IR spectrum: 1725 cm⁻¹ (C=O). Found: C 69.2; H 10.3%; MR_D 43.35. C₉H₁₆O₂. Calculated: C 69.1; H 10.3%; MR_D 43.22. The 2,4-dinitrophenylhydrazone had mp 177-178°C. Found: N 16.7%. C₁₅H₂₀N₄O₅. Calculated: N 16.7%.

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1-METHOXY-3,5-DIARYL-2-OXABICYCL0[4.4.0]DEC-3-ENES FROM "SEMICYCLIC"

1,5-DIKETONES

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It was established that "semicyclic" 1,5-diketones are capable of reacting with methanol by the catalytic action of hydrogen chloride and are capable of forming 1methoxy-3,5-diary1-2-oxabicyclo[4.4.0]dec-3-enes — cyclic acetals that include an alkoxydihydropyran ring. In addition, 2,4-darylbicycle[3.3.1]non-2-en-9-ones, which are formed from 1,3-diary1-3-(2-oxocyclohexy1)propan-1-ones by an intramolecular condensation of the erotonic type, are detected as side products. The possible mechanism of the reaction of 1,3-diary1-3-(2-oxocyclohexy1)propan-1-ones with methanol in the presence of hydrogen chloride is discussed.

It is well known that "semicyclic" 1,5-diketones that contain a methyl or methylene group in the α position with respect to one of the carbonyls easily undergo intramolecular condensation of the aldol-crotonic type under conditions of both basic and acid catalysis [1, 2].

1,5-Diketones that contain anyl groups in the α positions are capable of undergoing conversion to pyrylium salts under the influence of acids [3, 4].



Allen and Sallans [2] have observed that under the influence of sulfuric acid 1,3diphenyl-3-(2-oxocyclohexyl)propanone (I) reacts with methanol to give a cyclic acetal, i.e., 1-methoxy-3,5-diphenyl-2-oxabicyclo[4.4.0]dec-3-ene (VIII).

During a study of the reaction of diketone I with hydrogen sulfide in methanol under the influence of hydrogen chloride we observed that diketone I underwent reaction with methanol rather than with hydrogen sulfide to give acetal VIII, which is identical to the substance obtained by Allen and Sallans [2].

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	· · ·	IR spectrum, cm ⁻¹			Found, %			Calc., %		
Compound	mp, °C (crystalliza- tion solvent)	c-0c	C≖C	C—H(OCH ₃)	с	н	Em piri- cal for- mula	с	н	Yield, 7/0
VIII IX XI XII XIII XIII XIV	169-170 (benzene) 134-136 (benzene) 109-110 (benzene) 152,5-153,5 (benzene- acetone 1 : 2) 150-151 petroleum- ether) 156-158 (petroleum- ether) 152-153 (chloroform- methanol)	1027, 1087 1025, 1087 1038, 1080 1027, 1083 1032, 1087 1035, 1070 1030, 1085	1650 1650 1653 1648 1646 1650	2832 2830, 2840 2840 2835 2835 2845 2845 2830	82,1 78,7 78,6 75,6 83,9 81,0 77,9	8,0 7,1 7,0 7,3 7,0 7,2 7,3	$\begin{array}{c} C_{22}H_{24}O_2\\ C_{23}H_{26}O_3\\ C_{23}H_{26}O_3\\ C_{24}H_{28}O_4\\ C_{26}H_{26}O_2\\ C_{27}H_{28}O_3\\ C_{28}H_{30}O_4\\ \end{array}$	82,5 78,8 78,8 75,9 84,3 81,0 78,2	7,6 7,5 7,4 7,1 7,1 7,0	70 75 60 70 33 13 66

TABLE 1. 1-Methoxy-2-oxabicyclo[4.4.0]dec-3-enes

We attempted to ascertain the behavior of other "semicyclic" 1,5-diketones (II-VII), which differ with respect to the aryl substituents attached to the C_1 and C_3 atoms, toward the simultaneous action of methanol and hydrogen sulfide under similar conditions and also their behavior with respect to methanol in the absence of hydrogen sulfide, as well as to ascertain the effect of electronic and steric factors on the character of the transformation. It was found that diketones I-VII, including those that contain methoxyphenyl (II-IV, VI, VII) and naphthyl substituents (V-VII) attached to the C_1 or C_3 atoms at 5-15°C and under the influence of hydrogen chloride or the latter and sulfuric acid, react with methanol to give bicyclo[4.4.0]dec-3-enes VIII-XIV (see Table 1). In all cases the reaction mixture was a suspension of the diketone in methanol saturated with hydrogen chloride.

I. VIII $Ar = Ar' = C_6H_5$; II, IX $Ar = C_6H_5$, $Ar' = 4 \cdot CH_3OC_6H_4$; III, X $Ar = 4 \cdot CH_3OC_6H_4$, $Ar' = C_6H_5$; IV, XI, XV $Ar = C_6H_5$, $Ar' = 3,4 \cdot (CH_3O)_2C_6H_3$; V, XII, XVI $Ar = 2 \cdot C_{10}H_7$, $Ar' = C_6H_5$; VI, XIII, XVII $Ar = 2 \cdot C_{10}H_7$, $Ar' = 4 \cdot CH_3OC_6H_4$; VII, XIV $Ar = 2 \cdot C_{10}H_7$, $Ar' = 3,4 \cdot (CH_3O)_2C_6H_3$

As in the case of diketone I, reaction with hydrogen sulfide was not observed in the case of action of hydrogen chloride on hydrogen sulfide-saturated suspensions of diketones II, IV, and VII in methanol. Instead of the expected 3,5-diaryl-2-thiabicyclo[4.4.0]dec-3-enes [5, 6], one observes the formation of their oxygen analogs IX, XI, and XIV; when hydrogen sulfide is introduced into the reaction mixture, the yields of methoxydihydropyrans IV, XI, and XIV increased sharply: from 29 to 75% in the case of diketone II (no explanation was found for this fact). In addition, the addition of concentrated sulfuric acid (10% of the amount of methanol) promotes the formation of methoxydihydropyrans: The yield of methoxydihydropyran X increases from 29 to 60%.

In addition to XI-XII, diketones IV-VI under the conditions presented above give 9-oxo-2,4-diarylbicyclo[3.3.1]non-2-enes (XV-XVII) — the products of intramolecular crotonic condensation. The addition of sulfuric acid to a methanol solution of the diketone saturated with hydrogen chloride promoted the formation of XV-XVII. Thus, the yield of bicyclononene XVI from diketone V increased from 25 to 47% when sulfuric acid was added.

The starting diketones exist in the diketone form in the solid state, as evidenced by their IR spectra. It may be assumed that protonation of the more active alicyclic carbonyl group of the diketone to give carbonium ion A occurs in acidic media. The stabilization of the latter may probably take place via pathway (1) through cyclic carbonium ion B or via pathway (2) through hemiacetal C, leading to methoxydihydropyrans. Pathway (2) seems most likely to us, since it is well known that cyclohexaneone and its derivatives under similar conditions give hemiacetals [7, 8]. In addition, the ability of bicyclanes to undergo conversion to cyclic hemiacetals is well known [9]. Under acid-catalysis conditions the intramolecular condensation of the crotonic type evidently proceeds via pathway (3) and leads to the formation of bicyclononenes.

The IR spectra of VIII-XIV contain the absorption band of a double bond at 1648-1653 cm⁻¹ and in the 1000-1100 cm⁻¹ region one should note the two most intense absorption bands at 1025-1038 and 1070-1087 cm⁻¹, which are characteristic for the C-O-C-O-C grouping in cyclic acetals [10].



The PMR spectra of VIII-XIV contain signals of heteroring protons with an integral intensity of one proton: 5.34-5.8 (d, 4-H), 3.26-3.68 (dd, 5-H), and 2.33-2.50 ppm (m, 6-H) (${}^{3}J_{4,5} = 2.5-2.6$; ${}^{3}J_{5,6} = 10.5-11.0$ Hz). The protons of the methoxy groups here give signals at 3.2-3.35 ppm, whereas in the case of aryl substituents they are found at weaker field at 3.67-3.76 ppm. The multiplets at 1.45-1.60 and 6.60-7.68 ppm correspond to the alicyclic and aromatic protons.

The interpretation of the PMR spectra of VIII-XIV presented above, which was made with the use of the methods of total and inverse double resonance, makes it possible to identify them as 2-oxabicyclo[4.4.0]dec-3-enes and to refine the structure of VIII, which was previously described [2] as 2-methoxy-2,4-diphenyl-2,3,5,6,7,8-hexahydrochromene.

The use of the angular correlation of the SSCC of the vicinal protons of the heteroring and the effect of an aromatic solvent on the chemical shifts of the protons made it possible to establish the configuration of VIII-XIV [6]:



In the case of X the configuration was also confirmed by the results of x-ray diffraction analysis [11].

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded with a UR-20 spectrometer. The PMR spectra of 0.3 m solutions of the compounds in CDCl₃ were obtained with Tesla BS-447 (60 MHz) and RYa-2306 (60 MHz) spectrometers at room temperature with hexamethyldisiloxane as the internal standard. The chemical shifts are presented on the δ scale with an accuracy up to 0.02 ppm. The resonance signals were identified by the method of total and inverse double resonance (INDOR).

<u>1-(4-Methoxyphenyl)-3-phenyl-3-(2-oxocyclohexyl)propanone (III)</u>. A 12-g (0.05 mole) sample of benzylidene-p-methoxyacetophenone was added to a refluxing mixture of 50 ml (0.5 mole) of cyclohexanone and 150 ml of a 0.3 N solution of sodium hydroxide in ethanol. Diketone III was removed by filtration after cooling and partial evaporation of the reaction mixture. The yield of product with mp 135-137°C (from ethanol) was 10.8 g (65%). IR spectrum: 1680, 1720 cm⁻¹ (C=0). Found: C 78.2; H 7.3%. $C_{22}H_{24}O_{3}$. Calculated: C 78.6; H 7.1%.

<u>1-(2-Naphthyl)-3-(3,4-dimethoxyphenyl)propanone (VII)</u>. This compound was similarly obtained from 0.24 mole of cyclohexanone and 0.08 mole of chalcone in 180 ml of a 0.3 N solution of sodium hydroxide in ethanol. The yield of product with mp 140.5-141.5°C [from ethanol-benzene (1:1)] was 13.7 g (51%). IR spectrum: 1680, 1720 cm⁻¹ (C=O). Found: C 77.6; H 6.8%. $C_{27}H_{28}O_4$. Calculated: C 77.9; H 6.8%.

<u>1-Methoxy-3,5-diaryl-2-oxabicyclo[4.4.0]dec-3-enes(VIII-XIV)</u>. A suspension of 0.01 mole of the diketone in 30-50 ml of absolute methanol was saturated with dry hydrogen chloride in the course of 4-12 h at 5-15°C, and the mixture was then allowed to stand at room temperature for 12 h. The precipitated cyrstals were separated, washed with water and methanol, and re-crystallized from an appropriate solvent (Table 1).

9-0xo-2,4-diarylbicyclo[3.3.1]non-2-enes (XV-XVII) were obtained in addition to methoxydihydropyrans XI-XIII from diketones IV-VI. The reaction products were separated and purified by chromatography with a column filled with aluminum oxide [petroleum ether-ethyl acetate (10:1)].

<u>9-0xo-2-phenyl-4-(3,4-dimethoxyphenyl)bicyclo[3.3.1]non-2-ene (XV).</u> This compound was obtained in 65% yield and had mp 125-127°C. IR spectrum: 1700 (C=0); 1635 (C=C); 1605, 1595, and 1502 cm⁻¹ (C=CAr). PMR spectrum: 6.70-7.20 (m, Ar), 6.30 (d, 3-H), 4.05 (dd, 4-H), 3.76 (d, 0CH₃), 1.90 ppm (m, CH₂), Found: C 79.4; H 7.1%. C₂₃H₂₄O₃. Calculated: C 79.3; H 6.9%.

9-0xo-2-(2-naphthy1)-4-phenylbicyclo[3.3.1]non-2-ene (XVI). This compound was obtained in 47% yield and had mp 160-162°C. IR spectrum: 1732(C=O); 1640(C=C); 1605, 1590, and 1505 cm⁻¹ (C=CAr). PMR spectrum: 7.35-8.08 (m, Ar), 6.30 (d, 3-H), 4.20 (dd, 4-H), and 2.08 ppm (m, CH₂). Found: C 88.0; H 6.8%. C₂₂H₂₂O. Calculated: C 88.9; H 6.6%.

<u>9-0xo-2-(2-naphthyl)-4-(4-methoxyphenyl)bicyclo[3.3.1]non-2-ene (XVII)</u>. This compound was obtained in 20% yield and had mp 133-134°C. IR spectrum: 1734 (C=O); 1642 (C=C); 1622, 1597, and 1520 cm⁻¹ (C=CAr). PMR spectrum: 6.72-7.70 (m, Ar), 6.50 (d, 3-H), 4.25 (dd, 4-H), 3.80 (s, OCH₃), and 2.02 ppm (m, CH₂). Found: C 85.0; H 6.9%. C₂₆H₂₇O₂. Calculated: C 84.8; H 6.6%.

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