibid.*, **84**, 3918 (1962).

(7) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966).

(8) D. J. Thecker and J. P. Henry, *ibid.*, **85**, 3204 (1963).

(9) R. S. Neale and E. B. Whipple, *ibid.*, **86**, 3130 (1964).