CYCLIC UNSATURATED COMPOUNDS COMMUNICATION 52. SYNTHESIS, CONFIGURATION, AND DEHYDRATION OF 2.2- AND 5.5-DIMETHYL-1.3-CYCLOHEXANEDIOLS*

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5,5-Dimethyl-1,3-cyclohexadiene (I) served as one of the objects when studying the thermal transformations of substituted cyclohexadienes [2]. The present communication is devoted to the development of a synthesis method for this hydrocarbon.

Diene (I) was obtained for the first time from dimedon (II) by successive treatment with PCl_5 and Na (45% yield) [3, 4], but the purity of (I) was not determined. Later [5] diene (I) was synthesized in three steps in a yield of 43% from 4,4-dimethylcyclohexene, which is quite difficultly accessible [6].

As a potential intermediate in the synthesis of diene (I) it is possible to consider the previously unknown 5,5-dimethyl-1,3-cyclohexanediol (III) (cf. [7]):



It is possible to assume that 3,3-dimethyl-1,4-cyclohexadiene (V) can be obtained by the dehydration of 2,2-dimethyl-1,3-cyclohexanediol (VII).

Previously the catalytic hydrogenation of dimedon (II) had been studied repeatedly [8-11]. It was found that 3,3-dimethyl-1-cyclohexanol is formed when the hydrogenation is run in aqueous medium in the presence of Pt catalysts [9]. Besides the 3,3-dimethylcyclohexanol, $\sim 10\%$ of dimethylcyclohexane is formed when the hydrogenation is run in alcohol [10], dioxane, ether, or CH₃COOH [8]. In the presence of skeletal Ni in alcohol solution, at 180°C and 100 atm [11], the main reaction product is also the dimethylcyclohexanol. \dagger

*See [1] for Communication 51.

[†]In [11] the theory was expressed that the by-product of the given reaction, which is formed in very low yield, has the structure of 5,5-dimethyl-1,3-cyclohexanediol (III). However, a comparison of the data given in [11] (mp 146°) with the experimental data given below discloses that this theory is wrong.

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In the present paper we were able to select conditions for the hydrogenation of diketones (II) and (VI)* that made it possible to obtain diols (III) and (VII) in a respective yield of 94 and 91%. The hydrogenation was run over skeletal Ni in methanol at 80° and 150 atm. Diols (III) and (VII) were converted to diacetates (IV) and (VIII) by treatment with CH_3COCl in the presence of diethylaniline (in a respective yield of 81 and 92%).

The structure and stereochemistry of diols (III) and (VII) and of their diacetates (IV) and (VIII) were established on the basis of the IR and NMR spectra. Based on the data of the IR spectra, the compounds contain a gem-dimethyl grouping (double bond in the 1370-1380 cm⁻¹ region). The intense bands of hydroxyl groups, attached by strong intermolecular hydrogen bonds (~ 3300 cm⁻¹ in the crystal), are present in the IR spectra of diols (III) and (VII). The presence of two hydroxyl groups in compounds (III) and (VII) is corroborated by the fact that during acetylation they respectively form diacetates (IV) and (VIII) [(IV) $\nu_{C=O}$ 1735; (VIII) $\nu_{C=O}$ 1745 cm⁻¹].

The NMR spectra of diacetates (IV) and (VIII) are in good agreement with the structure adopted for them. Thus, in their NMR spectra are present a singlet signal, corresponding to the two acetyl groups [(IV) δ 1.92; (VIII) δ 1.87 ppm], and also signals from the two CH₃ groups [(IV) δ 0.98 (singlet); (VIII) δ 0.82 and 0.88 ppm].

The data of the IR and NMR spectra for diols (III) and (VII), and also for their diacetates (IV) and (VIII), also make it possible to establish their configuration and conformation (cf. [14-16]). It is known that in a six-membered ring the $\nu_{\rm C-O}$ vibration frequency of the hydroxyl group, having an equatorial conformation (1020-1045 cm⁻¹), is noticeably higher than the analogous vibration frequency of the axial hydroxyl (990-1020 cm⁻¹).[†] One band at 1031 cm⁻¹ is present in the indicated region in the IR spectrum of diol (III), which corresponds to the absorption of an equatorial hydroxyl group. At the same time, two bands, at 987 and 1018 cm⁻¹, are present in the discussed region in the IR spectrum of diol (VIII), which can respectively be assigned to the vibrations of the axial and equatorial hydroxyl groups.

In support of the e,e-conformation (and correspondingly of the cis-configuration) of diol (III) is also the absence of an intramolecular hydrogen bond in the compound, which is incapable of being realized in the given conformation. At the same time, a band that is characteristic for a hydroxyl group that takes part in the formation of an intramolecular hydrogen bond \ddagger (3500-3510 cm⁻¹) was detected in the IR spectrum of diol (VII), which is in agreement with an e,a-conformation (trans-configuration) of the compound.

It is known [15, 16, 18] that the $\nu_{\rm C-O}$ vibration frequencies in the IR spectra of the equatorial and axial acetoxy groups in the 1000-1040 cm⁻¹ region obey the same rules as hold in the spectra of the hydroxyl-containing compounds.** Thus, the sole $\nu_{\rm C-O}$ frequency in this region at 1031 cm⁻¹ in the spectrum of diacetate (IV) evidently corresponds to an equatorial acetoxy group. At the same time, two bands are present in the given region in the spectrum of diacetate (VIII), with frequencies that are characteristic for equatorial (1031 cm⁻¹) and axial (1007 cm⁻¹) acetoxy groups.

In the NMR spectrum of diacetate (IV) the protons at the C atoms, substituted by acetoxy groups, appear as a symmetrical quintet with a center at δ 5.01 ppm; this makes it possible to assume that the given protons are equivalent or, in other words, are arranged in the same manner with respect to the adjacent methylene groups. In the NMR spectrum of diacetate (VIII) the protons in a similar position form a complex multiplet in the δ 4.4 ppm region, which testifies to their nonequivalence.

As a result, a combination of the data indicates that diol (III) and its diacetate (IV) have a cis-configuration and exist preferably in an e,e-conformation, whereas diol (VII) and its diacetate (VIII) have a trans-configuration (e, a-conformation).

 $\overline{*2,2-Dimethyl-1,3-cyclohexanedione}$ (VI) was obtained in 68% yield by the methylation of 2-methyl-1,3cyclohexanedione (IX) as described in [12]. Diketone (IX) was obtained from resorcinol in 47% yield under conditions comparable to those described in [13].

[†]The region ν_{O-H} 3600 cm⁻¹ for the unbound hydroxyl [for (III) and (VII) 3610 cm⁻¹ in 0.005 M CCl₄ solution] is less characteristic in the given respect [17]. It is known that the shape of the discussed band of the equatorial and axial hydroxyl differs (symmetrical in the first case and unsymmetrical in the second case). In our case the indicated band is symmetrical in the spectrum of diol (III) and less symmetrical in the spectrum of diol (VII).

[‡]The frequency of a free hydroxyl of medium strength is also present in the spectrum (see above). **The 1240 cm⁻¹ ν_{C-O} region is less characteristic in this respect, and in the given case the IR spectrum of diacetate (IV) contains one band at 1237 cm⁻¹ in the indicated region (complex structure), whereas the spectrum of diacetate (VIII) contains, besides the indicated band, an additional band at 1220 cm⁻¹. It should be mentioned that the hydrogenation of the diketones is accomplished stereoselectively and one of the steric isomers is formed in high yield as a reaction result.

Diols (III) and (VII) were dehydrated by distillation with phthalic anhydride. Here a mixture of hydrocarbons was obtained from diol (III) in 50% yield, which, based on the GLC data, contained 84% of 5,5-dimethyl-1,3-cyclohexadiene (I), 8% of 3,3-dimethyl-1-cyclohexene (X), and 8% of 4,4-dimethyl-1-cyclohexene (XI). The pure diene (I) (the purity was at least 99.5%) was isolated from the mixture by distillation through a column (~ 100 theoretical plates). The structure of diene (I) was confirmed on the basis of the NMR spectrum, which shows the presence of a gem-dimethyl grouping (δ 0.88 ppm, singlet, 6H), a methylene group (δ 1.97 ppm, quadruplet, 2H), and four protons at the double bond.

The corresponding adduct, the anhydride of 7,7-dimethylbicyclo[2.2.2]-2-octene-5,6-dicarboxylic acid (XII), was obtained in 69% yield when diene (I) was refluxed with maleic anhydride in ether. Only one steric isomer is formed selectively as a reaction result, which follows from the identity in the IR spectra of the crude substance and the pure compound (XII). It is possible to assume that the given isomer has an endo-configuration of the anhydride ring. The structure of anhydride (XII) was established on the basis of its IR and NMR spectra [presence of an unsubstituted double bond; IR spectrum: 1620 (v.w, C=C), 3050 (m = C-H) cm⁻¹; NMR spectrum: δ 6.24 (doublet of quadruplets, 2H, =C-H) ppm], and two methyl groups at one C atom of the bridge [NMR spectrum: δ 0.85 (singlet, 3H) and 1.03 (singlet, 3H) ppm]. The structure of adduct (XII) once more corroborates the validity of establishing the structure of the starting diene (I).

The fractional distillation of the mixed dehydration products of diol (III) gave olefins (X) and (XI) as 70-80% concentrates. The mentioned compounds were purified by preparative GLC. The structure of compounds (X) and (XI) was established from an examination of the UV, IR, NMR, and mass spectra. Based on the data of the UV spectrum, a conjugated diene system is absent (absence of the characteristic absorption maximum) in compounds (X) and (XI). A total of one band is present in the IR spectra in the $\nu_{C=C}$ region, which is characteristic for a single unsubstituted double bond in a cyclohexene ring [(X) 1620; (XI) 1625 cm⁻¹]. In addition, a doublet band appears in the IR spectra of the discussed compounds in the 1370-1380 cm⁻¹ region, which shows the presence of a gem-dimethyl grouping. Signals are present in the NMR spectra of these compounds from the two methyl groups at one C atom [(X) δ 0.96 (singlet, 6H); (XI) δ 0.98 ppm (singlet, 6H)], three methylene groups, and two protons at a double bond [(X) δ 5.50 (multiplet, 2H); (XI) δ 5.65 ppm (multiplet, 2H)]. Of the two possible structures for gem-dimethylcyclohexene:



the data of the NMR spectrum make it possible to assign the structure of (X) to the compound with the lower boiling point [and correspondingly the structure of (XI) for the higher boiling compound]. Thus, a shift of the signal from the protons of the CH_3 groups downfield in compound (X) [when compared with the position of the same signal in the spectrum of compound (XI)] can be associated with the effect of the adjacent double bond. Besides this, the multiplet from =C-H in the NMR spectrum of compound (XI) is much broader, which is caused by the appearance of additional couplings with the adjacent methylene group [there is one such group in structure (X), and two in structure (XI)]. The structure of compounds (X) and (XI) was additionally confirmed by counter synthesis: a mixture of the mentioned olefins in a respective ratio of 1:2.9 was obtained in 67% yield by the reduction of diene (I) with potassium in tert-amyl alcohol.

The dehydration of diol (VII) under the conditions described above for diol (III) led in low yield (~20%) to a complex mixture of products, which, based on the GLC data, contained at least 13 components, of which the principal ones are toluene and the m- and p-xylenes. In the obtained mixture the C_8 dienes are present in amounts less than 10-15%. Based on the data of the IR spectrum, certain amounts of unsaturated ketones and hydroxyl-containing compounds are also present in the mixture. Consequently, the dehydration of diol (VII) cannot serve as a method for the synthesis of 3,3-dimethyl-1,4-cyclohexadiene (V).

EXPERIMENTAL METHOD

The IR spectra were obtained on a UR-10 spectrometer [(III), (VII), and (VIII) as KBr pellets, (I) and (IV) as a thin layer, and (III) and (VII) as a 0.005 M solution in CCl_4]. The Raman spectra were obtained by the photographic method on an ISP-51 spectrograph, and the intensities of the lines were read on a visual ten-point scale. The NMR spectra were obtained on a Varian DA-60-IL radiospectrometer at 60 MHz, relative to hexamethyldisiloxane as the internal standard. The UV spectra were obtained on an SF-4A spectrophotometer.

The GLC was run on a "Khrom-2" chromatograph using a column (6 m \times 4 mm) filled with Apiezon M, deposited (10%) on Chromosorb W (40-60 mesh), at 70°C, and a nitrogen flow rate of 120 ml/min. Under the indicated conditions the exit time of the hydrocarbons was: (I) 5.4, (X) 8.1, and (XI) 9.2 min. The purification of the compounds by preparative GLC was done under the same conditions, but using a 9 m \times 8 mm column.

<u>2-Methyl-1,3-cyclohexanedione (IX)</u>. Diketone (IX) was obtained in two steps in an overall yield of 47%, under conditions similar to those described previously [13]. The alkaline solution, obtained in the hydrogenation of resorcinol over skeletal Ni at 40° and 120 atm, was filtered from the catalyst, and the filtrate (without removing the dihydroresorcinol) was refluxed with CH_3I until the temperature of the mixture reached 70° (5-6 h). The solution was cooled, and the obtained crystals were separated, washed three times with water, then with methanol and ether, and dried; mp 208-209°. From [13]: mp 209-210°.

2,2-Dimethyl-1,3-cyclohexanedione (VI). Diketone (VI) was obtained in 68% yield as described in [12], by the methylation of diketone (IX) with CH_3I in methanol in the presence of CH_3OK ; bp 104-106° (8 mm); n_D^{20} 1.4568; the compound crystallized on standing; mp 33.5-34° (from a 5:1 ether-isopentane mixture). From [12]: bp 94-96° (9 mm); [19]: bp 98-100° (10 mm); bp 39-40° [12, 19].

5,5-Dimethyl-1,3-cyclohexanedione (III). The hydrogenation of 100 g of dimedon (II) in 300 ml of methanol over 10 ml of skeletal Ni in a 1-liter rotated autoclave at 80° and 150 atm gave, as the result of the standard workup, 91.5g (94%) of diol (III); mp 93-94° (from a 1:1 ether_isopentane mixture). Found: C 66.64; H 11.16%. C₈H₁₆O₂. Calculated: C 66.63; H 11.18%.

5,5-Dimethyl-1,3-cyclohexanediol Diacetate (IV). To a stirred mixture of 0.52 g of diol (III), 2 ml of absolute ether, and 1.39 g of diethylaniline was added 0.74 g of CH₃COC1, after which the mixture was refluxed for 8 h, allowed to stand overnight, and treated with 10 ml of water. The aqueous layer was separated and extracted with ether (6×3 ml). The combined extracts were washed with water, twice with 5% HCl solution, three times with water, and dried over MgSO₄. Then the ether was removed and the residue was distilled to give 0.67 g (81%) of diacetate (IV); bp 103° (3 mm); n_D^{20} 1.4569. Found: C 63.17; H 8.88%. C₁₂H₂₀O₄. Calculated: C 63.13; H 8.83%.

2,2-Dimethyl-1,3-cyclohexanediol (VII). The hydrogenation of 10 g of diol (VI) under the conditions described above for the hydrogenation of diketone (II) gave 9.35 g (91%) of diol (VII); mp 109-110.5° (from ether). Found: C 66.71; H 11.21%. $C_8H_{16}O_2$. Calculated: C 66.63; H 11.18%.

2,2-Dimethyl-1,3-cyclohexanediol Diacetate (VIII). Under conditions similar to those described above for the synthesis of diacetate (IV), from 1.5 g of diol (VII) we obtained 2.18 g (92%) of diacetate (VIII); mp 63.5-64.5° (from isopentane). Found: C 63.24; H 8.76%. $C_{12}H_{20}O_4$. Calculated: C 63.13; H 8.83%.

Dehydration of 5,5-Dimethyl-1,3-cyclohexanediol (III). A mixture of 157.2 g of diol (III) and 179 g of phthalic anhydride was heated in a distillation apparatus at 220-250°; the temperature of the collected vapors was 100-160°. The distillate was separated from the water, washed three times with 3% NaHCO₃ solution, then with water, and dried over CaCl₂. Distillation gave 57.9 g (50%) of a mixture of hydrocarbons; bp 65-75° (120 mm); n_D^{20} 1.4619, which, based on the GLC data, contained 84% of diene (I), 8% of (X), and 8% of (XI). Distillation of the mixture through a column (~100 theoretical plates), using tetralin as carrier, gave a chromatographically homogeneous (I); bp 47.1-47.2° (90 mm); n_D^{20} 1.4590; d_4^{20} 0.8100; m/e 108. λ_{max} (in heptane) 257 nm, ε 4840. Found: C 88.66; H 11.35%. C₃H₁₂. Calculated: C 88.82; H 11.18%. Infrared spectrum (ν , cm⁻¹): 1360-1370 (strong, twin, gem-CH₃), 1580 (m, $\nu_{C=C}^{S}$), 1638 (m, $\nu_{C=C}^{aS}$), 3028, 3040, and 3055 (m. =C-H).

Raman spectrum $(\Delta \nu, \text{ cm}^{-1})$: 264 (8br), 308(4), 339(4), 386(2), 406(3), 485(4), 563(5), 608(0), 639(2), 685(1-2), 709(10), 764(2), 854(5), 895(3), 915(3), 940 (9br), 1123(8), 1154(8), 1173(9), 1233(4), 1273(3), 1314(4), 1425(2), 1442(2), 1458(3), 1479(1), 1519(4), 1579(10br), 1639(0-1), 2784(3), 2816(3), 2871(6), 2920(6), 2964(7), 3046(7 v. br).

NMR spectrum (δ , ppm): 0.88 (singlet, 6H, CH₃), 1.97 (quadruplet, 2H, -CH₂-), 5.35-5.85 (multiplet, 4H, =C-H). Literature data: bp 110-111.5° [3]; 111° [4], 111.6-111.8° (749 mm) [5]; n_D¹⁸ 1.4563 [4]; n_D²⁰ 1.4558 [5]; d₁₅¹⁵ 0.8153 [3]; d₁₈¹⁸ 0.814 [4]; d₄²⁰ 0.8081 [5]; λ_{max} 258 nm [5]. Infrared spectrum [5]: 6.10 μ (w, 1640 cm⁻¹), 6.30 μ (w, 1585 cm⁻¹).

Fractional distillation of the mixture through a column (~100 theoretical plates) gave olefins (X) and (XI) as 70-80% concentrates. The pure hydrocarbons (X) and (XI) were isolated from the concentrates by

preparative GLC: (X); bp 117-118°; n_D^{20} 1.4440; m/e 110. Found: C 87.00; H 12.83%. C₈H₁₄. Calculated: C 87.19; H 12.81%. Infrared spectrum (ν , cm⁻¹): 1370-1380 (twin, gem-CH₃), 1620 (m, -C=C), 3030 (m, =C-H). NMR spectrum (δ , ppm): 0.96 (singlet, 6H, CH₃), 1.90 (multiplet, 6H, -CH₂-), 5.50 (multiplet, 2H, =C-H); an absorption maximum is absent in the UV spectrum; (XI): bp 119-120°; n_D^{20} 1.4420; m/e 110. Found: C 87.10; H 12.79%. C₈H₁₄. Calculated: C 87.19; H 12.81%. Infrared spectrum (ν , cm⁻¹): 1372-1380 (twin, gem-CH₃), 1625 (m, C=C), 3030 (m, =C-H). NMR spectrum (δ , ppm): 0.93 (singlet, 6H, CH₃), 1.80 (multiplet, 6H, -CH₂-), 5.65 (multiplet, 2H, =C-H); an absorption maximum is absent in the UV spectrum. From [6]: bp 115.5-118°; n_D^{20} 1.4414.

Adduct (XII) of 5,5-Dimethyl-1,3-cyclohexadiene with Maleic Anhydride. A solution of 1.5 g of diene (I) and 1.36 g of maleic anhydride in 10 ml of absolute ether was refluxed for 20 h. Distillation of the residue gave 1.98 g (69%) of adduct (XII); bp 92-93° ($1.2 \cdot 10^{-3}$ mm); n_D^{20} 1.5101. Found: C 70.07; H 6.85%. C₁₂ \cdot H₁₄O₃. Calculated: C 69.88; H 6.84%.

The compound crystallized on standing; mp 63.5-64.5° (from a 1:3 ether-isopentane mixture). Infrared spectrum (ν , cm⁻¹): 1620 (w, C=C), 1777 and 1857 (s, C=O), 3050 (m, =C-H). NMR spectrum (δ , ppm): 0.85 (singlet, 3H, -CH₃), 1.03 (singlet, 3H, -CH₃), 6.24 (doublet of quadruplets, 2H, =C-H).

3,3-(X) and 4,4-(XI)-Dimethylcyclohexenes. To a solution of 1.62 g of diene (I) in 20 ml of tert-amyl alcohol was added 2.1 g of K, the mixture was refluxed until the potassium had dissolved (4.5 h), and then it was poured into 70 ml of water. The organic layer was separated, while the aqueous layer was extracted with ether (3×10 ml); the combined extracts were washed well with water and then dried over CaCl₂. Distillation gave 1.11 g (67%) of a mixture of olefins; bp 120-122°; n_D^{20} 1.4451. Based on the GLC data, the mixture contained respectively 26 and 74% of hydrocarbons (X) and (XI). The pure components of the mixture were isolated by preparative GLC: (X); bp 117-118°; n_D^{20} 1.4439; m/e 110. (XI); bp 118-120°; n_D^{20} 1.4419; m/e 110. The IR spectra of the given and above described samples of (X) and (XI) showed good agreement.

Dehydration of 2,2-Dimethyl-1,3-cyclohexanediol (VII). Under conditions similar to those described above for the dehydration of diol (III), from 8.5 g of diol (VII) we obtained 3.5 g of a complex mixture of compounds (at least 13 components when based on the GLC data), which contained less than 10-15% of compounds with an exit time corresponding to the C₈ hydrocarbons. Based on the data of the IR spectrum (ν , cm⁻¹): 1599 m, 1646 m, 1729 v. w, 3010w, 3052w, 3085 v.w, and 3500 s, the dehydration products of diol (VII) contain ketones (mainly saturated), aromatic, and hydroxyl-containing compounds.

CONCLUSIONS

1. The hydrogenation of dimedon gave 5,5-dimethyl-1,3-cyclohexanediol in 94% yield, which has a cis-configuration, while the hydrogenation of 2,2-dimethyl-1,3-cyclohexanedione gave 2,2-dimethyl-1,3-cyclohexanediol, which has a trans-configuration.

2. The dehydration of 5,5-dimethyl-1,3-cyclohexanediol under the influence of phthalic anhydride is a convenient method for the synthesis of 5,5-dimethyl-1,3-cyclohexadiene.

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