798. *The Tautomerism of* $\Delta^{1(9)}$*-Octal-2-one.*

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Some cyclisations leading to $\Delta^{1(9)}$-octal-2-one have been studied. As ordinarily prepared this compound contains its $\Delta^{9(10)}$-isomer.

IN connection with other work, we required $\Delta^{1(9)}$-octal-2-one (II; R = H) and as we had already made a quantity of 2-hydroxymethylenecyclohexanone we decided to prepare it from this compound. Treatment with 4-diethylaminobutan-2-one methiodide and sodium ethoxide in anhydrous ethanol furnished the adduct (I; R = H). When 2-hydroxymethylenecyclohexanone was refluxed with methyl vinyl ketone and a trace of potassium hydroxide *in the absence of solvent*, the product (85%) was the adduct (I; R = CHO). When methanol was present, partial cyclisation occurred as shown by absorption at 238 mμ (in ethanol). Both compounds (I; R = H and CHO), when refluxed with potassium hydroxide in methanol, gave the octalone (II; R = H).

We also tried the effect of toluene-*p*-sulphonic acid in refluxing benzene on the aldehyde (I; R = CHO) in the hope that the formyl group might be retained to produce the octalone (II; R = CHO), a simple route to which might be of value. With a catalytic amount of acid two compounds were formed and isolated as their 2,4-dinitrophenylhydrazones: one was clearly that of the octalone (II; R = H), the other from elemental analysis and light absorption studies was formulated as that of the bridged compound (III).[1] No trace of the octalone (II; R = CHO) or of the spiro-ketone (IV) was detected. With more toluene-*p*-sulphonic acid the octalone (II; R = H) was the chief product.

One curious feature of the octalone (II; R = H) was the presence of a shoulder (for some specimens a small band) in the infrared absorption spectrum at 1710 cm.$^{-1}$. At first this was thought to be due to a saturated carbonyl-bearing impurity but when other routes [2,3,4] to compound (II; R = H) were followed all the products had this absorption.

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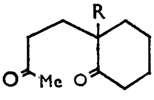
[1] For similar compounds see Johnson, Korst, Clement, and Dutta, *J. Amer. Chem. Soc.*, 1960, **82**, 614.

[2] du Feu, McQuillen, and Robinson, *J.*, 1937, 53.

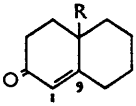
[3] Mannich and Braun, *Ber.*, 1920, **53**, 1874; Mannich, Koch, and Borkowsky, *Ber.*, 1937, **70**, 355.

[4] Pappo and Tsatsos, quoted by van Tamelen and Proost, *J. Amer. Chem. Soc.*, 1954, **76**, 3632.

By successive distillations this absorption was diminished but not eliminated; concomitantly absorption at 238 mμ (αβ-unsaturated ketone) increased slightly. Extraction with aqueous sodium hydrogen sulphite solution did not purify the compound.



(I)



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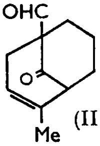
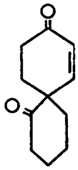
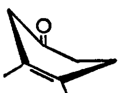


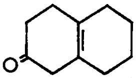
(III)



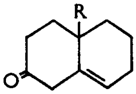
(IV)



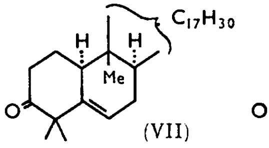
(Va)



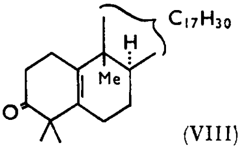
(V)



(VI)



(VII)



(VIII)

The 2,4-dinitrophenylhydrazone [2] of the octalone (II; R = H) was prepared and was chromatographically homogeneous. Unfortunately it required vigorous conditions for its hydrolysis.[5] However, the semicarbazone,[2] also apparently homogeneous, was hydrolysed quantitatively with warm 1·5% aqueous hydrochloric acid. The regenerated octalone still possessed the 1710 cm.$^{-1}$ absorption and appeared to be identical with the starting material. The only reasonable conclusion is that compound (II; R = H), as ordinarily prepared, contains the ketones (V) and (VI; R = H) and is probably in equilibrium with either or both. The lack of infrared absorption near 820 cm.$^{-1}$ (>C=CH–) supports structure (V) rather than (VI; R = H).

Conformational analysis shows that on the usually accepted chair and half-chair ring conformations the sum of the non-bonded interactions is virtually identical for structures (II) and (VI). The energy difference will thus be the resonance energy of compound (II). When the angular-substituted compounds (II; R = Me and CO_2Et), for which a tautomeric structure (V) is impossible, were made, they were found to be spectrally pure and not to undergo equilibration to the isomers (VI) on treatment with mild basic catalysts. The tautomer of compound (II; R = H) is thus (V).

A model of structure (V) shows that, provided the atoms have their normal valency angles, a cyclohex-3-enone ring is a half-boat (Va). However, only one eclipse is present, that of the carbon chain $C_{(1)}$–$C_{(4)}$ (in the case of the cyclohexene half-boat the C–H bonds are also eclipsed). The bow and the stern axial hydrogen atoms (2·74 Å apart) do not interfere. The tetrasubstituted bond evidently confers considerable stability on this structure. The isomerisation [6] of glutinone (VII) to glut-5(10)en-3-one (VIII) is of interest in this connection.

EXPERIMENTAL

2-3′-*Oxobutylcyclohexanone*.—4-Diethylaminobutan-2-one methiodide (50 g.) in absolute ethanol (150 ml.) was added, during 1 hr., to an ice-cold, stirred solution of 2-hydroxymethylenecyclohexanone (15 g.) in ethanolic sodium ethoxide [from sodium (2·2 g.)] in absolute ethanol (180 ml.). The mixture was stored overnight at room temperature, refluxed for 3 hr., cooled, and extracted with ether. The extract was washed with water and dried ($MgSO_4$). Evaporation and distillation gave the *diketone* (11·6 g., 58%), b. p. 110°/1·0 mm., n_D^{23} 1·4675 (Found: C, 72·2; H, 9·4. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%).

2-*Formyl*-2-3′-*oxobutylcyclohexanone*.—(*a*) 2-Hydroxymethylenecyclohexanone (8 g.), methyl vinyl ketone (6·7 g.), quinol (trace), and potassium hydroxide (~ 0·05 g.) were refluxed for 5 hr.

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[5] The method of Robinson (*Nature*, 1954, **173**, 541) was not successful with this compound.

[6] Chapon, *Bull. Soc. chim. France*, 1955, 1076; Beaton, Spring, Stevenson, and Stewart, *Tetrahedron*, 1958, **2**, 246; Paton, Spring, and Stevenson, *J.*, 1958, 2640.

After cooling, a few drops of concentrated hydrochloric acid were added. The product was then distilled, to give 2-formyl-2-3′-oxobutylcyclohexanone (10·5 g., 85%), b. p. 113—116°/0·02 mm., $n_D^{19.5}$ 1·4833 (Found: C, 67·2; H, 8·5. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%), $\nu_{max.}$ (film) 2750, 1713, 1444, 1420, 1340, 1170, 1130, 1098, 1068, and 960 cm.$^{-1}$.

(*b*) The formylcyclohexanone (6·3 g.) was refluxed for 18 hr. with a solution of 4-diethylaminobutan-2-one (8·6 g.) and pyridine (4·3 ml.) in dry benzene (60 ml.), cooled, washed with dilute hydrochloric acid, water, and brine, and dried ($MgSO_4$). Distillation gave formylcyclohexanone (2·1 g.) and the formyl adduct, as above (1·13 g., 11·5%), b. p. 110—113°/0·03 mm., n_D^{18} 1·4830.

$\Delta^{1(9)}$-*Octal*-2-*one*.—(*a*) The formyl adduct (7·0 g.) in methanol (800 ml.) and aqueous 45% potassium hydroxide solution (100 ml.) was refluxed under nitrogen for 24 hr. After cooling, the solution was poured into brine and extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and evaporated. Distillation afforded the octalone (3·5 g., 56%), b. p. 90—93°/0·25 mm., n_D^{16} 1·5250. After two further distillations it had $\lambda_{max.}$ (in EtOH) 238 mμ (ε 13,720), $\nu_{max.}$ (film) 1710, 1674, and 1622 cm.$^{-1}$. The 2,4-dinitrophenylhydrazone crystallised from ethyl acetate as scarlet plates, m. p. 170—172°, and from ethanol–ethyl acetate as needles, m. p. 176—177°, $\lambda_{max.}$ (in $CHCl_3$) 390 mμ (ε 24,850). The semicarbazone crystallised from ethanol as prisms, m. p. 207—208°, $\lambda_{max.}$ 269 mμ (ε 23,700).

(*b*) The formyl adduct (3·72 g.) was heated under reflux for 19 hr. with toluene-*p*-sulphonic acid (0·2 g.) in dry benzene (125 ml.). The solution was then washed with water, dried ($MgSO_4$), and evaporated. Distillation gave a pale yellow liquid (2·2 g.), b. p. 90—112°/0·04 mm., whose 2,4-dinitrophenylhydrazone was chromatographed in chloroform on bentonite–kieselguhr, to yield the bis-2,4-dinitrophenylhydrazone of compound (III) as yellow platelets (from ethyl acetate, insoluble in the cold), m. p. 245° (decomp.) (Found: C, 51·75; H, 4·4; N, 20·5. $C_{23}H_{22}N_8O_8$ requires C, 51·3; H, 4·1; N, 20·8%), $\lambda_{max.}$ (in $CHCl_3$) 360 mμ (ε 29,880), and the 2,4-dinitrophenylhydrazone of (II; R = H), m. p. 176—177°.

No other products were isolated.

(*c*) The formyl adduct (28 g.) was refluxed with toluene-*p*-sulphonic acid (7·0 g.) in benzene (750 ml.) for 1½ hr., after which the theoretical amount of water (2·90 ml.) had been collected. The product was worked up as usual and gave the octalone (II; R = H) (14·0 g.).

(*d*) 2-3′-Oxobutylcyclohexanone (I; R = H) (10 g.) was refluxed with toluene-*p*-sulphonic acid (5·0 g.) in dry benzene (500 ml.). The theoretical amount of water had collected after 30 min. Working up in the usual way gave the octalone (II; R = H) (8·5 g.).

The semicarbazone of $\Delta^{1(9)}$-octal-2-one was hydrolysed with 1·5% aqueous hydrochloric acid on a water bath for 5 min. The ketone was regenerated quantitatively.

Ethyl 2-*Oxo*-1-3′-*oxobutylcyclohexanecarboxylate*.—Ethyl 2-oxocyclohexanecarboxylate (20 g.) was refluxed for 4 hr. with methyl vinyl ketone (15 g.) and potassium hydroxide (~0·2 g.). After cooling, chloroform was added and the solution washed with water and dried ($MgSO_4$). Distillation afforded the adduct (21·25 g., 55%), b. p. 133—135°/0·6 mm., n_D^{18} 1·4748 (Found: C, 65·5; H, 8·3. Calc. for $C_{13}H_{20}O_4$: C, 65·0; H, 8·4%). The 2,4-dinitrophenylhydrazine crystallised from ethanol in yellow needles, m. p. 178°.

Ethyl 3-*Oxo*-$\Delta^{4(10)}$-*octalin*-9-*carboxylate*.—The above adduct (17·4 g.) was treated with toluene-*p*-sulphonic acid (10 g.) in refluxing benzene (800 ml.) under a water separator for 1½ hr., after which the theoretical amount of water (1·3 ml.) had separated. Working up in the usual way gave the octalone (15·48 g., 95%), b. p. 120°/0·45 mm., n_D^{20} 1·5070, $\nu_{max.}$ (film) 1724, 1676, 1629, 1450, 1331, 1298, 1258, 1229, 1184, 1089, 1016, 940, and 858 cm.$^{-1}$.

10-*Methyl*-$\Delta^{1(9)}$-*octal*-2-*one*.—This compound was made, according to the directions of Yanagita *et al.*,[7] in 30% yield and had b. p. 96—100°/0·5 mm., n_D^{15} 1·5235.

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[7] Yanagita and Yamakawa, *J. Org. Chem.*, 1957, **22**, 291.