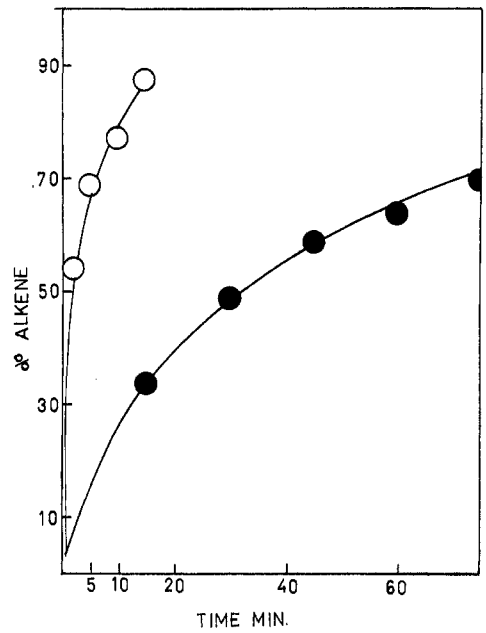

Figure 1.—Reaction of *cis*- and *trans*-4-*tert*-butylcyclohexanols with methyltriphenoxyphosphonium iodide in hexamethylphosphoramide at 75°. Reactions were 0.2 *M* in the alcohol, 0.4 *M* in the iodide. The percentages of alkenes were determined by glpc analysis using internal standards: ●, *cis*-4-*tert*-butylcyclohexanol; ○, *trans*-4-*tert*-butylcyclohexanol.

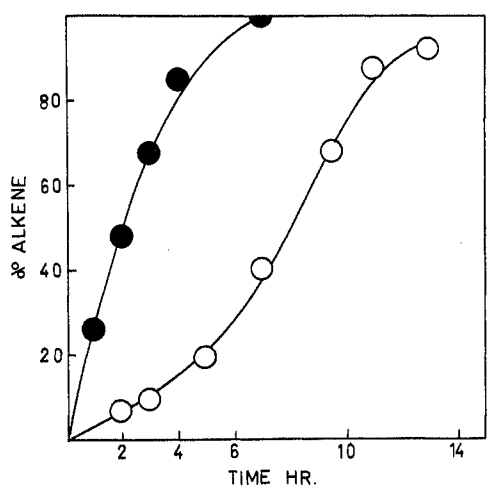

Figure 2.—Dehydrohalogenation of 2-iodooctane in hexamethylphosphoramide at 75°. Reactions were 0.2 *M* in 2-iodooctane. The percentages of alkenes were determined by glpc using internal standards: ●, no methyltriphenoxyphosphonium iodide; ○, solution 0.4 *M* in methyltriphenoxyphosphonium iodide.

prepared as described[3] and stored under dry ether. The alcohols used were commercial products except for *cis*- and *trans*-4-*tert*-butyl and *cis*- and *trans*-2-phenylcyclohexanols which were prepared by stereoselective reductions of the ketones ($IrCl_4$ complex for the cis,[7] $LiAlH_4$–$AlCl_3$ for the trans[8]).

Dehydration of Alcohols. General Procedure.—The method is presented in the text. The relative amount of solvent may be reduced for preparative applications. The isolation procedure is illustrated for the preparation of (*E*)-stilbene.

(*E*)-Stilbene.—A solution of 1,2-diphenylethanol (1.19 g, 6.0 mmol) and MTPI (5.4 g, 12 mmol) in 20 ml of HMPA was stirred at 75° for 1.0 hr, poured into 100 ml of aqueous KOH, and extracted three times with 25 ml of cyclohexane. The cyclohexane solution was washed three times with water and dried ($MgSO_4$). Removal of the solvent at reduced pressure and recrystallization of the resulting solid from ethanol afforded 928 mg (86%) of product as colorless plates, identical in all respects with authentic (*E*)-stilbene.

(7) E. L. Eliel, T. W. Doyle, R. O. Hutchins, and E. C. Gilbert, *Org. Syn.*, **50**, 13 (1970).

(8) E. L. Eliel, R. J. L. Martin, and D. Nasipuri, *ibid.*, **47**, 16 (1967).

Registry No.—**1**, 937-06-4; **2**, 937-05-3; **3**, 80-97-7; **4**, 57-88-5; **5**, 7443-70-1; **6**, 7443-52-9; **7**, 16201-63-1; **8**, 2362-61-0; **9**, 1490-04-6; **10**, 1724-39-6; **11**, 623-93-8; **12**, 1120-06-5; **13**, 2653-34-6; **14**, 614-14-2; **15**, 614-29-9; **16**, 112-53-8; **17**, 2198-72-3; **18**, 5445-30-7; MTPI, 17579-99-6; HMPA, 680-31-9.

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Oxidation Products of Ethyl α-Safranate

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Carotenoids with six-membered alicyclic end groups are widespread in nature.[1] Many organisms are capable of introducing carbonyl and/or alcohol functions at C-3 and C-4 into the α- or β-ionone rings of such carotenoids, while a few bacteria and the Japanese sea sponge have the ability to dehydrogenate the terminal cyclohexene rings to their aromatic counterparts. Relatively few methods have been developed for the total synthesis of such end groups[2] and it became of interest to inquire whether ethyl α-safranate (**1**), for which we recently described a simple and efficient synthesis,[3] could be transformed to versatile monocyclic intermediates and then to carotenoids.

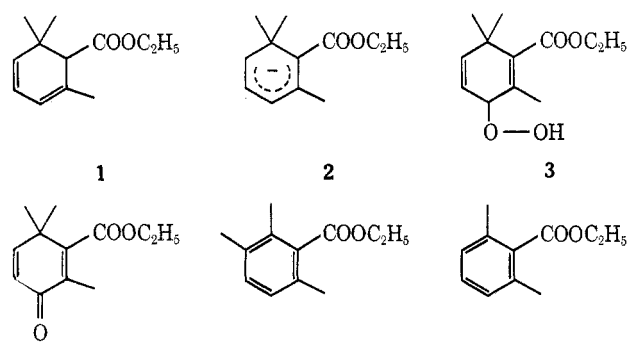
Addition of ethyl α-safranate (**1**) to a solution of potassium *tert*-butoxide in glyme produced an orange solution undoubtedly containing the anion **2**. This color was discharged quickly when oxygen was bubbled through the solution and after work-up the hydroperoxide **3** (34%), the keto ester **4** (43%), and ethyl 2,6-dimethylbenzoate (**6**) (3%) could be isolated by chromatography. The structures of **3** and **4** rest on their spectral properties exclusively (see Experimental Section) while the aromatic ester **6** was compared with an authentic sample. The relative proportions of hydroperoxide **3** and ketone **4** depend on the method of isolation, and not unexpectedly the hydroperoxide **3** turned out to be a very labile compound and readily lost the elements of water, giving the ketone **4**. Injection into a gas chromatograph caused its decomposition to a mixture of **4**, **5**, and **6** in a ratio of 8:1:1. Mechanistic studies on the formation and decomposition of the hydroperoxide **3** were not undertaken but it seems to be the initial product derived from addition of oxygen

(1) B. C. L. Weedon in "Carotenoids," O. Isler, Ed., Birkhäuser Verlag, Basel, 1971, p 29.

(2) H. Mayer and O. Isler in "Carotenoids," O. Isler, Ed., Birkhäuser Verlag, Basel, 1971, p 325.

(3) G. Büchi and H. Wüest, *Helv. Chim. Acta*, **54**, 1767 (1971).

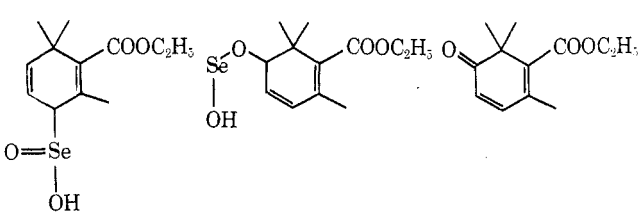
to the U-shaped pentadienyl carbanion **2**. Such anions are known to be protonated preferentially at the central carbon atom[4] and there is no reason to suspect that oxygen addition should occur elsewhere, particularly when the steric crowding around the termini of the anion is taken into account. The keto ester **4** and the two aromatic esters **5** and **6** produced from the hydroperoxide **3** on chromatography seem to be the result of acid-catalyzed heterolysis.[5] Protonation of the hydroxylic oxygen followed by O–O heterolysis gives the ketone **4**, while protonation of the other oxygen atom followed by loss of hydrogen peroxide leads to a carbonium ion which can undergo a Wagner–Meerwein rearrangement to ethyl 2,3,6-trimethylbenzoate (**5**) or fragment to ethyl 2,6-dimethylbenzoate (**6**).



1 **2** **3**

4 **5** **6**

In the course of efforts to introduce oxygen at C-2 ethyl α-safranate (**1**) was oxidized with selenium dioxide. In hot acetic acid ethyl 2,3,6-trimethylbenzoate (**5**) was formed in 63% yield. Oxidation in refluxing dioxane gave a new keto ester **9** with intense ultraviolet absorption at 309 nm, while the isomeric ester **4** absorbs at 241 nm. The formation of the two oxidation products can be rationalized if the allyl selenic acid[6] **7** undergoes a [2,3] sigmatropic rearrangement[7] to the selenium(II) ester **8**. In acetic acid solution this ester undergoes solvolysis with concurrent Wagner–Meerwein rearrangement, while in dioxane solution it decomposes to the ketone **9** and selenium.



7 **8** **9**

(4) R. B. Bates, D. W. Gosselink and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(5) R. Hiatt in "Organic Peroxides," Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, p 1.

(6) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).

(7) This mechanism of olefin oxidation by selenium dioxide was suggested to us by Professor K. B. Sharpless, M. I. T., who will publish his observations elsewhere. It has advantages over those proposed previously: ref 6; J. P. Schaefer, B. Horvath, and H. P. Klein, *J. Org. Chem.*, **33**, 2647 (1968); E. N. Trachtenberg, C. H. Nelson, and J. R. Carver, *ibid.*, **35**, 1653 (1970); D. H. Olson, *Tetrahedron Lett.*, 2053 (1966).

Experimental Section

Microanalyses were performed in the laboratory of Dr. F. Gautschi, Firmenich et Cie., Geneva. Boiling points are uncorrected. Gas–liquid chromatography was performed on a F & M 720 instrument, using silicon rubber gum SE-30 and Carbowax 20M columns. Silicic acid "Mallinckrodt" 100 mesh was used for column chromatography. The following spectrometers were used: nmr, Varian T-60; ir, Perkin-Elmer Model 247; uv, Cary Model 14; mass spectrum, Hitachi RM-U6D.

Autoxidation of Ethyl α-Safranate (1).—To a solution of 3.4 g (30 mmol) of potassium *tert*-butoxide in 150 ml of glyme (distilled from $LiAlH_4$) was added, at −70°, 5.8 g (30 mmol) of ethyl α-safranate (**1**) in 60 ml of dry ether. Oxygen was then bubbled through the mixture at −70°. When the initially orange color turned to light yellow (~20 min), 5 ml of acetic acid was added, followed by evaporation of most of the solvent *in vacuo*. The mixture was extracted with hexane, washed with water, dried (Na_2SO_4), and evaporated. The remaining oil (6.0 g) was chromatographed on 175 g of silicic acid. Elution with hexane and 2% AcOEt gave 0.3 g of a mixture of starting material and ester **6**. With hexane and 10% AcOEt 1.8 g of keto ester **4** was eluted: bp 72° (0.1 mm); ir ($CHCl_3$) 1715, 1655, 1630 cm^{-1}; uv (EtOH) 241 nm (ε 13,200); nmr (CCl_4) δ 1.3 (6 H, s), 1.3 (3 H, t, J = 7 Hz), 1.8 (3 H, s), 4.3 (2 H, q, J = 7 Hz), 6.1 (1 H, d, J = 11 Hz), 6.7 (1 H, d, J = 11 Hz); mass spectrum (70 eV) m/e (rel intensity) 208 (18), 135 (100).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.01; H, 7.51.

Later fractions eluted with hexane and 20% AcOEt yielded 1.8 g of a mixture of keto ester **4** and hydroperoxide **3**, followed by 1.4 g of pure hydroperoxide **3**: ir ($CHCl_3$) 3550, 3400, 1715 cm^{-1}; nmr (CCl_4) δ 1.1 (3 H, s), 1.2 (3 H, s), 1.3 (3 H, t, J = 7 Hz), 1.8 (3 H, s), 4.2 (2 H, q, J = 7 Hz), 4.5 (1 H, s), 5.7 (2 H, m), 8.5 (1 H, broad).

Injection of hydroperoxide **3** on glc (4-ft Carbowax 20M at 180°, injection port temperature 250°) produced compounds **5**, **6**, and **4** in the ratio of ~1:1:8. Retention times and spectra of collected samples were identical with those of authentic samples.

Selenium Dioxide Oxidation of Ethyl α-Safranate (1). A.—A mixture of 1.94 g (10 mmol) of ethyl α-safranate (**1**), 1.33 g (10 mmol) of selenium dioxide, and 12 ml of acetic acid was heated at 100–110° for 15 min. Water was added and the mixture was extracted with pentane. The organic layer was washed with 5% sodium bicarbonate solution and water and then dried (Na_2SO_4) and evaporated. Distillation of the residue afforded 1.22 g (63%) of ester **5**: bp 61° (0.1 mm); ir ($CHCl_3$) 1720 cm^{-1}; uv (EtOH) 235 nm (ε 1610), 277 (900); nmr (CCl_4) δ 1.3 (3 H, t, J = 7.5 Hz), 2.1 (3 H, s), 2.2 (6 H, s), 4.3 (2 H, q, J = 7.5 Hz), AB system centered at 6.9 (2 H); mass spectrum (70 eV) m/e (rel intensity) 192 (54), 147 (100).

B.—A solution of 5.82 g (30 mmol) of ethyl α-safranate and 3.55 g (32 mmol) of selenium dioxide in 50 ml of dioxane was heated at reflux for 30 min. The mixture was poured into water and extracted several times with ether. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated. Chromatography on silicic acid with hexane and 15% AcOEt as eluent yielded 2.47 g (40%) of keto ester **9**: bp 59° (0.1 mm); ir ($CHCl_3$) 1710, 1665, 1635 cm^{-1}; uv (EtOH) 309 nm (ε 6150); nmr (CCl_4) δ 1.3 (6 H, s), 1.35 (3 H, t, J = 7 Hz), 2.0 (3 H, s), 4.3 (2 H, q, J = 7 Hz), 6.0 (1 H, d, J = 10 Hz), 6.8 (1 H, d, J = 10 Hz); mass spectrum (70 eV) m/e (rel intensity) 208 (60), 134 (100).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.26; H, 7.59.

Registry No.—**1**, 35044-57-6; **3**, 36596-64-2; **4**, 36596-65-3; **5**, 36596-66-4; **6**, 36596-67-5; **9**, 36596-68-6.

Acknowledgment.—We are indebted to Firmenich et Cie., Geneva, for generous financial support.