that amino acid insertions, though possible, are not significant side reactions under the usual conditions of solid phase peptide synthesis.

Experimental Section[14]

Glycyl Resin.—A solution of N-*t*-butyloxycarbonylglycine[13] (1.31 g, 7.48 mmol) and triethylamine (1.04 ml, 7.48 mmol) in 60 ml of ethanol was added to 10.00 g of chloromethylated polystyrene–2% divinylbenzene copolymer, 200–400 mesh[2] (0.374 mmol of Cl/g). The mixture was stirred under reflux for 46 hr and filtered. The resin was washed with ethanol and acetic acid followed by treatment with trifluoroacetic acid for 15 min. The resin was washed with chloroform, ethanol, and methylene chloride. The trifluoroacetate was neutralized by treatment with triethylamine (10%) in chloroform followed by washes of chloroform, ethanol, and methylene chloride. A sample was hydrolyzed in 1:1 dioxane–12 *N* HCl for 24 hr at 110°. Amino acid analysis gave a glycine content of 0.128 mmol/g.

Coupling Reaction I.—Glycyl resin (3.00 g, 0.384 mmol) was placed in a reaction vessel and treated in the following manner: (1) washed (three 30-ml portions) with methylene chloride, (2) introduced N-*t*-butyloxycarbonylglycine (0.740 g, 4.22 mmol) in 30 ml of methylene chloride and mixed for 10 min, (3) introduced N,N′-dicyclohexylcarbodiimide (0.910 g, 4.42 mmol) and allowed to react for 24 hr, (4) washed (three 30-ml portions) with methylene chloride, (5) washed (three 30-ml portions) with dimethylformamide, (6) washed (three 30-ml portions) with acetic acid, (7) washed (three 30-ml portions) with ethanol, (8) washed (three 30-ml portions) with methylene chloride, and (9) dried *in vacuo* to yield product **1**.

Coupling Reaction II.—A portion (1.00 g) of product **1** was treated in the manner described above for the conversion of N-*t*-butyloxycarbonylglycyl resin to glycyl resin. The resulting resin was then treated according to the procedure used for coupling reaction I, with the exception that a 22-fold excess of N-*t*-butyloxycarbonylglycine and a 24-fold excess of N,N′-dicyclohexylcarbodiimide were used to prepare product **2**.

Characterization of Products 1 and 2.—Portions (0.500 g) of **1** and **2** were treated in the following manner: (1) washed (three 15-ml portions) with methylene chloride, (2) mixed with trifluoroacetic acid–methylene chloride (2:3) for 15 min, (3) washed (three 15-ml portions) with methylene chloride, (4) washed (three 15-ml portions) with ethanol, (5) washed (three 15-ml portions) with chloroform, (6) mixed with triethylamine (10%) in chloroform, (7) washed (three 15-ml portions) with chloroform, (8) washed (three 15-ml portions) with methylene chloride, (9) suspended in trifluoroacetic acid (20 ml) and treated with a stream of hydrogen bromide for 30 min, (10) washed (two 15-ml portions) with trifluoroacetic acid, (11) washed (two 15-ml portions) with trifluoroacetic acid–methylene chloride (1:1), and (12) washed (two 15-ml portions) with methylene chloride. The filtrates from steps 9–12 were pooled and evaporated *in vacuo* at 20°. The resultant residues were dissolved in 1% HCl and subjected to paper chromatography and ion exchange chromatography using an amino acid analyzer.

The presence of only glycine (R_f 0.26) and diglycine (R_f 0.38) was indicated by paper chromatography of the cleavage products from **1**. The amino acid analyzer indicated the presence of 38.4 μmol glycine/g (54.8%) and 31.6 μmol diglycine/g (45.2%) in **1**. The cleavage products from **2** were glycine (R_f 0.27), diglycine (R_f 0.37), and triglycine (R_f 0.50), as determined by paper chromatography. The amino acid analyzer indicated the presence of 5.3 μmol glycine/g (6.0%), 40.4 μmol diglycine/g (46.1%), 41.8 μmol triglycine/g (47.7%), 0.2 μmol tetraglycine (0.2%), and an unidentifiable trace peak equal in area to that of the presumed tetraglycine.

(14) Reference 5 gives detailed instructions on the methodology used for solid phase peptide synthesis. Paper chromatography was performed using the ascending method on Whatman No. 1 filter paper developed with phenol–water in a ratio of 75:25. Ninhydrin was used for revealing the chromatograms. Amino acids and peptides were quantitatively determined with a Technicon amino acid autoanalyzer as described by A. R. Mitchell and R. W. Roeske, *J. Chromatogr.*, **43**, 266 (1969). A buffer gradient from pH 3.10 to pH 3.80 allowed the resolution of glycine, diglycine, triglycine, and tetraglycine at elution times of 95, 189, 199, and 172 min, respectively. Glycine, diglycine, triglycine, and tetraglycine were purchased from Mann Research Laboratories, New York, N. Y.

Products of the Action of Peracetic Acid on Isolongifolene

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Treatment of isolongifolene[1] with perbenzoic acid has been reported to give the corresponding epoxide.[2] We have attempted to carry out this reaction using peracetic acid. Commercial peracetic acid brought to pH 3.6 with sodium acetate reacted sluggishly with isolongifolene. A 65% yield of the isolongifolene was recovered, and the remainder consisted of a mixture of a ketone (VI),[2] a lactone (V),[2] and an alcohol (VII) in a ratio of 14:1:4 along with a trace of an epoxide (III).[2] The alcohol, $C_{15}H_{24}O$, was assigned the structure VII on the basis of the following considerations.

(a) The infrared spectrum exhibits a hydroxy stretching vibration at 2.94 μ (Nujol), indicating the presence of alcohol.

(b) The nuclear magnetic resonance spectrum of VII is in accord with the assigned structure. It exhibits the following resonances: δ 5.51 (d, 1 H, corresponding to one olefinic proton, >=CH—C, J = 3 cps), 3.7 (t, 1 H, HCOH, J = 7.5 cps), 0.89, 0.86, 0.80, and 0.70 (4 s, 12 H, four methyl groups), 1.0–1.58 (m, 8 H, $>CH_2$), and 2.1 (m, 1 H, corresponding to the group C=C—CH—C).

(c) The mass spectrum shows a parent peak at *m/e* 220, 177 (M − 43), 164, etc.

The structure is further supported by the chemical evidence. Oxidation by the Jones reagent gave a ketone to which the structure VIII is assigned on the basis of the spectral data.

(a) The infrared spectrum (film) exhibits a carbonyl stretching band at 5.87 μ, indicating a six-membered unconjugated ketone.

(b) The ultraviolet spectrum exhibits λ_{max} 221 (ϵ_{max} 300), ruling out the possibility of a conjugated ketone.

(c) The nuclear magnetic resonance spectrum of VIII supports the above-assigned structure, indicating signals at δ 5.6 (d, 1 H, assigned to olefinic proton, >C=C—C, J = 3 cps), 0.68, 0.80, 0.82, and 0.86 (4 s, 12 H, *gem*-dimethyls), and 1.0–1.57 (m, 8 H, $>CH_2$).

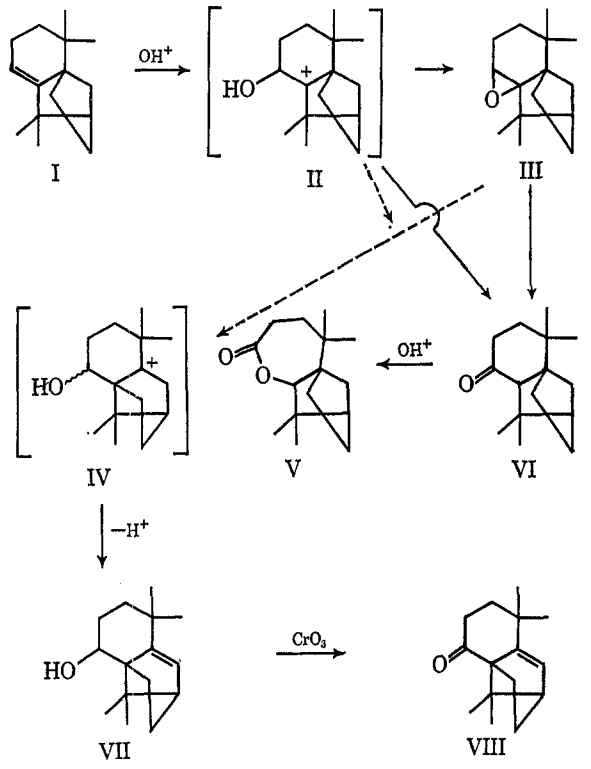
(d) The mass spectrum shows ions at *m/e* 218 (parent peak), 175 (M − 43), etc.

It was of interest to see if epoxide III, when treated with peracetic acid under the same conditions, would give the same products. Isolongifolene epoxide (III) was treated with peracetic acid buffered at pH 3.6 and gave at 60° three major products. They were shown by spectral analysis to be VI, V, and VII in a ratio of 15:1:5. These products suggest that the epoxide III could be an intermediate to give all the products shown in Scheme I.

(1) U. Ramdas Nayak and Sukh Dev, *Tetrahedron*, **8**, 42 (1960).

(2) S. Dev, J. Prahlad, R. Ranganathan, U. Ramdas Nayak, and T. S. Santhanakrishnan, *Tetrahedron Lett.*, No. 8, 417 (1964).

SCHEME I



Experimental Section[3]

Reaction of Isolongifolene (I) with Peracetic Acid.—In a 500-ml flask fitted with stirrer, condenser, and addition funnel was placed 100 g (0.5 mol) of isolongifolene and 12.5 g (0.15 mol) of sodium acetate. The mixture was heated to 60° and 95 g (0.5 mol) of 40% peracetic acid was added dropwise over a period of 45 min, while the temperature was maintained at 60°. After the addition, the mixture was stirred at 60° for 3 hr. It was then cooled, washed with water and 1% sodium sulfite solution, and extracted with toluene. The organic layer was washed once with water and dried over magnesium sulfate. The solvent was removed *in vacuo*. After 65 g of the starting material had been recovered *in vacuo*, the product obtained in an overall yield of 30% consisted of a mixture of previously unknown alcohol VII, ketone VI,[2] and lactone V[2] in a ratio of 4:14:1, respectively.[4] The compounds were isolated by preparative glpc using an 8 ft × 0.25 in., 20% SE-30 column at 200°. Alcohol VII had a melting point of 143–144°.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.57; H, 10.90. Found: C, 81.37; H, 10.89.

Ketone VIII.—In a flask fitted with stirrer, condenser, and addition funnel was placed 42.0 g (0.19 mol) of alcohol VII and 300 ml of acetone. To this mixture was added 85 ml (0.18 mol) of Jones reagent at 15° during a period of 45 min, and the solution was then further stirred at the same temperature for 45 min. After the solids had been filtered off, the acetone was removed *in vacuo* and the crude product was distilled to give 29.0 g of the ketone VIII, 70% yield, bp 106–107° (3.7 mm).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.50; H, 10.10. Found: C, 82.31; H, 9.90.

The 2,4-dinitrophenylhydrazone had mp 181–182°.

Anal. Calcd for $C_{21}H_{26}N_4O_4$: C, 62.29; H, 6.51; N, 14.10. Found: C, 62.89; H, 6.48; N, 13.90.

Reaction of Isolongifolene Epoxide (III) with Peracetic Acid.—Isolongifolene oxide, 1.1 g, mixed with 0.28 g of sodium acetate, was treated with 0.96 g of 40% peracetic acid. The mixture was heated slowly to 60°, and stirred at 60° for 3 hr. The mixture was cooled and extracted with chloroform, and the extract was washed with water and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the products were separated by preparative glpc (8 ft × 0.25 in., SE-30 column, 20%, 200°). The three products were shown by spectral analysis to be V, VI, and VII.

Registry No.—Peracetic acid, 79-21-0; I, 1135-66-6; VII, 22979-29-9; VIII, 22979-30-2; VIII-2,4-dinitrophenylhydrazone, 22979-31-3.

Acknowledgment.—The authors express their thanks to Dr. W. I. Taylor for his helpful suggestions and continued interest. We are also thankful to the Analytical Group for running various spectra and for their help in gas chromatography.

(3) All the nmr spectra were run on a Varian HA-100 spectrometer. Tetramethylsilane was used as an internal standard. The C and H analyses were run by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(4) The ratio of the products varies with the varying amounts of sodium acetate used.

The Reactions of Organophosphorous Compounds with α- and β-Diphenylacyl Bromides

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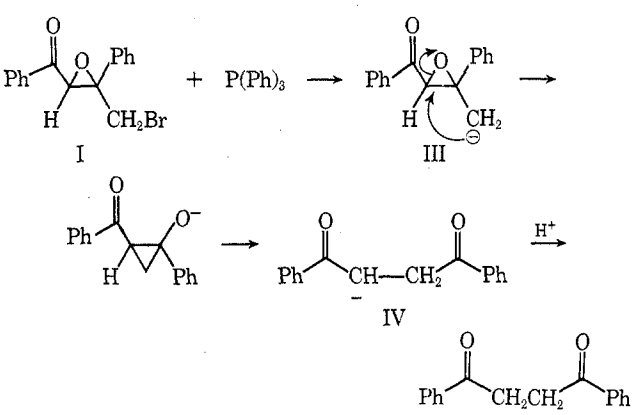
Relatively little attention has been directed to the preparation and reactions of organophosphorous compounds that possess an epoxide function in the β,γ position.[2] In the course of a study on the reactivity of small-membered rings, we investigated the reactions of *cis*- and *trans*-1,3-diphenyl-2,3-epoxy-4-bromo-1-butanone (I and II) with several organophosphorous compounds in an attempt to prepare a β,γ-epoxy phosphorous ylide.



In our studies, we have found that the reaction of *cis*-1,3-diphenyl-2,3-epoxy-4-bromo-1-butanone (I) with triphenylphosphine in refluxing toluene affords dibenzoylethane (55%), *trans*-dibenzoylethylene (5%), phenacyltriphenylphosphonium bromide (30%), benzoylmethylenetriphenylphosphorane (8%), and some triphenylphosphine oxide. Similar results were obtained with the *trans* epoxide (II).

A plausible explanation for the formation of dibenzoylethane involves attack of triphenylphosphine on bromine leading to anion III, which then rearranges to

(1) Alfred P. Sloan Foundation Fellow, 1968–1970

(2) For some pertinent references, see C. E. Griffin and S. K. Kundu, *J. Org. Chem.*, **34**, 1532 (1969).