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SYNTHESIS OF BRIDGED RING SYSTEMS RELATED TO CLOVENE*

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IN view of a recent publication by Murray *et al.*[1], we are prompted to report our results on a synthetic approach to the ring-system related to clovene. The novelty of the present communication is the synthesis of a hydrindane derivative (XII) with appropriate functional groups and having the desired stereochemistry at all the asymmetric centres.

The bicyclic ketone V was singled out to be a potential intermediate for this purpose in view of the successful observations made in this laboratory in a related field and the synthesis of the ketone was achieved through the following steps. The conjugate addition of methylmagnesium iodide to ethyl α-cyano-β-(*p*-methoxyphenyl)-crotonate I[2] was effected in the presence of cuprous iodide[3] resulting in the formation of the product II, b.p. 167-174°/0.6 mm. β-Methyl-β-(*p*-methoxyphenyl)-butyric acid (III), m.p. 89-90° obtained on hydrolysis and decarboxylation was cyclized with polyphosphoric acid[4] to the indanone IV, red *2,4-dinitrophenylhydrazone* (m.p. 266-267°).

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* Analysis of all the compounds described corresponded to the calculated values.

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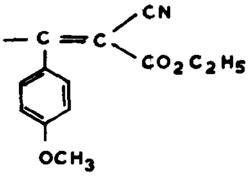
[1] R.D.H. Murray, W. Parker and R.A. Raphael, *Tetrahedron* **16**, 74 (1961).

[2] W. Baker, J.F.W. McOmie and A.S. Weaving, *J. Chem. Soc.* 2018 (1956).

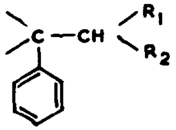
[3] A.J. Birch and R. Robinson, *J. Chem. Soc.* 501 (1943); W. Parker and R.A. Raphael, *Ibid*.1723 (1955).

[4] Sukh Dev, *J. Indian Chem. Soc.* **32**, 255 (1955).

The reduction of the ketone to the corresponding hydrocarbon was successfully effected through catalytic hydrogenation in presence of small amount of perchloric acid.[5] The aromatic ring of the indane was further reduced with sodium in liquid ammonia[6] and the resulting product isomerized with

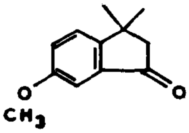


I



II, R_1 = CN, R_2 = $CO_2C_2H_5$

III, R_1 = H, R_2 = CO_2H



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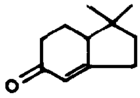
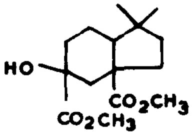
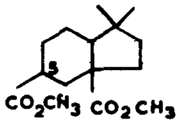


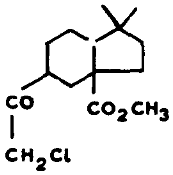
V



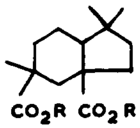
VI



VII

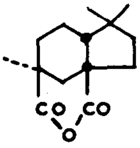


VIII

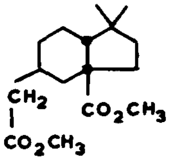


IX, R = CH_3

X, R = H



XII



XI

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[5] K.W. Rosenmund and E. Karg, Ber. Dtsch. Chem. Ges. 75, 1850 (1942); W.S. Johnson, R.G. Christiansen and R.E. Ireland, J. Amer. Chem. Soc. 79, 1995 (1957).

[6] A.J. Birch, Quart. Rev. 4, 69 (1950).

dilute sulphuric acid. The unsaturated ketone V [λ_{max} 230 mμ (log ε 3.9)], thus obtained, afforded a red 2,4-dinitrophenylhydrazone (m.p. 168°) and a semicarbazone (m.p. 215°). An acidic material could be isolated in a satisfactory yield on conjugate addition of potassium cyanide to V in aqueous alcoholic solution and subsequent alkaline hydrolysis and this on esterification with diazomethane afforded a neutral liquid, VI, b.p. 147-155°/4 mm. VI was further converted to the chloro-compound and finally to VII on boiling with zinc dust in acetic acid. In order to introduce the methyl group at 5-position in VII this was partially hydrolysed to the ester-acid, characterized through the crystalline anilide (m.p. 121°). This was successively converted to the acid-chloride, to diazoketone with diazomethane and finally to the chloro-ketone VIII with dry hydrogen chloride.[7] This was subjected to Favorskii rearrangement in the presence of sodium methoxide[8] and the desired diester IX was isolated in a poor yield, the major product being XI. Drastic alkaline hydrolysis of IX afforded the di-acid X, m.p. 171-172° which underwent easy conversion to the anhydride XII, m.p. 98-99° (ν_{max} 5.56 μ; 5.68 μ). Development of the third ring, characteristic of the clovene ring-system, is in active progress along well-tried methods.

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[7] Ch.R. Engel and G. Just, J. Amer. Chem. Soc. 76, 4909 (1954).

[8] R.B. Loftfield and L. Schaad, J. Amer. Chem. Soc. 76, 35 (1954); H.O. House and W.F. Gilmore, Ibid. 83, 3980 (1961).