ment M − 42 (ketene). We did not observe any M − 42 peaks from **2c** or **4b**.

Experimental Section

Isolation of β-Citraurol. Robinson fruits grown in Florida were collected during December and January. The peels were frozen and then extracted with dichloroethane–methanol (1:1) and $MgCO_3$ in a Waring blender. The filtered extract was dried, redissolved in ether, and saponified with 10% methanolic KOH. After washing and drying, the carotenoids were partitioned in hexane–methanol (90:10). A preliminary separation of the pigments in the methanol layer was made on a column filled with MgO–Celite (1:1) activated at 240°C overnight. The solvent mixture consisted of starting with hexane and using increasing amounts of dichloroethane. β-Citraurol was slightly less polar than zeaxanthin. The fraction containing **2b** was acetylated in pyridine with acetic anhydride. The β-citraurol acetate was purified by passing through a column packed with alumina Woelm W 200 basic acitivity II–III. Starting with a solvent mixture of 10% benzene in hexane, fractions were eluted, collected, and monitored by visible absorption spectra. By this means, the trans isomer was separated from the cis forms. The trans β-citraurol diacetate **2c** was crystallized from benzene–methanol yielding small, orange needles: λ_{max} (*n*-hexane) 403, 425, 450 nm; ir (KBr) 3040–2860 (CH), 1740 (C=O), 1445 (CH_2, CH_3), 1365 (CH_3), 1245 (CO–), 1030 and 970 cm^{-1} (trans CH=CH–) cm^{-1}; NMR (100 MHz, $CDCl_3$, Me_4Si) δ 6.7–6.1 (olefinic protons), ca. 5.05 (H of C-3), 4.58 s (CH_2 of C-8′), 2.36 and 2.24 (CH_2 of C-4), 2.10 s (CH_3 of acetate at C-8′), 2.06 s (CH_3 of acetate at C-3), 1.98 s (CH_3 at C-9, 13 and 13′), 1.85 (CH_3 at C-8′), 1.73 s (CH_3 at C-5), 1.52 s (impurity H_2O), 1.26 s (impurity), 1.12 and 1.08 (2 CH_3 at C-1), 0.89 and 0.84 ppm (impurities); mass spectrum M^+ 518.3430 (calcd for $C_{34}H_{46}O_4$, 518.3393); isotope ratio (M^+):(M + 1):(M + 2) 100:38:10 (calcd, 100:43:9), 474.3257 (M − 44 or M − C_2H_4O, calcd for $C_{32}H_{42}O_3$, 474.3133), 460.3336 (M − 58 or M − $C_2H_2O_2$, calcd for $C_{32}H_{44}O_2$, 460.3340), 458.3173 (M − 60 or M − $C_2H_4O_2$, calcd for $C_{32}H_{42}O_2$, 458.3184), 426 (M − 92), 414.2872 (M − 44 − 60, calcd for $C_{30}H_{38}O$, 414.2923), 400.3052 (M − 58 − 60, calcd for $C_{30}H_{40}$, 400.3129), 398 (M − 60 − 60), 366 (M − 60 − 92), 352 (M − 60 − 106), 263 (M − 60 − 195).

β-Citraurol Diacetate (2c). A solution of β-citraurin (**3a**) in tetrahydrofuran was reduced with lithium aluminum hydride,[15,16] followed by acetylation with acetic anhydride in pyridine[15,17] to obtain small, orange needles: λ_{max} (hexane) 404, 426, 452 nm; ir (KBr) 3040–2860 (CH), 1740 (C=O), 1445 (CH_2, CH_3), 1365 (CH_3), 1240 (CO–), 1025 and 965 cm^{-1} (trans CH=CH–); NMR (100 MHz, $CDCl_3$, Me_4Si) δ 6.9–6.1 (olefinic protons), ca. 5.05 (H of C-3), 4.56 s (CH_2 of C-8′), 2.36 and 2.24 (CH_2 of C-4), 2.09 s (CH_3 of acetate at C-8′), 2.05 s (CH_3 of acetate at C-3), 1.98 s (CH_3 at C-9, 13 and 13′), 1.86 s (CH_3 at C-8′), 1.74 s (CH_3 at C-5), 1.56 (impurity H_2O), 1.12 and 1.08 (2 CH_3 at C-1); mass spectrum M^+ 518.3426 (calcd for $C_{34}H_{46}O_4$, 518.3393), 474.3158 (M − 44 or M − C_2H_4O, calcd for $C_{32}H_{42}O_3$, 474.3133), 460.3355 (M − 58 or M − $C_2H_2O_2$, calcd for $C_{32}H_{44}O_2$, 460.3340), 458.3172 (M − 60 or M − $C_2H_4O_2$, calcd for $C_{32}H_{42}O_2$, 458.3184), 426 (M − 92), 414.3013 (M − 44 − 60, calcd for $C_{30}H_{38}O$, 414.2923), 400.3157 (M − 58 − 60, calcd for $C_{30}H_{40}$, 400.3129), 398 (M − 60 − 60), 366 (M − 60 − 92), 352 (M − 60 − 106).

8′-Apo-β-caroten-8′-ol Acetate (4b). This compound was prepared by reducing 8′-apo-β-caroten-8′-al with lithium aluminum hydride followed by acetylation with acetic anhydride in pyridine: mass spectrum M^+ 460.3340 (calcd for $C_{32}H_{44}O_2$, 460.3340), 416 (M − 44), 402.3260 (M − 58, calcd for $C_{30}H_{42}$, 402.3286), 400.3112 (M − 60, calcd for $C_{30}H_{40}$, 400.3129), 368.2725 (M − 92, calcd for $C_{25}H_{36}O_2$, 368.2714), 354.2537 (M − 106, calcd for $C_{24}H_{34}O_2$, 354.2557), 310.2604 (M − 58 − 92, calcd for $C_{23}H_{34}$, 310.2660), 308.2517 (M − 60 − 92, calcd for $C_{23}H_{32}$, 308.2503), 296.2462 (M − 58 − 106, calcd for $C_{22}H_{32}$, 296.2504), 294.2341 (M − 60 − 106, calcd for $C_{22}H_{30}$, 294.2347).

Oxidation of β-Citraurol (2b). β-Citraurol was dissolved in 0.5 ml of benzene and treated with *p*-chloranil (1 mg).[18] After 15 h there was almost complete conversion of **2b** to β-citraurin (**3b**). Characterization of **3b** was by visible spectrum in hexane and ethanol and by TLC using an authentic sample of β-citraurin (**3b**) for comparison.

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Registry No.—**2b**, 57593-78-9; **2c**, 57593-79-0; **3a**, 650-69-1; **4b**, 38699-13-7.

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Mechanism of Ozonolysis. Triphenylphosphine Reduction of Methylisopropylethylene Ozonide-^{18}O

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When diisopropylethylene is ozonized in the presence of acetaldehyde-^{18}O, methylisopropylethylene ozonide-^{18}O is produced. The position of ^{18}O enrichment in the ozonide provides mechanistic information. In one study,[1] it was concluded that 68–77% of the ozonide formed by a pathway which placed the ^{18}O label at the peroxy site. This analysis included reduction of the ozonides by $LiAlH_4$ or $LiCH_3$ followed by mass spectrometry of the ethanol and isobutyl alcohol that was obtained.

In a subsequent report on the same compound,[2] it was argued that such pathways are considerably less important. An upper limit of 10% was estimated for them by comparing the mass spectral intensities of the ozonide parent ions and the ether fragment ions (loss of O_2). Most of the total ^{18}O enrichment in the parent ion was also found in the ether fragment but a small difference was reported. This difference could be attributed to a competing process producing peroxy ^{18}O incorporation such as the aldehyde interchange mechanism[3] or the enrichment of ozone by exchange with ^{18}O-aldehyde.[4] Other possible explanations are that small amounts of scrambling occurred between peroxide and ether oxygens upon fragmentation or that a systematic error occurred owing to the weak intensities of the mass peaks (perhaps arising from an undetected trace impurity contributing to the intensities).

In order to test the possibility of ^{18}O enrichment at the peroxide site more directly and clarify if there is as much as 10% competition from such pathways, several samples from our previous study[2] were treated with Ph_3P. This produced Ph_3PO which was analyzed for ^{18}O content. The basis of the method is the work of Lorenz and Park[5,6] and Carles

Table I. Relative Intensities of Mass Peaks for Ph_3PO Produced from Reaction with Methylisopropylethylene Ozonide-^{18}O

Fragment	M − 1	M	M + 1	M + 2	M + 3
m/e	277	278	279	280	281
Run 1[a]	100[b]	54	8.4	2	0.0
2	100	56	9.2	1	0.1
3	100	60	10.1	1	0.1
Stnd	100	57	9.4	1	0.1

[a] Ozonides used in runs 1–3 are described in the text and ref 2. Stnd is the standard sample of Ph_3PO. [b] Deviation in the relative intensity of the M and M + 1 fragments was about 2 and 0.5, respectively (90% confidence level). The M + 2 and M + 3 fragments were too weak to statistically estimate uncertainties.

and Fliszár[7] which shows that the reaction is quantitative and that Ph_3P selectively attacks the peroxidic oxygens.[8]

The three samples of methylisopropylethylene ozonide-^{18}O that were used were estimated to contain the following percentages of total ^{18}O enrichment and ^{18}O at the ether site:[2] run 1, 54.7 and 52.1; run 2, 54.6 and 53.0; run 3, 54.7 and 49.0. The pertinent mass spectrum for Ph_3PO produced from these ozonides as well as a standard Ph_3PO sample is listed in Table I.

The four runs in Table I gave essentially the same fragmentation patterns with no evidence for ^{18}O enrichment in the Ph_3PO. From examination of the intensity ratios of the 277/279 fragments after correction for naturally occurring heavy isotopes, the upper limit of ^{18}O enrichment in the Ph_3PO is estimated to be 0.7%. This gives an upper limit of 2.6% for pathways that produce ^{18}O at the peroxide site. This estimate assumes that attack by Ph_3P is equally probable at either peroxide site and normalizes for the original ^{18}O content in the ozonides.

In summary, the Ph_3PO analysis supports the main conclusion obtained by direct mass analysis of the ozonides themselves[2] that most of the ^{18}O label occurs at the ether site. Compared to the direct analysis of the ozonides, the Ph_3PO procedure sets a lower estimate for processes that produce ^{18}O label at a peroxide site and it is quite consistent with such processes being mechanistically insignificant. Also, the small apparent loss of ^{18}O enrichment at the ether site when the ozonides are mass analyzed is not recovered by ^{18}O enrichment at the peroxide site. It must arise from some other effect such as discussed above implying that caution should be exercised when mass analyzing ozonides of this type.

Placing these results in a larger framework, the lack of evidence for peroxidic incorporation in this system and most others[10,11] and the recent revision of the Criegee mechanism[12] rationalizing much stereochemical data remove considerable support for competition by an aldehyde interchange mechanism.[3] Another basis for that hypothesis was the ^{18}O studies on the ozonide produced in the isobutyraldehyde–diisopropylethylene system.[13] It is interesting to note that the mass spectral method of analysis and the estimated peroxy ^{18}O enrichments overall in that work are similar to that first discussed by us in ref 2. Therefore it is attractive to extrapolate our present results to that system also whereupon the main isotopic evidence for peroxidic incorporation (and the aldehyde interchange pathway) would be removed.[14]

Experimental Section

The preparation of the ^{18}O-labeled ozonides and determination of their ^{18}O content has been described elsewhere.[2]

Ph_3PO. Pure Ph_3PO was obtained by passing ozone into a saturated solution of Ph_3P in heptane at room temperature followed by recrystallization. The mass spectrum and melting point were used for identification.

Ozonide Reduction with Ph_3P. The procedure in the literature was employed.[5-7] Heptane was the solvent. Because of the small amounts of samples, transfers on a vacuum line were convenient. The reaction proceeded for 6–8 h followed by isolation of Ph_3PO and mass analysis.

Mass Spectra. An AEI MS-902 mass spectrometer was used with ionizing voltage of 70 V and source temperature of about 175–200 °C. Direct introduction of the samples was employed and the vapor pressures were sufficient to easily obtain intense spectra.

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Registry No.—Ph_3PO, 791-28-6; Ph_3P, 603-35-0; ozone, 10028-15-6; methylisopropylethylene ozonide-^{18}O, 57719-20-7.

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