

(2) \rightarrow octenoate. The alcohol (7) was obtained as a solid, m.p. 58–64°, which by fractional crystallisation could be separated into two extreme fractions, m.p. 65.5–67° and 54–61°; again we were unable by any physical method to estimate the purity of these fractions. Determination of the extent of direct formation of acrylate from the intermediates was simple since a control experiment showed that under our conditions stearaldehyde and the phosphonate anion did not react. As a check on this the acrylate obtained from both fractions of [3-²H]-(7) showed complete retention of deuterium, while measurement of the yields of stearaldehyde obtained by base-induced decomposition of compound (7) showed 59% reversion from the high-melting fraction and 76% from the lower. Here $k_{-1} \gg k_1$ holds; we are unable to offer any definite explanation for this 'long-chain' effect.*

Because of the uncertainty regarding the composition of the fractions of (7) we are unable to make any quantitative comments regarding k_{-1} and k_2 for (C) and (T), but it is clear that k_2 for (C) must be very small, since no *cis*-ester was isolated though one or other of the fractions must have contained appreciable quantities of (C). It is also clear that k_{-1} and k_2 for (T) must be of similar magnitude. After the completion of this work it was suggested that the diastereoisomers corresponding to (2) could be interconverted directly without reversion to starting materials.⁴ We have no information on this point.

Pyrolysis⁵ of the hydroxy-phosphonate (6) at 110° also yielded the acrylate (35% from the borohydride-generated alcohol and 38% from that produced by hydrogenation); no *cis*-isomer was detected and a control showed that hexanal and the phosphonate did not react under these conditions. *trans*-Octenoate was also generated by the reaction of compound (8) with aqueous sodium hydroxide; a control demonstrated that the ester could have arisen by both the 'direct' and 'indirect' routes.

EXPERIMENTAL

1-(Diethoxyphosphorylmethylene)hexyl Ethyl Carbonate (5).—Sodium hydride (106 mg of a 60% dispersion in oil) was added to diethyl 2-oxoheptylphosphonate⁵ (500 mg) in tetrahydrofuran (10 ml). The mixture was stirred under nitrogen until effervescence ceased, then ethyl chloroformate (218 mg) was added and the mixture was stirred overnight at room temperature. Addition of water, acidification, and extraction with ether gave (after evaporation and purification by t.l.c.) the enol carbonate (5) (300 mg) as an oil, ν_{\max} 1755, 1265, 1235, 1040, and 980 cm^{-1} , τ (CCl_4) 4.72 (1H, d, J 9 Hz), 5.9 (6H, m), and 7.65 (2H, m). On refluxing in ethanolic sodium ethoxide the starting phosphonate was regenerated.

Ethyl 2-Diethoxyphosphoryl-3-oxo-octanoate (3).—Sodium hydride (4 g of a 60% dispersion in oil) was added in portions

to ethyl diethoxyphosphorylacetate⁶ (22.4 g) in tetrahydrofuran (40 ml) at 0°. When the effervescence ceased freshly distilled hexanoyl chloride (13.5 g) in tetrahydrofuran (20 ml) was added. The mixture was stirred for 1.5 h at room temperature, then poured into 2N-sulphuric acid and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate, water, and then 10% sodium hydroxide (3 \times 60 ml). Acidification of the latter extracts with 6N-sulphuric acid and extraction with ether, followed by concentration, yielded the keto-ester (3) (7.65 g) as an oil, ν_{\max} 1735, 1710, and 1585 cm^{-1} . Addition of the ester (3) (1 g) to sodium hydroxide (500 mg) in water (3 ml) with vigorous agitation followed by cooling to 0° gave a solid (250 mg) which was filtered off and recrystallised from ethanol to give the *salt*, m.p. 180–183°, λ_{\max} (EtOH) 260 nm (ϵ 11,400), λ_{\max} (EtOH-acid) 244 nm (ϵ 7700), ν_{\max} 1650 cm^{-1} (Found: C, 48.9; H, 7.6. $\text{C}_{14}\text{H}_{26}\text{O}_6\text{P}$ requires C, 48.8; H, 7.6%).

Ethyl 2-diethoxyphosphoryl-3-oxoicosanoate (4) was also prepared by this procedure and purified by t.l.c.

Ethyl 2-Diethoxyphosphoryl-3-hydroxyeicosanoate (7).—The ketone (4) (100 mg) and orthoboric acid (326 mg) were dissolved in ethanol (7 ml) and sodium borohydride (50 mg) was added. After 2 h at ambient temperature the mixture was poured into 6N-sulphuric acid. Extraction with ether and concentration yielded a partially crystalline alcohol (100 mg) which was recrystallised from light petroleum (b.p. 60–80°); m.p. 58–64°, ν_{\max} 3400 and 1720 cm^{-1} , τ (CDCl_3) 6.92 (1H, dd, J 9 and 20 Hz) (Found: C, 63.5; H, 10.7. Calc. for $\text{C}_{26}\text{H}_{52}\text{O}_6\text{P}$: C, 63.4; H, 10.8%).

Recrystallisation of the alcohol mixture from light petroleum (b.p. 60–80°) (2 \times) and then from methanol (3 \times) gave a fraction of m.p. 65.5–67°; recrystallisation of the material from the mother liquors from light petroleum (b.p. 60–80°) gave another fraction, m.p. 54–61°.

Ethyl 2-Diethoxyphosphoryl-3-hydroxyoctanoate (6).—This alcohol was prepared similarly and the oil obtained characterised by dehydration with acetic anhydride and pyridine to ethyl 2-diethoxyphosphoryloct-2-enoate (8), ν_{\max} 1720 and 1610 cm^{-1} , b.p. 90° (bath) at 10⁻⁵ mmHg (Found: C, 54.9; H, 8.8. $\text{C}_{14}\text{H}_{27}\text{PO}_5$ requires C, 54.9; H, 8.9%). Dissolution of the olefin (8) in ethanol-aqueous 10% sodium hydroxide (2 : 1) generated ethyl *trans*-oct-2-enoate (40%).

Ethyl 3-Oxoicosanoate.—Dry *t*-butyl alcohol (2.43 g) was added to a stirred suspension of lithium aluminium hydride (380 mg) in ether (50 ml). After being stirred for 30 min the suspension was allowed to settle, the supernatant ether was removed, and tetrahydrofuran (25 ml) was added, followed by the ketone (250 mg) in tetrahydrofuran (10 ml). The mixture was stirred for 30 min, water (20 ml) was carefully added, and the mixture was acidified with 6N-sulphuric acid. Extraction with ether and concentration gave a mixture, separated by t.l.c. into starting ketone and the *keto-ester*, m.p. 45–46°, ν_{\max} 1725 and 1710 cm^{-1} , λ_{\max} (EtOH) 245 nm (ϵ 1480), λ_{\max} (base) 274 nm (ϵ 22,000), τ (CDCl_3) 5.8 (1H, q, J 7 Hz) (Found: C, 74.5; H, 11.9. $\text{C}_{22}\text{H}_{42}\text{O}_3$ requires C, 74.6; H, 11.8%).

Decomposition of the Alcohols (7) by Base.—(a) The alcohol (7) (m.p. 65.5–67°) (10 mg) and ethanolic sodium ethoxide [1.4 ml of a solution from sodium (33.4 mg) in ethanol (100

⁴ G. Lefebvre and J. Seyden-Penne, *Chem. Comm.*, 1970, 1308.

⁵ E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, 1966, **88**, 5654.

⁶ R. C. Freeman and A. J. Speziale, *J. Org. Chem.*, 1958, **23**, 1883.

* We have observed this effect in other cases, e.g. the anion of ethyl α -phosphonatohexanoate smoothly condenses with diethyl α -ketoglutarate; the corresponding phosphonate anion of ethyl laurate does not.

ml)] were set aside for 15 min. Addition of water and extraction with ether gave the product mixture. G.l.c. (methyl stearate as internal standard; Silicone grease column at 220°) indicated a 59% yield of octadecanal.

The fraction of m.p. 54–61° yielded 76% of octadecanal under the same conditions.

(b) The alcohol fractions (7) were prepared by reduction with sodium borodeuteride. Decomposition as in (a) but in the presence of octadecanal gave a mixture of the latter substance and ethyl eicos-2-enoate which could not be separated by t.l.c. However after reduction with sodium borohydride t.l.c. separation was possible and the ethyl eicos-2-enoate isolated from each fraction was shown to have the same $(M + 1) : M$ peak ratios on an MS9 mass spectrometer as did the dehydration product (9) of the alcohols (7).

Decomposition of the Alcohols (6) by Base.—The alcohol (6) [from reduction of (3) with sodium borodeuteride] (49.6 mg), hexanal (27.8 mg), and naphthalene (32.0 mg) were dissolved in ethanol (2 ml), and ethanolic sodium ethoxide [0.85 ml of a solution of sodium (45.5 mg) in ethanol (10 ml)] was added. After 3 min g.l.c. of the mixture (Carbowax column at 150°) indicated a 92.6% yield of ethyl *trans*-oct-2-enoate as judged by the relative peak heights of ester and naphthalene and comparison of these with known calibration mixtures. Work-up in the usual way and

preparative t.l.c. gave the octenoate, whose mass spectrum (MS 9 instrument) showed that 53.5% monodeuterio-ester was present. Dehydration of the starting alcohol to olefin (8) and mass spectroscopy showed it to be 85% monodeuterio-compound: thus [$^2\text{H}_1$]- (6), 0.13 mmol; [$^2\text{H}_0$]- (6), 0.024 mmol; hexanal, 0.28 mmol; and [$^2\text{H}_1$]octenoate/- [$^2\text{H}_0$]octenoate = 1.15

$$= \frac{0.13(1-x) + [0.13x/(0.154x + 0.28)] \times 0.9 \times 0.154x}{0.024(1-x) + [(0.024x + 0.28)/(0.154x + 0.28)] \times 0.9 \times 0.154x}$$

where x is the fraction which reverts to hexanal. The assumption is made that the decomposition of (7) to octenoate + hexanal + phosphonate anion is quantitative, and control experiments show that the combination of the latter two compounds to give the former is 90% efficient.

Solution of the foregoing equation shows that 49% of (6) reverts to starting materials.

When heated at 110° for 70 h the alcohol (6) was converted into ethyl *trans*-oct-2-enoate (35%). A control experiment established that it was formed by direct decomposition

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