Tetrahedron, 1963, Vol. 19, pp. 2269 to 2280. Pergamon Press Ltd. Printed in Northern Ireland

# STUDIES IN SESQUITERPENES—XIX*

## ACTION OF PERBENZOIC ACID ON LONGIFOLENE†

U. RAMDAS NAYAK‡ and SUKH DEV‡
Organic Chemistry Department, Indian Institute of Science, Bangalore, India

(*Received* 9 *July* 1963)

**Abstract**—Oxidation of longifolene, a mono-olefinic sesquiterpene, with a chloroform solution of perbenzoic acid proceeded to almost two mole consumption of the peracid to furnish a number of products, important ones being an α-ketol, a norketone (longicamphenilone) and the corresponding $C_{14}$-alcohols. Under certain conditions it has been possible to arrest the reaction at one mole consumption and to isolate longifolene-α-epoxide, which is the major product; some amounts of epimeric longifolaldehydes and longicamphenilone were also formed. Further action of perbenzoic acid on longifolene oxide and longifolaldehydes has been investigated and the results used to interpret the mechanism of abnormal peracid oxidation of longifolene.

THE action of perbenzoic acid (PBA) on longifolene (I) was first studied by Naffa and Ourisson,[1] who observed that longifolene, which contains a single ethylenic linkage, on treatment with PBA in chloroform solution at −5° consumed peracid as follows: 1·27 equivalents in 12 minutes, 1·70 equivalents in 1 hour and 1·73 equivalents in 45 hours. By conducting the oxidation with 2 moles of PBA (in $CHCl_3$) at ice-temperature for 3 days, these authors succeeded in isolating a norketone (longicamphenilone, II) in 68% yield; α-longiforic anhydride (III) could also be isolated in yields of less than 10%. Although Meerwein,[2] in 1926, had shown that olefins of type IV normally consumed an excess of the peracid, the consumption of the second mole of the peracid was generally slow and incomplete; for example the closely related camphene (V) did not react beyond 20% of the calculated amount of the second mole of the peracid, and the chief product was found to be the epoxide only. Thus, this rather unusual reaction of longifolene with PBA, prompted us to investigate the reaction in some detail. The problem was divided in three phases, viz: a reinvestigation of the uncontrolled PBA oxidation of longifolene, controlled peracid oxidation of the hydrocarbon in order to isolate the primary reaction product, and a study of the further action of PBA on this intermediate.

### *Uncontrolled perbenzoic acid oxidation*

Oxidation of longifolene by PBA in chloroform, carried out in the usual manner, gave results which only qualitatively agreed with those of the previous workers.[1] The $C_{14}$-ketone could only be isolated in a much reduced yield (25–30%), and no evidence for the formation of the anhydride (III) could be gathered (*vide* Experimental). The formation of some 2–4% of longidione (VI) could be established spectrophotometrically.

---

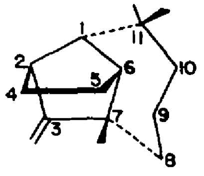
* Part XVIII: *Tetrahedron* **9**, 1 (1960).

† In part abstracted from the Ph.D thesis (Madras University, 1957) of U. R. Nayak.

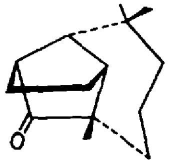
‡ Present address: Division of Organic Chemistry, National Chemical Laboratory, Poona 8, India.

[1] P. Naffa and G. Ourisson, *Bull. Soc. Chim. Fr.* 1115 (1954).

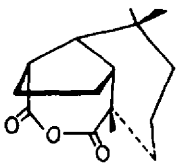
[2] H. Meerwein, *J. Prakt. Chem.* **113**, 9 (1926).



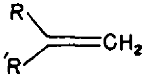
I



II

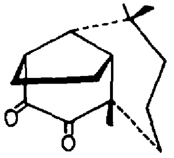


III

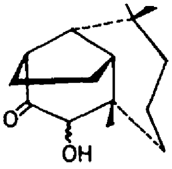


IV

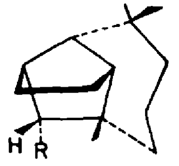
V



VI



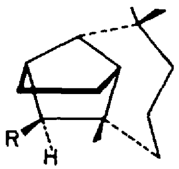
VII



VIII : R = OH

IX : R = COOH

X : R = CHO



XI : R = OH

XII : R = COOH

XIII : R = CHO

From a consideration of possible mechanistic path (*vide* Discussion) leading to the longidione, it was suspected that the α-ketol (VII) may be one of the products of the reaction. This could be established experimentally by oxidation of the crude reaction product with cupric acetate in acetic acid, when the longidione content (based both on spectrophotometric estimation and actual isolation) increased to ~20%. In a few perbenzoic acid oxidations, carried out in the early stages of this work, the dione content (spectrophotometric estimation) of the crude oxidation product after cupric acetate oxidation, was found to be as high as 45–50%; that this reflected a higher initial concentration of the α-ketol in the original peracid oxidation product is borne out by a comparison of the I.R. spectrum of an old sample with those of the products from more recent experiments, which showed considerable reduction in the intensity of the 3521 and 1695 $cm^{-1}$ bands (assignable to the α-ketol), and an increase in that of the 1725 cm$^{-1}$ band (partly resolved; assignable to longicamphenilone[3]). In an attempt to locate this discrepancy, the PBA oxidation of longifolene has been carried out under varied conditions and the dione content measured before and after cupric acetate oxidation. As is clear from these data (Table 1) the source of discrepancy could not be traced[4]; however, it is interesting to note that while a small percentage of pyridine cuts down the α-ketol formation considerably, addition of ethanol to the reaction mixture results in a more or less complete inhibition of the formation of the α-ketol.

TABLE 1. YIELD OF α-KETOL IN THE VARIOUS PERBENZOIC ACID OXIDATIONS OF LONGIFOLENE USING TWO MOLES OF PERACID IN CHLOROFORM

| No. | Experimental variation | % Dione* Before | After |
|---|---|---|---|
| | | Treatment with | Cu(OAc)$_2$ |
| 1 | Dry PBA solution | 3·3 | 19·4 |
| 2 | Wet PBA solution | 1·1 | 15·7 |
| 3 | Addition of pyridine | 1·0 | 9·1 |
| 4 | Addition of gaseous HCl | 5·2 | 21·2 |
| 5 | Addition of EtOH (2%) and conc. HCl (0·2%) | 2·8 | 22·0 |
| 6 | Addition of EtOH (10%) | 0 | 0 |

* The percentage of dione after cupric acetate oxidation, should represent the amount of α-ketol initially formed.

TABLE 2. PRODUCT ANALYSIS OF THE CUPRIC ACETATE-TREATED OXIDATION MIXTURE FROM LONGIFOLENE AND TWO MOLES OF PERBENZOIC ACID IN CHLOROFORM

| No. | Experimental variation | % yield (based on longifolene) Hydrocarbon | $C_{14}$-ketone | Dione | $C_{14}$-alcohols | Longifolic acids |
|---|---|---|---|---|---|---|
| 1 | Dry PBA solution | 14 | 31 | 19 | 10 | 9 |
| 2 | Wet PBA solution | 13 | 33 | 16 | 8 | 5 |
| 3 | Addition of pyridine | 22 | 27 | 7 | ? | 13 |
| 4 | Addition of EtOH (2%) conc. HCl (0·2%) | 15 | 27 | 25 | ? | ? |
| 5 | Addition of EtOH (10%) | 14 | 51 | 0 | ? | 9 |

In each of the experiments listed in Table 1, the product after cupric acetate oxidation was resolved by chromatography over alumina in order to establish its composition. These results have been summarized in Table 2. The amount of longidione thus, actually isolated in each case, agreed closely with that expected on the basis of spectrophotometric analysis. The major product in each case is shown to be the nor-ketone, longicamphenilone; it is significant that whereas the addition of some 10% ethanol to the reaction medium completely inhibits the formation of longidione, it increases the yield of longicamphenilone considerably. The hydrocarbon fraction isolated, in all cases except from experiments (3) and (5), displayed similar

---

[3] Pure longicamphenilone has $\nu^{C=O}$ 1740 cm$^{-1}$

[4] cf. footnote 7.

I.R. absorption and appeared to consist essentially of longifolene and longicyclene.[5] Other products formed included $C_{14}$-alcohols (VIII; XI) and longifolic acids[6] (IX, XII).

### *Controlled peracid oxidation*

In order to gain some definite information about the primary oxidation product, it was planned to arrest the peracid reaction at the stage of one mole consumption of the peracid. For this purpose, the rate of this reaction with three different peracid reagents was measured and the results are shown graphically in Fig. 1 and significant points have been summarized in Table 3. It is apparent from these data that percamphoric and possibly perbenzoic acid in benzene–toluene could be utilized to isolate the primary oxidation product. In fact, a preparative scale oxidation of

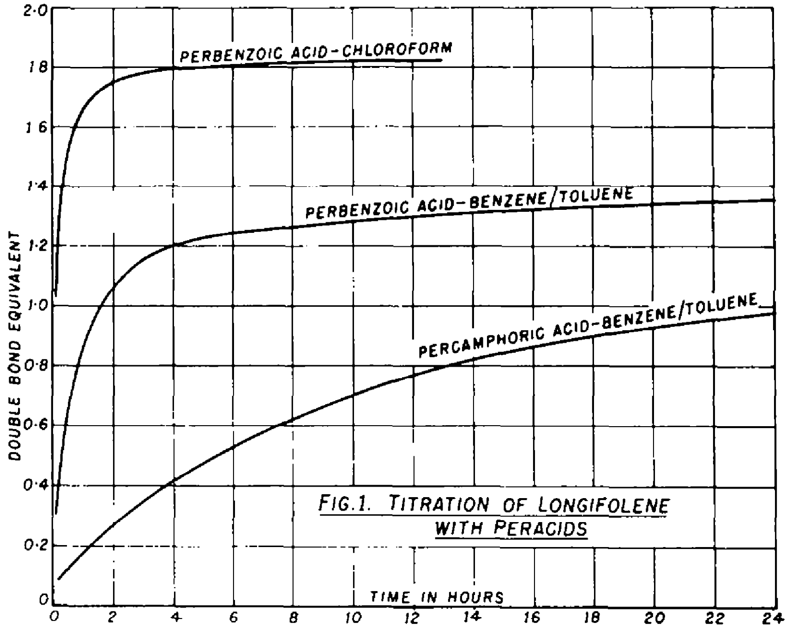


Fig. 1. Titration of longifolene with peracids at 0°.

Table 3. Peracid consumption of longifolene (at 0°)

| No. | Peracid | Solvent | Double bond equivalent after | | | | Time taken for one mole consumption |
|---|---|---|---|---|---|---|---|
| | | | 5 min | 2 hr and 20 hr | | "end"* | |
| 1 | Perbenzoic acid | Chloroform | 1·03 | 1·75 | 1·85 | 1·90 | <5 min |
| 2 | Perbenzoic acid | Benzene–toluene | 0·31 | 1·05 | 1·33 | 1·42 | 100 min |
| 3 | Percamphoric acid | Benzene–toluene | 0·08 | 0·24 | 0·93 | 1·17 | 32 hr |

* This indicates the value at which peracid absorption almost ceased, the time taken being 39, 116 and 68 hr respectively.

---

[5] U. R. Nayak and Sukh Dev, *Tetrahedron Letters* 243 (1963).

[6] For a clarification of the chemistry of longifolic acids see: U. R. Nayak and Sukh Dev, *Tetrahedron* **19**, XXI (1963).

longifolene with one mole of either perbenzoic acid in benzene–toluene or percamphoric acid in the same solvent, yielded essentially identical products. The reaction mixture has been shown to consist of unchanged hydrocarbon (~10–15%), longicamphenilone (~5–10%) longifolaldehydes (~5%) and a solid $C_{15}H_{24}O$ compound (70–80%) which, as will be shown in the sequel, was the expected longifolene-α-epoxide (XIV).[7]

I.R. spectrum (Fig. 2) of the solid $C_{15}H_{24}O$ compound, which displayed the bands (1290, 1270, 930 and 858 $cm^{-1}$) characteristic of an α-epoxide,[8] is in good accord with its formulation as an oxirane. Its PMR[9] spectrum displayed the two oxirane ring protons[10] as a pair of two doublets centered at 158 and 168 cps (Jab: 5 cps). Since longifolene system is sterically less accessible[11] from the side of the fused 7-membered ring, the attack by the peracid should yield the endo-isomer[12] (XIV). Longifolene epoxide is thermally quite stable and can be distilled (135°/7 mm) without any significant isomerization. However, it is very sensitive to base or acid-catalysed rearrangement to the aldehyde; all attempts to isolate the epoxide from the reaction

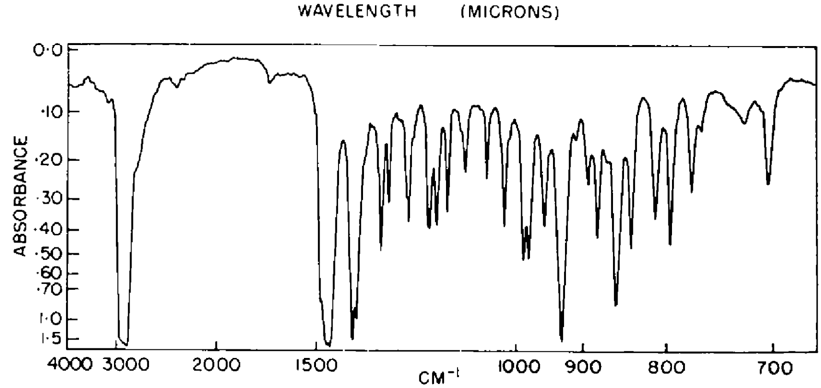


Fig. 2. Infrared spectrum of longifolene epoxide.

---

[7] It must be pointed out that in these peracid oxidations also, like the uncontrolled peracid oxidation discussed earlier, our experiments carried out at that time and in a manner exactly as described now, gave results which we have failed to reproduce now. The earlier experiments (five in all, carried out at different intervals during six months) yielded, besides some (15–20%) hydrocarbon fraction, a 65–70% yield of a liquid $C_{15}H_{24}O$ compound, shown to be chiefly longifolaldehyde (X) (Semicarbazone, m.p. 218° decomp; crude product of m.p. 195–200° obtainable in a yield of ~95%; longifolene epoxide does not react with semicarbazide under these conditions). A comparison of the IR spectrum of this material with that of pure longifolene epoxide, now available, showed complete absence of the 930 $cm^{-1}$ band so very characteristic of the longifolene epoxide (Fig. 2).

Longifolene used in the earlier as well as in the later experiments was of the same purity, though isolated from two different batches of "secondary residue" received at different times.

[8] W. A. Patterson, *Analyt. Chem.* **26**, 823 (1954).

[9] Kindly determined in Prof. G. Ourisson's Laboratory (Strassbourg) on a Varian Associates A-60 spectrometer for a 10% solution in $CCl_4$ with tetramethylsilane as the internal standard. The values are in cps from tetramethylsilane.

[10] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 55, Pergamon Press, London (1959).

[11] G. Ourisson, *Bull. Soc. Chim. Fr.* 895 (1955).

[12] The term endo has the same steric significance as is obtained in bicyclo [2,2,1] heptane; for this purpose, following Ourisson,[11] only this bicyclic part in longifolene is considered.

mixture by chromatography over washed alumina, magnesium silicate or silicic acid resulted in extensive rearrangement.

### *Action of perbenzoic acid on longifolene epoxide and longifolaldehydes*

Action of a chloroform solution of PBA on longifolene epoxide and longifolaldehydes was, next, investigated. The epoxide consumed one mole of the peracid at ~0° during 50 hours to give a material, qualitatively agreeing with the product of uncontrolled PBA oxidation. This was further treated with cupric acetate and the products separated by column chromatography. The results have been summarized in Table 4.

TABLE 4. PRODUCTS OF PBA OXIDATION OF LONGIFOLENE EPOXIDE AND LONGIFOLALDEHYDES

(After further treatment with cupric acetate)

| Product | Percent yield | |
|---|---|---|
| | From epoxide | From aldehyde |
| $C_{14}$-Ketone | 25 | 9 |
| Dione | 30 | 0 |
| $C_{14}$-Alcohols | 6 | 41[a] |
| Longifolic acids | 23[b] | 14[c] |

[a] Exo/endo ratio: 37/63

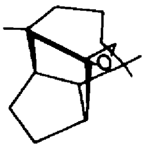
[b] Exo/endo ratio: 57/43

[c] Exo/endo ratio: 47/53

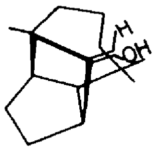
Under the same conditions, longifolaldehydes mixture was less reactive and even after a period of 93 hours, traces of PBA remained unconsumed, but the reaction mixture was worked up and further treated with cupric acetate as described above. The results have been collected in Table 4.

## DISCUSSION

It is clear from the data presented so far that the abnormal consumption of PBA by longifolene in chloroform is due to the further reaction of the epoxide. The susceptibility of longifolene epoxide to further peracid attack may have its origin in the steric compression at $C_3$ in the epoxide, which is relieved by its isomerization to the enol in which the bulkier oxygen atom is no longer attached to $C_3$. This would encourage rapid isomerization to the aldehydes (X, XIII) through the enol (XV), due to a decreased energy barrier between the epoxide and the enol. Thus the products of such an oxidation, should be those originating in the attacks of the peracid on the



XIV



XV

enol and the aldehyde, each giving rise to a set of products and the overall yield of each depending upon the moles of aldehyde and enol consumed as such for further oxidation. As discussed later, aldehydes lead to $C_{14}$-alcohols and longifolic acids, while the enol gives rise to the $C_{14}$-ketone and the ring-expanded product, the relative yields of the products depending in a complex manner on the rates ($k$, $k_1$, $k_2$, $k_3$, $k_4$) of different reactions. In a qualitative way, one could say that longifolene epoxide might yield an excess of products resulting from the enol (cf. Table 4) and from a comparison of the results of uncontrolled PBA oxidation (vide Table 2) of longifolene with those shown in Table 4, one could conclude that as longifolene is consumed, some concentration of aldehydes, at the expense of the epoxide, is built up.

$$\begin{tikzcd}
\text{Epoxide} \arrow[r, "k"] & \text{Enol} \arrow[r, shift left, "k_1"] \arrow[d, "k_3"] & \text{Aldehydes (partly equilibrated)} \arrow[l, shift left, "k_2"] \arrow[d, "k_4"] \\
 & \begin{array}{c}\text{C}_{14}\text{-ketone}\\ \alpha\text{-Ketol}\\ \text{Longidione}\end{array} & \begin{array}{c}\text{Acids}\\ \text{C}_{14}\text{-alcohols}\end{array}
\end{tikzcd}$$

The formation of longifolic acids from the aldehydes is in accord with the oxidation[13] of aldehydes to acids by peracids, while the $C_{14}$-alcohols would originate from the formates resulting from the peracid attack on the aldehydes in a manner well established for the interaction of ketones with peracids.[13]

The formation of the $C_{14}$-ketone and longidione deserves some comment. Though the carbon-carbon fission of an indole to a dicarbonyl derivative[14] by peracids, is a fairly general reaction in heterocyclic chemistry, this cleavage of a carbon-carbon linkage in carbocyclic compounds (apart from the perester rearrangement mentioned above) is quite uncommon. Apparently, this fission was first noticed with longifolene, and since then, at least one more case has been recorded.[15] The unlikely possibility that the $C_{14}$-ketone might have originated from the oxidation of the $C_{14}$-alcohols, was ruled out, when in an experiment it was shown that $C_{14}$-alcohols could be recovered unchanged from a treatment with PBA. It appears attractive to postulate that the cleavage involved in the $C_{14}$-ketone formation may be operative as shown in Fig. 3. As indicated there, the same intermediate (XVI) would, by a skeletal 1,2-shift, give rise to the $\alpha$-ketol (VII). As a matter of fact, this mechanistic reasoning had led us to look for the $\alpha$-ketol in the uncontrolled peracid oxidation. Further oxidation of the $\alpha$-ketol to the longidione could have occurred during work up, as the former is very susceptible to air oxidation, or alternately, oxidation of the ketol to the dione might have been effected by PBA, a reaction which can be realised in practice.

Based on these mechanistic considerations, one should expect the hydroxy aldehyde (XVII) as one of the important reaction products in this uncontrolled peracid oxidation. In fact, 1-phenyl-1(o-diphenyl) ethylene (XVIII) is known[16,17] to yield the

---

[13] C. H. Hassal in *Organic Reactions* **9**, pp. 73–106, John Wiley, New York (1957).

[14] B. Witkop and H. Fiedler, *Liebig's Ann.* **558**, 91 (1947).

[15] G. Chiurdoglu and P. Tullen, *Bull. Soc. Chim. Belg.* **66**, 169 (1957).

[16] C. K. Bradsher, *J. Amer. Chem. Soc.* **65**, 45 (1944).

[17] F. L. Weisenborn and D. Taub, *J. Amer. Chem. Soc.* **74**, 1329 (1952).

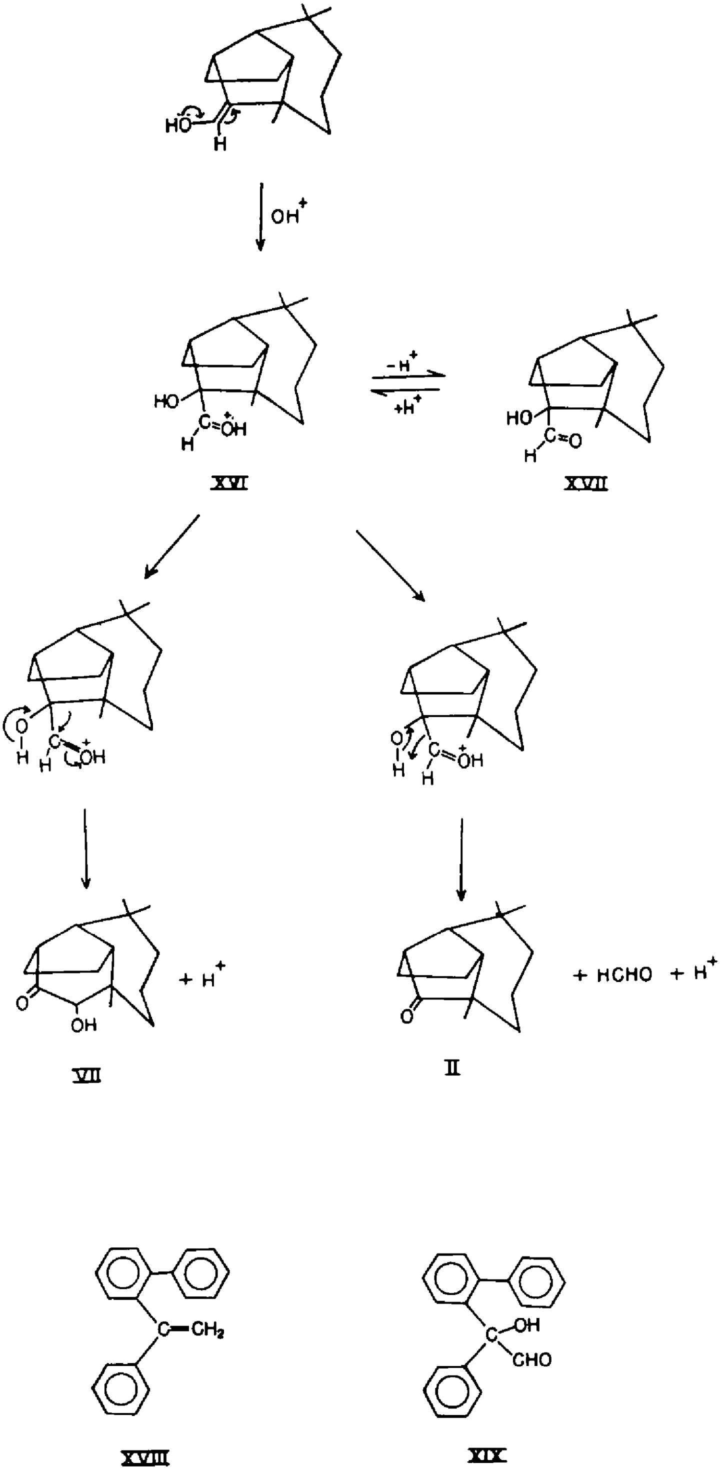

HO
H
OH⁺
HO
C=OH
H
-H⁺
+H⁺
HO
C=O
H
XVI
XVII
O
H
H
C
OH
O
H
C=OH
H
O
OH
+ H⁺
O
+ HCHO + H⁺
VII
II
C=CH₂
C
OH
CHO
XVIII
XIX

FIG. 3

hydroxyaldehyde (XIX) as the major product in peracid oxidations. However, in the case of longifolene, no evidence (*vide* Experimental) for the formation of the hydroxy aldehyde (XVII) could be gathered.

## EXPERIMENTAL

All m.ps. and b.ps. are uncorrected. Solvent extracts were finally washed with brine and dried ($Na_2SO_4$). Pet. ether refers to the fraction of b.p. 40–60°. Neutral alumina ($HNO_3$ method), Brockmann grade II, was employed throughout.

Specific rotations were measured in ethanol. The I.R. spectra were taken on a Perkin-Elmer Infracord model 137-B spectrophotometer either as smears (liquids) or in Nujol (solids), unless specified otherwise. U.V. measurements were made on a Beckman DU spectrophotometer employing solutions in 95% ethanol.

*Longifolene.* Longifolene was isolated, as described,[18] from the 'Secondary Residue' obtained from the essential oil of *Pinus longifolia.* The material used for the present investigations had $\alpha_D$ +39°, $n_D^{25}$ 1·5030 and was over 90% pure by gas liquid chromatography (GLC).

### *Uncontrolled perbenzoic acid oxidation*

*Peracid oxidation.* Longifolene (14·9 g, 0·073 mole) in purified chloroform[19] (65 ml) and a thoroughly dried ($Na_2SO_4$) solution of PBA[20] in chloroform (0·8855 N, 328 ml, i.e. containing 0·146 mole PBA) were separately cooled (−13°) in a freezing mixture. The peracid solution was, then, added slowly (15 min) from a dropping funnel to the hydrocarbon solution under stirring and cooling, such that the reaction temp did not go beyond −5°. The reaction mixture was then set aside at ~0° for 48 hr. At the end of this period, 1·93 mole equiv. of PBA had been consumed, when the almost colourless reaction mixture was worked up by extraction with 5% $NaHCO_3$ aq. (200 ml × 4), washing with brine and drying. Removal of solvent gave a pale yellow syrup (17·5 g). The aq. alkaline washings gave only benzoic acid on work up.

The above experiment was repeated (on half the scale) by adding the chilled longifolene solution to the peracid solution, i.e. the inverse addition. The product was essentially the same.

A part (7 g) of the product (in this and the other experiments the product refers to that obtained by the "normal" procedure) was fractionated, the fraction (1·7 g; b.p. 123–125°/3 mm) being collected separately. This was shown by its I.R. spectrum to be essentially longicamphenilone.

Another part (7 g) was dissolved in chloroform (70 ml) and digested with a 10% $Na_2CO_3$ aq. (70 ml) by refluxing on a water-bath for 4 hr. The aq. alkaline part, on acidification with HCl gave a gum, which was extracted out with ether. Removal of ether furnished an impure acid (~350 mg), m.p. 115–118°, which was found to consist of some benzoic acid (separable by sublimation) and longifolic acids. Since no α-longiforic acid could be isolated in this alkali digestion, it proved the absence of the anhydride in the oxidation product. α-Longiforic anhydride (m.p. 94–95°) can be quantitatively extracted (as the acid) from its chloroform solution by the above method.

Absence of hydroxyaldehyde (XVII) in the oxidation product was proved from the non-formation of any formic acid (in fact, any volatile, water soluble acid) when the product (2 g in methanol) was oxidized with sodium metaperiodate (1·5 g in 7·5 ml water) at room temp (25–30°) for 3 days.

The total oxidation product was found to turn more yellow on keeping, especially if exposed to air. Immediately after work up, the longidione content was estimated spectrophotometrically (see below) and was found to be 2–4%.

*Further oxidation with cupric acetate.* The peracid oxidation product (2·1 g), powdered cupric acetate (6·0 g) and 70% acetic acid (50 ml) were mixed and refluxed for 3 hr. The reaction mixture was diluted with water (200 ml), extracted with pet. ether (25 ml × 4), washed with 10% HCl aq. (25 ml × 1) then with brine and dried. The solvent was flashed off to yield a bright yellow oil (1·7 g; 20% dione content as estimated spectrophotometrically). The material (1·47 g) was diluted with pet. ether (20 ml) and chromatographed over alumina (45 g; 16 × 2·5 cm).

First fraction (pet. ether, 100 ml; 0·22 g) was shown to be a mixture of longifolene and longicyclene by a combination of GLC and I.R. spectroscopy. The next fraction (pet. ether/50% benzene, 100 ml

---

[18] U. R. Nayak and Sukh Dev, *Tetrahedron* **8**, 42 (1960).

[19] I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Poly. Sci.* 199 (1957).

[20] G. Braun, *Org. Syn. Coll. Vol. I*, p. 431. John Wiley, New York (1941).

and, benzene, 100 ml; 0·485 g) crystallized out; this was recrystallized from aq. ethanol at 0° to yield white flakes (0·35 g), m.p. 50–51° undepressed by an authentic sample (m.p. 50–51°) of longicamphenilone. The third fraction which was deep yellow in colour was eluted with benzene (100 ml × 6; 0·350 g) and crystallized from aq. ethanol at 0° in yellow needles, m.p. 93–94°; this was identified as longidione by its I.R. ($\nu^{C=O}$ 1705, 1725 $cm^{-1}$) and mixed m.p.

Next, benzene–5% methanol (100 ml) eluted (0.154 g) a product which after two recrystallizations from aq. ethanol yielded colourless needles m.p. 84–94° (Found: C, 80·29; H, 11·40. $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%). This material (20 mg) in acetone (1 ml) was oxidized with chromic acid reagent, prepared as described by Curtis *et al.*,[21] at room temp (26°) for 2·5 hr, when the resulting orange brown solution was diluted with water (50 ml) and extracted with hexane (15 ml × 4). Removal of solvent and crystallization of the product from aq. ethanol yielded soft white flakes identified as longicamphenilone by m.p. (50–51°) and mixed m.p. with an authentic specimen. The identification of this fraction as a mixture of epimeric $C_{14}$-alcohols was completed by comparing its I.R. spectrum with that of an epimeric longicamphenilols mixture (m.p. 84–94°, mixed m.p. same) obtainable[1] by the sodium-n-propanol reduction of longicamphenilone.

Finally, the alumina column was washed with 10% $Na_2CO_3$ aq. (200 ml). The alkaline washings on acidification yielded (0·158 g) a product which crystallized from aq. ethanol as colourless needles m.p. 136–138°. This proved to be 1:1 mixture of longifolic and isolongifolic acids.[6]

*Variations in peracid oxidation procedure.* The experimental data collected in Tables 1 and 2 was obtained on PBA oxidations carried out on 3·0 g of longifolene (with proportionate reduction in PBA in $CHCl_3$) with the modifications outlined below; the product in each case was further oxidized with cupric acetate as already described. (i) The moist peracid solutions obtained after preparation was used as such without drying ($Na_2SO_4$). (ii) Dry pyridine (1 ml) was mixed with the hydrocarbon before treatment with PBA. (iii) Absolute ethanol (1 ml) and conc. HCl aq. (0·1 ml) were added to the PBA solution before use. (iv) Anhydrous ethanol (5 ml) was mixed with the PBA solution before reaction. (v) Gaseous HCl saturated (at 0°) chloroform (1 ml; 0·073N) was mixed with the PBA solution prior to oxidation.

*Spectrophotometric estimation of longidione.* Analytically pure longidione (m.p. 93–94°) was dissolved in 95% ethanol and the $\lambda_{max}$ and optical density determined for some concentrations (0·1 to 0·3%). This way $\lambda_{max}$ and $\varepsilon_{max}$ were established as 440 m$\mu$ and 49 respectively. The product (~100 mg) of cupric acetate oxidation was dissolved in 95% ethanol (10 ml) and the optical density determined at 440 m$\mu$; a standard of known dione content was run side by side. From these data the dione concentration in the unknown was calculated as usual.

### *Controlled peracid oxidations*

*Kinetic runs; peracids.* Perbenzoic acid in purified chloroform (1·031N) was prepared as described earlier. Perbenzoic acid in thiophene-free benzene was obtained, likewise, by substituting this solvent for chloroform in the PBA preparation; the solution was 0·9168N in PBA. Percamphoric acid in thiophene-free benzene (0·3751N) was prepared according to the method of Milas and McAlevy[22] except that when the peracid was regenerated from its sodium salt solution, benzene was used for its extraction.

*Procedure.* An exact quantity (0·5 1·0 g) of pure longifolene was dissolved in 10 ml $CHCl_3$ or toluene and cooled to 0°. A blank (10 ml) of the solvent was, likewise, cooled to the same temp. A known volume (100% excess) of the peracid solution (at 5°) was pipetted into the reaction mixture and the blank. The reaction mixture was maintained at 0° for the entire reaction period. Aliquot portions (1 ml) were withdrawn at suitable time intervals and at once added to a solution of KI (2 g in 50 ml water) containing acetic acid (5 ml) and $CHCl_3$ (5 ml). The liberated iodine was titrated against standard $Na_2S_2O_3$ solution in the usual manner, 3 experiments being carried out for each reagent.

*Longifolene epoxide.* Longifolene (36·9 g) in pure benzene (40 ml) and a benzene solution of PBA (330 ml of 1·0967N), containing an equimolar amount (25·0 g) of the peracid, were separately cooled in an ice bath, and the latter rapidly added to the former with cooling. After 1·5 hr at 0°, all the peracid had been consumed. The reaction mixture was extracted with 6% $Na_2CO_3$ aq. (100 ml × 5), washed and dried. The solvent was flashed off from a water-bath (~80°), under suction, to yield a

---

[21] R. G. Curtis, I. Heilbron, E. R. H. Jones and G. F. Woods, *J. Chem. Soc.* 457 (1953).

[22] N. A. Milas and A. McAlevy, *J. Amer. Chem. Soc.* **55**, 349 (1933).

colourless oil (39·6 g). In the I.R. this material displayed a strong band at 930 cm$^{-1}$ (longifolene epoxide) and weak bands assignable to longicamphenilone and longifolaldehydes. The composition of crude reaction product was approximated as follows: The unreacted hydrocarbon was estimated by passing an n-hexane solution of the product (1 g) through a column of silica gel (12·5 cm × 2·2 cm; 30 g) and weighing the material eluted with n-hexane. Longicamphenilone and the aldehydes were approximated by inspection of the I.R. spectra. A check for these values was made by making a synthetic mixture of this composition (*vide* Theoretical part) and comparing its I.R. spectrum with that of the reaction product.

It has been found difficult to isolate pure longifolene epoxide in good amounts due to its non-amenability to column chromatography and its solubility characteristics. Reasonable quantities were obtained in the following manner. The product (30 g) was diluted with pet. ether (5 ml) and chilled in a freezing mixture (−10°) for several hr. The separated crystalline material was freed, as much as possible, of the mother liquor by inverse filtration in the cold. The residual solid was twice crystallized from pet. ether in the cold, as before. Finally the product was recrystallized (−10°) from the same solvent and collected on a filter, to yield colourless prisms (3–4 g), m.p. 42–43°, $[\alpha]_D$ +4·5° (*c*, 4·7%). (Found: C, 82·15; H, 10·79. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%).

*Longifolaldehyde.* It has already been stated that earlier experiments, carried out exactly as described above, yielded a product practically devoid of the longifolene epoxide, as revealed by its I.R. spectrum (before distillation). The material on fractionation (6″-Vigreux column) gave a fraction (65–70%) b.p. 114–115°/1·5 mm, $n_D^{23}$ 1·5090, $d_4^{23}$ 1·014, $[\alpha]_D$ −32·6° (*c*, 5%), I.R. spectrum: very similar to that of the undistilled material, aldehyde bands at 2680, 1712 cm$^{-1}$. (Found: C, 81·58; H, 10·8. $C_{15}H_{24}O$ requires: C, 81·83; H, 10·91%).

When the above fraction (1 g) was treated with semicarbazide hydrochloride (1 g) and sodium acetate (1 g) in aq. ethanol at room temp the *semicarbazone* soon started separating and was collected (1·25 g, m.p. 195–200°) after several hr. Recrystallization (0·3 g) from aq. ethanol containing a few drops of pyridine gave shining white flakes, m.p. 217–218° (Found: N, 15·6. $C_{17}H_{27}ON_3$ requires: N, 15·2%). A mixed m.p. with the semicarbazone of isolongifolaldehyde (m.p. 217–218°)[23] was 190–200°.

The 2,4-*dinitrophenylhydrazone* was prepared from the pure semicarbazone in the usual manner and was finally obtained as orange crystals, m.p. 172–173° (Found: N, 14·4; $C_{21}H_{28}O_4N_4$ requires: N, 14·0%).

The product on exposure to air, slowly deposited a solid, which was crystallized from aq. ethanol to yield colourless needles, m.p. 137–139°; this proved to be a 1:1 mixture of longifolic and isolongifolic acids.[6]

### *Further reactions with peracid*

*Action of PBA on longifolene epoxide.* Crystalline longifolene epoxide (1·1 g, 0.005 mole) was treated at 0° with a cold solution (10 ml) of PBA in chloroform containing an equimolar amount (0·69 g) of the peracid. After 50 hr at 0°, the reaction mixture, which was by now free of the peracid, was extracted with $Na_2CO_3$ aq. (2 g in 30 ml water), washed and dried. The chloroform solution, freed of solvent, yielded 1·14 g of a yellowish liquid (I.R. spectrum similar to that of the product of uncontrolled PBA oxidation of longifolene). The product was refluxed with cupric acetate (3·0 g) in 70% acetic acid (25 ml) for 3 hr and worked up as described earlier. The product (0·93 g) was chromatographed over alumina (30 g, 11 × 2·2 cm):

| | | |
|---|---|---|
| Frac. 1: | Pet. ether (100 ml × 2) | 71 mg ? |
| Frac. 2: | Pet. ether/50% benzene (100 ml) | 242 mg of II |
| Frac. 3: | Benzene (100 ml × 3) | 331 mg of VI |
| Frac. 4: | Benzene–5% MeOH (100 ml) | 63 mg of VIII + XI |
| Frac. 5: | $Na_2CO_3$ aq., 10% (50 ml) | 261 mg of IX + XII |

The various compounds were identified as described earlier. The isomer ratio for fraction 4 was established by its GLC, while that of fraction 5 by the GLC of its methyl ester.[6]

*Action of PBA on longifolaldehydes.* Crystalline longifolene epoxide (1·5 g) in pet. ether (20 ml) was passed through a column (7 × 3·5 cm) of silica gel (−100, +200 mesh, washed and activated at

---

[23] J. L. Simonsen, *J. Chem. Soc.* **123**, 2642 (1923). An authentic sample was prepared from crude isolongifolaldehyde obtained by the pyridine-chromic acid oxidation of isolongifolol.

120°/12 hr) and the column immediately washed further with benzene (500 ml). Solvent removal and distillation of the residue gave[6] a mixture of aldehydes (X, XIII), 1·27 g, b.p. 113–115°/1·5 mm.

The aldehyde mixture (1·1 g, 0·005 mole) was treated with PBA exactly as described above for the epoxide; the reaction, which was conducted side by side with that of the epoxide, was considerably slower (93 hr). The product (1 g) was further treated with cupric acetate and then chromatographed over alumina, exactly as detailed above, except that for fraction 3 a total of 100 ml × 5 of benzene was collected.

*Action of PBA on α-ketol.* The crystalline α-ketol (colourless needles, m.p. 105–107°; 0·35 g), obtainable[23] by the zinc-acetic acid reduction of longidione, was dissolved in $CHCl_3$ (5 ml) and treated at 0° with 5 ml $CHCl_3$ solution of PBA (1·174N). The reaction which was conducted under $N_2$ was allowed to proceed at 0° for 48 hr. The yellow reaction mixture on work up yielded crude longidione (m.p. 78–81°), which after two crystallizations from pet. ether gave pure dione, m.p. and mixed m.p. with an authentic sample, 93–94°.

*Gas liquid chromatography.* Gas liquid chromatography was carried out on a Perkin-Elmer Vapour Fractometer model 154-C on 20% diethylene glycol succinate on celite (60–100 mesh) using hydrogen as the carrier gas.