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STUDIES IN SESQUITERPENES—XLII

ISOLONGIFOLENE (PART 3): SYSTEMATIC DEGRADATION*

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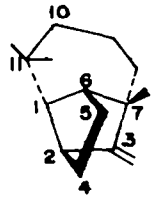
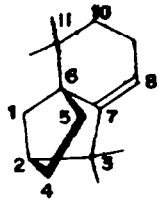
Abstract—Isolongifolene has been systematically degraded to a bisnor-keto acid, the spectral characteristics of which are in full accord with the structure (II) assigned earlier to isolongifolene.

IN AN earlier publication,[1] structure II has been deduced for isolongifolene, an acid-catalysed rearrangement product of longifolene (I). In order to put this structure on an unequivocal footing it was planned to investigate products of its catalytic



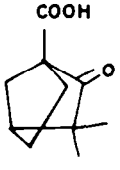
I



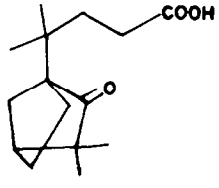
II

dehydrogenation as well as to carry out its systematic degradation to a known structure. The results of dehydrogenation, fully supporting the formulation II, have been described[2] and now, we report on its stepwise degradation.

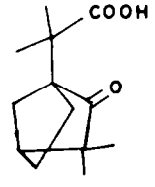
The degradation of isolongifolene to the known[3] camphenonic acid (III) of well-proven structure, through the already described[1] C_{15}-keto acid (IV) appeared to be the obvious choice. The acid IV has now been transformed into the bis-nor-keto acid (V), further degradation of which to III, by several routes, however proved abortive. This situation has, however, been by-passed by an unequivocal synthesis of the bis-nor-keto acid (V) reported in the succeeding communication.



III



IV



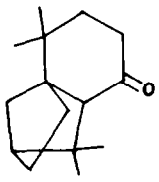
V

* Communication No. 1329, National Chemical Laboratory, Poona.

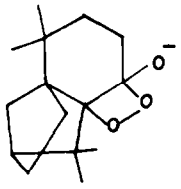
Preparation of C_{15}*-keto acid* (IV)

The previously reported[1] degradation of isolongifolene to IV, though straightforward, involves a sequence of five steps (epoxidation, BF_3-rearrangement, Baeyer-Villiger oxidation, hydrolysis and CrO oxidation) and it was thought worthwhile to see if a simpler route to IV could be developed. Two methods could be successfully worked out.*

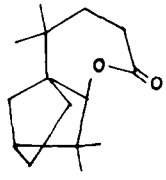
In view of the known[4] oxygenation of certain cyclic ketones to the corresponding ring-cleaved keto-acids, in presence of a strong base, the base-catalysed oxygenation of the C_{15}-ketone (VI) has been investigated. This ketone on reaction with oxygen in presence of t-BuOK at room temperature and pressure, readily consumed one



VI



VII



VIII

mole of oxygen to give the desired keto-acid (IV) in a yield of 60–65%. The mechanism of such reactions, which is expected to proceed through an intermediate such as VII has been discussed.[5]

It was found that unlike the reaction[1] of a benzene solution of perbenzoic acid (PBA) with isolongifolene, its reaction with $CHCl_3$ solution of PBA[6] takes a different course. Reaction of isolongifolene with excess of PBA led to the consumption of almost 2 moles of the peracid to give a product, which was found to contain over 60% of lactone VIII; interruption of the reaction at one mole consumption led, as expected, to the isolation of the saturated ketone (VI). Thus, this unexpected short-cut to the preparation of VIII, provided an easy access to the desired keto acid (IV).

Degradation to the bis-nor keto acid (V)

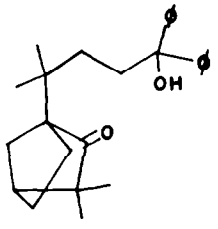
Action of a slight excess of PhMgBr on the methyl ester of the above keto acid furnished two isomeric, $C_{27}H_{34}O_2$, compounds in 70 and 20% yields. The major product must be the expected diphenyl carbinol (IX) in view of its IR spectrum: OH 3472, 1167 cm^{-1}; C=O 1724 cm^{-1}. On treatment with acetic anhydride in acetic acid, it readily underwent dehydration, in over 90% yield, to the required diphenyl ethylene (X): λ_{max} 252 mμ,† ε 16070; IR: C=O 1730 cm^{-1}; PMR: —C=C<u>H</u>—CH_2—, 1H triplet centred at 368 c/s, J = 8 c/s.

The less abundant product of the above reaction shows no C=O absorption, but only OH absorption (*vide infra*) in its IR spectrum and hence is formulated as XI, which is mechanistically sound; the stereochemistry is based on the reasonable assumption that the C=O at C_7 will be attacked from the side opposite to the bridge. In accordance with this formulation, the compound on treatment with Ac_2O in

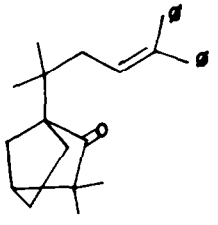
* Ozonolysis of isolongifolene proved to be abnormal and was not investigated further. Isolongifolene was found to be resistant to $KMnO_4$ oxidation in acetone soln; on the other hand use of $KMnO_4$ in AcOH resulted in a complex product.

† A trisubstituted 1,1-diphenyl ethylene usually displays λ_{max} 250 mμ[7].

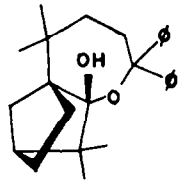
AcOH yielded the same diphenyl ethylene (X). The PMR spectrum of XI, which is in complete accord with this structure, has two special points of interest. Firstly, one of its quaternary methyls is highly shielded (3H singlets at 62, 53, 48 and 10 c/s) and the preferred conformation of the 7-membered ring should be such as to bring one of the quaternary Me's in the shielding cone[8] of a phenyl ring. Secondly, OH signal (sharp 1H singlet at 306 c/s; repeated shakings with D_2O were required to effect D exchange) was found to be concentration independent (in CCl_4), and hence must be internally H-bonded, evidently with the π-electron of the phenyl ring; several cases of π-HO bonding have been recorded.[9] As expected on this basis, IR spectrum (CCl_4) of XI shows two OH bands (main band at 3484 cm^{-1} and a minor one at 3590 cm^{-1}; $\Delta\nu$(OH) = 106 cm^{-1}), relative intensities of which are concentration (0·1, 0·05 and 0·01 molar) independent. An examination of models shows that due to



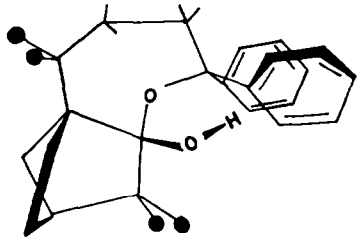
IX

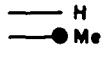


X



XI





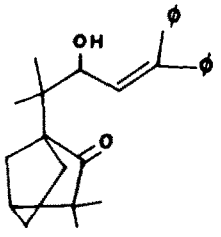
XII

the flexibility of the 7-membered ring, more than one conformation of XI, answering the above requirements is possible and, the most likely one is shown in XII.

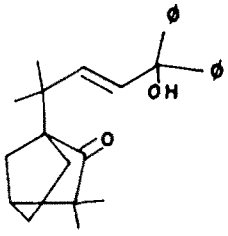
Once the nature of the products formed in the Grignard reaction had been established, in subsequent experiments, the total product was straightaway dehydrated with Ac_2O when the diphenylethylene (X) could be obtained in an overall yield of 63% from the keto ester.

The above olefin was brominated with NBS and the crude bromo derivative directly solvolysed in buffered aqueous dioxan[10] to give a product from which the major component crystallized to give a solid, $C_{27}H_{32}O_2$, m.p. 143–145°, in over 30% overall yield. In view of its UV (λ_{max} 250, ε 16180) and IR spectral (OH 3280,

1030 cm^{-1}; C=O 1711 cm^{-1}*) characteristics, this substance is formulated as the expected allylic alcohol XIII. Its PMR spectrum, though fully supporting this structure (one olefinic proton, 1H doublet centred at 362 c/s, J = 10 c/s) shows the CHOH† as a quartet (1H, centred at 241 c/s, J_1 = 10 c/s, J_2 = 2 c/s) rather than the expected doublet and, this must be ascribed to some long range spin–spin-coupling,[12] involving a preferred conformation of the side-chain. The IR spectrum of the non-crystalline part was essentially similar to that of XIII, hence as anticipated on energy consideration of the allylic carbonium ions involved, the allylic isomer XIV was not found to any significant extent.



XIII



XIV

The carbinol XIII on oxidation with CrO_3 in acetone solution[13] gave the bis-nor acid, $C_{13}H_{20}O_3$, in over 70% yield; it was found expedient to oxidize the total solvolytic product, to give the bis-nor acid in improved overall yields. The PMR spectrum of the acid ($\nu^{C=O}$ 1700, 1730 cm^{-1}) as well as its Me ester ($\nu^{C=O}$ 1735 cm^{-1}) clearly shows that of the four quaternary Me's, two, because of their down-field shift (Table 1), must be located on the carbon carrying the COOR group,[14] as indeed is required by the structure V for the keto acid. This degradation provides the first straightforward evidence for the location of a *gem*-dimethyl grouping at C_{11} in isolongifolene.

The above sequence of reactions represents a modified version of Barbier–Wieland degradation, leading to a *bis-nor* derivative.

After having prepared the C_{13}-keto acid (V) by the above route, ozonolysis of

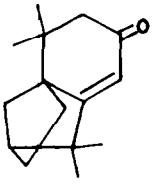
TABLE 1. PMR SIGNALS FOR THE QUATERNARY METHYLS IN THE ISOLONGIFOLENE SERIES

No.	Compound	Quaternary Me signals (in c/s)			
1	isolongifolane	51,	51,	51,	57
2	Isolongifolene	50,	57,	57,	62
3	9,10-Dehydro-isolongifolene (XVI)	53,	62,	62,	66
4	C_{15}-keto acid (IV)	60,	60,	60,	60
5	C_{13}-keto acid (V)	62,	62,	78,	79
6	Methyl ester of V	59,	61,	71,	76

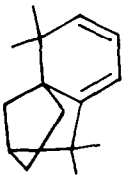
* In CCl_4 soln, $\nu^{C=O}$ 1724 cm^{-1}. The normal range of cyclopentanones being 1740–1750 cm^{-1}, this value is significantly low.

† The NMR spectra of all alcohols are measured before and after exchange with D_2O.

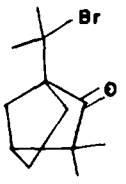
9-oxoisolongifolene[1] (XV) was studied in an effort to get V by a simpler method. However, the unsaturated ketone was recovered unchanged after ozonization at $-10°$ in $CHCl_3$. Likewise oxidation of 9,10-dehydro-isolongifolene (XVI), expeditiously obtained[15] from isolongifolene by allylic bromination (NBS) followed by dehydro-bromination (LiBr–Li_2CO_3-dimethylformamide), with RuO_4–$NaIO_4$[16] resulted in a complex acidic material (35%) containing only minor amounts of V.*



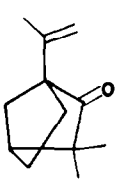
XV



XVI



XVII



XVIII

Attempted degradation of the keto acid (V) to the bromo derivative (XVII) by Hunsdiecker method,[17] or to the olefin, XVIII, by the Barton's decarboxylative elimination,[18] proved futile.

EXPERIMENTAL

For general remarks see Part XL of this series.

Action of PBA (*in* $CHCl_3$) *on isolongifolene*

(*i*) *Reaction with one mole equiv.* Isolongifolene ($\alpha_D = -82°$; 6·0 g) and a dry $CHCl_3$ soln of PBA (58 ml, 1·038N, 1 mole equiv), were separately cooled ($-10°$) and the latter soln added to the former in one lot. The reaction mixture was set aside at 0–5° for 17 hr (all per acid had been consumed) and then extracted with $NaHCO_3$ aq (5%, 70 ml × 3), washed with brine and dried. Solvent was flashed off to give a yellow oil (7·33 g), a part (2·03 g) of which was chromatographed over grade II Al_2O_3 (22 cm × 2·5 cm):

Fraction 1	light petroleum	100 ml	122 mg, oil
Fraction 2	50% C_6H_6 in light petroleum	100 ml	100 mg, oil
Fraction 3	C_6H_6	50 ml × 6	1·1 g, oil
Fraction 4	5% MeOH in C_6H_6	100 ml	413 mg, yellowish solid.

The various fractions were monitored by IR spectroscopy.

Fractions 2, 3 (IR spectrum: C=O 1698 cm^{-1}) were mixed and distilled to give a liquid (0·90 g, b.p. 122–123°/2 mm) identified (IR) as 8-oxo-7(αH)-isolongifolane (VI).[1]

Fraction 4 was recrystallized from hexane to give white needles, m.p. 141–143°. This is an unsaturated secondary alcohol and is discussed in detail in Part XLIV of this series.

(*ii*) *Reaction with 2 mole equiv.* To isolongifolene ($\alpha_D = -82°$; 12·24 g, 0·06 mole) cooled to $\sim -10°$, was rapidly added a similarly cooled soln of PBA in $CHCl_3$ (220 ml of 1·098N; 16·56 g of PBA, 0·12 mole). The reaction mixture was set aside first at 0–5° (20 hr) and then at room temp (27–28°, 70 hr), when no unchanged PBA remained. This was worked up as above to give a yellow viscous liquid (14·5 g; IR spectrum: intense band at 1730 cm^{-1}). Chromatography of a small portion (2·48 g) over neutral Al_2O_3 (grade II; 15 cm × 2·5 cm), essentially as described under (i), gave with benzene (100 ml) 300 mg of a solid (m.p. 62–64°), which was recrystallized from light petroleum to give colourless needles, m.p. 79–80°, and identified (IR, mixed m.p.) as the (±)-lactone[1] (VIII).

Hydrolysis (*vide infra*) of the total product showed it to contain ~60% of lactone [mixture of (±) and optically active product].

* Experiment carried out by Dr. R. R. Sobti of this Laboratory.

C_{15}-Keto acid (IV)

(*i*) *Directly from isolongifolene* via PBA *oxidation.* Oxidation of isolongifolene ($\alpha_D = -82°$) with two mole equivs of PBA in $CHCl_3$ was carried out, in several batches using 30 g of the hydrocarbon, exactly as described under (ii) above. The crude total product (83·8 g) and alcoholic KOH aq (84 g KOH, 200 ml H_2O and 550 ml EtOH) were mixed and refluxed on a steam-bath for 3 hr. The reaction mixture was cooled, diluted with water (550 ml) and distilled from a steam bath, under reduced press, to collect ~500 ml of distillate, which was rejected. The residue was cooled, extracted with ether (100 ml × 3) to remove neutral products (24·7 g, not investigated further) and the aqueous alkaline soln charcoaled and then acidified with conc HCl aq (Congo red). The precipitated gummy mass was taken up in ether (200 ml × 3), the extracts washed with brine, dried and the solvent flashed off to give the crude hydroxy acid as a brownish gum (55·0 g).

The above product (55·0 g) in acetone (100 ml) was stirred and treated dropwise (2 hr) with a soln of chromic acid (CrO_3 20 g, 60 ml H_2O and 18 ml conc H_2SO_4), such that the inside temp was 25–30°. After the addition, stirring was continued for another 1 hr and, the reaction mixture diluted with water (750 ml) and extracted with ether (150 × 3). The ether extract was washed with brine and then extracted with satd $NaHCO_3$ aq (200 ml × 3). The alkaline extract was charcoaled and acidified (conc HCl aq) to give a gum which was taken up in ether. The solvent was flashed off to give an almost colourless gum (43·75 g), which partly crystallised [mixture of (±) and (−) IV]. Crystallization from light petroleum gave white flakes (12·3 g, m.p. 102–104°), which were recrystallized (light petroleum) to give a product, m.p. 107–108°, identified (m.p. mixed m.p., IR) as the (±)-keto acid[1] (IV). The combined mother liquors were stripped off the solvent to furnish a gum (~33 g), which consisted essentially of IV (IR, GLC of derived Me ester[1]).

(*ii*) *By oxygenation of* 8-*oxo-isolongifolane.* To a soln of t-BuOK t-BuOH (0·87 g K, 25 ml t-BuOH), (±)-8-oxo-isolongifolane[1] (1 g; 0·0045 mole) was added and the soln shaken in an atmosphere of O_2 at 27°/700 mm till no more O_2 was consumed (122 ml in 7 hr). The resulting pale brown soln was diluted with water (100 ml) and acidified with 6N HCl. The product was taken up in light petroleum (50 ml × 6) and separated by $NaHCO_3$ aq into neutral (yellow oil, 340 mg, not studied further) and acidic product (690 mg, m.p. 100–101°). The acid was twice recrystallised from light petroleum to give glistening white flakes, m.p. 107–108°, identified (m.p., mixed m.p., IR) as IV.[1]

Degradation of IV *to bis-nor keto acid* (V)

(*i*) *Grignard reaction.* To an ethereal soln of PhMgBr (50 ml, 0·939 molar; 0·047 mole) was introduced, dropwise and with stirring, the methyl ester[1] of IV (5 g, 0·0188 mole) dissolved in ether (25 ml). The reaction mixture was gently refluxed for 4 hr and then poured onto ice (250 g) and NH_4Cl (30 g). The product was taken up in ether–benzene (1:1; 100 ml × 4), washed with brine and dried. Removal of solvent, left an orange yellow gum (9·69 g) which was chromatographed over neutral Al_2O_3 (grade II; 22·5 × 4·2 cm):

Fraction 1	light petroleum	200 ml × 13	0·9276 g, white solid, m.p. 60–63° diphenyl
Fraction 2	C_6H_6	200 ml × 5	0·0847 g, solid, rejected
Fraction 3	C_6H_6	200 ml × 13	1·0936 g, solid, m.p. 158–170°
Fraction 4	C_6H_6	200 ml × 6	0·9523 g, glass
Fraction 5	C_6H_6	200 ml × 17	2·1541 g, solid, m.p. 98–101°
Fraction 6	5% MeOH in C_6H_6	200 ml × 9	4·0253 g, brown gum
Fraction 7	MeOH	200 ml × 6	30 mg, rejected

Fraction 3 was twice recrystallized from light petroleum to give white needles, m.p. 180–181°, of XI; IR spectrum: OH 3400 and 1065 cm^{-1}; phenyl 1590, 1490, 748, 705 and 696 cm^{-1}. (Found: C, 83·12; H, 8·78. $C_{27}H_{34}O_2$ requires: C, 83·03; H, 8·78%).

Fraction 5 was recrystallized twice from light petroleum to furnish white needles (1·4 g), m.p. 100–100·5°, of IX. PMR spectrum: four quaternary Me's 53·5, 56, 56 and 56 c/s; aromatic protons, 10H multiplet centred at 432 c/s. (Found: C, 83·45; H, 8·80. $C_{27}H_{34}O_2$ requires: C, 83·03; H, 8·78%).

Mother liquors from the above crystallizations and fractions 4 and 6 were combined and rechromatographed over Al_2O_3, as above, to furnish 300 mg of crude XI (m.p. 175–179°) and 3·3 g of crude IX (m.p. 98–100°).

(*ii*) *Diphenyl ethylene* (X). The diphenylcarbinol (IX; 1 g) was refluxed with gl AcOH (5 ml) and Ac_2O (5 ml) for 3 hr, then diluted with ice-water (50 ml) and the product taken up in ether (50 ml × 3), which was washed with Na_2CO_3 aq (10%; 50 ml × 4), brine and dried. Solvent was removed and the residue, which slowly solidified, was twice recrystallized from light petroleum to furnish white crystals (695 mg), m.p.

114–115°; PMR spectrum: four quaternary Me's 54·5, 57, 61 and 61 c/s; vinyl proton, 1H triplet centred at 368 c/s, $J = 8$ c/s; 10 aromatic protons, essentially a singlet (428 c/s) with a broad base. (Found: C, 87·20; H, 8·80. $C_{27}H_{32}O$ requires: C, 87·05; H, 8·66%).

When XI (56·6 mg) was treated with gl AcOH (0·5 ml) and Ac_2O (0·5 ml) as above and, then worked up in the same manner, a solid product (50 mg) was obtained which on crystallization from light petroleum gave as the first crop (10 mg; m.p. 137–140°) unchanged XI, mixed with X, and a second crop (20 mg, m.p. 106–110°) identified as the diphenylethylene (X).

In subsequent experiments, the diphenyl carbinol (IX) and the hemiketal (XI) were not separated, but the mixture was dehydrated directly to get X. A typical example is described:

The total Grignard product from 4·7 g of keto ester [see (i) above] was chromatographed on Al_2O_3 (neutral/II; 20 cm × 4·2 cm) to separate diphenyl (1·5 g; light petroleum, 200 ml × 25) and collect together mixture of IX and XI (7·55 g; 3% MeOH in C_6H_6, 200 ml × 15). This product (7·4 g) was refluxed with gl AcOH (38 ml) and Ac_2O (38 ml) for 8 hr and then worked up as already described to get crude X, which was twice crystallized from light petroleum to get essentially pure X (4·14 g; overall yield, 63%), m.p. 111–113·5°. This product was straightaway used in the next step.

(*iii*) *Allylic bromination and hydrolysis.* The above diphenylethylene (1 g, 0·0027 mole), NBS (0·6 g, 0·003 mole) and CCl_4 (40 ml) were refluxed (2·5 hr) and worked up in the usual manner to get the crude bromo deriv (gum, 1·2 g). This was taken up in dioxan (33 ml), water (11 ml) and Li_2CO_3 (100 mg) added, and the reaction mixture refluxed for 4 hr. After concentrating it to ~ half its volume, it was diluted with water (20 ml) and the product taken up in ether (50 ml × 3), which was washed with brine and dried. Solvent was flashed off and the viscous residue diluted with light petroleum and chilled (−10°), when a solid (335 mg, m.p. 140–142°) separated, which was recrystallized from light petroleum to yield white flakes, m.p. 143–145° (m.p. 124–125°);* PMR spectrum: four quaternary Me's 46, 58·5, 58·5 and 63 c/s; 10 aromatic protons, ~5H singlets at 430 and 435 c/s. (Found: C, 83·10; H, 8·20. $C_{27}H_{32}O_2$ requires: C, 83·46; H, 8·3%).

(*iv*) C_{13}-*Keto acid* (V). The above allylic carbinol (80 mg) was taken up in acetone (5 ml) and treated at ~0° with a chromic acid soln (5·2 g CrO_3, 15 ml H_2O and 4·4 ml H_2SO_4) till a brown colour persisted (35 drops). The reaction mixture was kept aside at room temp (25–28°) for 19 hr and then worked up with water to get neutral (39 mg; mostly benzophenone) and acidic (52 mg) fractions. Acidic fraction slowly crystallized out and was recrystallized (light petroleum) to get colourless needles (30 mg), m.p. 110–112°. (Found: C, 69·56; H, 9·18. $C_{13}H_{20}O_3$ requires: C, 69·61; H, 8·99%).

9,10-*Dehydroisolongifolene* (XVI)

Isolongifolene (5·08 g), NBS (5·06 g) and CCl_4 (30 ml) were refluxed (2 hr) and worked up as usual to give 6·9 g of crude bromo derivative. This was taken up in dry dimethylformamide (50 ml), LiBr (3·0 g) amd Li_2CO_3 (4·1 g) added, and the whole stirred and heated (N_2) for 75 min at 120–125°. The reaction mixture was cooled, filtered and the filtrate, after dilution with water (100 ml), extracted with pentane–ether (1:1; 50 ml × 4). The combined extract was washed with brine and dried. Solvent was flashed off and the residue (4·52 g) filtered through a column of neutral Al_2O_3 (grade I; 10 cm × 1 cm) which was washed with light petroleum. From the combined eluates, solvent was removed and the residue distilled to give the diene (4·3 g), b.p. 77°/1·3 mm; its IR spectrum was superimposable on that of an earlier sample, prepared by a different route.[1]

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