6. N. O. Saldabol and S. A. Giller, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 5, 585 (1963).
7. N. O. Saldabol and S. A. Giller, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 6, 701 (1964).
8. N. O. Saldabol, A. Yu. Tsimanis, and S. A. Giller, USSR Inventor's Certificate No. 410015 (1974); Byul. Izobr., No. 1, 81 (1974).

EFFECT OF STRUCTURAL FACTORS ON THE REVERSIBLE 1,5-DIKETONE – HYDROXYDIHYDROPYRAN CONVERSION*

N. V. Vershinina, V. I. Vysotskii,
L. M. Eremeeva, V. A. Kaminskii,
and M. N. Tilichenko

UDC 541.623:547.815

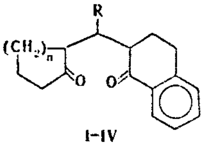
It is shown that δ-bicyclanones with five-membered rings have less of a tendency to undergo conversion to cyclohemiacetals than the analogous compounds with six-membered rings.

The reversible conversion of a 1,5-diketone (A) to a hydroxydihydropyran (B) has been previously established in the case of arylidenedicyclohexanones [2].

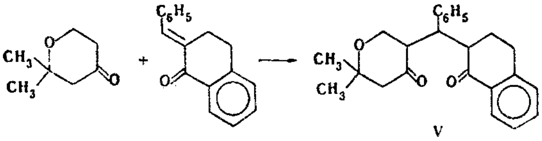
A B

In order to further investigate this conversion we synthesized 1,5-diketones I-VII and examined the forms in which they exist in the solid phase and in solutions and also carried out some reactions with them.

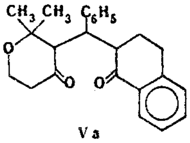
Diketones I and II were synthesized by condensation, respectively, of cyclopentanone and cyclohexanone with 2-dimethylaminomethyl-1-tetralone, and diketones III-V were synthesized by the addition of cyclopentanone, cyclohexanone, and 2,2-dimethyltetrahydro-4-pyrone to benzylidenetetralone.



I-IV



V



Va

I R=H, n=1; II R=H, n=2; III R=C$_6$H$_5$, n=1; IV R=C$_6$H$_5$, n=2

For the synthesis of diketones VI and VII we used the addition of cyclopentanone and cyclohexanone to 2,5-dibenzylidenecyclopentanone. Diketone VI was also obtained by dimerization of 2-benzylidenecyclopentanone under the influence of alkali. Diketone VII was previously described by one of us and Kharchenko [3], and we modified the method for its synthesis only somewhat. The structures of the diketones follow from the method by which they were synthesized and are in agreement with the analytical data. We consider structure Va for the product of addition of dimethyltetrahydropyrone to benzylidenetetralone unlikely, since participation of a sterically hindered methylene group in the Michael reaction is required for its formation.

---

*Communication XXVIII from the series "Reactions of 1,5-Diketones." See [1] for communication XXVII.

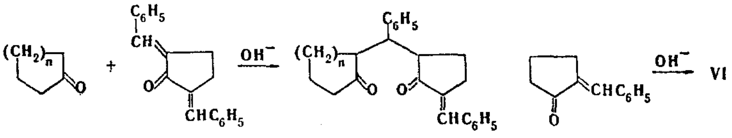
Far-Eastern State University, Vladivostok 690000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1315-1319, October, 1977. Original article submitted December 2, 1976.

TABLE 1. Properties of the Synthesized Compounds

Compound	mp, °C	Found, %		Empirical formula	Calc., %		$\nu_{C=O}$, cm^{-1}		Yield, %	Oxime			
		C	H		C	H	in the solid state	in solution		mp, °C	N found, %	empirical formula	N calc., %
I	50—51	80,0	7,4	$C_{16}H_{18}O_2$	79,3	7,5	1735 1685	1735 1685	71	153—155	5,3	$C_{16}H_{19}NO_2$	5,5
II	53—54	79,8	8,2	$C_{17}H_{20}O_2$	79,6	7,9	1700 1685	1705 1685	70	187—190	9,5	$C_{17}H_{22}N_2O_2$	9,8
III	85—87	83,1	6,9	$C_{22}H_{22}O_2$	83,0	7,0	1735 1685	1735 1685	90	180—183[a]	11,4	$C_{28}H_{26}N_4O_5$	11,2
IV	160—162	83,6	7,5	$C_{23}H_{24}O_2$	83,1	7,3	—	1715	80	139—141	7,0	$C_{23}H_{26}N_2O_2$	7,7
V	131—133	79,1	7,2	$C_{24}H_{26}O_3$	79,5	7,2	1705	1705	95	—	—	—	—
VI	144—146	83,9	6,8	$C_{24}H_{24}O_2$	83,7	7,0	1735 1700	1735 1700	90	158—160	3,5	$C_{24}H_{25}NO_2$	3,8
X	139—140	83,1	7,7	$C_{24}H_{26}O_2$[b]	83,2	7,6	—	—	95	—	—	—	—
XI	169—170	83,5	7,6	$C_{26}H_{28}O_2$[c]	83,8	7,5	—	—	92	—	—	—	—
XIV	99—101	87,8	7,3	$C_{22}H_{20}O$	88,0	6,7	—	—	74	—	—	—	—
XV	94—95	88,3	7,4	$C_{23}H_{22}O$	87,8	7,1	—	—	70	—	—	—	—

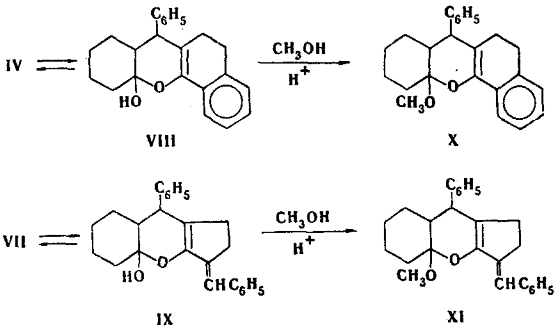
---

*2,4-Dinitrophenylhydrazone. [b]Found: CH_3O 9.2%. Calculated: CH_3O 9.0%. [c] Found: CH_3O 8.3%. Calculated: CH_3O 8.3%.

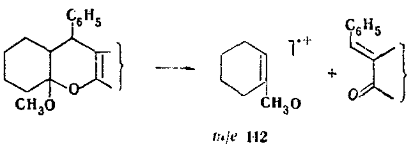


VI n=1; VII n=2

Carbonyl group absorption is observed in the IR spectra of I-III, V, and VI in the solid state and in solution (see Table 1). Crystalline samples of diketones IV and VII do not display carbonyl absorption. Bands at 3480 (OH), 1665 (IV), and 1650 cm^{-1} (VII) (C = C) are observed in their IR spectra. Absorption at 1715 cm^{-1} (C = O) appears in the IR spectra of solutions of IV and VII, in addition to hydroxyl and ethylene absorption. In conformity with [2], cyclohemiacetal structures VIII and IX should be assigned to the crystalline samples. The equilibria IV $\rightleftharpoons$ VIII and VII $\rightleftharpoons$ IX take place in solutions, however.

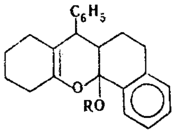


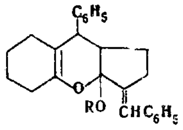
Compounds VIII and X are converted to acetals X and XI under the influence of a methanol solution of HCl. The absorption of a hydroxyl group vanishes from the IR spectra of X and XI, but the absorption of a double bond is retained (1660 cm^{-1}). The vibrations of methoxy groups appear at 2840 and 1100 cm^{-1}. Acetals X and XI decompose in the mass spectrometer to give an ion with m/e 112; this is in agreement with retrograde diene decomposition via the scheme



m/e 112

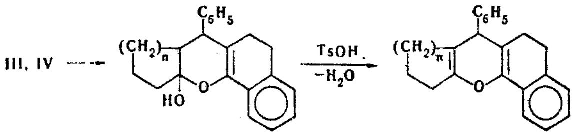
and makes it possible to exclude from consideration alternative formulas XII and XIII, which are, in principle, possible for cyclic derivatives of diketones IV and VII:


XII

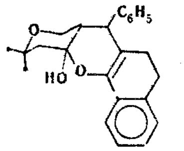

XIII

XII, XIII R=H or CH_3

Under the influence of p-toluenesulfonic acid in refluxing xylene, diketones III and IV are dehydrated to XIV and XV, evidently through the intermediate cyclohemiacetals:


XIV n=1 XV n=2

Thus the ability of 1,5-diketones to undergo conversion to cyclohemiacetals depends substantially on their structures. Whereas bicyclanone IV is cyclized to a considerable extent, the ability of its analog III to undergo this sort of transformation is lowered and is observed only indirectly (in the dehydration reaction). Compound VI does not undergo cyclization; its benzylidenebenzaldicyclohexanone analog, in which all of the rings are six-membered rings, undergoes cyclization in the solid state and in solutions [2]. Compound VII (with one five-membered ring) occupies an intermediate position, since it is only partially cyclized in solution. This is evidently explained by the fact that the carbonyl carbon atom in the six-membered ring has a tendency to undergo conversion from a planar to a tetrahedral configuration, while in the five-membered ring this conversion is associated with the development of shielded conformations and is therefore hindered. A comparison of the diketones II and IV shows that the substituent attached to the carbon atom that joins the two rings affects the ability of the diketone to undergo conversion to hydroxydihydropyrans. This effect has been previously noted [2]. In contrast to diketone IV, diketone V does not display a tendency to undergo cyclization. We explain this by the fact that cyclohemiacetal XVI is destabilized by a 1,3-diaxial interaction between the methyl and hydroxyl groups:


XVI

Under the influence of hydroxylamine, I, VI, and VII form monoximes, whereas II and IV give dioximes. The C = N absorption band is observed in its normal position (1680 cm^{-1}) in the IR spectra of the latter. From this it follows that the dioximes under consideration are not inclined to undergo the cyclization to oxadiazolines that was previously observed for dioximes of alkylidenedicyclohexanones [4].

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and 0.2 mole of solutions in carbon tetrachloride, chloroform, or methylene chloride were recorded with a UR-20 spectrometer. The mass spectra were recorded with an MKh-1303 mass spectrometer at 70 eV.

2-(2-Cyclopentanonylmethyl)-1-tetralone (I). A mixture of 61 g (0.3 mole) of 2-dimethylaminomethyl-1-tetralone and 75 g (0.9 mole) of cyclopentanone was heated in an argon atmosphere at 150-160°C until dimethylamine evolution ceased, after which the excess cyclopentanone was removed by vacuum distillation (with a water aspirator), and the residue was distilled at 170-175°C (1 mm). The distillate crystallized when it was cooled; the product can be recrystallized from alcohol.

2-(2-Cyclohexanonylmethyl)-1-tetralone (II). This compound was obtained by a similar procedure.

2-(2-Cyclopentanonylbenzyl)-1-tetralone (III). A mixture of 1 g (0.004 mole) of 2-benzylidene-1-tetralone, 1 g (0.012 mole) of cyclopentanone, and 12 ml of diethylamine was allowed to stand at room temperature for 5 days, after which it was diluted with 200 ml of 15% acetic acid. The resulting mass was triturated with water and, after complete solidification, was recrystallized from methanol.

2-(2-Cyclohexanonylbenzyl)-1-tetralone (IV). A 10-g (0.05 mole) sample of 2-benzylidenetetralone was dissolved in 70 ml of DMF, 20 g (0.2 mole) of cyclohexanone and 20 ml of 2 N alcoholic sodium hydroxide solution were added, and the mixture was allowed to stand at room temperature for 3 days. It was then diluted with water, during which the initially liberated oil crystallized rapidly. The reaction product was recrystallized from acetone–water (10 : 1).

2-(2,2-Dimethyl-5-benzyl-4-tetrahydropyronyl)-1-tetralone (V). This compound was similarly obtained from benzaltetralone and 2,2-dimethyltetrahydro-4-pyrone.

2-Benzylidene-5-(2-benzylcyclopentanonyl)cyclopentanone (VI). A 10-g (0.06 mole) sample of 2-benzylidenecyclopentanone was dissolved by heating in 110 ml of 10% alcoholic KOH solution in an argon atmosphere, and the solution was cooled to 0°C and allowed to stand at that temperature for 24 h. The precipitated diketone VI (4.7 g) was separated and recrystallized from ethyl ether (the solution was cooled to −75°C).

Compound VI was also obtained in the same way as VII (see below) from cyclopentanone and dibenzylidenecyclopentanone. The yield of VI with respect to this method is presented in Table 1.

2-Benzylidene-5-(2-benzylcyclohexanonyl)cyclopentanone (VII). A mixture of 19.2 g (0.2 mole) of cyclohexanone, 26 g (0.1 mole) of 2,5-dibenzylidenecyclopentanone, and 310 ml of 1 N alcoholic KOH solution was heated in an argon atmosphere on a water bath until a homogeneous solution formed (~ 10 min). The solution was allowed to cool, and it was then placed in a refrigerator. After 24 h, VII was removed by filtration and washed with 3% hydrochloric acid solution, water, and ethanol. Workup gave 21.7 g (61%) of VII with mp 159-161°C (154-156°C [3]).

4a-Methoxy-9-phenyl-5,6-benz-1,2,3,4,4a,7,8,9a-octahydroxanthene (X). A 1-g (0.003 mole) sample of IV was mixed with 15 ml of 0.25% HCl solution in absolute methanol, and the mixture was refluxed on a water bath for 2 h. It was then cooled, and 0.9 g of X was removed by filtration.

1-Methoxy-2-oxa-8-phenyl-4-benzylidenetricyclo[7.4.0.$0^{3,7}$]tridec-3(7)-ene (XI). This compound was similarly obtained.

9-Phenyl-5,6-benz-1,2,3,4,7,8-hexahydroxanthene (XV). A 0.5-g sample of IV was refluxed in 20 ml of m-xylene with a crystal of p-toluenesulfonic acid in a flask equipped with a Dean–Stark trap. After water liberation was complete, the xylene was vacuum evaporated, the residue was triturated with alcohol, and the resulting crystals were removed by filtration.

Compound XIV was similarly obtained.

Oximes of Diketones I-VII. These compounds were obtained by mixing alcohol solutions of 0.01 mole of the diketone and 0.03 mole of hydroxylamine acetate.

LITERATURE CITED

1. M. N. Tilichenko and T. I. Akimova, Zh. Org. Khim. (1977, in press).
2. V. I. Vysotskii, N. V. Vershinina, and M. N. Tilichenko, Khim. Geterotsikl. Soedin., No. 6, 898 (1975).
3. M. N. Tilichenko and V. G. Kharchenko, Dokl. Akad. Nauk SSSR, 110, 226 (1956).
4. V. K. Gamov, V. A. Kaminskii, and M. N. Tilichenko, Khim. Geterotsikl. Soedin., No. 11, 1525 (1974).