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CLEAVAGE OF COMPOUNDS RELATED TO 6-PHENYLBICYCLO(3,1,0)-HEXAN-2-ONE IN PRESENCE OF HYDROGEN CHLORIDE.

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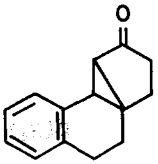
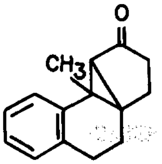
In connection with our programme devoted to the syntheses[1] of tricarbocyclic resin acids and related diterpenoids it became of our interest to undertake systematic investigation on the cleavage of suitably substituted phenylbicyclo(3,1,0)hexan-2-one systems under different conditions. Current interest in the syntheses[2,3] of such systems and recent findings on the mode of reductive opening[4,5] of conjugated cyclopropyl ketones prompted us to report here our initial results obtained on the hydrogen chloride induced cleavage of two model compounds I and II.

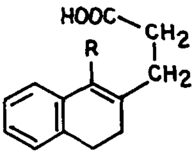
Syntheses of I and II were achieved through the general method[6] of internal addition of α-keto-carbene to a double bond. The diazoketones derived from β-(3,4-dihydro-2-naphthyl)-propionic acid[7] (IIIa) and the corresponding 1-methyl derivative IIIb (vide infra) were subjected to copper bronze catalysed ring-closure leading to the formation of 3,4-benztricyclo(5,3,$0^{1,7}$, $0^{2,7}$)decan-10-one (I) (23% yield), m.p. 130-131°, λ_{max}^{EtOH}235 mμ (log ε 4.07), $\nu_{max}^{CHCl_3}$ 1718 cm^{-1}, and 2-methyl-3,4-benztricyclo(5,3,$0^{1,7}$, $0^{2,7}$)decan-10-one II (40% yield), m.p. 89-90°. The latter was prepared earlier through a photolytic reaction[3] and its physical properties, λ_{max}^{EtOH} 240 mμ (log ε 4.01), $\gamma_{max}^{CHCl_3}$ 1712 cm^{-1} agreed well with the data recorded[3a] in the literature.



I

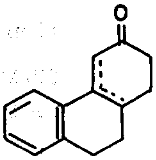


II

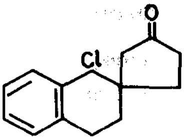


III a, R = H

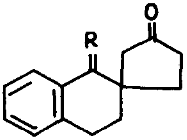
b, R = CH_3



IV

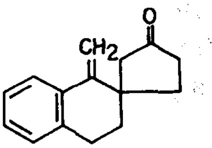


V

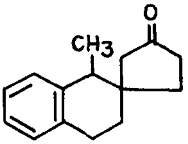


VI a, R = H_2

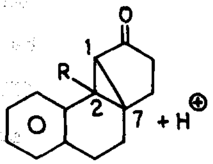
b, R = O



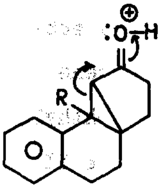
VII



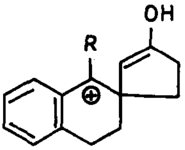
VIII



a



b



c

It has been reported[4] that a cyclopropane ring of a conjugated cyclopropyl ketone as a part of a bicyclo(3,1,0)hexane reacts differently to the reagents (a) lithium in liquid ammonia and (b) acids. While the lithium-liquid ammonia reduction cleaves[4,8] that bond of the cyclopropane ring possessing the maximum of orbital overap with the π system of the carbonyl group, the acid catalysed opening does not necessarily involve the same bond. Again, lumicholestenone and dihydrolumisantonin, although possessing a common bicyclo(3,1,0)hexanone moiety, upon treatment with acid cleave differently, the former undergoing a six[9] membered ring opening and the latter a five[10] membered one.

In view of the above findings our attention was directed to 6-phenylbicyclo(3,1,0)hexanone systems (as in I and II) in order to find out whether or not the compound I under the action of dry hydrogen chloride in chloroform would give rise to the formation of an unsaturated ketone (IV) and to compare the result with that of the lithium-ammonia reduction. The product obtained on acidic cleavage has now been characterised, through spectral studies and the synthesis[11] of a derivative VIa (vide infra), as a spiro chloro ketone V (90% yield), m.p. 114-115°, λ^{EtOH}_{max} 268 mμ (log ϵ 2.89), $\nu^{CHCl_3}_{max}$ 1740 cm^{-1} (cyclopentanone). The NMR spectral data revealed a characteristic signal at τ 5.06 (singlet) due to the single benzylic proton at the carbon atom bearing the chlorine residue. Catalytic reduction of V with 10% Pd/C in ethanol as well as the lithium in liquid ammonia reduction of I resulted in the formation of the cyclopentanone derivative VIa (above 90% yield), b.p. 125-126° (bath temp.)/0.2 mm., λ^{EtOH}_{max} 250 mμ (log ϵ 2.78), 266 mμ (log 2.84), 274 mμ (log ϵ 2.87), $\nu^{CHCl_3}_{max}$ 1740 cm^{-1}; semicarbazone m.p. 209-210°, melting point on admixture with the derivative of an authentic sample of VIa (synthesis vide infra) was found to be undepressed. Similarly the compound II on treatment with hydrogen chloride furnished the olefinic spiro cyclopentanone derivative VII (90%), b.p. 140° (bath temp.)

/0.25 mm., λ^{EtOH}_{max} 250 mμ (log ϵ 4.1), ν_{max} 1740 cm^{-1} (cyclopentanone), 1628 cm^{-1}; yellow 2,4-dinitrophenylhydrazone m.p. 203-204°. The same compound VII was previously obtained by Chapman et al[12] through a photolysis of II; and our spectral data are in accord with the reported values[3b]. Catalytic reduction of VII in presence of 10% Pd/C gave the saturated ketone VIII, b.p. 142° (bath temp.)/0.3 mm., ν_{max} 1738 cm^{-1}, which again was derived through the lithium in liquid ammonia reduction of II; yellow 2,4-dinitrophenylhydrazone m.p. 201-202° (mixture melting point undepressed). The rest of the compounds were synthesised in the following manner.

Treatment of β-(1-Oxo-1,2,3,4-tetrahydro-2-naphthyl)-propionic acid[13] with methylmagnesium iodide afforded the unsaturated acid IIIb (55% yield), m.p. 97-98°, λ^{EtOH}_{max} 265 mμ (log ϵ 4.15), τ 7.92 singlet (methyl attached to $Ph - C = C\langle$). Ethyl (1-Oxo-1,2,3,4-tetrahydro-2-naphthyl)-acetate on treatment with ethyl acrylate in presence of sodium ethoxide followed by hydrolysis and decarboxylation led to the formation of the diketone VIb (52% yield), b.p. 147-148° (bath temp.)/0.2 mm., λ^{EtOH}_{max} 252 mμ (log ϵ 4.02), $Y^{CHCl_3}_{max}$ 1740 cm^{-1}, 1670 cm^{-1} and 1600 cm^{-1}, evidently through a simultaneous Michael and Dieckman reaction. This was catalytically reduced in presence of perchloric acid to VIa (vide supra) in good yield.

As to the mechanism of the present cleavage reaction, it appears that the primary protonation step is followed by the preferential breaking of the $C_1 - C_2$ bond (stage b) so as to give rise to a benzyl carbonium ion (stage c) which either captures a chloride ion or generates a double bond. The cleavage of the same bond (vide supra) during the lithium-liquid ammonia reduction, however, is solely due to the known stereoelectronic factors[4,8] mentioned earlier. This is evident following constructions of Drieding models for I and II. That the greater tendency for a facile formation of a carbonium ion at the benzylic position is the guiding factor in determining the particular cyclopropane bond that breaks under the action of hydrogen chloride has been found to be true by extending our present studies to various analogues of I and II and 5-phenylbicyclo-(3,1,0)hexan-2-one systems also. Work is in progress to utilise our results for the construction of fused ring systems related to steroids and diterpenoids. The details will be published later.

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