Dihydropyran Cycloadducts. Part 4.[1] *X*-Ray and ^{13}C Nuclear Magnetic Resonance Studies on 2-Methyl-9-phenyl-4a-pyrrolidin-1-yl-1,2,3,4,4a,-5,6,7,8,9a-decahydroxanthen

György Oszbach * and Dezsö Szabó
Department of Chemistry, University Medical School, H-7601 PO Box 99, Pécs, Hungary
Gyula Argay, Alajos Kálmán, and András Neszmélyi
Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 PO Box 17, Budapest, Hungary

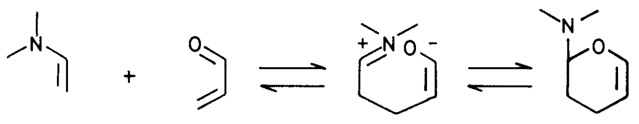
Based on *X*-ray data the relative configurations in the title compound are as follows: the cyclohexane and dihydropyran rings are *cis*-fused and the 9-phenyl group is *cis* to the annelated hydrogen atom. This is the first evidence for previous assumptions that the ring closure of cyclic enamines with heterodiene systems results in a *cis*-ring junction. However, the position of the 9-phenyl group is in contrast to earlier results, established by ^{1}H n.m.r. and chemical methods. The products from the reaction of different cyclic enamines with 2-benzylidenecyclohexanone show the same stereochemistry according to ^{13}C n.m.r. investigations.

Enamines have been known to form dihydropyrans with αβ-unsaturated aldehydes or ketones under mild conditions.[1-11] The first report [2] suggested a Diels–Alder type of reaction mechanism. In an extensive study Fleming and Karger suggested an equilibrium among a Michael type zwitterion adduct, a tautomeric dihydropyran, and a cyclobutane valence isomer.[5] The latter, two-step reaction mechanism was shown to occur by Risaliti *et al.*[9] (Scheme 1).

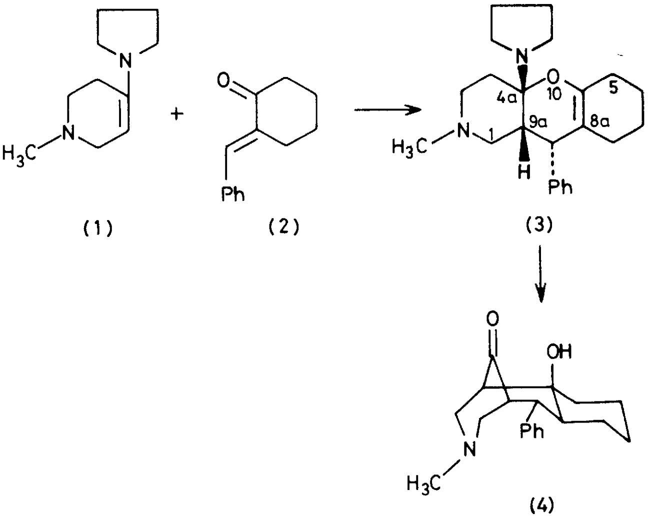
There is very little stereochemical information in the literature.[7,9,10] In our previous papers [1,11] the synthesis of dihydropyrans from enamines of 1-methyl-4-piperidone, cyclopentanone, and various benzylidene ketones was reported. Steric problems were also discussed. We found that the product from cycloaddition of 1-methyl-4-pyrrolidin-1-yl-1,2,5,6-tetrahydropyridine (1) with 2-benzylidenecylohexanone (2) had the relative configuration shown in Scheme 2.[11]

These steric considerations regarding the *cis*-ring closure are in agreement with results in the literature.[7,9,10] *cis*-Annelation is favoured because of the thermodynamically more stable equatorial position of the bulky amino-group. The position of the phenyl group was deduced from the structure of the hydrolysis product (4); however, inversion at C(9a) during hydrolysis could not be excluded.

This paper reconsiders the stereochemistry of the two-step cycloaddition reaction using physical evidence. Because of our particular interest in 2-azaxanthens of type (3), a model compound (5) was synthesized in order to exclude the nitrogen inversion in ring A. In principle, compound (5) may exist in the forms of eight different enantiomeric pairs. However, only one diastereoisomer could be isolated from the reaction mixture in good yield (72%). The steric structure of compound (5) has been established by *X*-ray diffraction.



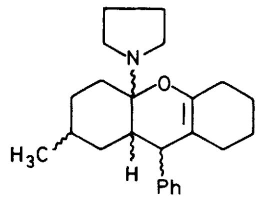
Scheme 1



Scheme 2

Crystal Structure.—As shown by the perspective view of structure (5) (Figure 1) rings A and B are *cis*-fused. The conformation about the C(4a)—C(9a) junction is depicted in Figure 2. The cyclohexane ring (A) assumes the optimal chair conformation bearing the 2-methyl group in the equatorial position. The pyrrolidine ring, which possesses an almost perfect twist (half-chair) shape, is bound axially to ring A. In accord with the C(5a)–C(8a) double bond [1.328(2) Å] both rings B and C are in the half-chair form. The puckering parameters [12] of the four non-planar rings along with the asymmetry parameters suggested by Duax *et al.*[13] are given in Table 6. The phenyl group with a pseudo-equatorial linkage to ring B is *cis* to H(9a). The amount of rotation (Table 5) of the planar phenyl ring about C(9)–C(15) reveals a synclinal [14] orientation with respect to the plane of the C(8), C(9), and C(9a) system. The bond lengths and angles (Tables 3 and 4) agree with those found in the literature for C(sp^3), C(sp^2), and C(aromatic) atoms. The difference between the C(sp^3)–O, 1.469(2) Å, and C(sp^2)–O, 1.378(1) Å, distances is rather pronounced. The N(1) atom in the five-membered ring has a trigonal pyramidal configuration formed by three C–N single bonds, one of which is slightly shorter than the other two.

Crystallographic Analysis of Compound (5).—A crystal of maximum dimension 0.3 mm was mounted on an Enraf–Nonius CAD-4 computer-controlled four-circle diffractomer equipped with graphite monochromater. Cell constants were



(5)

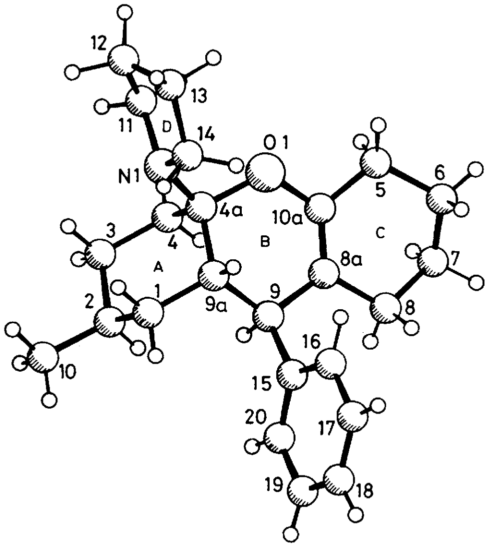


Figure 1. A perspective view of compound (5) indicating atomic numbering and ring labels. Atoms are carbon unless indicated otherwise. The hydrogen atoms in Tables 2 and 5 are numbered according to the carbon atoms to which they are linked

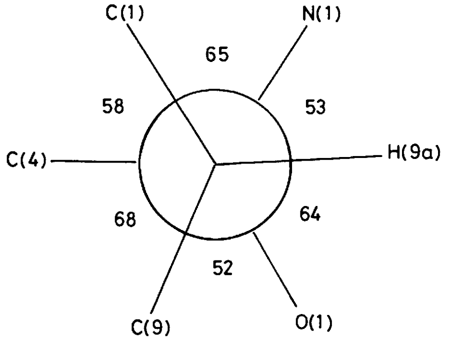


Figure 2. Newman projection down the C(9a)–C(4a) bond showing the conformation angles

Table 1. Atomic fractional co-ordinates of non-hydrogen atoms with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{eq} (Å^2)
C(1)	0.502 6(2)	0.344 4(1)	0.032 4(1)	3.48(5)
C(2)	0.583 7(2)	0.244 8(1)	0.083 3(1)	4.15(6)
C(3)	0.497 2(2)	0.215 5(1)	0.171 7(1)	5.03(6)
C(4)	0.340 7(2)	0.167 8(1)	0.107 4(1)	4.55(6)
C(4a)	0.263 0(2)	0.273 7(1)	0.063 1(1)	3.33(5)
O(1)	0.113 8(1)	0.221 3(1)	0.000 1(1)	4.14(4)
C(10a)	0.090 2(2)	0.124 9(1)	−0.127 7(1)	3.72(5)
C(5)	−0.061 5(2)	0.062 9(2)	−0.164 4(1)	4.87(6)
C(6)	−0.103 9(2)	−0.017 4(2)	−0.310 7(1)	4.65(6)
C(7)	0.017 7(2)	−0.108 6(2)	−0.366 5(1)	4.50(6)
C(8)	0.154 9(2)	−0.022 1(1)	−0.342 2(1)	4.08(6)
C(8a)	0.187 5(2)	0.093 0(1)	−0.206 7(1)	3.47(5)
C(9)	0.335 6(1)	0.164 9(1)	−0.162 6(1)	3.35(5)
C(9a)	0.345 4(1)	0.296 0(1)	−0.032 6(1)	3.14(4)
C(10)	0.738 2(2)	0.298 9(2)	0.149 8(2)	6.03(8)
N(1)	0.251 2(1)	0.402 0(1)	0.172 9(1)	3.57(4)
C(11)	0.183 4(2)	0.392 5(2)	0.276 7(1)	5.29(7)
C(12)	0.137 0(2)	0.536 9(2)	0.350 0(2)	7.28(9)
C(13)	0.094 9(2)	0.589 8(2)	0.248 9(2)	8.50(9)
C(14)	0.183 8(2)	0.516 1(2)	0.143 9(1)	4.82(6)
C(15)	0.382 2(2)	0.201 5(1)	−0.266 5(1)	3.36(5)
C(16)	0.300 0(2)	0.285 3(2)	−0.315 1(1)	4.85(6)
C(17)	0.341 5(2)	0.319 5(2)	−0.409 2(1)	5.84(7)
C(18)	0.466 3(2)	0.268 8(2)	−0.456 9(1)	6.44(7)
C(19)	0.548 7(2)	0.184 9(2)	−0.411 1(2)	6.90(8)
C(20)	0.507 3(2)	0.151 5(2)	−0.316 3(1)	5.13(7)

$B_{eq} = 4[(b_{11}b_{22}b_{33})/(a^2b^2c^2)]^{1/3}$ (Å^2).

determined during alignment procedures by least-squares refinement of the setting angles of 25 carefully centred reflections.

Crystal data. $C_{24}H_{33}NO$, $M = 351.54$, triclinic, $a = 9.356(3)$, $b = 10.603(3)$, $c = 11.433(2)$ Å, $\alpha = 114.43(2)$, $\beta = 99.77(2)$, $\gamma = 88.03(3)°$, $U = 1\,016.8(1.0)$ Å^3, $Z = 2$, $D_c = 1.148$ g cm^{-3}, $F(000) = 384$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, μ(Mo-K_α) = 7.4 mm^{-1}.

Intensity data were collected using the ω–2θ scan technique with Mo-K_α radiation for all reflections in the range $0 \leqslant 2\theta \leqslant 50°$. A total of 3 555 independent reflections was measured of which 2 803 had a net count greater than 2σ. The data were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods with the MULTAN program by the use of 304 normalized structure factors having $E \geqslant 1.7$. The E-map computed from the phase set possessing the best consistency revealed the positions of 22 of the 26 non-hydrogen atoms. One successive cycle of structure factor and Fourier calculations allowed the location of the missing four non-hydrogen atoms (R 0.43). Four cycles of full matrix least-squares refinement of atomic positions and isotropic temperature factors reduced the value of the agreement factor to 0.16. A further three cycles of anisotropic refinement lowered R to 0.116. At this stage hydrogen positions were generated from assumed geometries. In the subsequent three cycles of calculation the non-hydrogen positions were refined anisotropically (R 0.072). In the final three cycles hydrogen atom positions were refined in the isotropic mode along with an extinction coefficient which resulted in a structure factor agreement of 0.0039 for observed reflections ($R_{tot} = 0.046$). All calculations were performed on a PDP 11/34 minicomputer using the SDP-34 program package provided by Enraf–Nonius. Final atomic co-ordinates for non-hydrogen atoms are listed in Table 1, for hydrogen atoms in Table 2; anisotropic thermal parameters, and observed and calculated structure factors, are listed in Supplementary Publication No. SUP 23496 (22 pp.).*

We try to generalize some conclusions based on the X-ray study. We shall prove by ^{13}C n.m.r. that the same stereochemistry is valid for all cycloadditions between enamines and benzylidene ketones. Because ^{13}C n.m.r. chemical shifts are very sensitive to steric factors and to change of substituents, we compare the chemical shifts of cycloadducts (3) and (5)—(8).

Chemical shifts are shown in Table 7. The significant chemical shift changes in ring A are explained by substituent

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

Table 2. Atomic fractional co-ordinates of hydrogen atoms with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	B_{iso} (Å^2)
H(11)	0.504(1)	0.437(1)	0.108(1)	3.6(3)
H(12)	0.557(1)	0.359(1)	−0.028(1)	4.3(3)
H(2)	0.591(2)	0.157(1)	0.008(1)	5.2(4)
H(31)	0.499(2)	0.303(1)	0.253(1)	5.5(4)
H(32)	0.549(2)	0.147(1)	0.200(1)	6.0(4)
H(41)	0.336(1)	0.076(1)	0.028(1)	4.4(3)
H(42)	0.286(2)	0.152(1)	0.166(1)	4.8(3)
H(51)	−0.062(2)	0.002(1)	−0.120(1)	7.0(4)
H(52)	−0.127(2)	0.139(1)	−0.128(1)	6.4(4)
H(61)	−0.120(2)	0.051(1)	−0.353(1)	5.8(4)
H(62)	−0.193(2)	−0.071(1)	−0.332(1)	5.2(4)
H(71)	−0.011(1)	−0.166(1)	−0.461(1)	4.9(3)
H(72)	0.040(2)	−0.174(1)	−0.324(1)	6.1(4)
H(81)	0.143(2)	0.018(1)	−0.407(1)	4.9(3)
H(82)	0.238(2)	−0.085(1)	−0.357(1)	5.6(4)
H(9)	0.409(1)	0.099(1)	−0.147(1)	3.1(3)
H(9a)	0.298(1)	0.367(1)	−0.055(1)	2.7(3)
H(101)	0.793(2)	0.228(2)	0.178(2)	9.1(5)
H(102)	0.794(2)	0.315(2)	0.091(2)	10.5(5)
H(103)	0.738(2)	0.382(2)	0.229(1)	7.8(5)
H(111)	0.257(2)	0.362(1)	0.331(1)	7.0(4)
H(112)	0.100(2)	0.322(2)	0.238(1)	8.1(4)
H(121)	0.229(2)	0.595(2)	0.418(2)	12.5(5)
H(122)	0.059(2)	0.540(2)	0.401(2)	8.4(5)
H(131)	0.098(2)	0.682(2)	0.278(2)	10.1(5)
H(132)	−0.010(2)	0.558(2)	0.207(2)	15.6(6)
H(141)	0.262(2)	0.581(1)	0.148(1)	7.5(4)
H(142)	0.124(2)	0.477(1)	0.053(1)	6.3(4)
H(16)	0.210(1)	0.320(1)	−0.282(1)	5.0(3)
H(17)	0.282(2)	0.381(1)	−0.438(1)	5.8(4)
H(18)	0.492(2)	0.290(2)	−0.524(1)	8.4(5)
H(19)	0.637(2)	0.151(2)	−0.440(1)	8.4(5)
H(20)	0.567(2)	0.094(1)	−0.283(1)	6.3(4)

Table 3. Bond lengths (Å)

C(1)–C(2)	1.527(2)	C(8)–C(8a)	1.512(1)
C(1)–C(9a)	1.531(2)	C(8a)–C(9)	1.507(2)
C(2)–C(3)	1.526(1)	C(9)–C(9a)	1.550(1)
C(2)–C(10)	1.523(2)	C(9)–C(15)	1.523(1)
C(3)–C(4)	1.523(2)	N(1)–C(11)	1.476(1)
C(4)–C(4a)	1.529(2)	N(1)–C(14)	1.477(2)
C(4a)–O(1)	1.469(2)	C(11)–C(12)	1.500(2)
C(4a)–C(9a)	1.535(1)	C(12)–C(13)	1.475(2)
C(4a)–N(1)	1.437(1)	C(13)–C(14)	1.504(2)
O(1)–C(10a)	1.378(1)	C(15)–C(16)	1.382(2)
C(10a)–C(5)	1.502(2)	C(15)–C(20)	1.382(2)
C(10a)–C(8a)	1.328(2)	C(16)–C(17)	1.383(1)
C(5)–C(6)	1.516(1)	C(17)–C(18)	1.371(2)
C(6)–C(7)	1.515(2)	C(18)–C(19)	1.364(2)
C(7)–C(8)	1.521(2)	C(19)–C(20)	1.385(1)

Table 4. Bond angles (°)

C(2)–C(1)–C(9a)	113.3(2)	C(8)–C(8a)–C(9)	117.9(2)
C(1)–C(2)–C(3)	109.8(2)	C(8a)–C(9)–C(9a)	112.3(1)
C(1)–C(2)–C(10)	111.4(2)	C(8a)–C(9)–C(15)	112.2(2)
C(3)–C(2)–C(10)	112.7(2)	C(9a)–C(9)–C(15)	110.1(1)
C(2)–C(3)–C(4)	112.7(2)	C(1)–C(9a)–C(4a)	110.0(1)
C(3)–C(4)–C(4a)	111.3(2)	C(1)–C(9a)–C(9)	112.3(1)
C(4)–C(4a)–O(1)	108.9(1)	C(4a)–C(9a)–C(9)	111.8(1)
C(4)–C(4a)–C(9a)	109.2(2)	C(4a)–N(1)–C(11)	116.2(2)
C(4)–C(4a)–N(1)	110.8(2)	C(4a)–N(1)–C(14)	116.6(2)
O(1)–C(4a)–C(9a)	110.6(1)	C(11)–N(1)–C(14)	107.5(2)
O(1)–C(4a)–N(1)	106.3(1)	N(1)–C(11)–C(12)	104.3(2)
C(9a)–C(4a)–N(1)	111.1(1)	C(11)–C(12)–C(13)	104.1(2)
C(4a)–O(1)–C(10a)	118.6(1)	C(12)–C(13)–C(14)	106.7(2)
O(1)–C(10a)–C(5)	110.1(2)	N(1)–C(14)–C(13)	105.9(2)
O(1)–C(10a)–C(8a)	124.6(2)	C(9)–C(15)–C(16)	121.0(2)
C(5)–C(10a)–C(8a)	125.3(2)	C(9)–C(15)–C(20)	121.5(2)
C(10a)–C(5)–C(6)	111.6(2)	C(16)–C(15)–C(20)	117.5(2)
C(5)–C(6)–C(7)	110.5(2)	C(15)–C(16)–C(17)	121.5(2)
C(6)–C(7)–C(8)	111.0(2)	C(16)–C(17)–C(18)	119.9(2)
C(7)–C(8)–C(8a)	113.7(2)	C(17)–C(18)–C(19)	119.7(2)
C(10a)–C(8a)–C(8)	120.5(2)	C(18)–C(19)–C(20)	120.4(2)
C(10a)–C(8a)–C(9)	121.5(2)	C(15)–C(20)–C(19)	121.1(2)

Table 5. Relevant torsion angles (°)

C(1)–C(2)–C(3)–C(4)	52.5(2)
C(2)–C(3)–C(4)–C(4a)	−56.7(2)
C(3)–C(4)–C(4a)–C(9a)	58.3(2)
C(4)–C(4a)–C(9a)–C(1)	−57.8(2)
C(4a)–C(9a)–C(1)–C(2)	56.8(1)
C(9a)–C(1)–C(2)–C(3)	−53.1(2)
O(1)–C(4a)–C(9a)–C(9)	−52.1(1)
C(4a)–C(9a)–C(9)–C(8a)	39.1(1)
C(9a)–C(9)–C(8a)–C(10a)	−12.6(2)
C(9)–C(8a)–C(10a)–O(1)	−1.8(2)
C(8a)–C(10a)–O(1)–C(4a)	−12.6(2)
C(10a)–O(1)–C(4a)–C(9a)	39.4(1)
C(5)–C(10a)–C(8a)–C(8)	−5.3(2)
C(10a)–C(8a)–C(8)–C(7)	−10.1(2)
C(8a)–C(8)–C(7)–C(6)	42.7(2)
C(8)–C(7)–C(6)–C(5)	−61.0(2)
C(7)–C(6)–C(5)–C(10a)	45.2(2)
C(6)–C(5)–C(10a)–C(8a)	−12.9(2)
H(9a)–C(9a)–C(9)–H(9)	163.0(14)
H(9a)–C(9a)–C(9)–C(15)	47.9(10)
C(4a)–C(9a)–C(9)–H(9)	−79.9(10)
C(4a)–C(9a)–C(9)–C(15)	165.0(2)
C(9a)–C(9)–C(15)–C(16)	−67.5(2)
C(9)–C(9a)–C(4a)–N(1)	−169.8(2)
H(9a)–C(9a)–C(4a)–N(1)	−53.8(10)
C(9a)–C(4a)–N(1)–C(11)	−175.7(2)
C(9a)–C(1)–C(2)–C(10)	−178.7(2)
C(9a)–C(1)–C(2)–H(2)	64.0(12)

effects. Exchange of the pyrrolidine ring for a dimethylamino-group in the 4a-position does not alter significantly the chemical shifts of ring A. The chemical shifts of ring A in compounds (5) and (6) show that the 2-methyl group in compound (5) is equatorial. This finding is in accord with *X*-ray results (see above) and proves that the conformation of ring A is the same in the solid state as in solution. No substituent effect was observed on the chemical shifts of rings B and C carbon atoms. The ^{13}C n.m.r. shift data suggest that all the compounds reported have the same configuration.

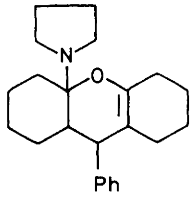
Our conclusions are as follows. (1) The reaction products formed from various enamines and (*E*)-2-benzylidenecyclohexanone are sterically uniform. (2) The first reaction step [nucleophilic attack of the enamine C(2) atom on the β-carbon of the unsaturated ketone] leads to the *erythro*-configuration with respect to the two new chiral centres [C(9) and (9a) in the products]. (3) *cis*-Ring closure occurs in the second reaction step, as it was stated earlier.[7,9,10] (4) Contrary to previous reports,[7,9,10] the 4a-dialkylamino-group is axial both in the solid and in solution; hence, the *cis*-ring fusion is not controlled by the bulky amine substituent.

Experimental

M.p.s were determined with a Boetius hot plate apparatus and are uncorrected. I.r. spectra were recorded with a Zeiss UR-10

Table 6. Puckering parameters (Q, ψ, θ) introduced by Cremer and Pople [12] and asymmetry parameters (ΔC_2 and ΔC_s) suggested by Duax *et al.*[13]

Ring	Q (Å)	ψ (°)	θ (°)	ΔC_2 [$a - b$] (°)	ΔC_s [a] (°)	Conformation
A	0.57	245	4	⟨3.7⟩	⟨2.7⟩	Chair
B	0.43	147	129	0.2 [C(5a)–C(8a)]	18.9 [C(4a)]	Half-chair
C	0.49	146	54	2.6 [C(6)–C(7)]	21.4 [C(6)]	Half-chair
D	0.32	55	—	1.5 [C(14)]	11.8 [C(12)]	Half-chair



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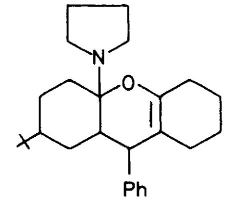

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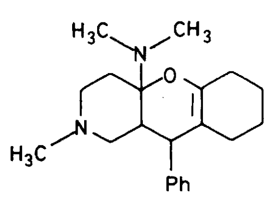

(8)

type spectrophotometer in KBr pellets. ^1H and ^{13}C n.m.r. spectra were obtained on a Varian XL-100-FT-15 instrument at 60 °C in $CDCl_3$ solution with tetramethylsilane as internal reference. In the case of ^{13}C spectra, the digital resolution was 5 Hz per point.

General Procedure for Cycloaddition Reactions.—(*E*)-2-Benzylidenecyclohexanone (2) (0.05 mol) and the appropriate enamine (0.05 mol) were refluxed for 1—8 h in absolute ethanol (50 ml). After cooling, crystals were filtered off, washed with absolute ethanol, and recrystallized from the solvent given below.

9-*Phenyl*-4a-*pyrrolidin*-1-*yl*-1,2,3,4,4a,5,6,7,8,9a-*decahydroxanthen* (6). The compound obtained was identical with that previously described.[7]

2-*Methyl*-9-*phenyl*-4a-*pyrrolidin*-1-*yl*-2,3,4,4a,5,6,7,8,9,9a-*decahydro*-1H-[1]*benzopyrano*[3,2-c]*pyridine* (3).* The preparation was described previously.[11]

2-*Methyl*-9-*phenyl*-4a-*pyrrolidin*-1-*yl*-1,2,3,4,4a,5,6,7,8,9a-*decahydroxanthen* (5). This was formed in 72% yield, m.p. 128—130 °C (from ethyl acetate) (Found: C, 82.5; H, 10.0; N, 3.85. $C_{24}H_{33}NO$ requires C, 82.0; H, 9.45; N, 4.0%); $\nu_{max.}$ (KBr pellet) 1 692 (enol ether) cm^{-1}; δ_H ($CDCl_3$; 100 MHz) 7.23 (5 H, quasi-s, Ph), 3.25 (1 H, br d, *J* 9.5 Hz, 9-H), and 0.85 (3 H, d, *J* 6 Hz, CH_3); ^{13}C n.m.r. see Table 7. The single crystal for *X*-ray analysis was prepared by further recrystallization from ethyl acetate.

2-*t*-*Butyl*-9-*phenyl*-4a-*pyrrolidin*-1-*yl*-1,2,3,4,4a,5,6,7,8,9a-*decahydroxanthen* (7). This was formed in 81% yield, m.p. 130—133 °C (from ethanol–ethyl acetate) (Found: C, 82.1; H, 9.9; N, 3.3. $C_{27}H_{39}NO$ requires C, 82.4; H, 10.0; N, 3.55%); $\nu_{max.}$ (KBr pellet) 1 689 (enol ether) cm^{-1}; δ_H ($CDCl_3$; 100 MHz) 7.17 (5 H, quasi-s, Ph), 3.26 (1 H, d, *J* 10 Hz, 9-H), and 0.82 (9 H, s, t-butyl CH_3); ^{13}C n.m.r. see Table 7.

Table 7. ^{13}C N.m.r. chemical shifts [δ (p.p.m.)] of compounds (3) and (5)—(8)

Carbon	(6)	(5)	(7)	(3)	(8)
1	23.5	32.1	27.7	54.5	54.9
2	20.0	26.2	41.0		
3	24.4	33.1	27.7	53.2	52.6
4	28.6	28.9	29.1	28.9	27.4
4a	90.6	90.8	90.6	88.6	88.7
5	28.0	28.0	27.9	27.9	26.8
6	24.7	24.9	24.1	24.8	23.2
7	24.7	24.9	24.9	24.8	23.2
8	27.0	27.0	26.9	26.9	26.7
8a	103.0	103.2	102.9	104.0	103.9
9	44.0	44.3	44.2	44.7	45.1
9a	45.1	46.0	45.6	45.0	45.6
10a	146.6	146.8	146.8	145.2	144.7
1′	43.7	43.7	43.5	43.9	36.6
		23.4	23.3		
2′	23.3			23.4	
		23.5	23.4		
1″	145.0	145.1	145.0	146.1	145.3
2″, 6″	129.0	129.0	128.9	129.1	129.0
3″, 5″	128.0	128.2	128.0	128.1	127.8
4″	126.0	126.0	125.9	125.9	125.7
CH_3		22.2		45.0	42.3
$\mathit{C}(CH_3)_3$			32.2		
$C(\mathit{C}H_3)_3$			24.8		

2-*Methyl*-4a-*dimethylamino*-9-*phenyl*-2,3,4,4a,5,6,7,8,9,9a-*decahydro*-1H-[1]*benzopyrano*[3,2-c]*pyridine* (8). This was formed in 77% yield, m.p. 79—80 °C (from acetonitrile) (Found: C, 77.55; H, 9.35; N, 9.35. $C_{21}H_{30}N_2O$ requires C, 77.25; H, 9.25; N, 8.6%); $\nu_{max.}$ (KBr pellet) 1 690 (enol ether) cm^{-1}; δ_H ($CDCl_3$; 100 MHz) 7.16 (5 H, quasi-s, Ph), 3.40 (1 H, br m, 9-H), 2.25 [6 H, s, $N(CH_3)_2$], and 2.21 (3 H, s, NCH_3); ^{13}C n.m.r. see Table 7.

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