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Abstract

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DEHYDRATION OF CYCLOALIPHATIC α-KETOLS OF THE CYCLOHEXANE AND Δ^3-CYCLOHEXENE SERIES

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In studying transformations of various types of compounds containing a cyclohexane, Δ^1- or Δ^3-cyclohexene ring, we have repeatedly noted a substantial difference in their behavior. Compounds of the Δ^1- and Δ^3-cyclohexene series possess many distinctive features absent in the corresponding compounds of the cyclohexane series ([1], [2]). In further development of the studies carried out earlier, it was of interest to examine the behavior of α-ketols of types I—III and X—XIII under dehydration conditions, in order to establish the influence on this process of the Δ^3 double bond and of substituents located in the ring.

The starting ketols X—XIII were obtained in high yield by hydration of the corresponding acetylenic alcohols ([1], [2]), whereas subsequent hydrogenation of these ketols made it possible to pass readily to the corresponding compounds I—III.

As a result of dehydration of the α-ketols of the cyclohexane series I—III with P_2O_5 in toluene (boiling for 2 hours), vinyl ketones IV—VI are formed; the presence in them of the α,β-unsaturated ketone grouping was demonstrated by studying the ultraviolet absorption spectra of their 2,4-dinitrophenylhydrazones. At the same time, catalytic hydrogenation of ketone IV gave the ketone VII known in the literature ([3]), while hydrogenation of ketones V and VI led to ketones VIII—IX. These same ketones VII—IX were obtained by one of us (together with V. Vidugirene) by another route, namely by oxidation of the corresponding unsaturated secondary alcohols with chromic anhydride. It is evident that, in the formation of ketones IV—VI, the dehydration process is preceded by isomerization of the α-ketol grouping in the starting compounds I—III ($RCHOHCOCH_3 \rightarrow RCOCHOHCH_3$), and the final result does not depend on the position of the substituents in the cyclohexane ring.

An entirely different picture is observed in the case of α-ketols with a Δ^3-cyclohexene ring X—XIII, where the direction of the dehydration process is determined by the presence and position of methyl groups in the ring. Of these α-ketols, only compound XI, having a methyl group in position 2, is dehydrated analogously to α-ketols I—III, forming (best of all in the presence of *n*-toluenesulfonic acid) vinyl ketone XIV, hydrogenation of which gives ketone VIII. The presence in ketone XIV of only one double bond conjugated with the carbonyl group was confirmed by studying the ultraviolet absorption spectrum of its 2,4-dinitrophenylhydrazone. On the other hand, ketone XIV was later synthesized by one of us (together with V. Vidugirene) by oxidation of the corresponding acetylenic secondary alcohol followed by hydrogenation of the triple bond in the presence of Lindlar catalyst (4). As for α-ketol X, which has no methyl group in the ring, its dehydration with $KHSO_4$ at 160–210° and under slight vacuum led to formation of the previously known ketone XV (5), containing two double bonds conjugated with the carbonyl group. Catalytic hydrogenation of this ketone gave ketone VII.

Table 1

No.	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Calculated, % C	Calculated, % H	2,4-Dinitrophenylhydrazones m.p., °C	2,4-Dinitrophenylhydrazones found, % C	2,4-Dinitrophenylhydrazones found, % H	2,4-Dinitrophenylhydrazones calculated, % C	2,4-Dinitrophenylhydrazones calculated, % H	UV spectra λ_{max}, mμ
I	90	75–76/2	1.4726	1.0161	69.30	10.45	69.19	10.32						
II	89	88–89/3	1.4726	0.9940	70.89	10.80	70.55	10.66						
III		110–111/7	1.4690	0.9958	70.57	10.69	70.55	10.66						
IV	20	93–94/12	1.4870		78.10	10.03	78.25	10.14	205–206	56.42	5.68	56.60	5.70	378
V									164–165	58.10	6.10	57.83	6.03	378
VI									196–197	57.62	6.23	57.83	6.03	379
VII									150–151	56.35	6.44	56.25	6.29	363
VIII		90–92/12	1.4650	0.9268	78.05	11.99	77.87	11.76	93–94	57.28	6.46	57.48	6.58	363

No.	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Calculated, % C	Calculated, % H	2,4-Dinitrophenylhydrazones m.p., °C	2,4-Dinitrophenylhydrazones found, % C	2,4-Dinitrophenylhydrazones found, % H	2,4-Dinitrophenylhydrazones calculated, % C	2,4-Dinitrophenylhydrazones calculated, % H	2,4-Dinitrophenylhydrazones UV spectra λ_{max}, mμ
IX									114–115	57.46	6.75	57.48	6.58	
XIV									201–202	57.94	5.85	58.18	5.49	378
XVI	5	74–76/3	1.5100	0.9720	79.74	9.52	79.95	9.39	128–129	58.28	5.55	58.18	5.49	388
XVII*									159–160	55.13	5.59	55.17	5.79	361
XVII									188–190	59.00	4.60	58.90	4.30	380–382
XVIII	48	59–60/2	1.4890	1.0067	79.78	9.45	79.95	9.38	183–184	57.92	5.50	58.18	5.49	363
XIX									122–123	58.11	5.81	57.83	6.03	
XX	91	97–98/14	1.4800	0.9823	78.85	10.40	78.89	10.59	187–188	57.86	5.86	57.83	6.03	
XXI	85	83–85/4	1.5070	1.0147	81.64	9.04	81.77	9.15						
XXII	81	81–83/4	1.5000	0.9870	80.74	10.04	80.90	10.10						
XXIII	64	60–62/4	1.5020	0.9240	89.74	10.04	90.00	10.00						

* The 2,4-dinitrophenylhydrazone contains one molecule of water.

Dehydration of ketol XIII, which has a methyl group in position 6, proceeds differently. In contrast to the preceding cases, on heating with $KHSO_4$ at 160–

reaction scheme

Figure 1: reaction scheme

210° under a slight vacuum, two ketones were obtained—XVIII (yield about 30%) and XVI (yield about 5%). The structure of the latter compound was proved by studying the UV absorption spectrum of its 2,4-dinitrophenylhydrazone and the IR spectrum of the ketone itself (an absorption band at 1660 cm^{-1} characterizes the presence of a carbonyl group conjugated with two double bonds (^{5}), and a band at 1560 cm^{-1} indicates the presence of double bonds). In addition, catalytic hydrogenation of ketone XVI gave compound VIII. It should be emphasized that upon dehydration of ketol XII with $KHSO_4$ the corresponding dienone of type XV-XVI is not formed at all (it was not detected among the reaction products even spectrographically). In this case only the bicyclic ketone XVII, analogous to XVIII, is obtained.

I, IV, VII, X, XV: R_1=R_2=R_3=H; III, VI, IX, XII, XVII, XVIIa, XIX: R_1=R_3=H; R_2=CH_3
II, V, VIII, XI, XIV: R_2=R_3=H; R_1=CH_3; XIII, XVI, XVIII, XVIIIa, XX: R_1=R_2=H; R_3=CH_3

The structure of ketones XVII and XVIII was proved as follows. It was established from the UV absorption spectra of their 2,4-dinitrophenylhydrazones that the carbonyl group is not conjugated with the double bond. In the IR spectra of these ketones there is a strong absorption band in the region of 1745 cm^{-1}, which could be assigned to a ketone group located in a five-membered ring (^{7}). Even under vigorous catalytic hydrogenation both ketones add only 1 mole of hydrogen. The presence of a five-membered ring in the bicyclic ketone XVIII was confirmed by its reduction by the Kishner method followed by aromatization over Pd/C, as a result of which the literature-known 5-methylindane (^{8}) was obtained; this was then oxidized with 10% HNO_3 to 1,2,4-benzenetricarboxylic acid, characterized in the form of its anhydride (^{8}). To determine the position of the carbonyl group in ketones XVII-XVIII, the first of them was aromatized with 10% palladized charcoal, after which 2,4-dinitrophenylhydrazone of 5-methylindanone XVIIb was isolated from the reaction products; judging from its UV spectrum (λmax 380-382 mμ), in this compound the carbonyl group is conjugated with the aromatic ring. Hence the structure of the ketones under consideration could correspond to formulas XVII-XVIII or XVIIa-XVIIIa. To resolve the latter

these ketones were first oxidized with KOJ and then dehydrogenated with Pd/C to the corresponding aromatic compounds, oxidation of which with HNO_3 in both cases gave only *m*-phthalic acid.

$$\mathrm{XVII} \xrightarrow[\substack{2.\ \mathrm{Pd/C}(340\text{–}350^\circ)\\ 3.\ 10\%\ \mathrm{HNO_3}(180^\circ)}]{1.\ \mathrm{KOJ(NaOH,\ CH_3OH)}} \mathrm{HOOC{-}C_6H_4{-}COOH} \xleftarrow[\substack{2.\ \mathrm{Pd/C}(340\text{–}350^\circ)\\ 3.\ 10\%\ \mathrm{HNO_3}(180^\circ)}]{1.\ \mathrm{KOJ(NaOH,\ CH_3OH)}} \mathrm{XVIII}$$

It follows from this fact that the ketones obtained have structures XVII–XVIII, since, if formulas XVIIa–XVIIIa corresponded to them, successive oxidation, aromatization, and repeated oxidation should have led respectively to *p*-phthalic and *o*-phthalic acids.

It should be noted that ketone XVII was converted by us in good yield into triene XXIII according to the scheme:

$$\mathrm{XVII} \xrightarrow[\mathrm{Na,\ liquid\ NH_3}]{\mathrm{CH{\equiv}CH}} \mathrm{XXI} \xrightarrow{\mathrm{H_2/Pd}} \mathrm{XXII} \xrightarrow{\mathrm{KHSO_4}} \mathrm{XXIII}$$

The presence in hydrocarbon XXIII of one isolated and two conjugated double bonds was confirmed by the Raman-spectrum data for this compound—two lines were found, one with frequency 1666 cm^{-1} and integral intensity of about 30 units and the second with frequency 1636 cm^{-1} and integral intensity of 300 units ([9]). The properties of the compounds obtained are given in Table 1.

From a comparison of the results of dehydration of α-ketols of the cyclohexane and Δ^3-cyclohexene series, it follows that in both cases isomerization of the α-ketol grouping first occurs, and then the corresponding vinyl ketones are formed. However, in the case of α-ketols of the Δ^3-cyclohexene series, this reaction is in most cases accompanied by other transformations. Thus, if the methyl group is absent in the cyclohexene ring (ketol X), additional isomerization of the cyclic double bond from the Δ^3 position to Δ^1 occurs, with formation of dienone (XV). When a methyl group is present in position 6 (ketol XIII) of the cyclohexene ring, the process of cyclization predominates over the process of double-bond isomerization, leading to the predominant formation of bicyclic ketone XVIII. If the methyl group is located in the cyclohexene ring in position 4 (ketol XII), then only bicyclic ketone XVII is obtained. But the presence of a methyl group in position 2 (ketol XI) hinders both the isomerization of the double bond and the cyclization process, owing to which the reaction stops (analogously to α-ketols of the cyclohexane series) at the stage of formation of vinyl ketone XIV. The described difference in the behavior of α-ketols of the Δ^3-cyclohexene series is evidently due not only to structural factors but also to steric features of the cyclohexene ring.

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Note: Figure translations are in progress. See original paper for figures.