Tetrahedron Letters No.7, pp. 649-652, 1971. Pergamon Press. Printed in Great Britain.

THERMAL AND PHOTOCHEMICAL CYCLISATION OF 2-METHYL-3-(PENT-4-ENYL)-CYCLOHEX-2-EN-1-ONE

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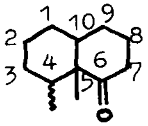
(Received in UK 30 December 1970; accepted for publication 19 January 1971)

During the course of other thermolysis studies,[1] we chose to apply the elegant cyclisation procedure of Conia[2] towards the synthesis of 4,5-dimethyldecal-6-one (1) system, bearing a $\Delta^{1,10}$ or $\Delta^{9,10}$ double bond. Thermolysis of (2) at 350° C in the gas phase has been shown, by Conia, to afford a stereoisomeric mixture of the <u>cis</u> and <u>trans</u> 4,5-dimethylhydrindanones (3) and (4) by way of the intermediate enol (5). Application of this cyclisation method to 2-methyl-3-(pent-4-enyl)-cyclohex-2-en-1-one (6) produced interesting divergences between thermal reactions carried out in the gas and liquid phases.

Reaction of the Grignard reagent derived from 1-bromopent-4-ene with the isobutyl enol ether (7)[3] of 2-methylcyclohexan-1,3-dione gave the required conjugated ketone (6) [b.p. 130°/20 mm.; ν_{max} 1670, 1630, 920 cm.$^{-1}$; λ_{max} 244 nm ε 9,400; N.M.R. τ 8.31 (s, 3H), 4.0-5.3 (m, 3H); g.l.c. carbowax coated capillary, 50 ft., 175° C, 12 psi R_t 5.10 min.; Found, C, 80.98; H, 10.05. $C_{12}H_{18}O$ requires C, 80.85; H, 10.18%.].

Depending on the direction of enolisation in (6), the intermediate enol would have the <u>endo</u> cyclic (8) or <u>exo</u> cyclic (9) double bond. Cyclisation via (8) would afford the known[1,4] dimethyldecalones (10) and (11). In the event, thermolysis of (6) in the gas phase at 325° (sealed tube) yielded four main products A, B, C, D in addition to recovered starting material. Component B predominated in the gas phase experiment and was assigned structure (11), on the basis of the following data (ν_{max} 1710 cm.$^{-1}$; λ_{max} nil; N.M.R. τ 9.20 (d, J=7cps., 3H), 8.74 (s, 3H), 4.37 (m, H). Mass spectral fragmentation 178 (M^+), 163 (M-15), 150 (M-28), 149 (M-29), 135 (M-43). Accurate mass 178.



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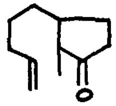

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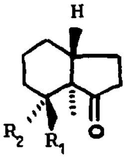
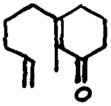


3. R_1 =Me, R_2 =H

4. R_1 =H, R_2 =Me

5.



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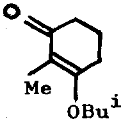

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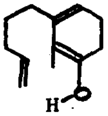

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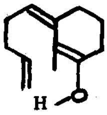

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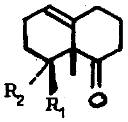
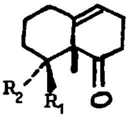


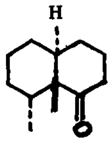
10. R_1 =Me, R_2 =H

11. R_1 =H, R_2 =Me



12. R_1 =Me, R_2 =H

13. R_1 =H, R_2 =Me



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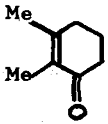

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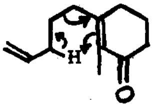

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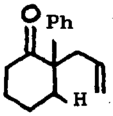

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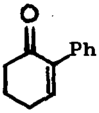

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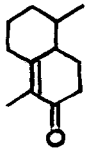

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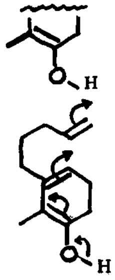

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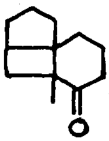

21.

135758.) It was found that B was not identical with either (10) or (11) by N.M.R. and g.l.c. (SE 30, 20%, 25 ft., 200°C, 25 psi), hence the *endo*cyclic isomer (8) must have been involved in the cyclisation. The choice between (12) and (13) was made by showing the identity of the hydrogenation product of B with (14), derived from the known decalone (11). Component C was found to be unstable and could not be purified satisfactorily. The *cis* dimethyl decalone (12), although an expected product, could not be isolated from the thermolysis mixture.

Thermolysis of (6) in the liquid phase at 350°C for 2.5 hr. gave a mixture consisting of mainly A and D, in which D predominated. Small amounts of B and C were detected by g.l.c. Components A and D were isolated by prepatative g.l.c.[carbowax 10% on chromasorb P, 11 ft., 210°C, 30 psi.] Component A (ν_{max} 1680, 1630 cm.$^{-1}$; λ_{max} 245 nm ε 7,500; N.M.R. τ 8.15 (s, 3H) 8.33 (s, 3H), no olefinic H. Mass spectral accurate mass 124.08906. $C_8H_{12}O$ requires 124.08881) was shown to be identical with 2,3-dimethylcyclohex-2-en-1-one (15), prepared by reaction of MeMgBr on (7). An analogy for this fragmentation (16), may be found in the work of Conia[2] who isolated (18) from thermolysis of (17).

The major product, D, from the liquid phase reaction was assigned structure (19) from the following data [ν_{max} 1670, 1630 cm.$^{-1}$; λ_{max} 247 nm. ε 11,000 (based on M.W. 178); N.M.R. τ 9.01 (d, J=5 cps, 3H), 8.32 (s, 3H), no olefinic H; Mass spectral accurate mass 178.136114. $C_{12}H_{18}O$ requires 178.135758]. Component D (19) could arise by an alternative mode of cyclisation, e.g. (20), of the enol derivative (8). This may be visualised as proceeding intermoleculary as shown; a situation favoured by liquid phase in contrast to the intramolecular process of the gaseous reaction.

In order to determine whether the enone (6) could be induced to enolise by photochemical excitation, it was irradiated in methanol, or benzene at 310 nm. (Westinghouse FS 20 sunlamp). The product was isolated by preparative g.l.c. (carbowax, 10%, 11 ft., 200°C, 30 psi.) and found to be a mixture of two isomers in the ratio 8:1, neither of which were produced in the thermolysis reactions. Structure (21) is favoured for the photochemical product, based on analogy[5] and spectral characteristics (ν_{max} 1700 cm.$^{-1}$; λ_{max}, nil; N.M.R. τ 9.08 (s, 3H), no olefinic H; mass spectral accurate mass 178.136150. $C_{12}H_{18}O$ requires 178.135758).

Acknowledgement

We thank The Colombo Plan Organisation for a maintenance award to A.S. and Professor D. Arigoni for invaluable discussion.

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