[Contribution from the Instituto de Química de la Universidad Nacional Autónoma de Mexico]

STRUCTURE AND PROPERTIES OF CYCLIC COMPOUNDS. IV.¹ THE DEHYDRATION OF CYCLIC ALLYLIC CARBINOLS

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In the course of another study (1) it was found that 1,3-dimethylcyclohex-2enol (Ia) dehydrates to give 1-methyl-3-methylenecyclohexene (IIa), and not 1,3-dimethylcyclohexadiene (IIIa). The structure follows from the fact that



the hydrocarbon had λ_{\max} 232 m μ , ϵ , 9,500. A dimethylcyclohexadiene would have λ_{\max} 265, ϵ , 5,000 [α -phellandrene has λ_{\max} 263, ϵ , 2,500 (2)], whereas a 3-methylenecyclohexene would absorb at 232 m μ [β -phellandrene has λ_{\max} 232 m μ , ϵ , 9,200 (2)]. It has generally been assumed that tertiary allylic alcohols similar to (I) will undergo endocyclic dehydration to a cyclohexadiene, but the above result suggested that this may not be so, and further examples were investigated.

Isophorone was reacted with methylmagnesium iodide and the resulting carbinol (Ib) was dehydrated by distillation from potassium bisulfate. The diene had λ_{max} 235 m μ , ϵ , 10,500 and showed no maximum at 260 m μ . This is in agreement with structure (IIb). Moreover, ozonolysis gave formaldehyde, showing the presence of a methylene group. A maleic anhydride adduct could not be obtained under normal conditions, and formation of an adduct from structure (IIb) would be contrary to Bredt's rule (3). The product must, therefore, be 1,5,5-trimethyl-3-methylenecyclohexene (IIb). Kharasch and Tawney (4) obtained a hydrocarbon by these reactions which they formulated as 1,3,5,5tetramethylcyclohexadiene, and from which they obtained a maleic anhydride adduct. When the present product was reacted with maleic anhydride in benzene in the presence of sulfuric acid (5) an adduct was obtained apparently identical with the acid adduct of these workers.

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Carvone (IV) was similarly reacted with the methyl Grignard reagent and



the intermediate carbinol was dehydrated to a hydrocarbon with λ_{max} 234 m μ , ϵ , 9,500. Such absorption can only be given by 2-methyl-3-methylene-5-isopropenylcyclohexene (V), and again exocyclic dehydration has occurred. Rupe and Liechtenhan (6) had previously carried out this reaction, but were uncertain of the structure of the product.

2-Methylcycloheptenone (VI) was prepared by the selenium dioxide oxidation of methylcycloheptene. The product had λ_{max} 233 m μ , the expected wavelength for a monoalkylated cycloheptenone (7). Its semicarbazone was identical with that of the ketone obtained by reacting cycloheptanedione with methylmagnesium iodide. Thus oxidation of methylcycloheptene takes place at the



allylic position adjacent to the methyl group, as does the oxidation of methylcyclopentene (8) and methylcyclohexene (9). The 2-methylcycloheptenone was reacted with methylmagnesium iodide and the product had λ_{max} 235 m μ , ϵ , 13,000. Thus again exocyclic dehydration has occurred, giving compound VII.

A search of the literature showed that similar reactions had been reported. Heilbron, Spring, and Bann (10) reacted 7-ketocholestene-5 with methylmagnesium bromide and obtained the hydrocarbon 7-methylenecholestene-5, and Weinhouse and Kharasch (11) found the same reaction to take place with 3-acetoxy-7-ketochloestene-5. Recently Musgrave (12) found that 4-cholesten-3-one gave 3-methylenecholestene-4 in a similar reaction. These results suggest that dehydration of compounds of the type (I) to compounds of type (II), and not of type (III), is a general phenomenon.

In view of this fact, the structures of a number of dienes, obtained by dehydration of cyclic allylic alcohols, probably have been incorrectly formulated in the literature. Haworth (13) reacted 2- and 3-methylcyclohexenone with methylmagnesium iodide and considered the products to be cyclohexadienes, and this, as shown above, is incorrect. Also, Downes, Gill, and Lions (14) carried out the same reaction on 3,4,6-trimethylcyclohexenone, and obtained a supposed tetramethylcyclohexadiene, which gave only a gummy maleic anhydride adduct, but the product is most probably the methylenecyclohexene. Similarly, Galloway, Dewar, and Reed (15) carried out this reaction with cryptone (4-isopropylcyclohexenone) and considered the product to be the cyclohexadiene, α -phellandrene. Their evidence, however, would support the formation of β -phellandrene, the more probable product.

The explanation for this mode of dehydration must be that, while for simple 1-alkylcyclohexanols endocyclic dehydration is preferred, since a double bond is more stable inside a cyclohexane ring (16), in the cases reviewed above the 1-alkylidenecyclohexene-2 (VIII) will be the more stable product, since it has a higher resonance energy than the cyclohexadiene (IX). Moreover the cyclohexadiene (IX).



hexadiene ring is a highly strained structure (17), whereas the strain in VIII is reduced by the bending of carbon atom 5 out of the plane of the ring.

EXPERIMENTAL

Grignard reaction on isophorone. Isophorone (13.8 g.) in ether (50 ml.) was added at 0° with stirring during $\frac{1}{2}$ hour to a Grignard solution prepared from methyl iodide (14.2 g.) and magnesium (2.4 g.) in ether (100 ml.). After stirring at room temperature for $\frac{1}{2}$ hour the reaction was worked up in the usual manner with aqueous ammonium chloride solution. The residue left after removal of the solvent was distilled from potassium bisulfate under reduced pressure (100 mm.) at a bath temperature 120–130°. The distillate was dried with sodium sulfate and redistilled giving the hydrocarbon (6.5 g.), b.p. 98–100°/200 mm., n_{z}^{20} 1.4705. Light absorption: λ_{max} 235 m μ , ϵ , 10,500, in purified 95% ethanol. No product of 1:4 addition was detected.

The hydrocarbon (1.36 g.) and maleic anhydride (0.90 g.) in benzene (2 ml.) containing 1 drop of concentrated sulfuric acid was allowed to stand at room temperature for 2 hrs. The precipitate (150 mg.) was recrystallized from aqueous methanol to m.p. 155°. Karasch and Tawney (4) give m.p. $154-155^{\circ}$.

Anal. Calc'd for C₁₄H₂₀O₄: C, 66.6; H, 8.0.

Found: C, 66.5; H, 8.0.

No adduct was formed in refluxing benzene solution in the absence of acid.

The hydrocarbon (1.2 g.) in ethyl acetate (20 ml.) was cooled in an ice-salt bath and ozonized oxygen was passed in for 30 minutes. The exit gases were passed through two bottles containing 5% methone in 10% ethanol-water. These solutions then were heated to boiling and were allowed to stand at room temperature overnight. The precipitate, m.p. 191°, 1.53 g. corresponded to a 60%, yield of formaldehyde. [Horning and Horning (18) give m.p. 191-191.5° for this derivative.]

Grignard reaction on carvone. Carvone (5.0 g.) in ether (30 ml.) was reacted with an ether solution of methylmagnesium iodide [from methyl iodide (5.3 g.) and magnesium (0.9 g.) in ether (40 ml.)] as above. The product (3.0 g.; 60%) had b.p. $81-83^{\circ}/18 \text{ mm.}, n_{p}^{20}$ 1.4975. Light absorption: λ_{max} 234 m μ , ϵ , 9,500. The product gave no precipitate with 2,4-dinitrophenylhydrazine solution and only polymeric resins with maleic anhydride in boiling benzene.

Methylcycloheptene. Cycloheptanone (12 g.) in ether (100 ml.) was reacted with excess methylmagnesium iodide solution in the usual manner and the crude carbinol product was dehydrated by distillation from iodine. The hydrocarbon (6.5 g.; 60%) had b.p. 92-98°/580 mm., n_p^{27} 1.4540. Ruzicka and Seidel (19) give b.p. 133.5°/720 mm., n_p^{22} 1.4575.

2. Methylcycloheptenone. A. 2-Methylcycloheptene (5.5 g.) in water (50 ml.) and purified dioxane (30 ml.) was stirred under reflux and selenium dioxide (7.9 g.) in hot water (20 ml.) was added over $\frac{1}{4}$ hr. The solution was stirred and refluxed for a further $\frac{1}{2}$ hours. The upper layer was decanted, poured into ice-water, and extracted with ether. The ethereal solution was washed with water, dried, and the solvent was removed. The residue was distilled giving the ketone (3.0 g.; 50%), b.p. 85-88°/20 mm., $n_{\rm p}^{25}$ 1.4938. Light absorption: $\lambda_{\rm max}$ 233 m μ , ϵ , 11,900.

A semicarbazide was prepared in the usual manner and had m.p. 202°, from ethanol.

Anal. Cale'd for $C_{9}H_{15}N_{3}O: C$, 59.7; H, 8.35; N, 23.2.

Found: C, 59.6; H, 8.5; N, 23.4.

2-Methylcycloheptenone. B. Cycloheptanedione, prepared by the selenium dioxide oxidation of cycloheptanone, was reacted with methylmagnesium iodide in the usual manner. The crude product, b.p. 86-90°/22 mm., $n_{\rm p}^{25}$ 1.4930, was converted to the *semicarbazone* (40%), m.p. 202°, from ethanol, undepressed by admixture with the semicarbazone above.

Grignard reaction on 2-methylcycloheptenone. 2-Methylcycloheptenone (2.2 g.) in ether (20 ml.) was reacted with excess methylmagnesium iodide [from methyl iodide (2.7 g.) and magnesium (0.45 g.)] in ether (30 ml.), as before. The product (1.2 g.; 55%), b.p. 80-82°/20 mm., n_{2}^{25} 1.4948, gave no precipitate with 2,4-dinitrophenylhydrazine reagent and no solid adduct with maleic anhydride in benzene. Light absorption: λ_{max} , 235 m μ , ϵ , 13,000.

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SUMMARY

It has been found that 1-alkylcycloalk-2-enols dehydrate, not to alkylcycloalkadienes, as has generally been assumed, but to the isomeric alkylidenecycloalk-2-enes.

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