TRANSFORMATIONS OF 2α-HYDROXY-2,6,6-TRIMETHYLBICYCLO[3.1.1]-HEPTAN-3-ONE UNDER CONDITIONS OF ACID CATALYSIS

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The transformations of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one under the conditions of acid catalysis have been studied. It has been shown that this compound can be used for the synthesis of products of various structures: a bridged bicyclic lactone (1,8,8-trimethyl-2-oxabicyclo[3.2.1]octan-3-one), an aromatic compound (carvacrol), and nitrogen-containing derivatives of p-menthane such as 8-acylamino-p-menth-6-en-2-ones. The structures of the compounds synthesized were shown by the results of ^1H and ^{13}C NMR spectroscopies.

In recent decades, the reactivity of natural monoterpene compounds has been widely studied with the aim of obtaining substances having properties of practical value [1-3]. In this connection, the availability of α-pinene (2,6,6-trimethylbicyclo[3.1.-1]hept-2-ene) (I), which is the main component of the turpentines obtained from coniferous species of trees, and the rich synthetic possibilities residing in this labile molecule make its use promising in the synthesis of various monoterpene derivatives.

TABLE 1. ^{13}C NMR Spectra of 1,8,8-Trimethyl-2-oxabicyclo[3.2.1]octan-3-one (III), 1,8,8-Trimethyl-2-azabicyclo[3.2.1]octan-3-one (V), and the 8-Acylamino-p-menth-6-en-2-ones (XVa-e)

Compound	Chemical shifts (δ, ppm) and multiplicities of the signals of the ^{13}C nuclei					
	1	2	3	4	5	6
III	—	—	179,0 s	38,7 t	42,9 d	30,0 t
V	45,2 s	—	176,6 s	38,5 t	42,8 d	30,0 t
XV a	135,2 s	200,0 s	39,8 t	41,4 d	27,7 t	145,4 d
XV b	135,6 s	199 9 s	39,8 t	41,8 d	27,7 t	145,2 d
XV c	135,9 s	199,9 s	40,0 t	41,8 d	28,1 t	145,6 d
XV d	135,4	s 199 9 s	40,0 t	41,5 d	27,9 t	145,6 d
XV e	135,4 s	200,0 s	39,9 t	41,6 d	27,7 t	145,1 d

Compound	Chemical shifts (δ, ppm) and multiplicities of the signals of the ^{13}C nuclei					
	7	8	9	10	11	R
III	37,8 t	45,2 s	23,7 q	18 3 q	21,8 q	
V	37,3 t	45,2 s	23,7 q	18,3 q	21,8 q	
XV a	15,6 q	55,4 s	25,8 q	26,3 q	170 2 s	26,1 q
XV b	15,9 q	56 3 s	24,0 q	24 3 q	169,3 s	43,1 t
XV c	15,9 q	55,9 s	24,0 q	24 3 q	170,0 s	45,9 t(COCH$_2$), 172,4 s(CO$\bar{O}$), 64,0 t(O$\bar{C}$H$_2$)
XV d	15,9 q	55,2 s	24,5 q	24,9 q	177,0 s	14 5 q (CH$_3$) 36,3 d(CH), 20,1 q, 20,3 q (CH$_3$)
XV e	15 7 q	56,3 s	24,3 q	24,7 q	170,'s	118, 3 s 126, 8 d 127,4 d, 128 6 d

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TABLE 2. ^{1}H NMR Spectra of the 8-Acylamino-p-menth-6-en-2-ones (XVa-e)

Compound	Chemical shift (δ, ppm) and multiplicities of the signals of the protons									
	C^3-H_a	C^3-H_e	C^4-H_a	C^5-H_e	C^5-H_a	C^6-H	C^1-CH_3	C^8-CH_3	NH	R
XVa	2,13 m	2,49 dd	2.92 tt	2,34 ddd	2,13 m	6,73 d	1,73 s	1.28 s, 1,31 s	5,72	1,92 s
XVb	2,15 m	2,52 dd	2,90 tt	2,37 ddd	2,15 m	6,73 d	1,74 s	1,33 s, 1,36 s	6,40	4,02 s
XVc	2,16 m	2,52 dd	2,90 tt	2,38 ddd	2,16 m	6,71 d	1,74 s	1,32 s, 1,35 s	5,96	1,25 t, 4,16 q, 2,86 s
XVd	2,14 m	2,48 dd	2,91 tt	2,33 ddd	2,14 m	6,73 d	1,73 s	1,30 s	5,49	2,28 m, 1,11 d
XVe	2,18 dd	2,57 dd	3,05 tt	2,40 ddd	2,18 dd	6,72 d	1,74 s	1,43 s	5,96 s	7,50 m

Compound	Spin–spin coupling constants of the protons, Hz				
	$^2J_{C^3-H_e,\ C^3-H_a}$	$^3J_{C^5-H_e,\ C^5-H_a}$	$^3J_{C^3-H_a,\ C^4-H_a}$ $^3J_{C^5-H_a,\ C^4-H_a}$	$^3J_{C^3-H_e,\ C^4-H_a}$ $^3J_{C^5-H_e,\ C^4-H_a}$	$^3J_{C^5-H_e,\ C^6-H}$
XVa	18,0	17,2	13,2	4,2	5.4
XVb	16.0	17,0	12 6	4,0	6 0
XVc	16.8	17,0	12.4	4,0	5,6
XVd	16,8	16,2	13,2	4,0	5,4
XVe	15,2	15.2	11,2	3,6	5.4

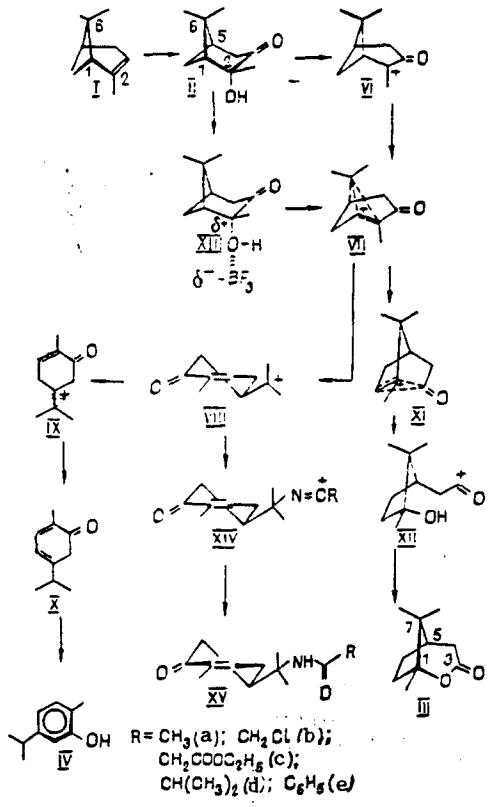
We have studied the transformations under the conditions of acid catalysis of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II), obtained by oxidizing α-pinene (I) with potassium permanganate [4]. It was established that the action of sulfuric acid on 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one leads to the formation of a mixture of 1,8,8-trimethyl-2-oxabicyclo-[3.2.1]octan-3-one (III) and carvacrol (IV) in a ratio of 1:1. The mixture was separated by two vacuum distillations with an efficient fractionating column. Proof of the structure of compound (IV) on the basis of the results of IR, mass, and ^{1}H NMR spectroscopies described in the Experimental part caused no difficulties.

The structure of the lactone (III) was confirmed by the results of IR, mass, and ^{1}H and ^{13}C NMR spectroscopies. Thus, in the IR spectrum of this compound there was a band at 1730 cm^{-1} which is characteristic for the vibrations of a carbonyl group and a band at 1120 cm^{-1} characteristic for the vibrations of the C—O—C bond. The mass spectrum of the compound had the peak of the molecular ion M^+ with an intensity of ~15% of the maximum peak in the spectrum. In the PMR spectrum, the signals of methyl groups were identified with chemical shifts (ppm) of 0.89 (8-CH_3-anti), 1.20 (8-CH_3-syn), and 1.28 (1-CH_3).

A signal with a chemical shift of 2.88 ppm in the form of a double doublet of doublets was assigned to the 4-H_{exo} proton; the spin-spin coupling constant (SSCC) of 22.7 Hz corresponded to geminal interaction with the 4-H_{endo} proton, a constant of 12.4 Hz to vicinal interaction with the 5-H proton, and a constant of 1.6 Hz to long-range spin-spin coupling with the 6-H_{exo} proton (^{W}J). A doublet of doublets with the chemical shift of 2.35 ppm was assigned to the 4-H_{endo} proton (^2J = 22.7 Hz, $^3J_{4\text{-}H_{endo}5\text{-}H}$ = 1.6 Hz) and a triplet of triplets with a shift of 2.56 to the 5-H proton ($^3J_{5\text{-}H,4\text{-}H_{exo}} = {}^3J_{5\text{-}H,6\text{-}H_{exo}}$ = 12.4 Hz, $^3J_{5\text{-}H,4\text{-}H_{endo}} = {}^3J_{5\text{-}H,6\text{-}H_{endo}}$ = 1.6 Hz).

The assignment of the other protons caused difficulties, since the spin-spin system of 2-oxabicyclo[3.2.1]octan-3-one has scarcely been described in the literature despite the fact that lactone (III) and its analogs, which are usually obtained by the Baeyer—Villiger oxidation of bicyclic ketones, are widely used in the stereoelective synthesis of various biologically active products [5, 6] (see scheme on following page).

The criterion for determining the structure of compound (III) as a bridged bicyclic lactone was provided by the results of ^{13}C NMR spectroscopy. As a comparison spectrum we used the spectrum of the model compound 1,8,8-trimethyl-2-azabicyclo [3.2.1]octan-3-one (V) [7]. The good agreement of the values of the chemical shifts of the carbon atoms of the lactone (III)



and its aza analog, the lactam (V) (apart from the shift of the C^2 carbon atom) unambiguously confirmed the structure of compound (III) (Table 1).

The formation of 1,8,8-trimethyl-2-oxabicyclo[3.2.1]octan-3-one (III) and carvacrol (IV) as the result of the reaction is explained by the fact that, under the action of an acid, the hydroxy group attached to the C^2 carbon atom is probably split out and the carbocation (VI) is formed, which is converted into the ion (VII) as the result of the conjugation arising between the C^2 carbon atom, bearing a positive charge, and the cyclobutane ring of the bicyclic system of pinane.

The intermediate (VII) can undergo rearrangement in two different directions. In the first case, the cyclobutane ring opens and the p-menth-6-en-2-on-8-yl cation (VIII) is formed which, as the result of a 4,8-hydride shift, is converted into the ion (IX). The latter, after the ejection of proton, gives the intermediate (X) which is rapidly stabilized through aromatization, leading to the formation of compound (IV). In the second case, the carbocation (VII) is converted as the result of migration of the gem-dimethyl bridge into the three-centered bicyclic cation (XI). The addition of a molecule of water to the latter, which takes place with cleavage of the C^1—C^2 bond leads to the ion (XII), which cyclizes into the lactone (III).

It must be mentioned that a mixture of the products (III) and (IV) in a ratio of 1:1 is formed in the action on compound (II) of both concentrated and dilute sulfuric acid, the only difference being that the rate of the transformation is considerably lower in the latter case. The limiting stage of the process is probably the splitting out of the hydroxy group of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one and the formation of the ion (VI) or (VII) while the subsequent rearrangement of the cation (VII) into ion (VIII) or (XI) depends little on the acidity of the reaction medium.

The action on 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II) of another acidic catalyst — boron trifluoride etherate — led to the selective transformation of compound (II) into carbacrol (IV). Such a result of the reaction under these conditions can be explained by two factors: either the rearrangement of the three-centered bicyclic cation (VII) into cation (XI) is reversible and the impossibility of the subsequent stabilization of the ion (XI) in absolutely anhydrous medium leads to the complete conversion of compound (II) into product (IV), or the intermediate (XIII) formed under the action of boron trifluoride etherate on 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II) is capable of undergoing rearrangement by only one pathway — into the monocyclic cation (VIII).

Under the action of sulfuric acid on 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II) in the presence of nitriles, the main direction of transformation becomes the formation of menthane derivatives — 8-acylamino-p-menth-6-en-2-ones (XV) — although small amounts of (III) and (IV) are formed together with them. The IR spectra of compounds (XVa-e) each has a band at ~3300 cm^{-1} characteristic for the vibrations of N—H group, a band at ~1720 cm^{-1} that is characteristic for the vibra-

tions of the C=O bond in ketones, a band at 1670 cm^{-1} that is characteristic for the vibrations of a carbonyl group in an amide (amide I), and a band at ~1550 cm^{-1} that is characteristic for vibrations of the N—H group in substituted amides.

The mass spectra of the compounds each had the peak of the molecular ion with an intensity of from 8 to 42% of the maximum peak in the spectrum. The assignment of the signals in the PMR spectra was made on the basis of the spin-spin coupling constants (SSCCs) of the protons, and also of a comparison of the spectra of the aminoketones synthesized with the spectra of analogs synthesized previously. Thus, in the spectrum of 8-acylamino-p-menth-6-en-2-one (XVa) singlets of the methyl groups 7-CH_3 (δ 1.73 ppm, s, 3H), 9-CH_3 (1.28 ppm, s, 3H), and 10-CH_3 (1.31, s, 3H) were identified, and so was the signal of the proton attached to the C^6 atom with a chemical shift of 6.73 ppm and a spin-spin coupling constant of 5.4 Hz.

A triplet of triplets with a chemical shift of 2.92 ppm was ascribed to the 4-H proton; axial-axial interaction of the 4-H proton with axial 3-H and 5-H protons corresponds to a constant of 13.2 Hz, and interaction of the 4-H proton with the equatorial protons attached to the same atoms to a constant of 4.2 Hz.

A doublet of doublets with a chemical shift of 2.49 ppm was ascribed to the 3-H equatorial proton (^2J = 18.0 Hz, $^3J_{4\text{-H},3\text{-H}_e}$ = 4.2 Hz) and a signal in the form of a double doublet of doublets with a chemical shift of 2.34 ppm to the 5-H equatorial proton (^2J = 17.2 Hz, $^3J_{4\text{-H},5\text{-H}_e}$ = 4.2 Hz, $^3J_{5\text{-H}_e,6H}$ = 5.4 Hz). A multiplet with a chemical shift of 2.13 ppm (2H) was ascribed to the 3-H_a and 5-H_a axial protons.

The PMR spectra of compounds (XVb-e) had a similar form (Table 2). The assignment of the signals in the ^{13}C NMR spectra was made on the basis of the multiplicities of the lines in the spectra recorded without the suppression of interactions with protons and also of a comparison of the values of the chemical shifts of the ^{13}C carbon atoms of the amidoketones synthesized with those for analogs obtained previously (Table 1). It is obvious that the formation of the amidoketones (XV) took place as the result of the addition of a nucleophile (nitrile) to the cation (VIII).

The yield of an amidoketone (XV) depended both on the nature of the nitrile used and the conditions of the reaction. Thus, in the presence of a large excess of sulfuric acid, and at temperatures above room temperature, the yields of amidoketones (XV) did not exceed a few parts percent, while under milder conditions the yield of the amide (XVa) reached 44%.

It must be mentioned that among the compounds formed in the Ritter reaction no products of the addition of nitriles to the bicyclic cation (XII) were detected. It is likely that the exceptional transformation of the latter into 1,8,8-trimethyl-2-oxabicyclo[3.2.1]octan-3-one (III) is controlled by thermodynamic factors and is due to the high stability of the lactone (III).

On the interaction of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one with acetonitrile in the presence of boron trifluoride etherate as acid catalyst, just as in catalysis by sulfuric acid, the predominant formation of 8-acetylamino-p-menth-6-en-2-one (XVa) took place. The only by-product of the reaction in this case was carvacrol (IV).

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker WM-360 spectrometer with a resonance frequency of 360.134 MHz for ^1H nuclei and 90.56 MHz for ^{13}C. The concentration of the solutions was ~10% in deuterochloroform. Chemical shifts were determined relative to an internal standard — HMDS. IR spectra were taken on a UR-20 instrument. Mass spectra were recorded on a MKh-1320 instrument. The course of the reaction was monitored and the purity of the products synthesized was determined by the GLC method using a Chrom-5 chromatograph with a glass column (2 × 2000 mm) filled with Chromaton N-AW-DMCS (0.16-0.20) impregnated with Apiezon L.

2α-Hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II), obtained by the procedure of [4], had bp 107-108°C (4 mm Hg), n_D 1.4884. IR spectrum (λ_{max}^{KBr}, cm^{-1}): 3450 (OH), 3000-2850 (CH), 1730 (C=O). PMR spectrum (δ, ppm): 0.91 (s, 3H, 6-CH_3-*syn*), 1.38 (c, 3H, 6-CH_3-*anti*), 1.40 (s, 3H, 2-CH_3), 1.70 (d, J = 11.0 Hz, 1H), 2.12 (m, 2H), 2.32 (1H, OH), 2.47 (dt, J_1 = 11.0 Hz, J_2 = 6.0 Hz, 1H), 2.63 (t, 2H, J = 1.8 Hz). According to the literature: bp 113-115°C (17 mm Hg), n_D^{28} 1.4877. PMR spectrum (CCl_4, δ, ppm): 2.60-1.65 (m, 7H), 1.38 (s, 3H, 2-CH_3), 1.32 (s, 3H, 6-CH_3-*anti*), 0.88 (s, 3H, 6-CH_3-*cis*) [4].

Action of Sulfuric Acid on 2α-Hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II). With cooling in an ice bath, 4.0 g of sulfuric acid was carefully added dropwise to 10 g of compound (II). The mixture was stirred with cooling for another 6 h, and then its temperature was allowed gradually to rise to that of the room. After the end of the reaction, the mixture was poured into an excess of aqueous ammonia and was extracted with ether, and the extract was dried with $MgSO_4$. The oil obtained after the solvent had been evaporated off was distilled in vacuum with an efficient fractionating column.

Lactone (III) and carvacrol (IV) form an azeotropic mixture on distillation, but the composition of the condensate was inhomogeneous: a low-boiling fraction [bp 90-100°C (4 mm Hg)] consisted predominantly of carvacrol (IV), and a higher-

boiling fraction [bp 120-126°C (4 mm Hg)] was enriched with product (III). Redistillations of these fractions gave compounds (III) and (IV) in states suitable for spectral studies (purity greater than 90% according to GLC).

1,8,8-Trimethyl-2-oxabicyclo[3.2.1]octan-3-one (III). IR spectrum (λ_{max}^{KBr}, cm^{-1}): 2980-2880 (CH), 1730 (C=O), 1120 (C—O—C). Mass spectrum, m/z: 168 (M^+, 15%), 153, 124, 111, 108, 99 (100%), 85, 71, 55, 44. PMR spectrum (δ, ppm): 0.89 (s, 3H, 8-CH_3-*anti*), 1.20 (c, 3H, 8-CH_3-*cis*), 1.29 (s, 3H, 1-CH_3), 1.43 (dd, 1H, J_1 = 16.0 Hz, J_2 = 11.2 Hz), 1.72 (d, 1H, J_1, J_2 = 16.0 Hz, J_3 = 11.2 Hz), 2.09 (m, 1H), 2.35 (dd, 1H, J_1 = 22.7 Hz, J_2 = 1.6 Hz, 4-H_{endo}), 2.56 tt, 1H, J_1 = 11.2 Hz, J_2 = 1.6 Hz, 5-H), 2.88 (ddd, 1H, J_1 = 22.7 Hz, J_2 = 11.2 Hz, J_3 = 1.6 Hz, 4-H_{endo}).

Carvacrol (IV). IR spectrum (λ_{max}^{KBr}, cm^{-1}): 3400 (OH), 2980-2920 (aliphatic C—H), 3020 (aromatic C—H), 1640, 1530 (aromatic C=C). Mass spectrum (m/z): 150 (M^+, 7%), 135, 121, 108, 79, 77, 71 (100%). PMR spectrum (δ, ppm): 1.13 (d, 6H, $CH(\underline{C}H_3)_2$), 2.14 (s, 3H, CH_3), 2.74 (m, 1H, $\underline{C}H(CH_3)_2$), 5.00 (1H, OH), 6.6-7.1 (m, 3H, aromatic H's).

Action of Boron Trifluoride Etherate on 2α-Hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II). To 6.8 g of compound (II) was carefully added 11 ml of a solution of boron trifloride etherate. The mixture was stirred at room temperature until the reaction was complete, and then an excess of aqueous KOH was carefully added, the mixture was extracted with ether, and the extract was dried with $MgSO_4$. The oil obtained after the solvent had been evaporated off was distilled in vacuum, bp 103-105°C (4 mm Hg). The product obtained consisted of the individual compound (IV).

The Ritter reaction was performed in the following way. A mixture of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II) and a nitrile was cooled in an ice bath and then sulfuric acid was added dropwise, very slowly, with avoidance of the heating of the reaction mixture, since the reaction is extremely exothermic. The mixture was stirred with cooling for another 4 h, and then its temperature was allowed gradually to rise to that of the room and stirring was continued until the reaction was complete (monitoring by GLC). The reaction mixture was poured into an excess of cooled aqueous ammonia and was extracted with ether, and the extract was dried with $MgSO_4$. The oil obtained after the solvent had been evaporated off was distilled in vacuum.

8-Acetylamino-p-menth-6-en-2-one (XVa) was obtained from 10 g of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II), 9.6 g of acetonitrile, and 7.4 g of sulfuric acid with a yield of 5.4 g (44%). bp 170-175°C (4 mm Hg). IR spectrum (λ_{max}^{HBr}, cm^{-1}): 3340 (NH), 2980-2930 (CH), 1720 (ketone C=O), 1670 (amide C=O), 1550 (NH). Mass spectrum (m/z, %): 209 (M^+, 16), 194, 189, 174, 166, 150, 138, 145, 124, 107, 100, 96, 86, 82, 81, 79, 77, 69, 67, 58 (100), 43, 41.

8-(Chloroacetylamino)p-menth-6-en-2-one (XVb) was obtained from 10 g of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II), 16.0 g of chloroacetonitrile, and 7.4 g of sulfuric acid with a yield of 4.8 g (33%). bp 198-196°C (4 mm Hg). IR spectrum (λ_{max}^{KBr}, cm^{-1}): 3350 (NH), 2980-2800 (CH), 1730 (ketone C=O), 1680 (amide C=O), 1560 (NH). Mass spectrum (m/z, %): 245 and 243 (M^+, 6 and 18), 209, 208, 172, 168, 150, 135 (100), 134, 108, 58, 54, 44, 43.

8-(Ethoxycarbonylacetylamino)-p-menth-6-en-2-one (XVc) was obtained from 10 g of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.-1]heptan-3-one (II), 18.0 g of ethyl cyanoacetate, and 7.4 g of sulfuric acid with a yield of 4.4 g (26%). bp 221-227°C (4 mm Hg). IR spectrum (λ_{max}^{KBr}, cm^{-1}): 3350 (NH), 2980-2890 (CH), 1740 (ketone C=O), 1720 (ester C=O), 1660 (amide C=O), 1550 (NH). Mass spectrum (m/z, %): 281 (M^+, 8), 269, 241, 209, 202, 191, 176, 174, 163, 150, 135 (100), 121, 108, 79, 77, 58, 43, 41.

8-Isobutyrylamino-p-menth-6-en-2-one (XVd) was obtained from 10 g of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II), 12.0 g of isobutyronitrile, and 7.4 g of sulfuric acid with a yield of 4.9 g (42%). bp 187-192°C (4 mm Hg). IR spectrum (λ_{max}^{KBr}, cm^{-1}): 3320 (NH), 2980-2800 (CH), 1710 (ketone C=O), 1670 (amide C=O), 1550 (NH). Mass spectrum (m/z, %): 237 (M^+, 20), 166, 150, 135 (100), 128, 96, 91, 71, 58, 43, 41.

8-Benzoylamino-p-menth-6-en-2-one (XVe) was obtained from 10 g of 2α-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-one (II), 9.3 g of benzonitrile dissolved in 10 ml of dibutyl ether, and 7.6 g of sulfuric acid. In the absence of the dibutyl ether an appreciable fall in the yield of amide (XVe) was observed because of the intensive hydrolysis of the benzonitrile. Yield 6.8 g (42%). bp 232-236°C (4 mm Hg). IR spectrum (λ_{max}^{KBr}, cm^{-1}): 3350 (NH), 1720 (ketone C=O), 1670 (amide C=O), 1590 (aromatic C=C), 1540 (NH), 1460 (aromatic C=C). Mass spectrum, m/z (%): 271 (M^+, 42), 251, 236, 202, 200, 163, 162, 150, 135, 105 (100), 77, 58, 43, 41.

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