pulsions exist in **3**, they would be removed through formation of **4**.[11]

(11) The hypothesis that an electronic substituent effect is the controlling factor in stabilizing the localization occurring in the observed pathway is not attractive. If one can transfer evidence from esr data for the electron distribution in the first excited state, it is clear that β positions in naphthalenes and in benzocyclobutenes have very little spin density to be stabilized or destabilized by substituents such as *tert*-butyl; see R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *J. Amer. Chem. Soc.*, **93**, 697 (1971), for benzocyclobutene esr data and I. Goldberg and B. M. Peake, manuscript to be published for *tert*-butylnaphthalene esr data.

(12) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for Grant 5150-D4 in support of R. W. F. We also acknowledge the National Cancer Institute for Grant 11,421-07 for support of W. L. M. We are grateful to Professor N. O. Smith for detailed discussions on the error analysis of our kinetic data. A part of this research has been presented by J. E. Anderson, R. W. Franck, and W. L. Mandella, 3rd Northeast Regional Meeting of the American Chemical Society, Abstracts, p 182.

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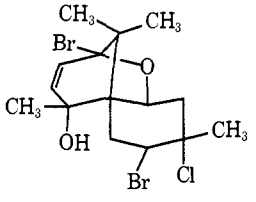
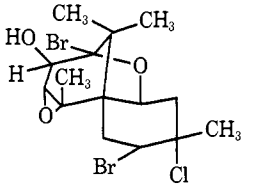
Marine Natural Products. IV. Prepacifenol, a Halogenated Epoxy Sesquiterpene and Precursor to Pacifenol from the Red Alga, *Laurencia filiformis*[1]

Sir:

Recently we described the isolation of pacifenol (**1**)[2] and johnstonol[1] (**2**) from *L. pacifica* and *L. johnstonii*, respectively. Marine algae of the genus *Laurencia* were first noted for producing terpenoids containing bromine.[3,4] In addition, the isolation of **1** and **2**, which contain both bromine and chlorine as well as an unusual tricyclic ring structure, makes this genus an important one for the study of marine natural products.



1



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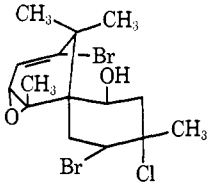

3

In the course of further work on this interesting group of algae, we have isolated the probable precursor of pacifenol, prepacifenol (**3**). Accordingly, hexane extraction of *L. filiformis* followed by evaporation of the hexane and recrystallization of the partly crystalline residue from hexane gave prepacifenol (**3**) (yield, 0.3% dry plant): $C_{15}H_{21}O_2Br_2Cl$; *m/e* M^+ = 430, 428, 426; high resolution $M^+ - H_2O$ *m/e* = 409.9477 (calcd for $C_{15}H_{19}O^{79}Br^{81}Br^{35}Cl$, 409.9472). The nmr spectrum (100 MHz, $CDCl_3$) of **3** indicated at δ 1.88 (s), 1.63 (s), 1.42 (s), and 1.24 (s) four methyl groups, at 2.4 (m) four methylene protons, at 3.02 (d, J = 3 Hz) one α-epoxy proton, at 4.72 (four lines, X of ABX) one proton α to bromine, at 4.41 (four lines) one proton α to hydroxyl, and at 6.25 (d, J = 3 Hz) one vinyl proton. That prepacifenol was an alcohol was indicated by infrared absorption at 3.5 μ coupled with the disappearance of a one-proton nmr signal (d, J = 5 Hz) at δ 1.50 after a D_2O exchange experiment. On analysis of these data for prepacifenol, in particular comparison of its nmr spectrum with the nmr spectra of **1** and **2**, structure **3** was proposed for prepacifenol. Confirmation of this structure was provided in convincing fashion by the conversion of **3** to **1** in almost quantitative yield upon treatment with *p*-toluenesulfonic acid in benzene. The pacifenol so produced was identical with that previously isolated from *L. pacifica*. The conversion of **3** to **1** also occurred on heating **3** to its melting point. Depending upon the rate of heating, **3** melts from 109 to 126°, solidifies, and remelts at 147°. Thin layer chromatography of the residue shows complete conversion to **1**. The cyclization also occurs in high yield under conditions of chromatography upon neutral alumina.

Our original isolation procedure for **1** from *L. pacifica* involved the use of silica gel chromatography and therefore it was possible that pacifenol was an artifact.[2] Indeed, chromatography of prepacifenol on silica gel resulted in quantitative conversion of pacifenol. We conducted a new extraction of *L. pacifica* using the procedure described above which led to the exclusive isolation of prepacifenol. The new extraction gave only prepacifenol and no pacifenol. Thus, our report that pacifenol is present as a natural product in *L. pacifica* is incorrect. However, pacifenol does exist as a natural product in *L. tasmanica*. Extraction of this alga using the new procedure led to pacifenol (0.25% of dry plant) as the major compound.

Acknowledgment. One of us (J. J. S.) wishes to express his gratitude to the Australian National University for a Research Fellowship (1971–1972) and to Professor A. J. Birch, Research School of Chemistry, Australian National University, for the hospitality of his laboratory where this work was carried out. We are grateful to Dr. H. B. S. Womersley, University of Adelaide, for identification of the algae.

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Short-Lived Intermediates. IV. Adamantene[1]

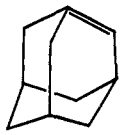
Sir:

The recent syntheses of bicyclo[3.3.2]non-1-ene[2] have generated considerable interest in the synthesis and

(1) For paper III of this series see: J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *Tetrahedron Lett.*, 195 (1972).
(2) J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *J. Amer. Chem. Soc.*, **93**, 3774 (1971).
(3) T. Irie, M. Suzuki, E. Kurosawa, and T. Masamune, *Tetrahedron*, **26**, 3271 (1970); M. Suzuki, E. Kurosawa, and T. Irie, *Tetrahedron Lett.*, 4995 (1970), and previous papers cited within.
(4) S. Itô, K. Eudo, T. Yoshida, and M. Kodama, *Chem. Commun.*, 186 (1967).

(1) Part III: J. E. Gano, *Chem. Commun.*, 1491 (1971).
(2) (a) J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967); (b) J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967).

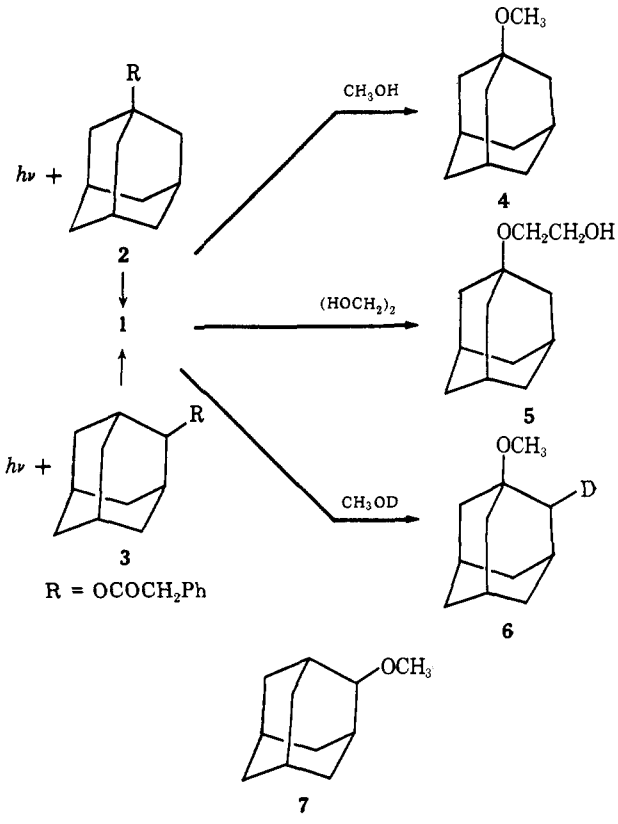
detection of substances which contain highly twisted double bonds.[3] Partly due to the great interest in adamantane chemistry and party to its inherent strain,[3a] the olefin adamantene, (**1**) has been extensively sought.[4]



1

Heretofore, this quest has been unsuccessful. We report here compelling evidence for the generation of adamantene in the type II photoelimination reaction of adamantyl esters.

Esters 1-adamantyl phenylacetate (**2**) and 2-adamantyl phenylacetate (**3**) were prepared by standard methods and irradiated in degassed solutions (0.02–0.3 *M*) of hydroxylic solvents with 254-nm light.[5] In addition to the expected free radical products (1-adamantanol, 23%; ethylene glycol; 2-phenylethanol, 6%; bibenzyl, 5%; adamantane, 4%), ester **2** in methanol also gave 1% 1-methoxyadamantane.[6] Except for giving 2-adamantanol (17%) in place of 1-adamantanol, ester **3** gave similar products (ethylene glycol; 2-phenylethanol, 14%; bibenzyl, 5%; adamantane, 1%) including 1-methoxyadamantane (2–3%). Addition of diazomethane to the photolysate caused the appearance of a new peak in the gas chromatogram which was identified as methyl phenylacetate in a yield comparable to 1-methoxyadamantane. Of particular significance is the fact that, within our limits of detection (0.05%), no 2-methoxyadamantane (**7**) was formed. Photolysis of ester **3** in ethylene glycol gave 2% of 1-(2-hydroxyethoxy)adamantane (**5**). Photolysis of ester **2** or **3** in methanol-*O*-*d* gave 1-methoxyadamantane which had incorporated one deuterium on the adamantyl skeleton, **6**, and both esters showed the same isotope effect for deuterium incorporation of $k_H/k_D \sim 3$.[7] Addition of 0.2 *M* biacetyl, an efficient quencher of phenylacetate triplets at this concentration,[5a] had little effect on the photolysis of **3** (0.3 *M*) in methanol. Neither the yield of **4**, the yields of the other major products, nor the per cent decomposition of ester were decreased by more than 18%.[7b]



The mechanism we propose which explains all of these observations involves type II photoelimination from the excited singlet state of ester **2** or **3** to give adamantene (**1**) and phenylacetic acid followed by ether formation by ionic addition of the hydroxylic solvent to **1**. This mechanism explains every available fact. For example, both esters gave only ether **4** and not **7**. This is consistent since all examples of strained olefins to date are known to add nucleophiles *only* in the Markovnikov sense.[3] Furthermore, the incorporation of one deuterium is consistent with this explanation. The kinetic isotope effect indicates rate-determining hydroxyl hydrogen transfer. In this case, that transfer would be protonation to give the 1-adamantyl cation. The common isotope effect indicates the same intermediate from **2** and **3**. Singlet excited state reactivity, as indicated by the lack of significant biacetyl quenching, is also consistent with the excited state assignment in phenylacetate type II photoelimination reactions.[5a,b]

Certain alternative explanations require consideration.[6b] The geometrical orientation of ester **3** is favorable for a 1,3-photoelimination to give the known 2,4-dehydroadamantane.[8] The dehydroadamantane once formed could have added methanol giving ether **4**.

(3) (a) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, 92, 956 (1970); (b) J. A. Marshall and H. Faubl, *ibid.*, 92, 948 (1970), and references cited therein.

(4) (a) R. B. Gagosian, J. C. Dalton, and N. J, Turro, *ibid.*, 92, 4752 (1970); (b) R. R. Sauers, M. Gorodetsky, J. Whittle, and C. K. Hu, *ibid.*, 93, 5521 (1971); (c) L. K. Montgomery and J. D. Roberts, *ibid.*, 82, 4750 (1960).

(5) Phenylacetate esters are structurally a poor choice for this experiment due to their propensity for competing type I α cleavage to form the benzyl radical. For an initial study, however, they offered the advantages of light absorption at a convenient wavelength and relatively efficient type II photoelimination in model compounds. In addition, they represent one of the few classes of esters where the photochemistry seems well understood. See, for example, (a) J. E. Gano, *Mol. Photochem.*, 3, 79 (1971); (b) R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, 93, 2685 (1971); (c) T. C. Meiggs and S. I. Miller, *ibid.*, 94, 1990 (1972).

(6) (a) All yields were based on decomposed ester. Time *vs.* concentration plots indicated all products mentioned arose from primary photochemical processes. The products were isolated by preparative glpc and identified by spectral and glpc comparison with authentic materials. (b) A control experiment showed 1-methoxyadamantane was not formed by an acetate type pyrolysis in the glpc injection port followed by methanol trapping.

(7) (a) Photolysis in 90 ± 2% deuterated methanol-*O*-*d* gave 1-methoxyadamantane from ester **2** with 32 ± 4% d_0 and 68 ± 4% d_1 and from ester **3** with 23 ± 2% d_0, 74 ± 4% d_1, and 3 ± 2% d_2 as determined by mass spectrometry. Location of the deuterium in the adamantyl radical was based on isotope analysis of the adamantyl ion at [M − OCH_3] which showed 29 ± 3% d_0 and 69 ± 3% d_1 for fragmentation of **6** from **3**. Assignment of the deuterium specifically in the two position is based only on the mechanistic considerations discussed herein. In addition, neither the other products nor the recovered starting material were found to have incorporated more than 6% deuterium. (b) Although even the phenylacetate singlet excited state should be quenched by biacetyl at a diffusion-controlled rate,[5] the observed inefficiency of singlet state quenching is not entirely unexpected since the singlet state lifetimes in related systems are approximately 12 nsec in 10^{-2} *M* sclutions, and the known self-quenching would be expected to considerably reduce such lifetimes at the 0.3 *M* concentrations used here.

(8) A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Commun.*, 657 (1966).

This is ruled out, however, because ionic addition to 2,4-dehydroadamantane has been studied and is known to give not **4** but **7**.[9] Alternatively, an unprecedented heterolytic photocleavage could have occurred in the polar solvent methanol giving an adamantyl cation which could have added methanol to form ether **4**. This explanation is satisfactory for ester **2** but not for ester **3**. The latter would give the 2-adamantyl cation which is known not to rearrange[10] but to give ether **7** which was not observed.

The evidence leaves little doubt that adamantene was formed. It is interesting to note that similar but unsuccessful attempts to generate this alkene from ketone precursors have been reported during this study.[4] Possibly the higher singlet excitation energy of esters accounts for this different behavior. Further studies are now in progress to increase the alkene yield[5] and to detail the properties of adamantene.

Acknowledgment. Partial support of this work by the donors of the Petroleum Research Fund (PRF-1511G), administered by the American Chemical Society, and the ardent competitory instigation of Dr. J. L. Fry are thankfully acknowledged.

(9) A. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968).

(10) (a) P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **8**, 529 (1969); (b) J. A. van Zorge, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **89**, 781 (1970).

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Phosphoranes as Nonobligatory Intermediates in Reactions of Alkoxyphosphonium Salts

Sir:

A number of reactions exist in the field of organophosphorus chemistry which involve the formation of an alkoxyphosphonium salt intermediate followed by dealkylation to the corresponding phosphoryl compound.[1] A few well-known examples of these reactions would include the Arbusov reaction,[2] the Perkow reaction,[3] as well as the acid-catalyzed hydrolysis of phosphorus esters.[4] In general, the dealkylation step involves a nucleophilic displacement at carbon of the alkyl group, with C–O bond cleavage.

In other reactions of alkoxyphosphonium salts such as alkaline hydrolysis,[5,6] the nucleophile attacks at phosphorus rather than at carbon resulting in P–O bond cleavage. The possibility exists that many nucleophiles, which ultimately react at carbon with C–O bond cleavage, may prefer attack at phosphorus to form a pentacoordinate intermediate but are prevented energetically from displacing the relatively poor alkoxy leaving group. Instead, return to phosphonium salt with subsequent attack at carbon would be the overall lower energy pathway. Thus, a pentacoordinate phosphorus intermediate may be involved only as a nonobligatory intermediate in the reaction of nucleophiles with alkoxyphosphonium salts.

We decided to test the possibility of a reversible phosphorane formation in competition with nucleophilic attack at carbon by investigating the stereochemistry of the reaction of various nucleophiles with a chiral phosphonium salt. Formation of the stereochemically nonrigid phosphorane[7] could lead to loss of stereospecificity in the overall reaction, rendering the phosphorane operationally detectable. Our results indicate that the reaction of nucleophiles with an acyclic dialkoxyphosphonium salt, menthoxymethoxymethylphenylphosphonium tetrafluoroborate (**1**), resulting in eventual C–O bond cleavage may proceed with either complete retention of configuration at phosphorus or loss of stereospecificity, depending on the nature of the nucleophile.

Pure $(S)_P$-**1**[8,9] (mp 67–69°), prepared by O-methylation[10] of $(S)_P$-menthyl methylphenylphosphinate, $(S)_P$-**2**,[11] was mixed with an equal molar amount (1 mmol) of the various nucleophiles in the solvents (10 ml) listed in Table I. After *ca.* 10 min, work-up by diluting with dichloromethane (100 ml), extracting with water,[12] drying, and reconcentrating under vacuum resulted in the quantitative formation of **2**. Thus cleavage of the $O–CH_3$ bond is the exclusive mode of reaction. The product stereochemistry was identified by ^1H nmr[11] and the results are indicated in Table I. The product phosphinate, **2**, was stereochemically stable to the reaction conditions, indicating that any loss in stereospecificity at phosphorus must have occurred prior to product formation.[13]

Table I. Stereochemistry of the Products from the Reaction of $(S)_P$-**1** with Various Nucleophiles

Nucleophile	Solvent	Products $(S)_P$-**2**	Products $(R)_P$-**2**	Stereochemistry
I^- (Li^+)	*a*	100	0	Retention
Br^- (Li^+)	*a*	100	0	Retention
Cl^- (Li^+)	*a*	100	0	Retention
F^- (Li^+)	*b*	60	40	Epimerization
$PhNH_2$	*b*	100	0	Retention
i-$PrNH_2$	*b*	60	40	Epimerization
Pyridine	*b*	100	0	Retention
Et_3N	*b*	60	40	Epimerization

[a] Acetone. [b] Dichloromethane.

(1) For recent reviews which include many examples, see R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965; A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967; "Organophosphorus Chemistry," S. Trippett, Ed., The Chemical Society, London: Vol. I, 1970; Vol. II, 1971; Vol. III, 1972.

(2) A. Michaelis and R. Kaehne, *Chem. Ber.*, **31**, 1048 (1898); A. E. Arbusov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906).

(3) W. Perkow, K. Ollerich, and F. Meyer, *Naturwissenschaften*, 39, 353 (1952).

(4) W. Gerrard, W. J. Green, and R. A. Nutkins, *J. Chem. Soc.*, 4076 (1952); L. Keay, *J. Org. Chem.*, **28**, 1426 (1963).

(5) G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, 91, 7023 (1969); R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *Chem. Commun.*, 1010 (1969).

(6) K. E. DeBruin and K. Mislow, *J. Amer. Chem. Soc.*, 91, 7393 (1969).

(7) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); K. Mislow, *ibid.*, **3**, 321 (1970).

(8) The configuration notations $(S)_P$ and $(R)_P$ refer to the stereochemistry at phosphorus.

(9) The ^1H nmr spectrum (CH_2Cl_2) of $(S)_P$-**1** featured PCH_3 (d, δ 2.5, J_{HCP} = 14 Hz) and $POCH_3$ (d, δ 4.2, J_{HCOP} = 12 Hz).

(10) K. E. DeBruin and J. R. Petersen, *J. Org. Chem.*, 37, 2272 (1972).

(11) O. Korpiun, R. A, Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968); R. A. Lewis, O. Korpiun, and K. Mislow, *ibid.*, **90**, 4847 (1968).

(12) $(S)_P$-**1** in the absence of a nucleophile is stable to these work-up conditions.