viously reported for us for this reaction,[9] 3-[3-(hydroxymethyl)phenyl]-*NNO*-azoxybenzaldehyde, has been withdrawn; it is not produced in the photoreaction). We now report that this photoreaction is catalyzed by the hydronium ion. The effect of medium acidity (aqueous H_2SO_4) on Φ_m/Φ_m^0, where Φ_m^0 is the quantum yield for the formation of **4** in water at pH 7, was determined by monitoring the increase in optical density at 233 nm due to the formation of product **4**, using a merry-go-round apparatus, with 254-nm irradiation. The results are shown in Figure 2. Identical results for Φ_m/Φ_m^0 were obtained by preparative irradiation experiments. The efficiency of the photoreaction is observed to depend strongly on the medium acidity.[10] In addition, Φ_{H_2O}/Φ_{D_2O} (both solutions of pH 7) was found to be 1.30 ± 0.10, thus indicating that proton transfer from the solvent occurs in the product-forming process.

The quantum yield (absolute yield at pH 7, $\Phi_m^0 = 0.055$) was found not to depend on the substrate concentration from 10^{-4} and 10^{-3} M. This strongly suggests that a unimolecular process occurs, leading up to the product-forming step, which is inconsistent with the previously proposed mechanism.[9] Additional support for a unimolecular process is the observation that irradiation of an equimolar (10^{-4} M) mixture of nitrobenzene and benzyl alcohol in aqueous solution does not result in an analogous reaction.

α,α-Dideuterio-*m*-nitrobenzyl alcohol was synthesized and the isotope effect on quantum yield (Φ_m^H/Φ_m^D), where Φ_m^H and Φ_m^D represent the quantum efficiency for *m*-nitrobenzaldehyde formation for the undeuterated and deuterated alcohols, respectively, was measured. It gave 2.4 ± 0.1 in water at pH 7. A lower value (1.3 ± 0.1) was observed in 15% H_2SO_4. The observed isotope effect indicates that abstraction of the α-hydrogen is involved in the product-forming process.

It is clear from the results presented for the meta isomer that the mechanism of this reaction is more complex than for the para isomer: the meta isomer does not react via a simple intramolecular reduction–oxidation process. The fact that water is *essential* for the reaction, and that added hydronium ions can increase the efficiency of the photoreaction, suggests that protons, either donated from water or H_2SO_4, are required to "trap" the reactive triplet state, possibly via protonation of the nitro group. It is not clear at this time why the para isomer does not react in an analogous reaction under these conditions.

At acidities greater than $H_0 = -2$, Φ_m/Φ_m^0 decreases dramatically. Since the estimated pK_{SH^+} of the CH_2OH group[11] is approximately −3 to −6, we propose that the protonated molecule (on the hydroxyl group) is less reactive than the free molecule in the photoreaction. However, we cannot as yet eliminate the possibility of nonproductive photophysical quenching processes at these acidities.

To summarize, we have uncovered a meta/para dichotomy in catalytic effects in the aqueous photochemistry of *m*- and *p*-nitrobenzyl alcohols: the meta isomer exhibits proton-catalyzed redox photochemistry, while, on the other hand, the para isomer exhibits hydroxide-catalyzed redox photochemistry. Neither photoreactions occur in organic media; hence both could be described as "water-catalyzed".[12] We are presently studying these and related reactions in detail, the results of which will be reported in due course.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this research, and for a postgraduate scholarship to one of us (P.W.).

(10) The possibility that these observations are due to a salt effect was eliminated since the presence of up to 3 M NaCl or $LiClO_4$ failed to enhance Φ_m/Φ_m^0 to the extent observed in Figure 2. Typically we find Φ(2 M NaCl)/Φ(0 M NaCl) ≈ 1–2. However, the observation of a salt effect implicates the possible existence of polarized intermediates on the reaction pathway.

(11) Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.

(12) Preliminary results show that the photochemistry of the ortho isomer (to give *o*-nitrosobenzaldehyde) is not subject to catalysis by proton or hydroxide ions. It reacts equally efficiently in water and in organic media.

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Methyl 5-(Triphenylphosphoranylidene)levulinate: A Reagent for Homologation of Aldehydes to δ-Ene γ-Keto Esters

Summary: Methyl 5-(triphenylphosphoranylidene)-levulinate has been synthesized and shown to condense with aldehydes to afford *E* δ-ene γ-keto esters in good yield.

Sir: γ-Keto esters are useful as synthetic intermediates, and subsequently a number of synthetic sequences for their production have been developed.[1] In the course of a natural product synthesis we wished to homologate an aldehyde to the corresponding *E* δ-ene γ-keto ester. To our knowledge no methodology had been reported to effect this transformation in a single synthetic operation.

We have developed two syntheses of ylide **1** and herein report its reaction with aldehydes in DMF proceeds in good to excellent yield. Ketones appear to be unreactive toward the reagent, though an exhaustive study has not been undertaken.

Ylide **1** may be prepared either by condensation of 2 equiv of methylenetriphenylphosphorane with 3-carbomethoxypropionyl chloride in THF at −78 °C or by condensation of triphenylphosphine with methyl 5-bromolevulinate[2] in refluxing benzene, followed by deprotonation with aqueous sodium carbonate (Scheme I).[3]

Ylide **1** is a stable crystalline solid, readily soluble in DMF, and condenses with aldehydes under mild conditions (Table I).[3] Products (as determined by ^1H NMR) are generally greater than 95% "*E*", with the exception of the homatropaldehyde adduct **4d**, which is approximately 85% "*E*".

A total synthesis of (±)-γ-dodecanolide (**3**), sex pheremone of the Rove beetle, has been completed in 68% overall yield from heptanal (Scheme II) to demonstrate the viability of the reagent for production of γ-lactones.

Though compound **3** has been previously synthesized in optically active form,[4] this synthesis illustrates the po-

(1) (a) Woessner, W. D.; Solera, P. S. *Synth. Commun.* **1978**, *8*, 279–283. (b) Ryu, I.; Matusumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283–4286. (c) Miyashita, M.; Kumazawa, T.; Yoshikoshi, A. *Chem. Lett.* **1980**, 1043–1044 and references therein.

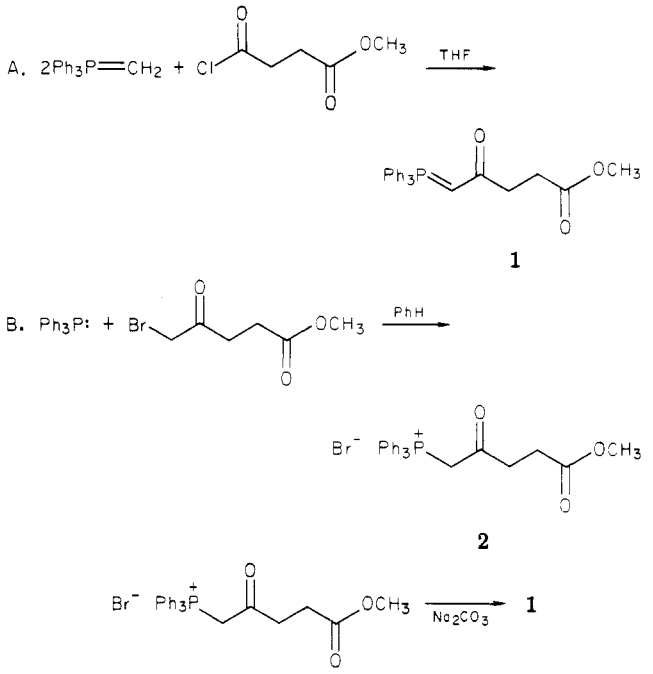
(2) For preparation, see: MacDonald, S. F. *Can. J. Chem.* **1974**, *52*, 3257–3258.

(3) See paragraph at the end of paper concerning supplementary material. The ^1H NMR spectra of ylide **1** is noteworthy in that the α- and β-carbomethoxy protons appear magnetically equivalent, registering as a 4-proton singlet (δ 2.55) even at 200 MHz.

(4) Pirkle, W. H.; Adams, P. E. *J. Org. Chem.* **1979**, 2169–2175. Alternate syntheses are referenced by Pirkle and Adams.

0022-3263/83/1948-0138$01.50/0

Scheme I



Scheme II

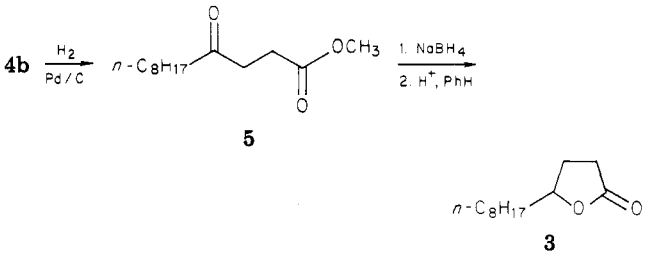
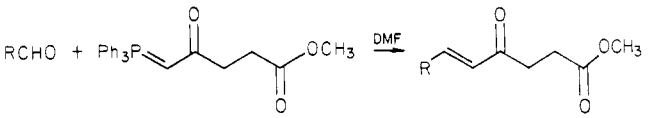
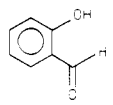
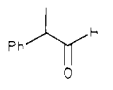
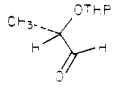
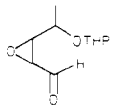


Table I



aldehyde	temp, °C	time	product	% yield[a,b]
PhCHO	55	2 days	4a	90
n-$C_6H_{13}CHO$	reflux	2 days	4b	71
	25	24 h	4c	70
	65	2 days	4d	80
	65	24 h	4e	87
	25	18 h	4f	93

[a] All products gave satisfactory elemental analysis and exhibited consistent spectral properties. [b] All yields are unoptimized.

tential for application to butanolide synthesis. Details of other reactions of ylide 1, and total synthesis of other, dissimilar, natural products will be reported in due course.

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Registry No. 1, 84028-77-3; 2, 84028-78-4; (±)-3, 57084-18-1; 4a, 84028-79-5; 4b, 84028-30-8; 4c, 84028-81-9; 4d, 84028-82-0; 4e, 84028-83-1; 4f, 84028-84-2; 5, 33566-59-5; $Ph_3P{=}CH_2$, 3487-44-3; Ph_3P, 603-35-0; PhCHO, 100-52-7; n-$C_6H_{13}CHO$, 111-71-7; 3-carbomethoxypropionyl chloride, 1490-25-1; methyl 5-bromolevulinate, 53856-93-2; salicylaldehyde, 90-02-8; α-methylbenzeneacetaldehyde, 93-53-8; (*S*)-2-[(tetrahydropyran-2-yl)oxy]-propionaldehyde, 76438-34-1; 2-[[1-(tetrahydropyuran-2-yl)oxy]ethyl]oxiranecarboxyaldehyde, 84028-85-3.

Supplementary Material Available: Experimental procedures for preparation of compounds 1-3 and 5, plus a general procedure for aldehyde homologation, and NMR, IR, and analytical data for 1, 2, 4a-f, and 5 are included (3 pages). Ordering information is given on any current masthead page.

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Stereocontrolled Synthesis of (±)-Modhephene via the Weiss Reaction[1]

Summary: A stereocontrolled synthesis of (±)-modhephene (1) has been realized. The key steps were the facile generation of the [3.3.3] propellane system 7 via the Weiss reaction and the stereospecific incorporation of the chiral methyl function into the modhephene skeleton by addition of (dimethylcopper)lithium to the strained, diactivated cyclopropyl ketone 6. Alkylation of the resulting enolate provided the tetramethyl derivative 12, which was converted to 1 in three routine steps.

Sir: Modhephene (1), the first carbocyclic propellane from a natural source, was isolated by Zalkow in 1978[2] and soon attracted considerable synthetic interest.[3-8] In 1979[9] we proposed to synthesize 1 by an approach that was designed to be completely stereocontrolled. Our route was based on the preparation of the strained, monoactivated cyclopropyl ketone 2, which would permit regiospecific incorporation of the *gem*-dimethyl group (see 3), followed by stereospecific introduction of the isolated methyl function of 4 with (dimethylcopper(I))lithium. The introduction of the fourth methyl group by alkylation of the enolate from the cyclopropane opening and the conversion of the ketone into an olefin were to complete the synthesis as illustrated in Scheme I. Although the opening of monoactivated cyclopropanes (especially, strained ones) has

(1) Dedicated to Dr. Ulrich Weiss, National Institutes of Health, on the occasion of his 75th birthday.
(2) Zalkow, L. H.; Harris, R. N., III; Van Derveer, D. *J. Chem. Soc., Chem. Commun.* **1978**, 420.
(3) Smith, A. B.; Jerris, P. J. *J. Org. Chem.* **1982**, *47*, 1845. Smith, A. B.; Jerris, P. J. "Abstracts of Papers", 179th National Meeting of the American Chemical Society, Houston, TX, March 24-28, 1980; American Chemical Society: Washington, DC, 1980; ORGN 63.
(4) Karpf, M.; Dreiding, A. S. *Tetrahedron Lett.* **1980**, *21*, 4569.
(5) Schostorez, H.; Paquette, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 722.
(6) Oppolzer, W.; Marazza, F. *Helv. Chim. Acta* **1981**, *64*, 1575.
(7) Oppolzer, W.; Battig, K. *Helv. Chim. Acta* **1981**, *64*, 2489.
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(9) Mitschka, R.; Gawish, A.; Wieringa, C.; Weiss, U.; Cook, J. M. "Abstracts of Papers", presented at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept 10-14, 1979, American Chemical Society: Washington, DC, 1979; ORGN-146.

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