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Intramolecular Cyclization of Alicyclic 1,5-Di- and 1,3,5-Triketones

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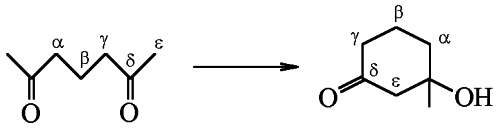
Abstract—On a series of 44 alicyclic 1,5-di- and 1,3,5-triketones was studied the influence of various structural factors (size of the 5–7-membered ring, positions of the substituents) on the capability for intramolecular aldol condensation and on its direction. The most prone to this reaction are compounds possessing a 6-membered cycle and a substituent in the β-methylene bridge. The substituent in α-position to one of the carbonyl groups can affect the reaction in two ways depending on the degree of shielding of this position.

The δ-diketones with methyl, methylene, or methine group in ε-position to one of the carbonyl groups are known for a long time to undergo cyclization in the presence of bases into β-hydroxycyclohexanones.



An early example of this reaction was contained in the discussion of Knoevenagel and Rabe that lasted for 40 years on the nature of the condensation product of ethyl acetoacetate with formaldehyde: Whether the substance was methylene bisacetoacetate or the corresponding β-ketol [1–4]. On development of IR spectroscopy numerous products of aldehydes condenstion with ethyl acetoacetate regarded as cyclic 1,5-diketones were actually proved to be 3-hydroxycyclohexanones [5]. The condensation direction of the acyclic δ-diketones was repeatedly subjected to investigations; for instance, it was demonstrated that 7-alkyl-2,6-heptanediones cyclized mainly at the methylene and not methyl group [6, 7]. At present the studies are continued on the stereochemistry of cyclization [8], on the rate of aldolization of acyclic δ-ketones [9], and on the equilibrium position δ-diketone–3-hydroxycyclohexanone [10].

Yet in the series of alicyclic 1,5-diketones were studied only condensations of 2,2'-alkylidenedicyclohexanones [11–15] and 2-[2-oxocyclopentylmethyl(or benzyl)]cyclohexanones [16, 17] that afforded substituted 2-hydroxy-8-R-tricyclo[7.3.1.$0^{2,7}$]tridecan-13-ones and 2-hydroxy-8-R-tricyclo[7.2.1.$0^{2,7}$]dodecan-12-ones respectively. The effect of the ring size and of substituents in the cycle and in the alkylidene group connecting the rings (methane fragment) on the cyclization process was not studied.

We carried out evaluation of the relative capability for intramolecular cyclization on a series of alicyclic 1,5-diketones **Ia–XXXVa** and 1,5,9-triketones (**XXXVIa–XLIVa**) (Scheme 1, designation **a** was used for the diketo form of the compound, **b** corresponded to its ketol form). The most of the compounds under study were prepared by us or by our coworkers: compounds **I–VI, XXXVI–XXXVIII** [11], **VIII–X, XVII, XIX, XX, XXIV, XXV, XXVII, XLI** [18], **XIII, XIV** [19], **XV** [20], **XVI** [21], **XXI** [22], **XXVI** [17], **XXIX, XXXIII–XXXV** [23], **XXX, XXXI** [24], **XXXIX** [16]. Compounds **XXIII, XXXI, XL** were first obtained in [15], compounds **XVIII, XXII** in [25], **XI** in [26, 27], **XII** in [28]. In this study in order to refine some conclusions we additionally prepared diketones **VIIa, XXVIIIa**, and for compounds **XXVIIIa, XXXIa** was first observed cyclization into ketoles.

The intramolecular aldol cyclization to ketols occurs under treatment of diketone with 1 M solution of NaOH or KOH in alcohol. The arising ketols in contrast to the low-melting original diketones are high-melting (mp 160–180°C) well crystallized compounds that precipitate from the alcoholic solutions. Some diketones (**IIIa–VIa, XIa, XIIa**) already during the synthesis carried out under basic conditions cyclize at once into ketols **IIIb-VIb**, **XIb**, **XIIb**. As a rule the heating of ketols results in retroaldol reaction [11, 29]; however ketols **Vb, XIb** do not afford the

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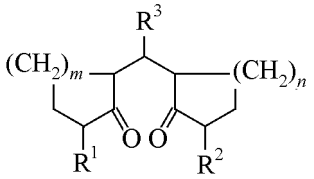
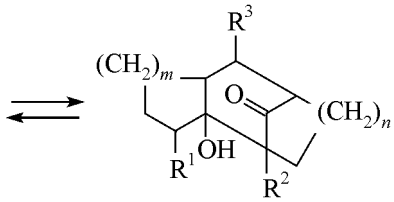
Scheme 1.



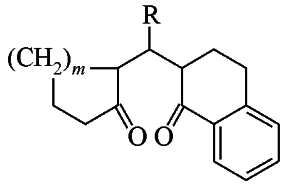
Ia–XXXIIa



Ib–VIb, XIb, XIIb, XXIIb–XXIVb, XXVIIIb, XXXIb

Ia, $m = n = 2$, $R^1 = R^2 = R^3 = H$; **IIa**, $R^3 = CH_3$, $R^1 = R^2 = H$; **IIIa**, $R^3 = Ph$, $R^1 = R^2 = H$; **IVa**, $R^3 = n\text{-}CH_3O\text{-}C_6H_4$, $R^1 = R^2 = H$; **Va**, $R^3 = p\text{-}N(CH_3)_2C_6H_4$, $R^1 = R^2 = H$; **VIa**, $R^3 = \alpha$-furyl, $R^1 = R^2 = H$; **VIIa**, $R^3 = R^1 = H$, R^2 = benzylidene; **VIIIa**, $R^3 = R^1 = H$, R^2 = 1-cyclohexenyl; **IXa**, $R^3 = H$, $R^1 = R^2$ = 1-cyclohexenyl; **Xa**, $R^3 = H$, $R^1 = R^2$ = 1-Cl-cyclohexyl; **XIa**, R^3 = spirocyclohexane; $R^1 = R^2 = H$; **XIIa**, R^3 = spirocyclohexane; $R^1 = H$, R^2 = 1-cyclohexenyl; **XIIIa**, $R^3 = CH_3$, $R^1 = H$, R^2 = benzylidene; **XIVa**, $R^3 = Ph$, $R^1 = H$, R^2 = benzylidene; **XVa**, $R^3 = Ph$, R^1 = 1-cyclohexenyl, R^2 = benzylidene; **XVIa**, $R^3 = H$, $R^1 = R^2$ = benzylidene; **XVIIa**, $m = n = 2$, $R^3 = H$, $R^1 = R^2$ = cyclohexylidene; **XVIIIa**, $m = n = 1$, $R^3 = R^1 = R^2 = H$; **XIXa**, $m = n = 1$, $R^3 = R^1 = H$, R^2 = cyclopentylidene; **XXa**, $m = n = 1$, $R^3 = H$, $R^1 = R^2$ = cyclopentylidene; **XXIa**, $m = n = 1$, $R^3 = H$, $R^1 = R^2$ = benzylidene; **XXIIa**, $m = 2$, $n = 1$, $R^3 = R^1 = R^2 = H$; **XXIIIa**, $m = 2$, $n = 1$, $R^3 = Ph$, $R^1 = R^2 = H$; **XXIVa**, $m = 2$, $n = 1$, $R^3 = p\text{-}CH_3OC_6H_4$, $R^1 = R^2 = H$; **XXVa**, $m = 2$, $n = 1$, $R^3 = H$, R^1 = cyclohexenyl, $R^2 = H$; **XXVIa**, $m = 2$, $n = 1$, $R^3 = R^1 = H$, R^2 = benzylidene; **XXVIIa**, $m = 2$, $n = 1$, $R^3 = R^1 = H$, R^2 = cyclopentylidene; **XXVIIIa**, $m = 2$, $n = 1$, $R^3 = Ph$, R^1 = 1-cyclohexenyl, $R^2 = H$; **XXIXa**, $m = 2$, $n = 1$, $R^3 = Ph$, $R^1 = H$, R^2 = benzylidene; **XXXa**, $m = 3$, $n = 1$, $R^3 = R^1 = R^2 = H$; **XXXIa**, $m = 3$, $n = 2$, $R^3 = R^1 = R^2 = H$; **XXXIIa**, $m = 3$, $n = 3$, $R^3 = R^1 = R^2 = H$.

corresponding diketones due to dehydration or thermal degradation [29]. Yet in solution both forms are in equilibrium, and in all reactions studied ketols serve as initial compounds alongside the corresponding 1,5-diketones. Even ketol **XIb** whose related diketone was not obtained in reaction with amines affords reaction product of the diketo form [30].



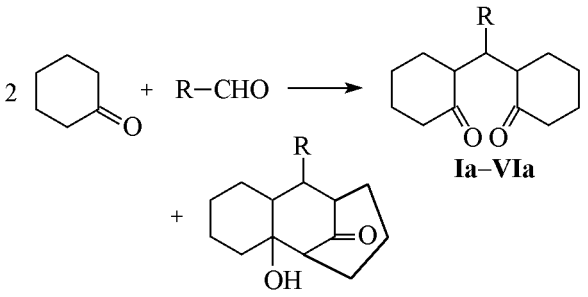
XXXIIIa–XXXVa

XXXIIIa, $m = 2$, R = Ph; **XXXIVa**, $m = 1$, R = H; **XXXVa**, $m = 1$, R = Ph.

Let us consider the effect of structural factors on the cyclization.

(1) The indispensable condition of intramolecular aldol condensation in 1,5-diketones with 5–7-membered rings is the presence of at least one cyclohexanone ring. This rule concerns both unsubstituted and substituted 1,5-diketones. The driving force of cyclization is apparently the quest of the carbonyl carbon of the cyclohexane ring for transition in sp^3-hybridized state with decreased number of eclipsed interactions. Unsubstituted diketones **Ia, XXIIa, XXXIa** containing a six-membered ring afford the corresponding ketols whereas the unsubstituted diketones with only 5-membered and 7-membered rings **XVIIIa, XXXa, XXXIIa** do not react under the same conditions. Diketone **XXIIa** that occupies an intermediate position between diketones **Ia** and **XVIIIa** yields ketol only in the presence of morpholine or piperidine, but an alkali shifts the equilibrium toward diketone [16].

(2) The presence of a substituent in the β-methylene bridge favors the cyclization of diketone into ketol, and the transformation is the easier the bulkier is the substituent. In some instances the transformation occurs already during the synthesis of the diketone. For example, compounds **I–V** can be prepared by condensation of cyclohexanone with appropriate aldehydes in a basic medium [11]. As the bulk of the substituent R grows, the fraction of ketol in the reaction product increases. Thus the condensation of cyclohexanone with formaldehyde gives rise to diketone **Ia** with a small impurity (about 5%) of the corresponding ketol **Ib**; in condensation with acetaldehyde in the reaction mixture diketone **IIa** and ketol **IIb** are present in nearly equal amounts, and with aromatic aldehydes cyclohexanone affords ketols **IIIb–VIb**. Diketones **XXIIIa** and **XXIVa** containing an aryl substituent in the β-position in contrast to



diketone **XXIIa** readily transform into the corresponding ketols **XXIIIb, XXIVb** when treated with alcoholic solution of alkali [17].

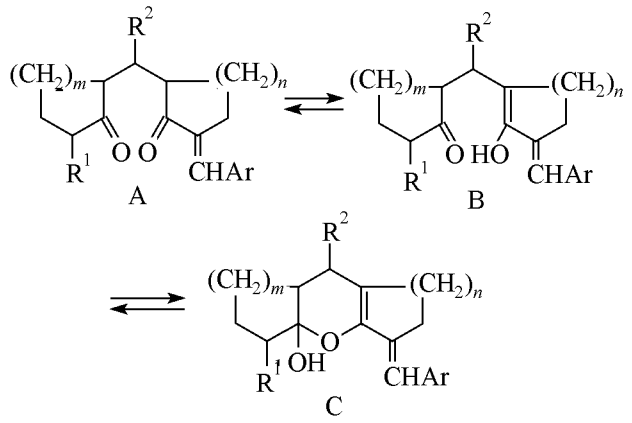
(3) The capability for cyclization of alicyclic 1,5-diketones having substituents in the α-position with respect to carbonyl groups and no substituents in the β-methylene bridge depends on the shielding extent of the interacting sites. The presence of bulky substituents in one or another ring prevents the cyclization of 1,5-diketones. Note for example diketones with such substituents as benzylidene (**VIIa** and **XXVIa**), 1-cyclohexenyl (**VIIIa, IXa, XXVa**), 1-chlorocyclohexyl (**Xa**), cyclopentylidene (**XXVIIa**), and fused benzene ring (**XXXIVa**). On the other hand 1,5,9-triketones **XXXVIa, XXXIXa, XLIVa** that may be regarded as 1,5-diketones with substituents in the α-position [(2-oxocyclohexyl)methyl or (2-oxocycloheptyl)methyl] readily undergo cyclization when treated with alkali. Apparently here the sterical factor is the most important, and since the shielding of the methylene component in the 1,5,9-triketones is less than in the mentioned diketones they are still capable of intramolecular cyclization.

Introduction of additional substituent into the β-position with respect to carbonyl groups of diketones that already have substituents in the α-position at one of the carbonyl groups facilitates their cyclization into ketols. For instance, in distinction from diketones **VIIIa, XXVa** that do not form ketols compounds **XIIa** and **XXVIIIa** with bulky substituents in the β-methylene bridge exist in ketol form: Compound **XIIb** forms just in the process of the synthesis [28], and ketol **XXVIIIb** is obtained from diketone at treatment with alkali. As exception may be cited the diketones with fused benzene ring **XXXIIIa, XXXVa** incapable of ketol formation.

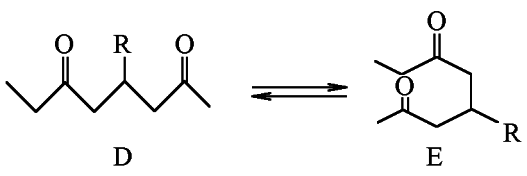
(4) 1,5-Diketones **XIIIa–XVa, XXIXa** containing in the structure simultaneously an arylidene substituent at CH_2 group in the α-position and an alkyl or aryl substituent in the β-position with respect to carbonyl groups are more prone not to aldol condensation but to intramolecular cyclization resulting in dihydropyrans C [23, 31] (Scheme 2). Apparently the arylidene subsituent in the molecule A favors enolization of the nearest carbonyl group of the cyclanone. The arising enol B can further transform into semiacetal C. However the necessary condition of this cyclization as show our examples is the presence of an alkyl or aryl substituent in the general β-position. Diketones **VIIa, XVIa, XVIIa, XXVIa, XXVIIa** lacking such substituent and those with five-membered cycles **XIXa–XXIa** are not inclined to cyclization in the basic medium.

The cyclization is observed not only in the presence of arylidene substituent but also with a fused benzene ring. Compound **XXXIII** in the crystalline state has a cyclic structure corresponding to the C form, and in CCl_4 and $CHCl_3$ solutions establishes an equilibrium of diketone and dihydropyran. Compounds of similar structure containing five-membered rings **XXXIVa, XXXVa** both in the crystalline state and in solution are present in diketo form [23]. They do not yield ketols under treatment with alkaline solutions.

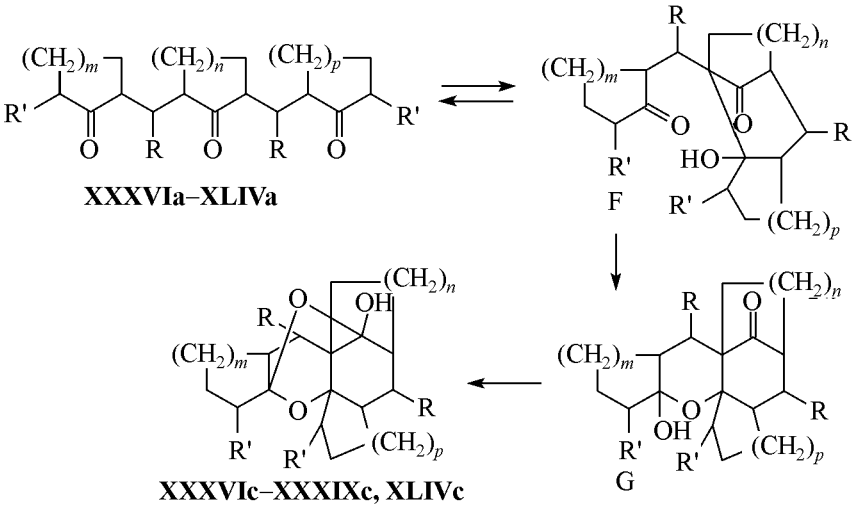
Scheme 2.



The same facilitating effect of substituents in the β-methylene bridge both on cyclization along Scheme 1 and 2 suggests that these induce the 1,5-diketones to take the conformation with the reaction sites close in space. The simulation with the use of models of probable conformations for 1,5-diketones showed that with a bulky substituent R in the β-position the most favorable conformation is E.



Scheme 3.



XXXVIa, $m = n = p = 2$, R = R' = H; **XXXVIIa**, $m = n = p = 2$, R = Ph, R' = H; **XXXVIIIa**, $m = n = p = 2$, R = α-furyl, R' = H; **XXXIXa**, $m = p = 2$, n = 1, R = R' = H; **XLa,** $m = n = p = 1$, R = R' = **H; XLIa,** $m = n = p = 1$, R = H, R' = cyclopentylidene; **XLIIa,** $m = n = p = 3$, R = R' = H; **XLIIIa,** $m = p = 3$, $n = 1$, R = R' = H; **XLIVa,** $m = p = 2$, $n = 3$, R = R' = H.

The direction of the intramolecular aldol condensation depends on the following factors.

(1) In alicyclic 1,5-diketones containing alongside 6-membered also 5- and 7-membered rings the cyclohexanone ring plays the part of the carbonyl component, and the cyclopentanone and cycloheptanone rings furnish methylene component, i.e., in the corresponding ketols $m = 2$ and a $n = 1, 3$ (Scheme 1). This behavior is observed with diketones **XXIIa–XXIVa, XXVIIIa, XXXIa** and triketones **XXXIXa, XLIVa**. In diketone **XXIXa** everything seemingly favors the action of the cyclopentanone ring as a carbonyl component (phenyl substituent in the β-methylene bridge, no CH_2 group in the α-position of the cyclopentanone ring); however this compound under the synthesis conditions yields at once the dihydropyran form C. (2) In 1,5,9-triketones **XXXVIa–XXXIXa, XLIVa** capable of intramolecular aldol condensation the cyclization occurs not at the free methylene group by at methine one. This cyclization direction was also observed with acyclic δ-ketones [6, 7].

Intramolecular aldol condensations in 1,5,9-triketones begin as an interaction between two rings to form ketols F like those arising from 1,5-diketones. The cyclization occurs at methine group providing a quaternary carbon atom in the compound; the latter atom is not bonded to oxygen. This structuer is impossible for the other directions of aldol condensation. The arising ketol F converts successively into semiacetal G and then into the final reaction product **XXXXIc–XXXIXc, XLIVc**. The first cyclization product of 1,5,9-triketones turned out to be compound **XXXVIc** that previously had been assigned another structure [32]. Yet later by separation of the intermediate cyclization products of triketone **XXXIXa** and proceeding from the data of IR, ^1H and ^{13} NMR spectroscopy was established the described above structure of compounds **XXXIXc** [33] and **XXXVIc** [16]. The structure of the latter compound was solved by X-ray diffraction analysis [34]; it showed that the tetrahydropyran rings in compound **XXXVIc** existed in the *boat* conformation.

The rules revealed for alicyclic 1,5-diketones hold also in the 1,5,9-triketone series. Triketones **XLa, XLIa, XLIIIa** lacking the cyclohexanone rings do not form intramolecular cyclization products when treated with alkali. In triketones **XXXIXa** and **XLIVa** containing alongside 6-membered ring also 5- and 7-membered rings the carbonyl component is also the cyclohexanone ring, and those of cyclopentanone and cycloheptanone provide methylene component.

The structure of compounds obtained **VIIa, XXVIIIa,b, XXXIb** was confirmed by IR, ^1H and ^{13}C NMR, and mass spectra.

Absorption bands frequencies for carbonyls in 6- and 7-membered rings are close in value: according to various publications their difference not exceeds 8–10 cm^{-1}. To reveal from which ring originates the

carbonyl group remaining in ketol **XXXIb** we registered under equal conditions the IR spectra of the original cyclohexanone, cycloheptanone, and the products obtained **XXXIa, XXXIb**. Under the same conditions were measured the IR spectra of diketone **Ia** and its ketol **Ib** to estimate the effect of the rigid ketol structure and of the size of 1–7-membered ring on the absorbance of the carbonyl group:

	Cyclohexanone	Cycloheptanone	**XXXIa**	**XXXIb**	**Ia**	**Ib**
ν(C= O), cm^{-1}	1705.6	1697.0	1706.6, 1695.7	1696.4	1706.8	1708.6
ν(OH), cm^{-1}	–	–	–	3448, 3588	–	3410, 3585

The data obtained unambiguously indicate that in ketol **XXXIb** the carbonyl group of cycloheptanone is retained; this is also confirmed by ^{13}C NMR spectra.

In the mass spectra of the compounds obtained is clearly seen the retro-Michael decomposition characteristic of 1,5-diketones.

EXPERIMENTAL

IR spectra (from KBr pellets) were recorded on Spectrum BX-II (Perking Elmer) instrument, mass spectra were measured on HÞ 5972 MSD/HÞ 5890 series II GC (Hewlet-Packard) device. ^1H and ^{13}C NMR spectra were registered in $CDCl_3$ on spectrometer Bruker AC-250 at operating frequencies 250 MHz (^1H) and 62.9 MHz (^{13}C), internal reference TMS. The assignment of signals was done with the use of *off-resonance* technique.

2-Benzylidene-6-(2-oxocyclohexylmethyl)-cyclohexanone (VIIa) (procedure [25]). A mixture of 3 g (0.016 mol) of 2-benzylidenecyclohexanone, 0.6 g (0.02 mol) of paraformaldehyde, 1.62 g (0.02 mol) of dimethylamine hydrochloride, 10 ml of 2-propanol, and 0.02 ml of concn HCl was refluxed at stirring for 20 min. The solvent was distilled off from the crystallized light-yellow precipitate, the latter (5 g) was dissolved in 10 ml of water, and the organic compounds were extracted with ether. To the water layer was added 40% solution of NaOH till alkaline pH, the Mannich base was extracted with ether, the extract was dried with Na_2SO_4, and the ether was distilled off. To the residue (4.5 g), Mannich base of 2-benzylidenecyclohexanone, was added 2 g (0.02 mol) of cyclohexanone, and the mixture was heated for 15 h on a sand bath at 180–200°C. After cooling the reaction mixture was distilled in a vacuum of oil pump to obtain 2.2 g (46%) of diketone **VIIa**, bp 230–235°C (4 mm Hg). The compound crystallized at cooling, mp 88–90°C (from ethanol). On mixing with 1 M alcoholic solution of NaOH diketone **VIIa** did not change. IR spectrum, cm^{-1}: 1704, 1679 (C=O), 1604, 1490 (Ph). Mass spectrum, *m/z* (I_{rel}, %): 296 (11) $[M]^+$, 278 (2) $[M–H_2O]^+$, 199 (37) $[M–C_6H_9O]^+$, 186 (100) $[C_6H_8OCHPh]^+$, 171 (12), 141 (21), 129 (37), 115 (62), 91 (46). ^1H NMR spectrum (δ, ppm) contained a group of multiplets in 1.2–3.0 (18H) region and a group of multiplets at 7.3–7.4 (6H, =CH) ^{13}C NMR spectrum in $CDCl_3$ (δ_C, ppm) showed the presence of two isomers (apparently, *treo*- and *erithro*-forms), all the signals were doubled save broadened signals at 22.5 and 28.7 ppm). Signals of methylene group carbons: 22.5, 24.7, 25.0, 28.0, 28.2, 28.7, 29.7, 30.1, 31.0, 31.7, 34.4, 34.8, 41.9, 42.3; signals of methine carbons appeared as two pairs of lines: 46.3, 48.0 and 47.2, 49.1 with intensity ratio 4:5; 128.2, 130.0, 134.4, 134.7 (=CH); 135.8, 137.5, 137.7 (=C); 204.2, 205.0, 213.3, 213.6 (C=O). Found, %: C 81.12; H 8.23. $C_{20}H_{24}O_2$. Calculated, %: C 81.08; H 8.11.

2-[α-(2-Oxocyclopentyl)benzyl]-6-(1-cyclohexenyl)cyclohexanone (XXVIIIa) (procedure [15] and 2-hydroxy-3-(1-cyclohexenyl)-8-phenyltricyclo-[7.2.1.0^{2,7}]dodecan-12-one (XXVIIIb). A mixture of 2 g (0.0075 mol) of 2-benzylidene-6-(1-cyclohexenyl)cyclohexanone, 1.15 g (0.0075 mol) of 1-cyclopentenylmorpholine, and 6 ml of anhydrous dioxane was refluxed for 40 h. The reaction progress was monitored by TLC. The cooled reaction mixture was diluted with water (15 ml), acidified to pH 3–4 with diluted (1:5) hydrochloric acid, the reaction product was extracted into ether, the extract was washed with water till pH 7, and dried with Na_2SO_4. The ether was evaporated on a water bath, and the residual solvent was removed in a vacuum of oil pump. We obtained 2.48 g (95%) of resinous substance. Further separation of the target product was carried out in two ways. (a) 0.48 g of the resinous substance was dissolved in 0.5 ml of 1 M NaOH alcoholic solution. In 10 min crystallized ketol **XXVIIIb**. Yield 0.41 g (85%).

(b) 1 g of resinous substance was mixed with 3 ml of hexane, the insoluble residue (0.57 g) was recrystalized from ethanol. From the ethanol solution separated 0.21 g of precipitate comprising a mixture of compounds **XXVIIIa** and **XXVIIIb**, and from the

filtrate was additionally isolated 0.1 g of diketone **XXVIIIa**. The obtained mixture (0.21 g) was dissolved in 1 ml of 1 M NaOH solution in ethanol, and in 2 h was filtered off 0.17 g of ketol **XXVIIIb**.

Retroaldol reaction of ketol XXVIIb. In a sealed capillary 50 mg of ketol **XXVIIIb** was heated for 15 min to 190°C. The melt on cooling was recrystallized from ethanol–water mixture (3:1) to obtain 40 mg of diketone **XXVIIIa** (identified by TLC, IR spectrum and melting point of the compound mixed with an authentic sample).

2-Hydroxytricyclo[7.4.1.0^{2,7}]tetradecanone (XXXIb). To 0.5 g of diketone **XXXIa** was added 0.5 ml of 1 M NaOH ethanol solution, and the yellow mixture was left standing at 0°C. 3 days later crystal precipitate was separated. Yield of ketol **XXXIb** 0.33 g (66%), mp 118–120°C (from hexane). IR spectrum see above. Mass spectrum, *m/z* (I_{rel}, %): 222 (59.5) $[M]^+$, 204 (7.3) $[M–H_2O]^+$, 125 (47.2) $[C_7H_{11}OCH_2]^+$, 124 (99.1) $[M–C_6H_9O]^+$, 112 (99.1) $[C_6H_9OCH_2$ and $C_7H_{11}O]^+$, 98, 100 $[C_6H_9O]^+$. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.2–2.1 m (21H), 2.44 m (1H, C^{9}H), 2.75 t (1H, C^{1}H, *J* 5). ^{13}C NMR spectrum (δ_C, ppm): 20.7, 24.9, 25.9, 26.1, 26.3, 28.5, 32.7, 34.9, 35.0 (9$\underline{C}$H$_2$); 35.7, 48.1 (C^7, C^9); 61.0 (C^1), 76.1 (C^2), 215.4 (C^{14}). [To compare: ^{13}C NMR spectrum (δ_C, ppm) of diketone **XXXIa** contains signals from two carbonyl groups at 212.3 (in cyclohexanone) and 215.3 (in cycloheptanone).] Found, %: C 75.32; H 9.83. $C_{14}H_{22}O_2$. Calculated, %: C 75.68; H 9.91.

REFERENCES

1. Knoevenagel, E., *Lieb. Ann.*, 1894, vol. 281, pp. 25–126.
2. Rabe, P. and Elze, F., *Lieb. Ann.*, 1902, vol. 323, pp. 83–112.
3. Knoevenagel, E., *Ber.*, 1903, vol. 36, pp. 2118–2123.
4. Rabe, P. and Appuhn, K., *Ber.*, 1943, vol. 76B, pp. 979–982.
5. Finar, I.L., *J. Chem. Soc.*, 1961, no. 2, pp. 674–676.
6. Danishefsky, S., Nagel, A., and Peterson, D., *Chem. Commun.*, 1972, pp. 374–375.
7. Alexandre, C. and Rouessac, F., *Chem. Commun.*, 1975, pp. 275–279.
8. Agami, C., Platzer, N., and Sevestre, H., *Bull. Soc. Chim.*, 1987, no. 2, pp. 358–360.
9. Rutherford, A.R., Gibb, C.S., and Hartley, R.C., *Tetrahedron Lett.*, 1998, vol. 39, no. 7, pp. 685–688.
10. Guthrie, J.P. and Guo, J., *J. Am. Chem. Soc.*, 1996, vol. 118, no. 46, pp. 11472–11487.
11. Tilichenko, M.N., *Ezhegodnik Saratov. Univ.*, 1954, pp. 501–504.
12. Colonge, J., Dreux, J., and Deplace, H., *Bull. Soc. Chim.*, 1956, no. 11–12, pp. 1635–1640.
13. Plesek, J. and Munk, P., *Chem. Listy*, 1957, vol. 51, pp. 633–638.
14. Plesek, J. and Munk, P., *Coll. Chem. Commun.*, 1957, vol. 22, pp. 1596–1602.
15. Birkofer, L., Kim, S.M., and Engels, H.D., *Chem. Ber.*, 1962, vol. 95, no. 6, pp. 1495–1504.
16. Akimova, T.I., Kosenko, S.V., and Tilichenko, M.N., *Zh. Org. Khim.*, 1991, vol. 27, no. 12, pp. 2553–2560.
17. Akimova, T.I., Kosenko, S.V., Pavlenko, L.V., and Tilichenko, M.N., *Zh. Org. Khim.*, 1993, vol. 29, no. 2, pp. 287–296.
18. Akimova, T.I. and Tilichenko ,M.N., *Zh. Org. Khim.*, 1990, vol. 26, no. 6, pp. 1249–1257.
19. Minaeva, N.N. and Tilichenko, M.N., *Zh. Org. Khim.*, 1986, vol. 22, no. 9, pp. 1915–1920.
20. Akimova, T.I. and Tilichenko, M.N., *Zh. Org. Khim.*, 1983, vol. 19, no. 12, pp. 2496–2502.
21. Tilichenko, M.N. and Minaeva, N.N., *Zh. Org. Khim.*, 1983, vol. 19, no. 12, pp. 2516–2523.
22. Tilichenko, M.I., Koroleva-Vasil'eva, I.A., Akimova, T.I., *Zh. Org. Khim.*, 1986, vol. 22, no. 9, pp. 1920–1922.
23. Vershinina, N.V., Vysotskii, V.I., Eremeeva, L.M., Kaminskii, V.A., and Tilichenko, M.N., *Khim. Geterotsikl. Soed.*, 1977, no. 10, pp. 1315–1319.
24. Shumakov, S.A., Kaminskii, V.A., and Tilichenko, M.N., *Khim. Geterotsikl. Soed.*, 1990, no. 1, pp. 109–114.
25. Gill, N.S., James, K.B., Lions, F., and Potts, K.T., *J. Am. Chem. Soc.*, 1952, vol. 74, pp. 4923–4928.
26. Pettit, G.R. and Thomas, E.G., *Chem. Ind.*, 1963, vol. 44, pp. 1758–1760.
27. Rollin, P., *Bull. Soc. Chim.*, 1973, no. 4, pp. 1509–1514.
28. Rollin, P., *Bull. Soc. Chim.*, 1973, no. 5, pp. 1806–1810.
29. Vysotskii, V.I., Vershinina, N.V., and Tilichenko, M.N., *Dep. VINITI.*, no. 920-74; *Ref. Zh. Khim.*, 1974, 17Zh 227.
30. Eremeeva, L.M., Bratchikova, A.I., Kaminskii, V.A., and Tilichenko, M.N., *Khim. Geterotsikl. Soed.*, 1979, no. 9, pp. 1247–1250.
31. Starichkova, N.V., *Cand. Sci. (Chem.) Dissertation*, Vladivostok, 1977.
32. Tilichenko, M.N., *Zh. Org. Khim.*, 1966, vol. 2, no. 9, pp. 1615–1619.
33. Akimova, T.I., Kosenko, S.V., and Tilichenko, M.N., *Zh. Org. Khim.*, 1990, vol. 26, no. 11, pp. 2456–2457.
34. Akimova, T.I., Nesterov, V.V., Antipin, M.Yu., and Vysotskii, V.I., *Khim. Geterotsikl. Soed.*, 1999, no. 11, pp. 1491–1496.