mixture of regioisomeric enolates of which only **7** is alkylated by **2b**. Employing these bases, the adduct **8** was obtained in 71 and 53% yield, respectively, after chromatography on activity IV, neutral alumina with ether–petroleum ether (5:95). Finally, it is convenient, but not essential, to isolate and purify the adducts from the initial alkylation reaction. A detailed procedure given below for the preparation of **10** and **11** illustrates this point.

A solution of lithium 2,2,6,6-tetramethylpiperidide, prepared from 7.2 g (0.05 mol) of amine and *n*-butyllithium in 100 mL of THF, was cooled to −78 °C and 5.6 g (0.05 mol) of 3-methylcyclohexanone was added dropwise. The enolate solution was then transferred by canula to a slurry of **2b** (17.2 g, 0.05 mol) in 100 mL of THF cooled to −78 °C. After 3.5 h, the solution was allowed to warm to 25 °C, THF was removed, and the residue was taken up in ether. Ether was removed and the residue was taken up in methylene chloride. This was cooled to 0 °C and then treated with 7 mL of 48% aqueous HBF_4 (0.05 mol), dissolved in 40 mL of acetic anhydride. Reaction was continued for 30 min at 0 °C and then 500 mL of ether was added. The red oily product, which separated, was washed with ether and then taken up in 100 mL of acetone and treated with 7.5 g (0.05 mol) of sodium iodide for 30 min. Acetone was removed in vacuo and the residue was extracted with ether. The ether solution was concentrated to 10 mL, petroleum ether (200 mL) was added, and the solution was filtered. Removal of solvent and Kugelrohr distillation of the residue (0.1 mm, 25–60 °C) gave 3.5 g (46%) of a mixture of **10** and **11** (2:1) as a pale yellow oil.

Further applications of Fp(vinyl ether)BF_4 salts in synthesis are being pursued.

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Registry No. 2b, 78782-37-3; **3**, 1193-18-6; **4**, 78782-38-4; **5**, 78782-40-8; **6**, 529-01-1; **7**, 78782-00-0; **8**, 78782-41-9; **9**, 78782-42-0; **10**, 29606-79-9; **11**, 52152-10-0; **12**, 89-80-5; **13**, 491-07-6; **14** (isomer 1), 78791-20-5; **14** (isomer 2), 78853-56-2; (2-methylcyclohexanone)lithium enolate, 13670-84-3; (3-methylcyclohexanone)lithium enolate, 54526-74-8; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2.

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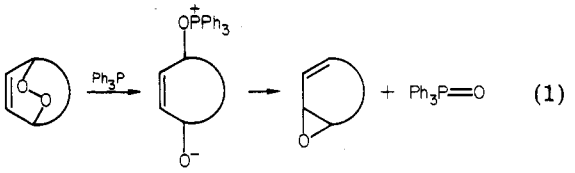
Interaction of Triphenylphosphine with 2,3-Dioxabicyclo[2.2.1]heptane

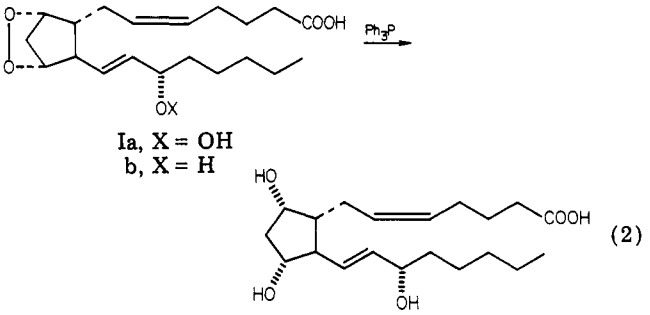
Summary: The reaction of triphenylphosphine with 2,3-dioxabicyclo[2.2.1]heptane resulted in the formation of a phosphorane that decomposed in the presence of water to give triphenylphosphine oxide and *trans*-1,3-cyclopentanediol.

Sir: The study of the interaction of triphenylphosphine (Ph_3P) with peroxides have been extensive. Peroxides that have been investigated include diacyl peroxides,[1] peresters,[2] dialkyl peroxides,[3] hydroperoxy endoperoxides,[4] ozonides,[5] and dioxetanes,[6] all of which react with formation of triphenylphosphine oxide and loss of one oxygen from the substrate. The reactions of Ph_3P with several unsaturated bicyclic peroxides have also been reported.[7] These reactions proceed by initial cleavage of the oxygen–oxygen bond followed by Sn2′ displacement to give the unsaturated epoxide and triphenylphosphine oxide (eq 1).



(1)

Hamberg and Samuelsson[8] in 1973 reported the first reactions of Ph_3P with two saturated bicyclic endoperoxides, PGG_2 and PGH_2 (I_a and $_b$). The product of the reactions was reported to be the cis 1,3-diol (eq 2). but no



(2)

mechanistic details were given. We report here the first mechanistic study of the reaction of Ph_3P with a saturated bicyclic endoperoxide, the prostaglandin endoperoxide model compound, 2,3-dioxabicyclo[2.2.1]heptane[9] (II).

II

Table I. Rate Constants for the Reaction of Triphenylphosphine and Peroxides[a]

compound (X)	[X], M × 10^{-3}	[Ph_3P], M × 10^{-3}	solvent	$10^2 k_2$, M^{-1} s^{-1}
II	10	0.1	$CHCl_2$[b]	0.99 ± 0.06[c,d]
II	10	0.1	benzene[b]	0.93 ± 0.06[c,d]
IV[e]	6.6	70	benzene	100 ± 10[f]
IV[e]	6.1	65	benzene/CH_3CN	100 ± 10[f]

[a] Disappearance of Ph_3P was pseudo first order through at least 3 half-lives (T = 24 °C). [b] Distilled off of EDTA before use. [c] Disappearance of Ph_3P monitored by observing decrease in absorbance at 290 nm. [d] The rate constants are the average of three experiments. [e] IV = tetramethyldioxetane. [f] Reference 6.

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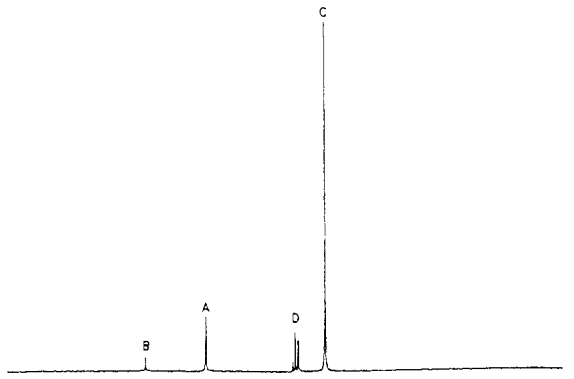
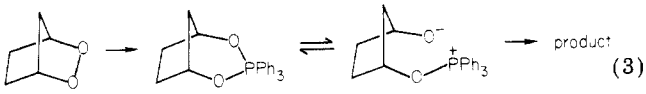


Figure 1. ^{31}P NMR of the reaction mixture illustrating the predominance of the phosphorane III at −63.89 ppm (peak C); peak A, triphenylphosphine; peak B, triphenylphosphine oxide; peaks D, minor phosphorus intermediates.

Treatment of II dissolved in moist methylene chloride with Ph_3P resulted in the slow decomposition of the peroxide and production of triphenylphosphine oxide, *trans*-1,3-cyclopentanediol (60–80%),[10] and trace amounts of two unidentified products, but no cis 1,3-diol.

We have measured the second-order rate constant for the reaction of Ph_3P with endoperoxide II and it is reported in Table I. Examination of this table reveals that the rate of the reaction is experimentally the same in benzene (E_t = 34.5)[11] and methylene chloride (E_t = 41.1).[11] This insensitivity of the reaction rate to solvent polarity is reminescent of the behavior reported by Bartlett[6] for the reaction of Ph_3P with the monocyclic peroxide tetramethyldioxetane.

The similarity of this reaction to the Bartlett reaction suggests that both reactions proceed via initial biphilic[12] insertion of Ph_3P into the oxygen–oxygen bond (eq 3). In



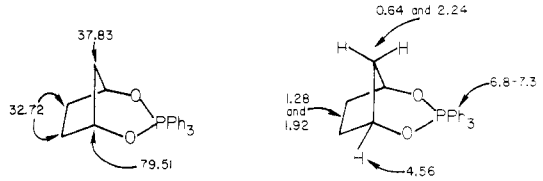
(3)

II III

the case of endoperoxide II heterolytic cleavage of the phosphorane intermediate III gives a zwitterion that reacts with water via backside displacement to give the trans diol. Further examination of Table I also reveals that bicyclic endoperoxide II reacts 100 times slower with Ph_3P than does tetramethyldioxetane, reflecting the increased steric interaction in the approach to the peroxide linkage and decreased strain in the (2.2.1) nucleus.

Examination of the initial interaction between Ph_3P and II under anhydrous conditions[13] by ^{31}P NMR provides evidence for intermediates as depicted in eq 3 and their ionic decomposition. At concentrations much higher than those used for kinetic work [Ph_3P] = 0.5 M and [II] = 0.5 M) three minor phosphorus-containing intermediates at

Scheme I



a carbon assignments b proton assignments

−47.51, −48,69, and −50.25 ppm and a major intermediate at −63.89 ppm were observed[14] (see Figure 1). All four of these peaks are in the chemical shift region expected for five-coordinate phosphorus species.[15]

The proton-decoupled ^{13}C NMR of the reaction mixture exhibits a two-carbon singlet at 32.72 ppm, a one-carbon doublet at 37.83 ppm, J_{P-C} = 12.7 Hz, a two-carbon doublet at 79.51 ppm, J_{P-C} = 11.1 Hz, and doublets at 127.24, J_{P-C} = 12.7 Hz, 132.20, J_{P-C} = 7.9 Hz, 134.09, J_{P-C} = 19 Hz, and 150.63 ppm, J_{P-C} = 125.4 Hz, for aromatic carbons. This spectral data is consistent with the suggestion that the intermediate appearing at −63.89 ppm in the ^{31}P NMR spectrum is the phosphorane III. The proton NMR supports this contention, exhibiting a two-proton pair of doublets at 0.64 and 2.04 ppm, J_{H-H} = 12.2 Hz, a four-proton pair of doublets at 1.28 and 1.92 ppm, J_{H-H} = 8.2 Hz, a two-proton doublet at 4.56 ppm, J_{P-H} = 21.1 Hz, and a multiplet for aromatic hydrogens at 6.8–7.3 ppm. Minor peaks in both the ^1H and ^{13}C NMR barely discernible above the base line noise are most likely due to the minor phosphorus-containing species. The assignment of these chemical shifts to the phosphorane intermediate are depicted in Scheme I.

The phosphorane intermediates decay very slowly in anhydrous benzene, E_t = 34.5 (ca. 80% of the original amount of intermediate is still present after 2 days), and slightly faster in tetrahydrofuran, E_t = 37.4, as expected for an ionic reaction to give a mixture of unidentified products. Addition of 1 equiv of water to the phosphorane resulted in its immediate hydrolysis and production of triphenylphosphine oxide and the trans 1,3-diol as the overwhelming products.

The observation of only four different carbons in the aromatic region suggests that phosphorane III is undergoing rapid pseudorotation[16] on the NMR time scale. Details of this dynamic process and the reactions of Ph_3P with other biologically important peroxides will be reported in the near future.

Acknowledgment. We thank the University of Wyoming for support of this work, the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE 78-18581, for the ^{31}P NMR data, and the National Science Foundation for providing funds for the purchase of a JEOL-270 multinuclear NMR utilized in this work.

Registry No. II, 279-35-6; III, 78870-51-6; IV, 35856-82-7; *trans*-

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1,3-cyclopentanediol, 16326-98-0; Ph_3P, 603-35-0.

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Asymmetric Synthesis of γ-Lactones. A Facile Synthesis of the Sex Pheromone of the Japanese Beetle

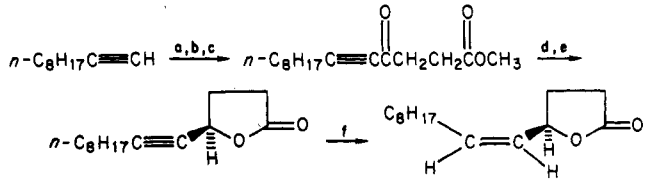
Summary: The sex pheromone of the Japanese beetle, (*R*)-(−)-(*Z*)-5-tetradecen-4-olide, has been prepared in essentially 100% optical purity by using the asymmetric reducing agent *B*-3-pinanyl-9-borabicyclo[3.3.1]nonane to introduce chirality.

Sir: Chirality often plays a critical role in the biological activity of molecules. This phenomenon is particularly important for the sex pheromone produced by the female Japanese beetle, *Popillia japonica*, which has been identified as (*R*)-(−)-(*Z*)-5-tetradecen-4-olide. As little as 1% of the *S,Z* isomer can significantly reduce the response of male beetles to the *R,Z* isomer. The *R* and *S* enantiomers of the pheromone were originally prepared from glutamic acid.[1] Unfortunately, only the more expensive *R*-(−)-glutamic acid leads to the correct enantiomer. More recently the pheromone has been prepared by resolution[2] and by asymmetric reduction[3] of an intermediate. However, these methods do not all give product of high optical purity.[4] Since the pheromone can be used to survey and control this major pest, effective methods for its synthesis would be useful.

We recently reported a route to γ-lactones through the asymmetric reduction of 4-oxo-2-alkynoates.[5] Application of this method to a synthesis of the Japanese beetle pheromone was complicated by the length of the synthesis and the need to manipulate sensitive intermediates. We now report a short synthesis which provides pheromone of essentially 100% optical purity.

The procedure is outlined in Scheme I. The propargyl ketone was prepared in 67% yield from 1-decyne and the acid chloride[6] by using the procedure of Normant.[7] By using the copper(I) bromide–methyl sulfide complex[8] the yield of the propargyl ketone could be increased to 85%. The chiral center was then introduced to asymmetric reduction of the propargyl ketone with *B*-3-pinanyl-9-borabicyclo[3.3.1]nonane (Alpine-borane).[9] The reagent from (+)-α-pinene produced the required *R* enantiomer in

Scheme I[a]



[a] Reagents: (a) *n*-BuLi. (b) CuI/LiI. (c) $ClCOCH_2CH_2CO_2CH_3$, 0 °C, 5 min. (d) Alpine-borane room temperature, 7 days. (e) NaOH/MeOH, reflux, 15 min. Neutralize, 1 N HCl, recrystallize with cyclohexylamine, H^+, distill. (f) $H_2Pd/CaCO_3$ poisoned with lead/quinoline.

70–75% chemical yield. Commercially available (+)-α-pinene (92% optical purity) gave product of 85–90% enantiomeric excess as judged by the use of a chiral NMR shift reagent. Using optically-pure (+)-α-pinene[10] resulted in a product in which none of the minor enantiomer could be detected by NMR (less than 3% *S* probably could not be detected). The crude ester was then saponified[11] and after neutralization the hydroxy acid was distilled [Kugelrohr, 140 °C (pot), 0.01 mm] to give the acetylenic lactone.[12] Reduction of the acetylene gave the pheromone in 80–90% overall yield from the ester. The product was eluted through a short silica gel column with methylene chloride/hexane/ethyl acetate (150/50/5). The α-pinene of 92% optical purity gave a final product of 78–88% optical purity, while optically-pure α-pinene gave product of 97% optical purity.[1]

The limiting factor in obtaining product of high optical purity with the Alpine-borane reagent is usually the optical purity of the α-pinene. High optical purity α-pinene is available.[10] However, the purification of the α-pinene requires extra steps. We therefore sought methods to enrich the desired enantiomer. All intermediates were oils and could not be crystallized. However, we found that the 4-hydroxy acid could be crystallized from acetonitrile as a cyclohexylamine salt[13] (mp 94–95 °C). After two recrystallizations, conversion to the pheromone gave material with a rotation of $[\alpha]^{26}_D$ −69.93° (9.84, $CHCl_3$) [lit. $[\alpha]^{26}_D$ −69.6 (5.0, $CHCl_3$);[1] $[\alpha]^{25}_D$ −70.0 (6.4, $CHCl_3$)[2a]], which was spectroscopically indentical with the natural material.

We have previously shown that Alpine-borane is an effective asymmetric reducing agent for a variety of propargyl ketones.[9] Thus by using different acetylenes it should be possible to produce a variety of optically-active γ-lactones by this route. The generality of recrystallizing the 4-hydroxy acids to optically pure products remains to be explored. These vinyl γ-lactones are of considerable interest in synthetic chemistry because they may be used to introduce chirality in acyclic systems through alkylations with organocopper or palladium reagents.[14]

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(10) Optically-pure α-pinene is available by a resolution process, Brown, H. C.; Yoon, N. M. *Isr. J. Chem.* **1976/1977**, *15*, 12, or by isomerization of β-pinene, Cocker, W.; Shannon, P. V. R.; Staniland, P. A. *J. Chem. Soc. C* **1966**, 41. However, in our hands commercial β-pinene gives α-pinene of only 92% optical purity, research in progress with R. Graham. We are indebted to Professor Harry Mosher for a gift of optically-pure α-pinene.
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(12) Rotation $[\alpha]^{25}_D$ −3.99 (2.2, $CHCl_3$), [lit.[2b] $[\alpha]^{22}_D$ −4.1 (1.658, $CHCl_3$)].
(13) A β-hydroxy acid has been enriched in 100% optically activity by recrystallization as a dicyclohexylamine salt. Tai, A.; Nakahata, M.; Harada, T.; Izumi, Y.; Kusumoto, S.; Inage, M.; Shiba, T. *Chem. Lett.* **1980**, 1125.
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