

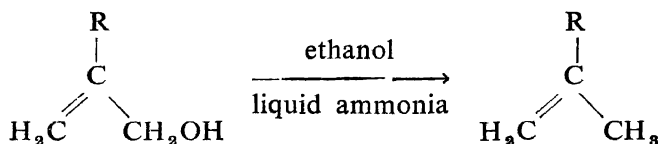
## Terpenoids : Part XXXI. A New Synthesis of Isopropenyl Mono-cyclic Terpenoids

O. P. Vig, Amrik Lal Khurana and K. L. Matta

Based on hydrogenolysis of suitably substituted  $\beta$ -allylic carbinols with sodium and alcohol in liquid ammonia, a new method of synthesising isopropenylic terpenes has been developed. The utility of this technique has been demonstrated by affecting new and facile syntheses of ( $\pm$ )-dihydrocarvone, ( $\pm$ )-carvone, ( $\pm$ )-perillaldehyde, ( $\pm$ )-4-methyl-isopropenyl cyclohexane and ( $\pm$ )- $\alpha$ -curcumene.

For the last few years, we have been interested in the syntheses of mono- and sesquiterpenoids particularly having isopropenyl grouping as a part of their constitution. Recently we reported the syntheses of dipentene<sup>1</sup>,  $\beta$ -terpineol<sup>2</sup>, isopulegone<sup>3</sup> and isolimonene<sup>4</sup> wherein isopropenyl group is sought through the application of Wittig's reaction<sup>5</sup> with methylene triphenylphosphorane on the appropriate substituted ketone to give the desired product. Another equally potential synthetic approach for the fixation of methylenic bond in such terpenic compounds, utilised in our laboratory is the Claisen rearrangement<sup>6</sup> of appropriate vinyl ether<sup>7</sup> prepared from suitably constituted allylic alcohol. This procedure has been employed as a key step for the clean syntheses of carvone<sup>8</sup>, dihydrocarvone<sup>9</sup> and perillaldehyde<sup>10</sup> which also possess isopropenyl chain in their formulation.

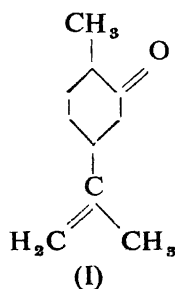
Besides the above mentioned unambiguous techniques for the synthesis of isopropenylic compounds, a new ancillary approach to their syntheses has been developed in the present studies. It is based upon the hydrogenolysis of suitably  $\beta$ -substituted allylic primary alcohol with sodium and ethanol in liquid ammonia according to the conditions laid down by Birch<sup>11</sup> and this results in the formation of isopropenyl group as under :



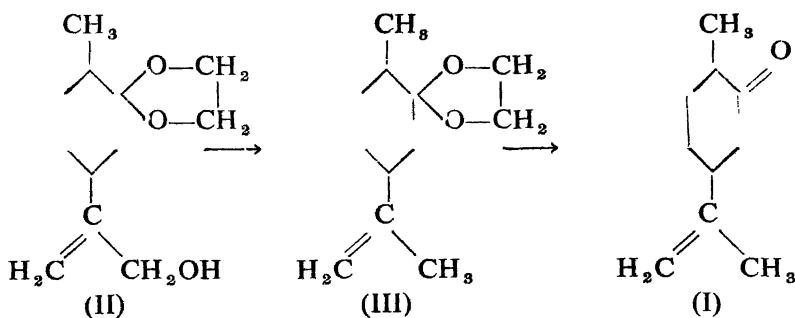
1. O. P. Vig, K. L. Matta, Amrik Lal and Inder Raj, *Jour. Indian Chem. Soc.*, 1964, 41, 142.
2. O. P. Vig, K. L. Matta and Inder Raj, *Idem*, 1965, 42, 581.
3. O. P. Vig, K. L. Matta and Inder Raj, *Idem*, 1965, 42, 841.
4. O. P. Vig and S. D. Sharma, *This Journal*, (communicated).
5. R. Greenwald, M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, 1963, 28, 1128.
6. A. W. Burgstahler and I. C. Nordin, *J. Amer. Chem. Soc.*, 1961, 83, 198.
7. W. H. Watanabe and L. E. Conlon, *J. Amer. Chem. Soc.* 1957, 79, 2828.
8. O. P. Vig, S. D. Sharma and Inder Raj, *Indian J. Chem.*, 1966, 4, 275.
9. O. P. Vig, S. D. Sharma and Inder Raj, *Idem*, 1965, 3, 425.
10. O. P. Vig, S. D. Sharma and Inder Raj, *Idem*, 1966, 4, 127.

The elegant technique of hydrogenolysis, investigated by Birch<sup>11</sup>, has been used for the reduction of many allylic alcohols. Its importance also lies in the synthesis of  $\beta$ -bisabolene from lanceol (which possesses isopropylidene form)<sup>12</sup>. However, this reaction has never been employed for the preparation of terpenes wherein isopropenyl grouping is secured after hydrogenolysis of a suitable allylic alcohol. The present investigations are directed towards the syntheses of the following terpenoids through the application of this method.

*Synthesis of ( $\pm$ ) dihydrocarvone* : Dihydrocarvone (I) has been isolated in the laevo rotatory form<sup>13</sup>. The preparation of the ketone (I) has been reported by the



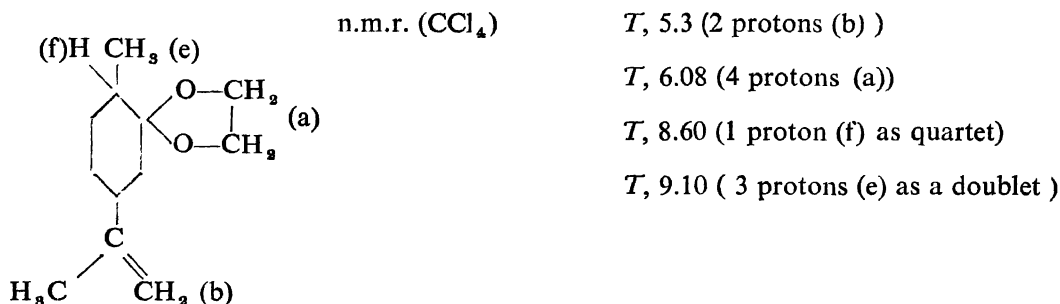
chromic acid oxidation of dihydrocarveol and selective reduction of carvone<sup>14</sup>. The syntheses of the compound (I) have been achieved by Vig et al<sup>9,15</sup>. However, in the present studies a new synthesis of this terpenic ketone (I) has been effected through the following steps :



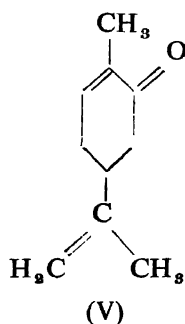
$\beta$ -(4-Methyl-3, 3-ethylene dioxy cyclohexyl) allyl alcohol, the starting material, prepared by the method described by Vig et al.,<sup>16</sup> was submitted to hydrogenolysis in liquid ammonia<sup>13</sup> with sodium and ethanol when 4-methyl-3, 3-ethylene-dioxy-

11. J. Bisch, *J. Chem. Soc.*, 809, 1945.
12. A. J. Birch and A. R. Murray, *J. Chem. Soc.*, 1951, 1888.
13. A. R. Pinder, "The Chemistry of Terpenes", Chapman and Hall Ltd., London, 1960, 74.
14. O. Wallach, *Ann.*, 1893, 275, 114.
15. O. P. Vig, *J. Gen. Org. Chem.*, USSR, 1961, 31, 669.
16. O. P. Vig and S. D. Sharma, *Jour. Indian Chem. Soc.*, (communicated)

isopropenyl cyclohexane (III) was obtained in 53 per cent yield after purification by chromatography on alumina column. It showed characteristic I. R. absorption peaks at 1640, 880 ( $\begin{matrix} R_1 \\ R_2 \end{matrix} > C = CH_2$ ) and 1045 (ketal)  $cm^{-1}$ . Further the structure of the compound (III) was supported through n. m. r. as follows :



G.L.C. of the given sample on a 6 ft. 10 per cent silicon oil column at 140° showed it to be a single component. The compound (III) on deketalisation with P.T.S and acetone<sup>17</sup> yielded 5-isopropenyl-2-methyl-cyclohexanone (I) in 90 per cent yield. Its 2:4-dinitrophenyl hydrazone and semicarbazone derivatives showed melting points close to those reported for (±) dihydrocarvone<sup>9</sup>. Its I. R. absorption spectrum was found to be superimposable with the spectrum of earlier synthesised product. Its identity was again supported by its conversion to carvone (V) through bromination of (I) with P.T.T. followed by dehydrobromination sequence exactly according to the conditions employed by French workers<sup>18</sup>.

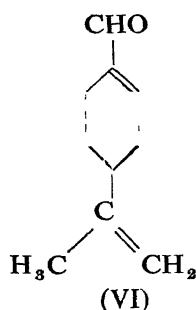


(±)-Carvone (V) obtained by the above procedure was characterised through its derivatives, 2:4-dinitrophenyl hydrazone and semicarbazone, and also by spectral evidence. I.R. absorption spectrum showed prominent peaks at 1695 (conj.-C=O) and 895 (terminal methylene)  $cm^{-1}$ , U. V. absorption spectrum showed maximum at  $\lambda_{max}^{EtOH} 235 m\mu$  ( $\log \epsilon = 3.9$ ). Lit.<sup>8</sup> reports  $\lambda_{max}^{EtOH} 235 m\mu$  ( $\log \epsilon = 3.9$ ).

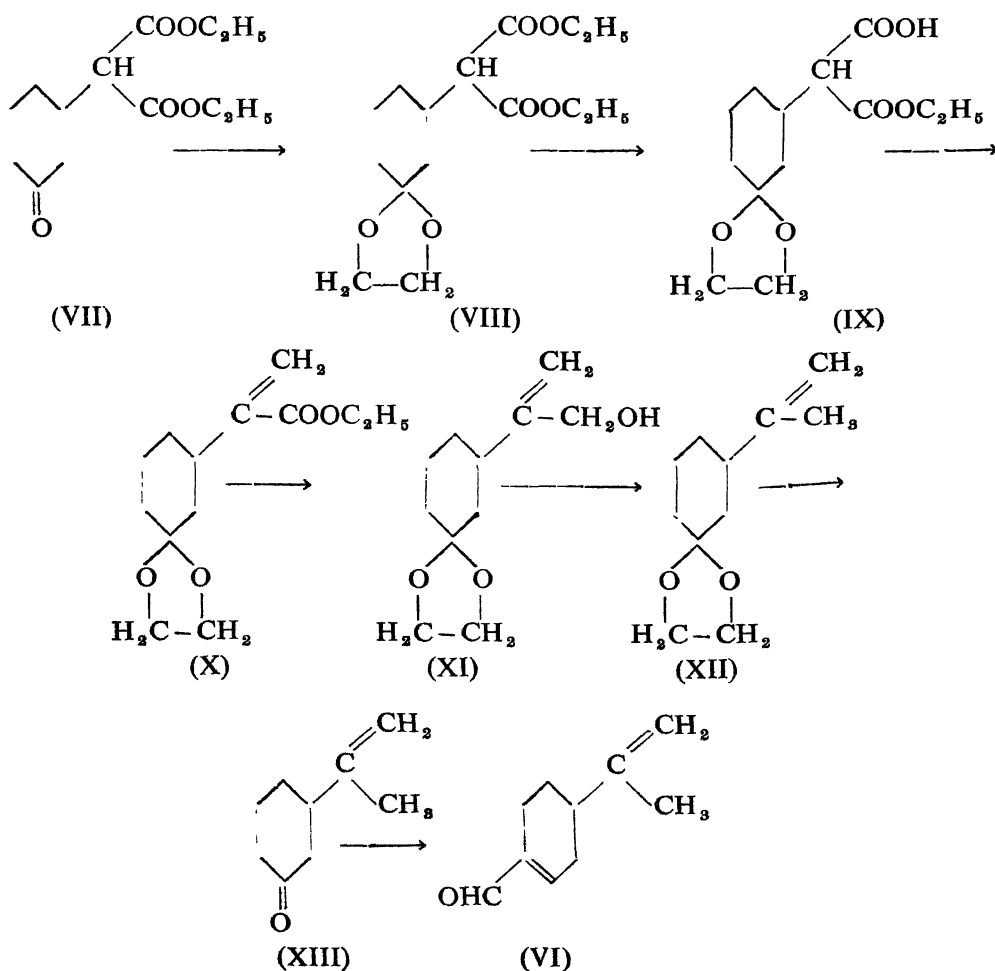
17. W. S. Johnson, J. D. Bass and K. L. Williamson, *Tetrahedron*. 1963, **19**, 861.

18. A. Marquet and J. Jacques, *Bull. Soc. Chim.*, France, 1962, 92.

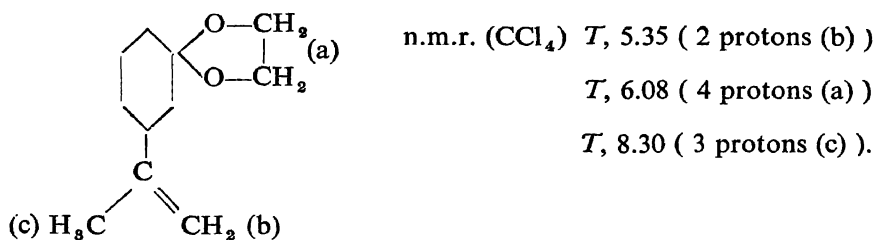
II. *Synthesis of ( $\pm$ )-perillaldehyde*: Perillaldehyde (VI) has been found to occur in nature in the laevo as well as in the dextro rotatory forms<sup>19</sup>.



A synthesis of ( $\pm$ )-perillaldehyde (VI) has been reported in the literature<sup>10</sup>. However, another straightforward synthesis of this aldehyde (VI) is sought through the present studies. The sequence of reactions is illustrated in the annexed diagram:



Ethyl (3-oxocyclohexyl) malonate (VII) was obtained in 80 per cent yield by Michael addition on cyclohexenone with diethyl malonate in sodium and ether<sup>20</sup>. The carbonyl group in the keto ester (VII) was protected by ketal formation<sup>21</sup> with ethylene glycol in presence of a catalytic amount of P.T.S when 90 per cent of the ketal diester (VIII) was obtained which exhibited I.R. absorption spectrum bands at 1740 (ester) and 1045 (ketal)  $\text{cm}^{-1}$ . The diester (VIII) was submitted to half hydrolysis<sup>22</sup> with methanolic sodium hydroxide (calculated amount) when  $\alpha$ -carbethoxy (3,3-ethylene dioxy) acetic acid (IX) was furnished in good yields. The compound (IX) showed characteristic I.R. absorption peaks at 3750-2500 (associated -OH), 1755-1710 (carbonyl of acid and ester) and 1045 (ketal) $\text{cm}^{-1}$ . The acid ester (IX), on exposure to formalin containing diethyl amine<sup>22</sup> provided  $\alpha$ -ethyl (3,3-ethylene dioxy cyclohexyl) acrylate (X) in 70 per cent yield. The presence of various functional groups in (X) was supported through I.R. absorption spectrum which showed characteristic peaks at 1725 (ester), 1045 (ketal), 925, and 895 (terminal methylene)  $\text{cm}^{-1}$ . The acrylic ester (X) was submitted to reduction with lithium aluminium hydride when  $\beta$ -(3,3-ethylene dioxy cyclohexyl) allyl alcohol (XI) was obtained in 70 per cent yield. This was characterised through its I.R. spectrum which exhibited bands at 3460 (OH), 925, 885 (terminal methylene), 1045-1030 (broad band OH and ketal)  $\text{cm}^{-1}$ . The allylic alcohol, on treatment with sodium and ethanol (absolute) in liquid ammonia under the usual conditions<sup>11</sup> and after purification by chromatography on alumina, furnished 3,3-ethylenedioxy isopropenyl cyclohexane (XII) in 50 per cent yield. It showed I.R. absorption peaks at 1645, 892 ( $\begin{matrix} R^1 \\ R_2 \end{matrix} > C = CH_2$ ) and 1042 (ketal)  $\text{cm}^{-1}$ . Its identity was further supported through n.m.r. as follows :



G.L.C. of the sample on 6 ft. 10 per cent silicon oil column at  $140^\circ$  showed it to be a single component. The ketal (XII) was stirred at room temperature with P.T.S. and acetone mixture<sup>17</sup> when 3-isopropenyl cyclohexanone (XIII) was obtained in 80 per cent yield. The I. R. spectrum of the compound (XIII) was found to be superimposable with the spectrum of the earlier synthesised ketone<sup>10</sup>. House et al<sup>23</sup> have reported the preparation of this ketone through abnormal Grignard reaction with 2-propenbromide on cyclohexenone. The compound (XIII) was converted to

20. D. K. Banerjee and P. S. Halwe, *Jour. Indian Chem. Soc* , 1960, 37, 669.

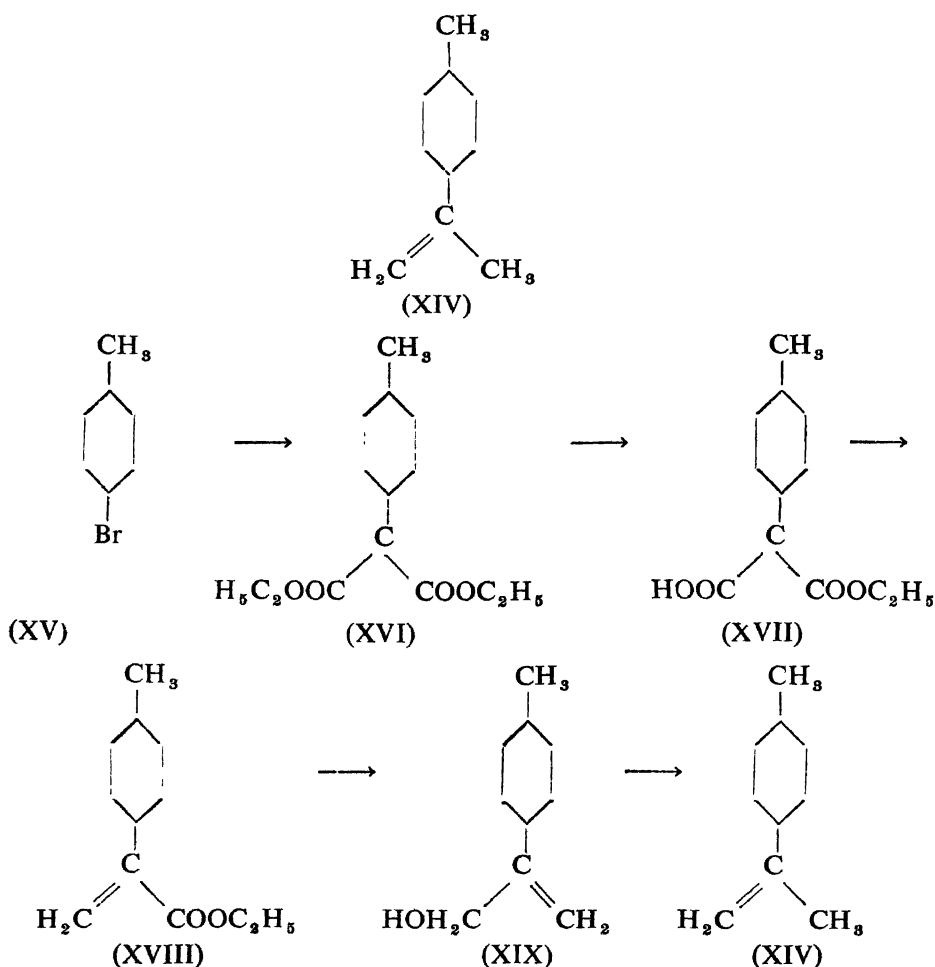
21. J. Samli, *Ber.*, 1938, 71B, 1803.

22. I. N. Nazarov, A. Titov and A. I. Kuznetsova, *Akad. Nauk, S. S. S. R. OTdel, Khim Nunk.*, 1959, 1412-1420.

23. H. O. House, R. A. Latham and C. D. Slater, *J. Org. Chem.*, 1966, 31, 2667.

(±)-perillaldehyde (VI) exactly on the same lines as already reported<sup>10</sup>. The synthetic aldehyde (VI) was characterised through its derivatives ( see experimental). Its I. R absorption spectrum showed characteristic peaks at 1700, 2790 ( $\alpha$ ,  $\beta$ -unsaturated aldehyde), 1660, 895 ( terminal methylene ) and 1470 (C-CH<sub>3</sub>) cm.<sup>-1</sup> U. V. absorption spectrum showed maximum at  $\lambda_{\max}^{\text{EtOH}}$  235 m $\mu$ . (log  $\epsilon$  = 3.6).

III. *Synthesis of 4-methyl-isopropenyl cyclohexane* : 4-Methyl-isopropenyl cyclohexane (XIV) has been reported to be the product of Wolff-Kishner reduction of dihydro carvone<sup>2,4</sup> and has also been prepared from *p*-menthanyl acetate<sup>2,4</sup>. The present synthetic route, based upon the application of hydrogenolysis, records the unambiguous synthesis of this hydrocarbon (XIV). The chart given below illustrates the sequence of reactions employed :

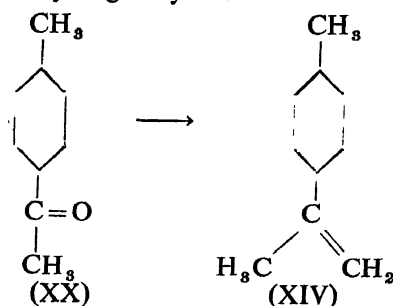


Diethyl malonate was alkylated with 4-methyl-bromocyclohexane in presence of sodium ethoxide in ethonal when ethyl (4-methyl cyclohexyl) malonate (XVI) was

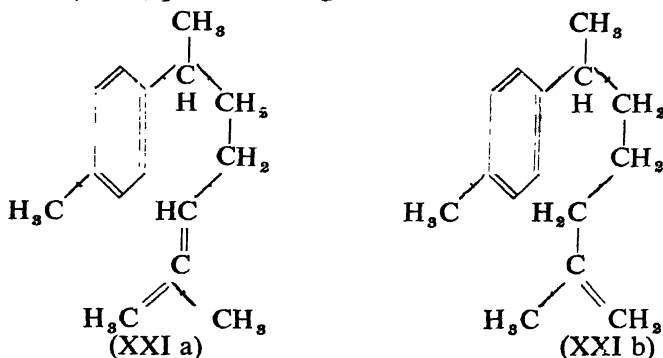
obtained in 75 per cent yield. It showed I. R. absorption characteristic peaks at 1740 (ester), 1370 and 1460 (C-CH<sub>3</sub>) cm<sup>-1</sup>.

Half hydrolysis<sup>22</sup> of the diester was carried out in methanolic sodium hydroxide when acid ester (XVII) was produced in 90% yield. This later on treatment with formaline and di-ethylamine<sup>22</sup> under the usual conditions afforded ethyl- $\alpha$ -(4-methyl-cyclohexyl) acrylate (XVIII) in 70 per cent yield. Its I. R. spectrum showed peaks at 1725 (ester), 930 and 825 (terminal methylene) cm<sup>-1</sup>. The acrylate (XVIII) on exposure to lithium aluminium hydride reduction provided  $\beta$ -(4-methyl-cyclohexane) allyl alcohol (XIX) in 78 per cent yield. It exhibited I. R. spectrum characteristic bands at 3460 and 1045 (primary-OH)cm<sup>-1</sup>. The allylic alcohol (XIX) was submitted to hydrogenolysis in liquid ammonia exactly according to the conditions as stated above<sup>12</sup> to give 4-methyl isopropenyl cyclohexane (XIV) in 69.9 per cent yield. The synthetic hydrocarbon was chromatographed on alumina for purification. Its I. R. absorption spectrum showed peaks at 1650 and 860 ( $\begin{matrix} R_1 \\ R_2 \end{matrix} > C = CH_2$ ) cm<sup>-1</sup>.

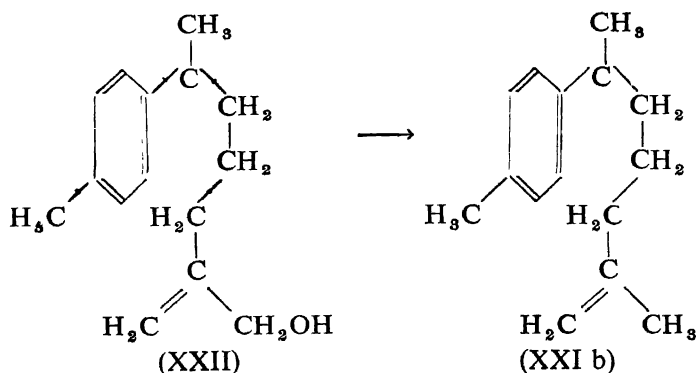
Another sample of the hydrocarbon (XIV) was prepared from 4-methyl-1-acetyl cyclohexane (XX) by employing the Wittig reaction with methylene triphenyl phosphorane according to the conditions laid down by Corey and coworkers<sup>5</sup>. The I.R. absorption spectra of the hydrocarbon obtained by these two different methods namely, Wittig reaction and hydrogenolysis were found to be superimposable.



IV. *Synthesis of ( $\pm$ )  $\alpha$ -curcumene (Isopropenyl form)*. The naturally occurring  $\alpha$ -curcumene, a monocyclic sesquiterpene hydrocarbon, exists in two forms (XXIa) and (XXIb) with (XXIa) predominating<sup>25</sup>.



Recently an unambiguous synthesis of ( $\pm$ )- $\alpha$ -curcumene (XXIb) has been reported<sup>26</sup>. In the present investigations (XXIb) form has been synthesised along the following lines :



2-Methylene-6 (*p*-tolyl) *n*-heptan-1-ol<sup>27</sup> (XXII) on submission to hydrogenolysis in liquid ammonia, furnished the hydrocarbon (XXIb) which was purified by chromatography on alumina (eluted with petroleum ether 40-60). It showed I.R. absorption peaks at 1660, 890 (terminal methylene), 1460, 1385 (C-CH<sub>3</sub>) and 817, 725 (1 : 4 benzene substitution) cm<sup>-1</sup>.

#### EXPERIMENTAL\*

*β*-(4-Methyl-3, 3-ethylenedioxy cyclohexyl) allyl alcohol (II) : This was prepared from ethyl  $\alpha$ -(4-methyl-3, 3-ethylene dioxy cyclohexyl) acrylate according to the procedure described in the literature<sup>16</sup>.

4-Methyl-3, 3-ethylenedioxy isopropenyl-cyclohexane (III) : Sodium metal (12 g.) was added in small pieces to a well stirred mixture of 12 g. of allyl alcohol (II) and absolute ethanol (60 ml.) contained in liquid ammonia (500 ml.) excluded from moisture. After the addition, the stirring was continued for another 3 hrs. Thereafter, the excess of liquid ammonia was allowed to evaporate and the solid cake left behind was decomposed with cold water (200 ml.). The resulting solution was extracted with ether and the ether extract after washing with brine was dried. The solvent was removed and the residue was chromatographed on alumina (eluted with petroleum ether 40-60). Fractionation under diminished pressure afforded 7.4 g. of (III) in 53 per cent yield, b.p. 98°10 mm.,  $\eta_D^{32}$  1.468.

Found : C, 73.74 ; H, 10.12, C<sub>12</sub>H<sub>18</sub>O<sub>2</sub> requires C, 73.43 ; H, 10.27%.

\* Melting and boiling points are uncorrected, microanalysis by Mr. B. N. Anand, Panjab University, Chemistry Deptt., Chandigarh. When not indicated otherwise, anhydrous sodium sulphate was used as drying agent.

26. O. P. Vig, J. P. Salota and B. Vig, *Indian J. Chem.*, 1966, 4, 323.

27. O. P. Vig, and B. Vig, *Jour. Indian. Chem. Soc.*, (communicated)



*2-Methyl-5-isopropenyl-cyclohexanone (dihydrocarvone) (I)*: To 6 g. of the above compound (III), was added 160 ml. of acetone, P.T.S (1 g.) and 10 ml. of water. The reaction mixture was stirred at room temperature for one and a half hour. It was diluted with sodium chloride solution (300 ml.) and extracted with ether. The ether extract was washed with brine and sodium bicarbonate solution (5%). After evaporating the solvent the residue was vacuum distilled to give the ketone (I) (3.6 g) in 77% yield, b.p. 89/5 mm.  $\eta_D^{32}$  1.4700. Found C, 79.25 ; H, 10.14,  $C_{10}H_{16}O$  requires C, 78.95 ; H, 10.53%.

2 : 4-Dinitrophenyl hydrazone derivative of (I) prepared by the sulphuric acid method in cold was crystallised from ethanol when yellow needles were obtained, m.p. 155°. Lit.<sup>28</sup> reports m.p. 155°. Found : N, 17.27.  $C_{16}H_{20}N_4O_4$  requires N, 16.87%.

Semicarbazone derivative of (I) after crystallisation from methanol melted at 166-67°. Lit.<sup>28</sup> reports m.p. 168°; Found : N, 19.86,  $C_{11}H_{19}N_3O$  requires N, 20.09%.

*2-Methyl-5-isopropenyl- $\Delta^2$ -cyclohexenone (V)*: 7.2 g. of the bromo reagent (P.T.T.) was added in small lots to 2.9 g. of the ketone (I) dissolved in anhydrous tetrahydrofuran (32 ml.) when the decolourisation occurred immediately. The reaction mixture was decomposed with 100 ml. of 5% solution of sodium bicarbonate and the organic product extracted with ether. The ether extract was washed with brine and dried. Removal of the solvent provided the bromo compound as a crude oil ( which was not distilled ). It was refluxed for 30 minutes with 40 ml. of pyridine. The contents were cooled, poured into water (150 ml.) and worked up in the usual way. On fractionation there was obtained 2.2 g. of carvone (V), b.p. 80-82/3 mm.  $\eta_D^{32}$  1.4985, Lit.<sup>29</sup> reports 1.5003. Found : C, 79.74 ; H, 9.36.  $C_{10}H_{14}O$  requires C, 80.0 ; H, 9.33%.

2:4-Dinitrophenyl hydrazone derivative prepared in the usual way was isolated as bright red needles, m.p. 186°, Lit.<sup>29</sup> reports m.p. 185°. Found : N, 16.82,  $C_{16}H_{18}N_4O_4$  requires N. 16.86%. Semicarbazone derivative of (V) was obtained as white needles after crystallisation from ethanol, m.p. 153-154°. Lit.<sup>29</sup> reports m.p. 154-156°. Found : N, 20.40.  $C_{11}H_{17}N_3O$  requires N, 20.28%.

*Ethyl (3-keto cyclohexyl) malonate (VII)*: To a mixture containing 1.8 g. of sodium, 4 ml. of absolute ethanol and anhydrous ether (20 ml.) was added cyclohexenone diethylmalonate (80 g.) followed by cyclohexenone (48 g.) dissolved in 100 ml. of anhydrous ether. A vigorous reaction started and ether began to reflux. In order to complete the reaction, the contents were refluxed for 6 hrs. The reaction mixture was decomposed by adding 50 ml. of water containing acetic acid. The ether layer was separated, washed with sodium hydroxide (2%), then with water and dried. The solvent was evaporated and the residual

28. J. Simonsen, "The Terpenes", University Press, Cambridge, 1947, 1, 252, 253, 358.

29. J. Simonsen, "The Terpenes", University Press, Cambridge, 1947, 1, 394.

oil on fractionation furnished (VII) b.p. 170-175/12 mm., yield 9.6 (70%)  $\eta_D^{30}$  1.4535. Found : C, 60.92 ; H, 7.79.  $C_{13}H_{20}O_5$  requires C, 60.92 ; H, 7.87%.

*Ethyl (3, 3-ethylene dioxy-cyclohexyl) malonate (VIII)* : A mixture of 64 g. of (VIII), 13 g. of ethylene glycol, anhydrous benzene (250 ml.) and P.T.S (100 ml.) was refluxed under a Dean and Stark apparatus till water ceased to collect in the limb (8 hrs.). Thereafter excess of P.T.S was destroyed with sodium bicarbonate (5%) and worked up in the usual way when 67.5 g. (90%) of the ketal diester (VIII) was obtained, b.p. 190-192/12 mm.  $\eta_D^{30}$  1.458. Found : C, 60.23 ; H, 7.78.  $C_{15}H_{24}O_6$  requires C, 59.98 ; H, 8.05%.

*$\alpha$ -Ethoxy carbonyl- $\alpha$  (3-3-ethylenedioxy-cyclohexyl) acetic acid (IX)* : To 4 g of sodium hydroxide dissolved in 32 ml. of methanol, was added the ketal diester from (VIII ; 30 g. ) and the contents were left 24 hrs, at room temperature. A solid mass was separated and dissolved in water (90 ml.). The resulting solution was washed with ether in order to remove the unhydrolysed material. The cooled contents were neutralised with 10 ml. of ice-cold hydrochloric acid. The half acid ester generated was immediately extracted with ether and worked up in the usual way. After removing the solvent the residue was distilled under diminished pressure, to afford the acid ester (IX) as a thick oil, b.p. 220°/6mm ; yield 22 g. (84%)  $\eta_D^{30}$  1.4665. Found : C, 57.47 ; H, 7.80.  $C_{13}H_{20}O_6$  requires C, 57.34 ; H, 7.40%.

*Ethyl- $\alpha$ (3,3-ethylene dioxy-cyclohexyl) acrylate (X)* : A mixture consisting of the above acid (IX), diethylamine (10 g.) and formaline (18 ml) was refluxed for 3 hrs. The contents were cooled, poured into 100 ml. of water and neutralised with hydrochloric acid. The organic material was extracted with ether. The ether extract after washing with water, was dried. The solvent was removed and the residue on fractionation provided acrylic ester (X) as a colourless oil, b.p. 145°/5 mm ; yield 18.1 g. (68%).  $\eta_D^{32}$  1.4765, Found : C, 64.78 ; H, 8.7.  $C_{13}H_{20}O_1$  requires C, 64.98 ; H, 8.39%.

*$\beta$ -(3, 3-Ethylenedioxy-cyclohexyl) allyl alcohol (XI)* : A solution of 18 g. of acrylic ester (X) in 75 ml. of anhydrous ether was added to a fine stirred suspension of 1.7 g. of lithium aluminium hydride, contained in 150 ml. of ether (anhydrous) at such a rate so as to maintain ether at a gentle reflux. The contents were further stirred at room temperature for 3 hrs. The reaction mixture was cooled and decomposed with ice cold sodium sulphate. The ether layer was separated and the aqueous layer extracted with ether. The combined ether extracts were dried. The solvent was evaporated and the residue on distillation furnished allyl alcohol (XI) 11.88 g. (80%), b.p. 144°/5 mm.  $\eta_D^{32}$  1.4930. Found : C, 66.87 ; H, 9.42.  $C_{11}H_{18}O_3$  requires C, 66.44 ; H, 9.15%.

3-3-Ethylenedioxy-isopropenyl cyclohexane (XII): Reduction of the allylic alcohol (XI) (11 g.), with sodium metal (11 g.) and absolute ethanol (50 ml.) in liquid ammonia (600 ml.), under the same conditions as already described in the preparation of (III), provided (XII), b. p. 105-107°/5 mm., yield 6.0 g. (66%)  $\eta_D^{32}$  1.4705. Found : C, 72.69 ; H, 9.86.  $C_{11}H_{18}O_2$  requires C, 72.49 ; H, 9.96%.

3-Isopropenyl-cyclohexanone (XIII) : 3, 3-ethylene dioxy-isopropenyl cyclohexanone (XII) (6 g.) was deketalised by stirring at room temperature for 2 hrs. with solution of P.T.S (1 g.) in acetone (100 ml.) containing 100 ml. of water. The contents were worked up in the usual manner. 4.1 g. (91% yield) of (XIII), b.p. 94-98°/4 mm. was obtained on fractionation,  $\eta_D^{36}$  1.4868. Found : C, 72.20 ; H, 9.99.  $C_9H_{14}O$  requires C, 78.21 ; H, 10.21%

Perillaldehyde (VI) : 3-Isopropenyl-cyclohexanone (4 g.) was converted to perillaldehyde exactly according to the conditions laid down in the literature<sup>10</sup>, b.p. 100-105°/6 mm.  $\eta_D^{36}$  1.4968. Lit.<sup>30</sup> records  $\eta_D^{23}$  1.5009, yield 1 g.

The  $\alpha$ ,  $\beta$ -unsaturated aldehyde furnished 2 : 4-dinitro phenylhydrazone derivative after crystallisation from ethanol which melted at 199-200°. Lit.<sup>30</sup> reports m.p. 200°. Found : N, 17.3.  $C_{16}H_{18}N_4O_4$  requires N, 16.96%.

The semicarbazone of (VI) after crystallisation from aqueous ethanol melts at 198°. Lit.<sup>30</sup> reports m.p. 199°. Found : N, 20.40.  $C_{11}H_{17}N_3O$  requires N, 20.27%.

Ethyl (4 methyl-cyclohexyl) malonate (XVI) : Diethyl malonate (40.0 g.) was introduced, with shaking, to a solution of sodium ethoxide, prepared from sodium metal (6.0 g.) in absolute ethanol (100 ml.). The contents were left at room temperature for 6 hrs. Thereafter, 50 g. of 4-methyl-1-bromo-cyclohexane was added. The reaction mixture was refluxed for 24 hrs. It was cooled, poured into excess of water and extracted with ether. The ether extracts were washed with brine solution and dried. On fractionation there was obtained (XVI) 40 g. (77%), b.p. 150°/5 mm. Found : C, 65.48 ; H, 9.35.  $C_{14}H_{24}O_4$  requires C, 65.59 ; H, 9.44%.

$\alpha$ -Ethoxy carbonyl-(4-methyl cyclohexyl) acetic acid (XVII) : 17.0 g. of the diester (XVI) on hydrolysis, with methanolic sodium hydroxide (35 ml.) (prepared from 2 g. of sodium hydroxide in methanol (35 ml.)) under the same conditions as already described in the preparation of (IX), provided half acid ester (XVII), 13.69 g. (85%), b.p. 190°/5 mm.  $\eta_D^{30}$  1.4610. Found : C, 63.02 ; H, 8.75.  $C_{12}H_{20}O_4$  requires C, 63.13 ; H, 8.83%.

*Ethyl- $\alpha$ (4-methyl cyclohexyl) acrylate (XVIII)*: A mixture of the above half acid (XVII, 12.6. g.), diethylamine (5 g.) and formalin (19 ml.) was refluxed for 3 hrs. After working in the usual manner as has been already described while preparing (X), there was obtained (XVIII), b.p. 130°/5mm, yield 7.9.g. (72%),  $\eta_D^{30}$  1.4665. Found : C, 73.35 ; H, 10.19.  $C_{12}H_{20}O_2$  requires C, 73.43 ; H, 10.27%.

*$\beta$  (4-Methylcyclohexyl) allyl alcohol (XIX)*: To a finer suspension of lithium aluminium hydride (0.95 g) in anhydrous ether (100 ml.) was added acrylic ester (XVIII, 7.2 g.) in anhydrous ether (300 ml.) at such a rate so as to maintain ether at a gentle reflux. The contents were further stirred for 3 hrs and worked up in the usual manner when 6 g. (85 %) of (XIX), b.p. 130°/5 mm. was obtained  $\eta_D^{30}$  1.476. Found : C, 77.65 ; H, 11.55.  $C_{10}H_{18}O$  requires C, 77.86 ; H, 11.76%.

*4-Methyl-1 acetyl -cyclohexane (XX)*: 4-Methyl-1-acetyl-cyclohexene<sup>81</sup> (5 g.) was reduced over palladium charcoal catalyst (5%, 0.3 g.) in ethanol (98%, 100 ml.) in a stream of hydrogen at a slight positive pressure. There was collected 5 g. (98%) of (XX), b.p. 85°/17mm. Found : C, 69.89 ; H, 11.25.  $C_9H_{16}O$  requires C, 77.09 ; H, 11.50%.

*4-Methyl-isopropenyl cyclohexane (XIV)*: A solution of sodium methyl sulphanyl carbanion was prepared under nitrogen atmosphere from sodium hydride (0.8 g.) and dimethyl sulphoxide (8.2 ml). This on treatment with triphenyl phosphonium iodide (6.8 g.) in dimethyl sulphoxide (16.4 ml.) furnished the yield. After stirring the yield for 10 min. the ketone (XX, 1.38 g.) in tetrahydrofuran (10 ml.) was added and stirring continued for 2 hrs. The contents were poured into ice-cold water and extracted with petroleum ether. After the removal of the solvent the contents were chromatographed on alumina. It was further distilled under reduced pressure to afford (XIV), b.p. 65°/17 mm.  $\eta_D^{25}$  1.445. Found : C, 86.22 ; H, 13.32.  $C_{10}H_{18}$  requires C, 86.88 ; H, 13.12%.

The compound (XIV) was also obtained through hydrogenolysis of allyl alcohol (XIX) (5 g.) with sodium metal (5 g.) and ethanol (25 ml.) in liquid ammonia (300 ml.) under the same conditions as has been already described while preparing (III). Yield 3 g. (69.9%), b.p. 62°/18 mm.,  $\eta_D^{23}$  1.4553 ; Found : C, 86.67 ; H, 13.03.  $C_{10}H_{18}$ , requires C, 86.88 ; H, 10.12.

*2-Methylene-6 ( p-tolyl )-n-heptan.-1-01 (XXII)*: This was prepared according to the method described in the literature<sup>27</sup>.

*2-Methylene-6-methyl ( p-tolyl )-hexanone (XXIb)*; Reduction of (XXII) (1.0 g.), with sodium metal (1.0 g.) and ethanol (5 ml) in liquid ammonia (150 ml.) under the

usual conditions, provided 0.6 g. (66.6%) of (XXI), b.p.  $107^{\circ}/5\text{mm}$ .  $\eta_{\text{D}}^{30}$  1.5127.  
Found : C, 89.02 ; H, 10.92.  $\text{C}_{18}\text{H}_{22}$  requires C, 89.04 ; H, 10.96%.

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