SYNTHESIS AND STRUCTURES OF 2,3,6-TRIARYL-1-ACYL-4-ACYLOXYPIPERIDEINES

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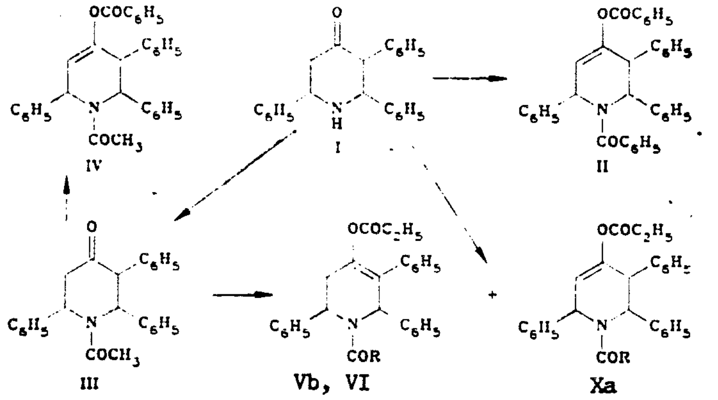
1-Acyl-4-acyloxy-2,3,6-triaryl-Δ^3- and Δ^4-piperideines were obtained by acylation of 2,3,6-triarylpiperidone and its 1-acetyl derivative with carboxylic anhydrides and chlorides. The molecular and crystal structures of 3-phenyl-2,6-bis(o-acetoxyphenyl)-1-acetyl-4-acetoxypiperidin-3-ene were established by x-ray diffraction analysis.

The information on ethers of enols of γ-piperidones is limited. The synthesis of 2,3,6-triphenyl-1-acetyl-4-acetoxypiperideines has been described [1]. Both isomeric (with respect to the position of the piperpideine double bond) piperideines were obtained by the reaction of 2,3,6-triphenyl-4-piperidinone with acetic anhydride in the presence of pyridine.

To develop methods to obtain and study the structures and physiological activities of similar enol ethers, we carried out the acylation of triaryl-substituted γ-piperidones with carboxylic acid chlorides and anhydrides in the presence of triethylamine which, being a relatively strong base, can promote stabilization of the enol form.

In the reaction of 2,3,6-triphenyl-4-piperidinone (I) with benzoyl chloride under these conditions one observes N- and O-benzoylation; this is associated with the rather high electrophilicity of the benzoyl cation. The principal product of enolization and acylation [2,3,6-triphenyl-1-benzoyl-4-benzoyloxypiperidin-4-ene (II)] was isolated in ~60% yield by crystallization.



Va, Vb R=CH_3; VI R=C_2H_5

The data from the IR spectrum of II (Table 1) confirm the presence of amido and ester groups, as well as an olefinic bond in the ring. The presence in the PMR spectrum of a doublet signal at 6.35 ppm (J = 4.8 Hz) and three broad singlets at 4.60-6.86 ppm (Table 2) provides evidence for the presence of a double bond in the $C_{(4)}$–$C_{(5)}$ position.

Only 2,3,6-triphenyl-1-acetyl-4-piperidinone (III) was obtained in the reaction of piperidone I with acetyl chloride in the presence of triethylamine. In this case the reaction proceeds through a step involving the formation of a ketene, which readily acylates amines. As a rule, the acetylation of enols with ketene takes place under acid-catalysis conditions and with prolonged heating [2].

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TABLE 1. Characteristics of II-VI and VIII

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}	Yield, %
II	$C_{37}H_{29}NO_3$	158 ... 159	1612, 1652, 1762	57
III	$C_{25}H_{23}NO_2$	176 ... 177	1647, 1727	55
IV	$C_{32}H_{27}NO_3$	204 ... 205	1607, 1647, 1747	47
Va	$C_{28}H_{27}NO_3$	137	1604 sh, 1634, 1772	34
Vb	$C_{28}H_{27}NO_3$	152 ... 153	1612, 1667, 1782	23
VI	$C_{29}H_{29}NO_3$	139 ... 140	1618, 1662, 1783	39
VIII	$C_{31}H_{29}NO_7$	202 ... 203	1610, 1666, 1776	90

TABLE 2. PMR Spectra of II-VI and VIII

Compound	Chemical shifts, δ, ppm						
	2-H*	3-H	5-H	6-H	CH_3	CH_2, q	aromatic ring, m
II	5,33 br.s	4,60 br.s	6,35d	6,86 br.d	—	—	8,0 ... 6,55
III	6,00 br.d	4,29 d	2,89m; 3,22m	5,77 br.t	1,88 s	—	7,2 ... 6,7
IV	5,37 br.s	4,65 br.s	6,25d	6,66 br.s	1,71 s	—	8,0 ... 6,9
Va	5,23 br.s	4,49 br.s	6,06 br.s	6,61 br.d	1,12 d; 1,68 s	2,4	7,45 ... 6,85
Vb	—	—	2,62m; 3,0 m;	5,23 br.t	1,12t; 2,07 s	2,4	7,6 ... 6,9
VI	—	—	2,62 m; 2,99 m;	5,32 t	1,12 t, 1,08 t	2,38 2,39	7,63 ... 6,87
VIII	—	—	2,70 m; 2,83 m;	5,35 t	1,98 s, 2,14s; 2,30 s; 2,34s	—	7,62 ... 6,88

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*In the aromatic region for Vb, VI, and VIII.

TABLE 3. Torsion Angles for VIII

Angle	τ°	Angle	τ°
$C_{(6)}—N_{(1)}—C_{(2)}—C_{(3)}$	−47,6 (0,2)	$C_{(4)}—C_{(3)}—C_{(31)}—C_{(36)}$	62,5 (0,3)
$C_{(6)}—N_{(1)}—C_{(2)}—C_{(21)}$	79,1 (0,2)	$C_{(3)}—C_{(4)}—C_{(5)}—C_{(6)}$	−30,1 (0,3)
$C_{(11)}—N_{(1)}—C_{(2)}—C_{(3)}$	114,6 (0,2)	$O_{(41)}—C_{(4)}—C_{(5)}—C_{(6)}$	150,1 (0,2)
$C_{(2)}—N_{(1)}—C_{(6)}—C_{(5)}$	19,5 (0,2)	$C_{(5)}—C_{(4)}—O_{(41)}—C_{(42)}$	76,3 (0,2)
$C_{(2)}—N_{(1)}—C_{(6)}—C_{(61)}$	−106,1 (0,2)	$C_{(4)}—C_{(5)}—C_{(6)}—N_{(1)}$	18,3 (0,2)
$C_{(11)}—N_{(1)}—C_{(6)}—C_{(5)}$	−142,2 (0,2)	$N_{(1)}—C_{(6)}—C_{(61)}—C_{(66)}$	14,5 (0,3)
$C_{(2)}—N_{(1)}—C_{(11)}—C_{(13)}$	176,1 (0,2)	$C_{(5)}—C_{(6)}—C_{(61)}—C_{(62)}$	66,2 (0,2)
$C_{(6)}—N_{(1)}—C_{(11)}—O_{(12)}$	160,4 (0,2)	$C_{(2)}—C_{(21)}—C_{(22)}—O_{(27)}$	−3,8 (0,3)
$N_{(1)}—C_{(2)}—C_{(3)}—C_{(4)}$	36,8 (0,2)	$C_{(26)}—C_{(21)}—C_{(22)}—O_{(27)}$	176,8 (0,2)
$N_{(1)}—C_{(2)}—C_{(3)}—C_{(31)}$	−146,5 (0,2)	$C_{(21)}—C_{(22)}—O_{(27)}—C_{(28)}$	96,0 (0,2)
$C_{(21)}—C_{(2)}—C_{(3)}—C_{(4)}$	−90,5 (0,2)	$C_{(22)}—O_{(27)}—C_{(28)}—O_{(29)}$	−8,6 (0,4)
$N_{(1)}—C_{(2)}—C_{(21)}—C_{(22)}$	75,0 (0,2)	$C_{(4)}—O_{(41)}—C_{(42)}—O_{(43)}$	5,4 (0,2)
$C_{(3)}—C_{(2)}—C_{(21)}—C_{(26)}$	20,9 (0,2)	$C_{(6)}—C_{(61)}—C_{(62)}—O_{(67)}$	0,2 (0,3)
$C_{(2)}—C_{(3)}—C_{(4)}—C_{(5)}$	0,9 (0,3)	$C_{(66)}—C_{(61)}—C_{(62)}—O_{(67)}$	178,9 (0,2)
$C_{(2)}—C_{(3)}—C_{(4)}—O_{(41)}$	−179,2 (0,2)	$C_{(61)}—C_{(62)}—O_{(67)}—C_{(68)}$	91,9 (0,2)
$C_{(31)}—C_{(3)}—C_{(4)}—C_{(5)}$	−175,4 (0,2)	$C_{(62)}—O_{(67)}—C_{(68)}—O_{(69)}$	−0,7 (0,3)
$C_{(2)}—C_{(3)}—C_{(31)}—C_{(32)}$	64,0 (0,2)		

From N-acetyl-substituted piperidone III we obtained ethers of its enol form with various O-acyl radicals. 2,3,6-Triphenyl-1-acetyl-4-benzoyloxypiperidin-4-ene (IV) is formed by heating III with benzoyl chloride and triethylamine in benzene. In the PMR spectra of N-acetyl derivatives II and IV the signals of the 2-H and 6-H protons show up in the form of broad lines; this is due to retarded rotation of the anil group about the N–C bond. In this connection the chemical shifts presented in Table 2 are averaged for both rotamers. The spin–spin coupling constants (SSCC) are also average (J = 4-8 Hz).

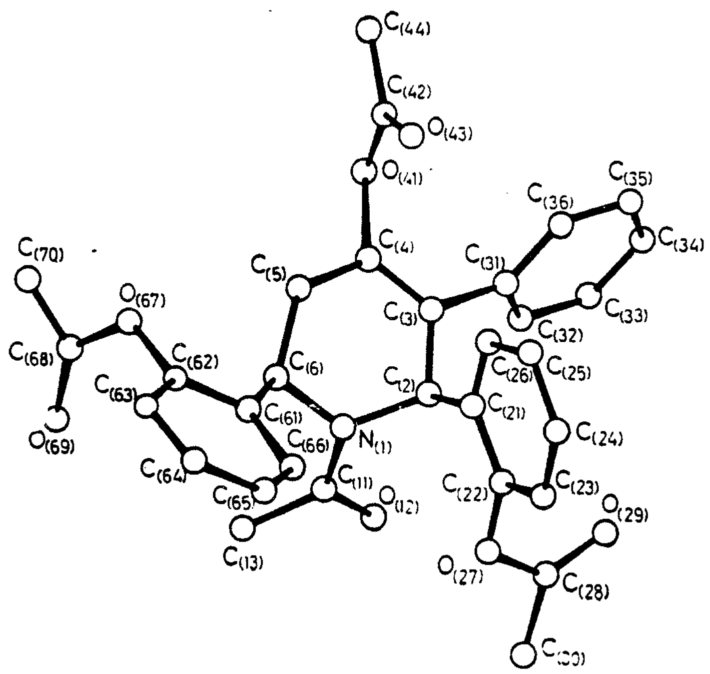
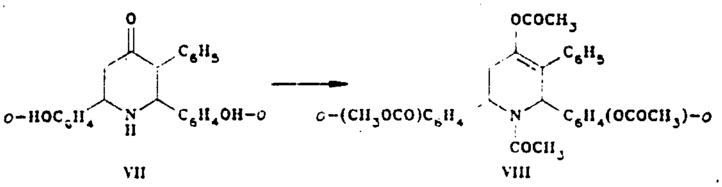


Fig. 1. Structure of the VIII molecule (without the hydrogen atoms).

The isomeric (with respect to the position of the double bond) 2,3,6-triphenyl-1-acetyl-4-propionoxypiperidin-4-ene (Va) and -piperidin-3-ene (Vb) were obtained in the reaction of piperidone III with propionic anhydride in pyridine. They were isolated by column chromatography in 34 and 23% yields, respectively. The structures of Va and Vb were confirmed by IR and PMR spectral data. 2,3,6-Triphenyl-1-propionyl-4-propionoxypiperidin-3-ene (VI) was similarly obtained from piperidone I. 3-Phenyl-2,6-bis(o-acetoxyphenyl)-1-acetyl-4-acetoxypiperidin-3-ene (VIII) was obtained in quantitative yield in the reaction of 3-phenyl-2,6-bis(o-hydroxyphenyl)-4-piperidinone (VII) with acetic anhydride in pyridine.



The structures of IV and V provide evidence that the first act in the enolization of piperidones under the influence of acid anhydrides is acylation of the piperidine nitrogen atom. The resulting enol hydroxy group is then acylated without participation of the N–O acyl shift.

According to the PMR spectral data, isomeric (with respect to the position of the double bond) piperideines, which cannot always be isolated, are formed in the syntheses of II and IV-VI. It must be noted that a certain dependence is observed between the nature of the acylating agent and the structure of the resulting enol ether; this dependence is evidently associated primarily with the steric accessibility of the enol hydroxy group to attack by the acylating reagent. Thus, in the case of benzoyl chloride, the piperideine in which the double bond is located in the $C_{(4)}$–$C_{(5)}$ position predominates in the mixture of isomers obtained (II and IV). The Δ^3-piperideine is formed in greater amounts in acylation with acylation with aliphatic acid anhydrides: VIII was isolated in 90% yield, while the ratio of the Δ^3 – (VI) and Δ^4-piperideine formed in the case of acylation of piperidone I with propionic anhydride was, according to PMR data, ~4:1.

The conformation and configuration of VIII were determined by x-ray diffraction analysis. The piperidine ring has a distorted boat conformation (Fig. 1 and Table 3), the basis of which are the $C_{(3)}$, $C_{(4)}$, $C_{(6)}$, and $N_{(1)}$ atoms (±0.05 Å), while the $C_{(2)}$ and $C_{(5)}$ atoms deviate from this basis by 0.5 and 0.28 Å, respectively.

The o-hydroxyphenyl substituents in the $C_{(2)}$ and $C_{(6)}$ positions are cis oriented. The substituents attached to the $C_{(2)}$ and $C_{(6)}$ atoms are axially oriented. The $N_{(1)}C_{(11)}O_{(12)}C_{(13)}$ amide fragment is planar (the sum of the angles at the $C_{(11)}$ atom is 360 ± 0.3°). The nitrogen center is coordinated in an almost planar-trigonal manner with a sum of the bond angles at 357.6°. The length of the $N_{(1)}$–$C_{(11)}$ bond is 1.372 Å; this indicates conjugation of the unshared electron pair of the nitrogen atom

TABLE 4. Coordinates of the Atoms (× 10^4) and Their Isotropic Temperature Factors for VIII

Atom	*x*	*y*	*z*	*B*, Å²
$N_{(1)}$	−1741(2)	753,6(6)	5407(1)	3,04(3)
$C_{(2)}$	−1384(2)	114,3(7)	6378(1)	3,00(4)
$C_{(3)}$	26(2)	1406,8(7)	6279(1)	2,83(3)
$C_{(4)}$	333(2)	1572,2(7)	5283(1)	3,08(4)
$C_{(5)}$	−626(2)	1495,3(9)	4273(2)	4,47(5)
$C_{(6)}$	−1606(2)	975,5(8)	4280(1)	3,13(4)
$C_{(11)}$	−1800(2)	188,9(8)	5581(2)	3,69(4)
$O_{(12)}$	−1538(2)	−17,7(6)	6500(1)	5,13(3)
$C_{(13)}$	−2254(3)	−177,1(9)	4614(2)	5,31(5)
$C_{(21)}$	−2566(2)	1526,9(8)	6610(1)	3,03(4)
$C_{(22)}$	−3788(2)	1343,8(8)	7087(2)	3,54(4)
$C_{(23)}$	−4887(2)	1697,9(9)	7301(2)	4,32(5)
$C_{(24)}$	−4786(2)	2255,7(9)	7065(2)	4,40(5)
$C_{(25)}$	−3583(2)	2453,6(9)	6602(2)	4,34(5)
$C_{(26)}$	−2491(2)	2095,2(8)	6374(2)	3,66(4)
$O_{(27)}$	−3961(2)	773,0(6)	7293(1)	4,48(3)
$C_{(28)}$	−3578(3)	593(1)	8325(2)	5,79(6)
$O_{(29)}$	−2975(3)	882,6(9)	8987(2)	10,35(7)
$C_{(30)}$	−3971(4)	−6(1)	8460(3)	7,94(8)
$C_{(31)}$	890(2)	1506,4(8)	7325(1)	2,96(3)
$C_{(32)}$	1411(2)	1056,3(8)	7950(2)	3,57(4)
$C_{(33)}$	2212(2)	1142(1)	8930(2)	4,46(5)
$C_{(34)}$	2465(2)	1675(1)	9306(2)	5,13(5)
$C_{(35)}$	1927(3)	2122(1)	8713(2)	5,14(5)
$C_{(36)}$	1154(2)	2041.9(8)	7718(2)	4,00(4)
$O_{(41)}$	1624(1)	1842,4(5)	5089(1)	3,32(3)
$C_{(42)}$	1527(2)	2407,8(8)	4934(2)	3.26(4)
$O_{(43)}$	447(1)	2652.2(6)	5040(1)	4,60(3)
$C_{(44)}$	2888(2)	2652(1)	4624(2)	4,89(5)
$C_{(61)}$	−3018(2)	1105.5(7)	3661(2)	3,11(4)
$C_{(62)}$	−3059(2)	1207,0(8)	2523(2)	3,63(4)
$C_{(63)}$	−4289(2)	1350.6(9)	1918(2)	4,80(5)
$C_{(64)}$	−5530(2)	1396(1)	2450(2)	5,24(5)
$C_{(65)}$	−5537(2)	1287(1)	3577(2)	4,82(5)
$C_{(66)}$	−4291(2)	1141.9(9)	4166(2)	4,00(4)
$O_{(67)}$	−1792(1)	1184.5(6)	1975(1)	4,34(3)
$C_{(68)}$	−1454(3)	685(1)	1531(2)	4,95(5)
$O_{(69)}$	−2168(2)	284.1(7)	1602(2)	6,53(4)
$C_{(70)}$	−87(3)	724(2)	976(2)	8,23(8)
$H_{(2)}$	−1310(20)	851(8)	7010(10)	1,1(4)
$H_{(5A)}$	0(30)	1430(10)	3640(20)	5,2(7)
$H_{(5B)}$	−1230(20)	1820(10)	4190(20)	3,2(5)
$H_{(6)}$	−1180(20)	693(8)	3920(20)	1,0(4)
$H_{(13A)}$	−2370(30)	−540(10)	4980(20)	6,6(8)
$H_{(13B)}$	−1390(30)	−230(10)	4150(30)	7,9(8)
$H_{(13C)}$	−2970(30)	−20(10)	4150(20)	5,5(7)
$H_{(30A)}$	−3510(30)	−240(10)	8020(20)	7,7(8)
$H_{(30B)}$	−5140(40)	30(20)	8480(30)	11(1)
$H_{(30C)}$	−3750(40)	−60(10)	9220(30)	10(1)
$H_{(44A)}$	3690(30)	2430(10)	5000(20)	7,4(8)
$H_{(44B)}$	2870(30)	3020(10)	4540(20)	8,2(8)
$H_{(44C)}$	3120(30)	2520(20)	3880(30)	10(1)
$H_{(70A)}$	710(30)	860(10)	1490(30)	10,6(9)
$H_{(70B)}$	190(40)	410(20)	820(30)	11(1)
$H_{(70C)}$	−190(40)	960(20)	470(30)	13(1)

with the carbonyl group (the length of the N–C bond in the absence of conjugation is 1.425 Å [3]). The length of the $C_{(11)}=O_{(12)}$ bond (1.228 Å) is somewhat greater than in the usual carbonyl group (1.215 Å), which is also due to conjugation and corresponds to the length of the amide C=O bond in N-benzoyldecahydro-4-quinolinone [4]. The analogous bond in the 1-benzoyl-2,5-dimethyl-4-piperidinone molecule [5] is lengthened to an even greater extent (to 1.240 Å) due to the additional formation of an intermolecular hydrogen bond.

Considering that the starting 2,6-diaryl-substituted piperidones have a chair conformation with a diequatorial orientation of the aryl substituents attached to the $C_{(2)}$ and $C_{(6)}$ atoms, one can conclude that ring inversion with the formation of piperideines with a distorted boat conformation with cis-diaxial orientation of the aryl radicals attached to the α-carbon atoms of the piperidine ring occurs during their N-acylation.

TABLE 5. Bond Lengths and Valence Angles for VIII

Bond	l, Å	Angle	ω°
$N_{(1)}$—$C_{(2)}$	1,482(2)	$C_{(2)}$—$N_{(1)}$—$C_{(6)}$	119,6(2)
$N_{(1)}$—$C_{(6)}$	1,476(2)	$C_{(2)}$—$N_{(1)}$—$C_{(11)}$	117,6(2)
$N_{(1)}$—$C_{(11)}$	1,372(2)	$C_{(6)}$—$N_{(1)}$—$C_{(11)}$	120,4(1)
$C_{(2)}$—$C_{(3)}$	1,517(2)	$N_{(1)}$—$C_{(2)}$—$C_{(3)}$	111,4(2)
$C_{(2)}$—$C_{(21)}$	1,530(2)	$N_{(1)}$—$C_{(2)}$—$C_{(21)}$	112,9(2)
$C_{(3)}$—$C_{(4)}$	1,317(2)	$C_{(3)}$—$C_{(2)}$—$C_{(21)}$	111,7(2)
$C_{(3)}$—$C_{(31)}$	1,482(2)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	117,0(1)
$C_{(4)}$—$C_{(5)}$	1,488(3)	$C_{(2)}$—$C_{(3)}$—$C_{(31)}$	116,6(2)
$C_{(4)}$—$O_{(41)}$	1,413(2)	$C_{(4)}$—$C_{(3)}$—$C_{(31)}$	126,3(1)
$C_{(5)}$—$C_{(6)}$	1,552(3)	$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	123,8(1)
$C_{(6)}$—$C_{(61)}$	1,521(2)	$C_{(3)}$—$C_{(4)}$—$O_{(41)}$	122,0(1)
$C_{(11)}$—$O_{(12)}$	1,228(2)	$C_{(5)}$—$C_{(4)}$—$O_{(41)}$	114,2(1)
$C_{(11)}$—$C_{(13)}$	1,504(2)	$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	115,4(1)
$C_{(21)}$—$C_{(22)}$	1,392(2)	$N_{(1)}$—$C_{(6)}$—$C_{(5)}$	112,2(2)
$C_{(21)}$—$C_{(26)}$	1,395(2)	$N_{(1)}$—$C_{(6)}$—$C_{(61)}$	113,9(2)
$C_{(22)}$—$C_{(23)}$	1,378(3)	$C_{(5)}$—$C_{(6)}$—$C_{(61)}$	109,8(1)
$C_{(22)}$—$O_{(27)}$	1,402(2)	$N_{(1)}$—$C_{(11)}$—$O_{(12)}$	122,0(1)
$C_{(23)}$—$C_{(24)}$	1,372(2)	$N_{(1)}$—$C_{(11)}$—$C_{(13)}$	117,9(1)
$C_{(24)}$—$C_{(25)}$	1,381(2)	$O_{(12)}$—$C_{(11)}$—$C_{(13)}$	120,1(1)
$C_{(25)}$—$C_{(26)}$	1,383(2)	$C_{(2)}$—$C_{(21)}$—$C_{(22)}$	120,3(1)
$O_{(27)}$—$C_{(28)}$	1,350(2)	$C_{(2)}$—$C_{(21)}$—$C_{(26)}$	123,3(1)
$C_{(28)}$—$O_{(29)}$	1,180(2)	$C_{(21)}$—$C_{(22)}$—$O_{(27)}$	119,3(1)
$C_{(28)}$—$C_{(30)}$	1,493(3)	$C_{(23)}$—$C_{(22)}$—$O_{(27)}$	118,1(1)
$C_{(31)}$—$C_{(32)}$	1,392(2)	$C_{(22)}$—$O_{(27)}$—$C_{(28)}$	116,7(1)
$C_{(31)}$—$C_{(36)}$	1,387(2)	$O_{(27)}$—$C_{(28)}$—$O_{(29)}$	122,0(2)
$C_{(32)}$—$C_{(33)}$	1,383(2)	$O_{(27)}$—$C_{(28)}$—$C_{(30)}$	110,7(2)
$C_{(33)}$—$C_{(34)}$	1,374(3)	$O_{(29)}$—$C_{(28)}$—$C_{(30)}$	127,2(2)
$C_{(34)}$—$C_{(35)}$	1,369(3)	$C_{(3)}$—$C_{(31)}$—$C_{(32)}$	119,8(1)
$C_{(35)}$—$C_{(36)}$	1,383(2)	$C_{(3)}$—$C_{(31)}$—$C_{(36)}$	121,4(1)
$O_{(41)}$—$C_{(42)}$	1,370(2)	$C_{(4)}$—$O_{(41)}$—$C_{(42)}$	115,2(2)
$C_{(42)}$—$O_{(43)}$	1,190(2)	$O_{(41)}$—$C_{(42)}$—$O_{(43)}$	121,5(1)
$C_{(42)}$—$C_{(44)}$	1,481(2)	$O_{(41)}$—$C_{(42)}$—$C_{(44)}$	111,9(1)
$C_{(61)}$—$C_{(62)}$	1,396(2)	$O_{(43)}$—$C_{(42)}$—$C_{(44)}$	126,6(2)
$C_{(61)}$—$C_{(66)}$	1,384(3)	$C_{(6)}$—$C_{(61)}$—$C_{(62)}$	119,5(1)
$C_{(62)}$—$C_{(63)}$	1,379(2)	$C_{(6)}$—$C_{(61)}$—$C_{(66)}$	123,8(1)
$C_{(62)}$—$C_{(67)}$	1,404(2)	$C_{(61)}$—$C_{(62)}$—$O_{(67)}$	119,0(1)
$C_{(63)}$—$C_{(64)}$	1,375(3)	$C_{(63)}$—$C_{(62)}$—$O_{(67)}$	118,3(1)
$C_{(64)}$—$C_{(65)}$	1,387(3)	$C_{(62)}$—$O_{(67)}$—$C_{(68)}$	116,7(1)
$C_{(65)}$—$C_{(66)}$	1,383(2)	$O_{(67)}$—$C_{(68)}$—$O_{(69)}$	122,7(2)
$O_{(67)}$—$C_{(68)}$	1,358(2)	$O_{(67)}$—$C_{(68)}$—$C_{(70)}$	110,7(2)
$C_{(68)}$—$C_{(69)}$	1,180(2)	$O_{(69)}$—$C_{(68)}$—$C_{(70)}$	126,7(2)
$C_{(68)}$—$C_{(70)}$	1,494(3)		

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in $CDCl_3$ were recorded with a Bruker WP-80 spectrometer (80 MHz) with tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained with an LKB-2091 spectrometer with an ionizing-voltage energy of 70 eV. Molecular-ion peaks corresponding to their molecular masses are present in the mass spectra of II-VI and VIII.

The results of elementary analysis for C, H, and N for II-VI and VIII were in agreement with the calculated values.

X-Ray Diffraction Analysis of 3-Phenyl-2,6-(o-acetoxyphenyl)-1-acetyl-4-acetoxypiperidin-4-ene (VIII). Crystals with the composition $C_{31}H_{29}NO_7$ grown from acetone were investigated with a CAD-4 automatic four-circle diffractometer using MoK_α emission (graphite monochromator). The following values were obtained: space group $P2_1/n$, monoclinic lattice parameters $a = 9.446(2)$, $b = 23.947(8)$, $c = 12.092(3)$ Å, $\beta = 93.46(2)°$, $V = 2732.71$ Å^3, $M = 527.57$, $\rho_{calc} = 1.282$ g/cm^3. A total of 3288 independent reflections were measured. The structure was found by the direct method and was refined by the total-matrix method of least squares. The positions of the hydrogen atoms were ascertained from differential synthesis and were refined within the anisotropic approximation. The final value of the R factor was 0.037 ($R_w = 0.051$). The coordinates of the atoms and their temperature factors (Table 4), the bond lengths and the bond (Table 5), and torsion angles (Table 3) were determined.

2,3,6-Triphenyl-1-benzoyl-4-benzoyloxypiperidin-4-ene (II). A 25 g (178 mmoles) sample of benzoyl chloride and 20 g (198 mmoles) of triethylamine were added simultaneously to a solution of 6 g (18 mmoles) of piperidone I in 100 ml of absolute benzene; the reagents were added gradually with stirring. The mixture was then heated for 5 h, after which it was cooled and treated with 100 ml of water. The aqueous mixture was extracted with 200 ml of ether, after which 190 ml of ether was removed by distillation. The residue was cooled, and the resulting precipitate was recrystallized from ethanol to give 5.3 g (54%) of II in the form of colorless crystals.

2,3,6-Triphenyl-1-acetylpiperidin-4-one (III). A 14.6-g (186 mmoles) sample of acetyl chloride and 43.6 g (430 mmoles) of triethylamine were added to a solution of 6 g (18 mmoles) of piperidone I in 100 ml of benzene, after which the mixture was heated for 8 h and treated with 100 ml of water. The aqueous mixture was extracted with ether, the ether extract was evaporated, and the residue (10 ml) was purified with a column packed with activity II Al_2O_3 (d = 2.5, h = 5 cm, elution with ether). The ether solution was cooled, and the resulting precipitate was separated and dried to give 3.65 g (55%) of III.

2,3,6-Triphenyl-1-acetyl-4-benzoyloxypiperidin-4-ene (IV). This compound was obtained in the same way as III from 2.4 g (6.5 mmoles) of III, 27.2 g (194 mmoles) of benzoyl chloride, and 47.8 g (474 mmoles) of triethylamine in 100 ml of benzene. The yield of IV was 1.44 g (47%).

2,3,6-Triphenyl-1-acetyl-4-propionoxypiperidin-4-ene (Va) and -piperidin-3-ene (Vb). A mixture of 2.2 g (6 mmoles) of piperidone III and 7.8 g (60 mmoles) of propionic anhydride in 5 ml of pyridine was heated for 4 h, after which it was treated with sodium carbonate to pH 7. The mixture was extracted with 150 ml of ether, the ether extract was evaporated, and the residue was purified by passing through a layer of activity II Al_2O_3 (d = 2.5, h = 5 cm, elution with ether). Cooling of the ether solution gave 1.45 g (57%) of a crystalline mixture of Va and Vb, which was chromatographed with a column packed with Al_2O_3 (d = 2.5, h = 25 cm, elution with ether). We initially isolated 0.58 g of Vb, with R_f 0.59, after which we isolated 0.87 g of Va with R_f 0.35 [ethyl acetate–heptane (3:1)].

2,3,6-Triphenyl-1-propionyl-4-propionoxypiperidin-3-ene (VI) and 3-Phenyl-2,6-bis(o-acetoxyphenyl)-1-acetyl-4-acetoxypiperidin-3-ene (VIII). The reaction of 2 g (6 mmoles) of piperidone I and 7.8 g (60 mmoles) of propionic anhydride gave 1.05 g (40%) of VI, while the reaction of 1.5 g of piperidone VII and 4.18 g of acetic anhydride gave 1.94 g (90%) of VIII. The reaction was carried out in the same way as the synthesis of Va and Vb in pyridine.

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