

*Anal.* Calcd for  $C_{33}H_{46}O_2$ : C, 83.47; H, 9.78. Found: C, 83.3; H, 9.81.

**Dehydration of 8'-Hydroxy-8',9'-dihydrocitra-naxanthin.**—A solution of 45 mg of the 8'-hydroxycitra-naxanthin in 50 ml of chloroform was treated with 10 drops of chloroform-HCl reagent<sup>8</sup> allowed to stand for 20 min, and then diluted with petroleum ether. The mixture was then washed with sodium bicarbonate solution and water, and dried over anhydrous sodium sulfate. The solvents were removed *in vacuo*, and the residue was dissolved in *n*-hexane and chromatographed on a column of deactivated alumina developed and eluted with 40% ether in *n*-hexane. The zone corresponding to the dehydration product was isolated and crystallized from *n*-hexane, yielding 12 mg, mp 156–158°, undepressed on admixture of synthetic citranaxanthin; both samples exhibited the same thin layer chromatographic behavior. The nmr spectrum<sup>2</sup> [singlets at  $\tau$  7.72, 8.02, 8.25, and 8.93; doublet at 2.52 ( $J = 16$  cps)] is in full accord with structure I. Further proof of identity with authentic sample of citranaxanthin was established by infrared and visible spectroscopy.

**8'-Hydroxy-8',9'-dihydrocitra-naxanthin (IV).**—A solution of 0.5 g of  $\beta$ -apo-8'-carotenal in 3 ml of acetone and 5 ml of ethanol was cooled to ca. 0° and added to a cold (ca. 0°) mixture of 0.5 ml of 0.1 *N* potassium hydroxide and 5 ml of ethanol. The reaction mixture was stirred, allowed to stand in the cold (ca. 0°) overnight, and then diluted with ether. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*; the residue was dissolved in 1% acetone-petroleum ether and was chromatographed on a column of Microcel C. IV was isolated and crystallized from peroxide-free ether-petroleum ether, yielding 80 mg, mp 145–147°. Both the synthetic and natural samples displayed the same thin layer chromatographic behavior. The nmr spectra (signals at  $\tau$  7.75, 8.03, 8.15, 8.25, and 8.97) is in full accord with structure IV. The infrared and visible spectra were superimposable on those of the natural sample.

*Anal.* Calcd for  $C_{33}H_{46}O_2$ : C, 83.47; H, 9.78. Found: C, 83.4; H, 9.71.

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(8) L. Wallcave and L. Zechmeister, *J. Am. Chem. Soc.*, **75**, 4495 (1953).

### Mechanism of the Reaction of Trialkylphosphine Dihalides with Alcohols. Isolation of an Alkoxytrialkylphosphonium Halide

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Wiley<sup>1</sup> recently described an extremely useful method for the conversion of alcohols to halides without isomer-

(1) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

ization. For example, a 91% yield of neopentyl bromide was obtained by treatment of neopentyl alcohol with tributylphosphine and bromine. As a result of a study of its stereochemistry and kinetics, Wiley<sup>2</sup> has proposed that the reaction probably proceeds by way of the rapid, irreversible formation of an alkoxytrialkylphosphonium intermediate followed by its slow decomposition to alkyl halide and trialkylphosphine oxide by way of an  $S_N2$  displacement.

In the course of preparing 2,2,2-triphenylethyl bromide, which was needed in another study, from 2,2,2-triphenylethanol by use of Wiley's procedure we have isolated from the reaction mixture (2,2,2-triphenylethoxy)tributylphosphonium bromide.<sup>3</sup> We believe that this isolation and the characterization<sup>4</sup> of the proposed intermediate constitutes strong supporting evidence for Wiley's mechanism. Within the framework of this mechanism, the successful isolation of the proposed intermediate in this particular case may be explained in terms of the difficulty of  $S_N2$  displacement at a center adjacent to a trityl group.

#### Experimental Section

2,2,2-Triphenylethanol (1.0 g, 0.0036 mole), prepared by lithium aluminum hydride reduction of triphenylacetic acid, and 1.0 ml (0.0040 mole) of tributylphosphine (Aldrich) in 3.4 ml of dimethylformamide (Matheson Coleman and Bell, stored over potassium hydroxide) were treated dropwise under nitrogen with 0.19 ml (0.0037 mole) of bromine, the temperature being maintained below 55°. The reaction mixture was poured into a mixture of 50 ml of water and 30 ml of ether. The aqueous phase was extracted with two 20-ml portions of ether and the combined organic phases washed with two 20-ml portions of water, dried with sodium sulfate, and evaporated under vacuum. Crystallization of the resulting 1.95 g of oil and solid from petroleum ether-benzene yielded 0.95 g<sup>6</sup> of (2,2,2-triphenylethoxy)tributylphosphonium bromide, mp 128–129°, whose nmr ( $CDCl_3$ ) spectrum consisted of absorption at  $\tau = 2.7$ –2.8, a poorly resolved doublet centered at  $\tau = 4.66$ , very broad absorption centered at  $\tau = 7.3$  and complex absorption centered at  $\tau = 8.6$  and 9.1 ppm, with relative areas of 15, 1.9, 5.4, and 21, respectively.

*Anal.* Calcd for  $C_{32}H_{44}BrOP$ : C, 69.18; H, 7.98; Br, 14.38. Found: C, 68.94; H, 8.19; Br, 14.67.

(2) G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Letters*, 2509 (1964).

(3) By using this nomenclature we do not imply anything about the nature of the phosphorus-bromine bond.

(4) In the only previous report<sup>5</sup> of the preparation (from  $R_2POR$  and  $R'I$ ) of an alkoxytrialkyl phosphonium halide, elemental analysis and the nature of the decomposition products were the basis of the assignment of structure.

(5) A. I. Razumov and N. N. Bankovskaya, *Dokl. Akad. Nauk S.S.S.R.*, **116**, 241 (1957).

(6) No attempt has been made to maximize the yield or to determine the total amount actually formed because the results reported here suffice to establish the principal point of this Note, that an alkoxytrialkylphosphonium halide is formed under the reaction conditions. It would of course be desirable, in addition to demonstrating the formation of the "salt" in the reaction mixture, to show that it is on the reaction path to product bromide. In view of the fact that this material is stable for many months at room temperature and melts without structural change at a temperature about 75° above the usual reaction temperature, we feel that the temperature necessary for the "salt" to decompose is sufficiently far from the reaction temperature so as to make any decomposition results inapplicable to the reaction as usually run.