Synthesis and Spectra of 7-(*o*- and *p*-*R*-Phenyl)-10,10-dimethyl-8,9,10,11-tetrahydrobenz[*c*]acridin-8-ones. Structure Correction of 1,2,3,4-Tetrahydro-2,2-dimethyl-5-aryl-6-aza-7,8-benzophenanthren-4-ones

Eduardo Cortés [1], Roberto Martínez, J. Gustavo Avila and R. Alfredo Toscano

Instituto de Química, Universidad Nacional Autónoma de México [2],
Circuito Exterior, Ciudad Universitaria,
Coyoacán 04510, México, D. F.

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It has been reported that dimedone added to α-arylidennaphthylamines in ethanol with formation of 1,4-addition products derivatives of 5-aryl-5,6,7,8,9,10-hexahydrobenzo[*c*]phenanthridin-7-ones, **III**, which are easily oxidized by chromic anhydride to the corresponding tetrahydro derivatives, **IV**. However, the attempted preparation of these compounds resulted instead of the formation of isomeric acridin-8-ones **V** and **VI**. Structures were confirmed by ir, ^{1}H nmr, ms and X-ray spectroscopy.

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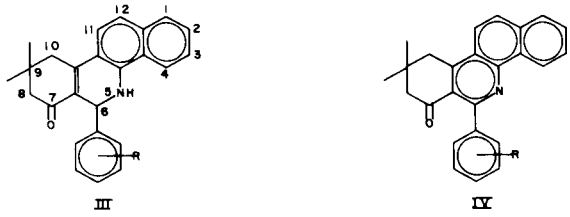
The synthesis of various series of azachrysenes **I** or **II** (Scheme 1) has been reported [3]. The exploration of these derivatives has provided a variety of pharmacologically active compounds or served as precursor to potential medicinal agents [4].

I II

Scheme 1

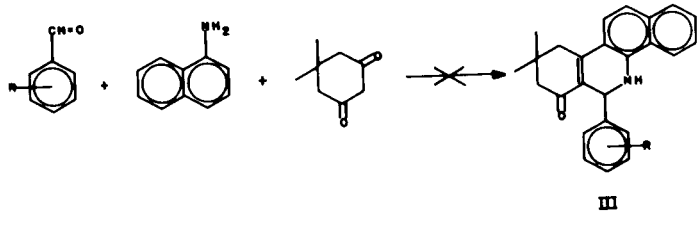
In the course of our synthetic and spectroscopic investigations of compounds with possible pharmacological activity, we undertook the study of the 5-azachrysenes, hexahydrobenzo[*c*]phenanthridines of general formula **III** and its tetrahydro derivatives **IV** (Scheme 2), since several reports indicated that some analogs exhibited antileukemic and antiinflammatory activities [5].



III IV

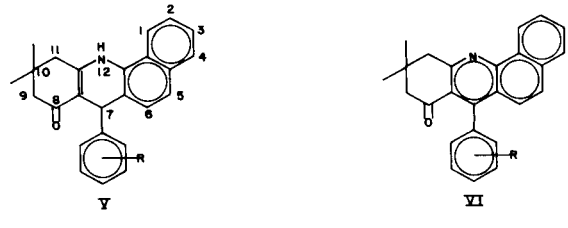
Scheme 2

Lielbriedis, Trusov and Gudrienice developed a one-step synthesis of **III** from dimedone, α-naphthylamine and the appropriate aromatic aldehydes in ethanol (Scheme 3) [6]. However, the attempted preparation of compounds **III** under these conditions or in benzene as solvent, resulted instead of the formation of isomeric benz[*c*]acridines **V** (Scheme 4), which were characterized by absorption spectra (Table 1). The ir spectra (nujol) for all the compounds showed very strong bands at 1590, 1510 (vinylogous amide) [7], 1490 and 3320 cm^{-1} secondary amine. The ^{1}H nmr spectra of the acridinones **V** showed a broad singlet at δ 8.55 (1H, N*H*), which was removed by deuterium oxide, other broad signal at δ 8.2 (1H, C_1-H) [8], as well as one singlet at δ 5.3 (1H, C_7-H). Further confirmation of the structure of the acridinones **V** is derived from their mass spectral data. All the compounds **V** showed the molecular ion and their base peak is the ion at m/z 276.



III

Scheme 3



V VI

o-R = -H, -Cl, -Me, -OMe.

p-R = -Cl, -Me, -OMe, -Br, $-NO_2$, $-NH_2$.

Scheme 4

Oxidation of compounds **V** with chromic anhydride in acetic acid afforded benz[*c*]acridin-8-ones, **VI** (Scheme 4) (Table 2). In agreement with the suggested structure, the ir spectra (nujol) of **VIa** (R = H) compound exhibited a strong ketone carbonyl band at 1690-1695 cm^{-1}. Its ^{1}H nmr spectrum showed a broad signal at δ 9.35 [9] for the

Table 1

Physical and Spectral Data for Compounds **V**

Compound No.	R	Mp °C	Yield %	Molecular Formula	Spectral Data
a [6]	-H	266-268	28	$C_{25}H_{23}NO$	ir (Nujol): 3300, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 8.55 (bs, 1H), 8.2 (m, 1H), 7.8-6.9 (m, 10H), 5.3 (s, 1H), 2.64 (s, 2H), 2.2 (s, 2H), 1.1 (s, 3H), 1.05 (s, 3H); ms: M^+ at m/z 353
b	*o*-Cl	273-275	31	$C_{25}H_{22}NOCl$	ir (Nujol): 3305, 1590 cm^{-1}; ^1H nmr (deuteriochloroform + dimethylsulfoxide): δ 8.92 (bs, 1H), 8.35 (m, 1H), 7.4-6.8 (m, 9H), 5.8 (s, 1H), 2.7 (s, 2H), 2.15 (s, 2H), 1.13 (s, 3H), 1.08 (s, 3H); ms: M^+ at m/z 387
c	*o*-OMe	263-265	46	$C_{26}H_{24}NO_2$	ir (Nujol): 3290, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.7 (m, 1H), 7.6-6.8 (m, 9H), 6.75 (bs, 1H), 5.85 (s, 1H), 3.86 (s, 3H), 2.52 (s, 2H), 2.25 (s, 2H), 1.13 (s, 6H); ms: M^+ at m/z 383
d [6]	*o*-Me	272-274	24	$C_{26}H_{24}NO$	ir (Nujol): 3310, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.8 (m, 1H), 7.7-6.85 (m, 9H), 6.8 (bs, 1H), 5.6 (s, 1H), 2.7 (s, 3H), 2.48 (s, 2H), 2.22 (s, 2H), 1.1 (s, 3H), 1.05 (s, 3H); ms: M^+ at m/z 367
e	*p*-Cl	267-269	24	$C_{25}H_{22}NOCl$	ir (Nujol): 3305, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.78 (m, 1H), 7.7-6.9 (m, 9H), 6.86 (bs, 1H), 5.36 (s, 1H), 2.48 (s, 2H), 2.24 (s, 2H), 1.08 (s, 3H), 1.0 (s, 3H); ms: M^+ at m/z 387
f	*p*-Br	276-278	35	$C_{25}H_{22}NOBr$	ir (Nujol): 3305, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.73 (m, 1H), 7.7-6.9 (m, 9H), 6.85 (bs, 1H), 5.37 (s, 1H), 2.54 (s, 2H), 2.28 (s, 2H), 1.15 (s, 3H), 1.04 (s, 3H); ms: M^+ at m/z 431
g [6]	*p*-NO_2	280-282	60	$C_{25}H_{22}N_2O_3$	ir (Nujol): 3310, 1590 cm^{-1}; ^1H nmr (deuteriochloroform + dimethylsulfoxide): δ 9.17 (bs, 1H), 8.45 (m, 1H), 8.1-7.0 (m, 9H), 5.45 (s, 1H), 2.7 (s, 2H), 2.4 (s, 2H), 1.15 (s, 3H), 1.03 (s, 3H); ms: M^+ at m/z 398
h [6]	*p*-OMe	260-262	27	$C_{26}H_{24}NO_2$	ir (Nujol): 3300, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.85 (m, 1H), 7.8-6.85 (m, 9H), 6.8 (bs, 1H), 5.32 (s, 1H), 3.18 (s, 3H), 2.48 (s, 2H), 2.25 (s, 2H), 1.1 (s, 3H), 1.04 (s, 3H); ms: M^+ at m/z 383
i	*p*-Me	298-300	24	$C_{26}H_{24}NO$	ir (Nujol): 3290, 1590 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.9 (m, 1H), 7.85-6.8 (m, 9H), 6.75 (bs, 1H), 5.35 (s, 1H), 2.52 (s, 2H), 2.28 (s, 2H), 2.23 (s, 3H), 1.15 (s, 3H), 1.09 (s, 3H); ms: M^+ at m/z 367

[6] Prepared by I. Lielbriedis and collaborators.

methine proton of C_1 as well as two singlets of the methylene protons joined to C_9 and C_{11} at δ 2.57 and 3.38 respectively. The signal for the methyl protons of C_{10} also appeared as a singlet at δ 1.2. Further evidence concerning the structure of the acridinones, **VI**, has been derived from their mass spectral data which gave the same pattern fragmentation with the molecular ion as the peak base [9].

Table 2

Bond Lengths (Å)

C(1)-C(2)	1.363(3)	C(1)-C(12b)	1.402(3)
C(2)-C(3)	1.390(4)	C(3)-C(4)	1.359(3)
C(4)-C(4a)	1.413(3)	C(4a)-C(5)	1.426(3)
C(4a)-C(12b)	1.412(3)	C(5)-C(6)	1.346(3)
C(6)-C(6a)	1.439(3)	C(6a)-C(7)	1.417(3)
C(6a)-C(12a)	1.410(3)	C(7)-C(7a)	1.387(3)
C(7)-C(15)	1.493(3)	C(7a)-C(8)	1.502(3)
C(7a)-C(11a)	1.409(3)	C(8)-C(9)	1.495(3)
C(8)-O(1)	1.207(3)	C(9)-C(10)	1.531(3)
C(10)-C(11)	1.533(3)	C(10)-C(13)	1.515(3)
C(10)-C(14)	1.527(3)	C(11)-C(11a)	1.507(3)
C(11a)-N(12)	1.327(3)	N(12)-C(12a)	1.352(2)
C(12a)-C(12b)	1.454(3)	C(15)-C(16)	1.372(3)
C(15)-C(20)	1.372(3)	C(16)-C(17)	1.386(4)
C(17)-C(18)	1.351(6)	C(18)-C(19)	1.358(6)
C(19)-C(20)	1.378(4)		

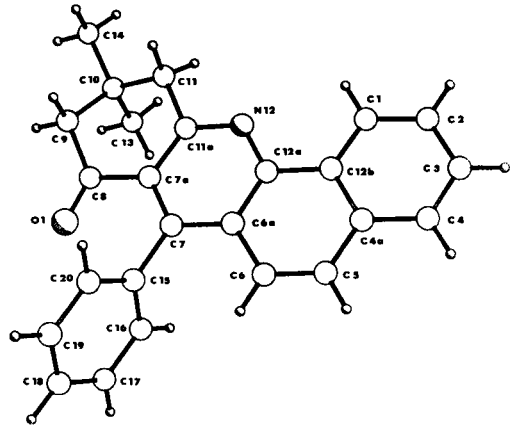


Figure 1

Table 3

Bond Angles (Degrees)

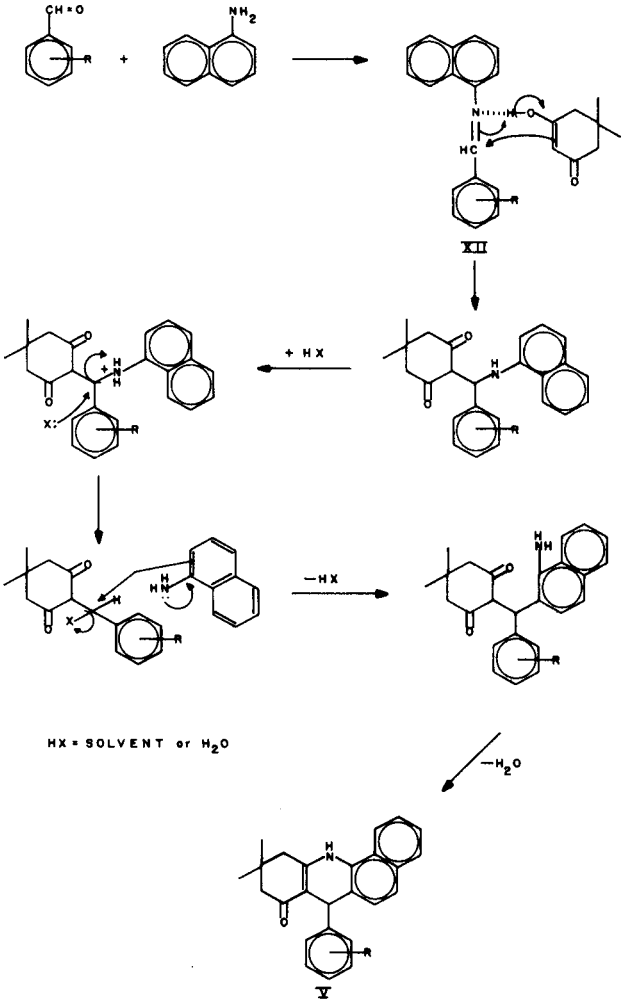
C(2)-C(1)-C(12b)	120.6(2)	C(1)-C(2)-C(3)	120.7(2)
C(2)-C(3)-C(4)	120.0(2)	C(3)-C(4)-C(4a)	121.1(2)
C(4)-C(4a)-C(5)	122.5(2)	C(4)-C(4a)-C(12b)	118.3(2)
C(5)-C(4a)-C(12b)	119.1(2)	C(4a)-C(5)-C(6)	121.9(2)
C(5)-C(6)-C(6a)	121.2(2)	C(6)-C(6a)-C(7)	123.4(2)
C(6)-C(6a)-C(12a)	118.7(2)	C(7)-C(6a)-C(12a)	117.8(2)
C(6a)-C(7)-C(7a)	118.6(2)	C(6a)-C(7)-C(15)	119.1(2)
C(7a)-C(7)-C(15)	122.3(2)	C(7)-C(7a)-C(8)	122.4(2)
C(7)-C(7a)-C(11a)	119.2(2)	C(8)-C(7a)-C(11a)	118.3(2)
C(7a)-C(8)-C(9)	116.5(2)	C(7a)-C(8)-O(1)	121.9(2)
C(9)-C(8)-O(1)	121.5(2)	C(8)-C(9)-C(10)	111.9(2)
C(9)-C(10)-C(11)	107.2(2)	C(9)-C(10)-C(13)	110.4(2)
C(11)-C(10)-C(13)	110.6(2)	C(9)-C(10)-C(14)	109.4(2)
C(11)-C(10)-C(14)	109.6(2)	C(13)-C(10)-C(14)	109.5(2)
C(10)-C(11)-C(11a)	115.3(2)	C(7a)-C(11a)-C(11)	121.7(2)
C(7a)-C(11a)-N(12)	122.9(2)	C(11)-C(11a)-N(12)	115.4(2)
C(11a)-N(12)-C(12a)	118.6(12)	C(6a)-C(12a)-N(12)	122.9(2)
C(6a)-C(12a)-C(12b)	119.8(2)	N(12)-C(12a)-C(12b)	117.3(2)
C(1)-C(12b)-C(4a)	119.2(2)	C(1)-C(12b)-C(12a)	121.5(2)
C(4a)-C(12b)-C(12a)	119.2(2)	C(7)-C(15)-C(16)	121.1(2)
C(7)-C(15)-C(20)	120.0(2)	C(16)-C(15)-C(20)	118.8(2)
C(15)-C(16)-C(17)	119.5(3)	C(16)-C(17)-C(18)	121.2(3)
C(17)-C(18)-C(19)	119.6(3)	C(18)-C(19)-C(20)	120.1(3)
C(15)-C(20)-C(19)	120.8(3)		

On the other hand, the ir spectra of the acridinones, **VI**, (R = H, *p*-NO_2, *p*-OMe and *o*-OMe) obtained in ethanol as solvent (Russian's conditions) and the ir spectra of the same compounds obtained in benzene as solvent (our conditions) were virtually identical. This indicated that the compounds are benz[*c*]acridin-8-ones, **VI**, and not tetrahydrobenzo[*c*]phenanthridin-7-ones, **IV**, which was proved unequivocally by means of X-ray crystallography.

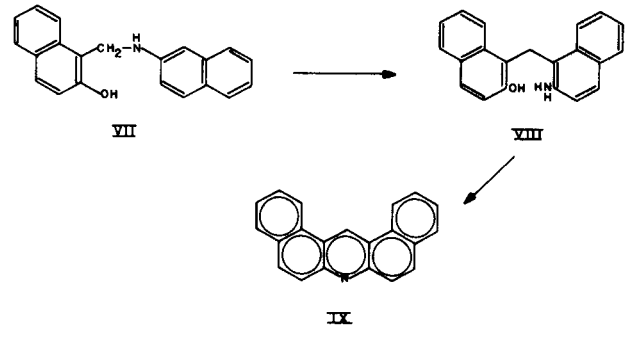
The X-ray crystallographic data for 7-phenyl-10,10-dimethyl-8,9,10,11-tetrahydrobenz[*c*]acridin-8-one, **VIa**, (R = H), (Figure 1), show that the tetrahydro ring on the acridine moiety adopts a half-chair conformation, meanwhile the rest of this group is planar and form a dihedral angle of 105.2° with the also planar phenyl substituent at C_7. The bond lengths and bond angles for compound **VIa** (R = H) are shown in Tables 2 and 3.

A similar production of an anomalous product has been reported in several ring closure of arylaminomethylene cyclohexanes [10], however they need catalytic amounts of an acid. Particularly, the use of lactic or zinc chloride gave a preponderance of the acridine system [11]. In our case, the mechanism of the presumed rearrangement could occur as shown in Scheme 5, which is analogous to proposed by Walker and Hael for production of benz[*c*]acridines from 2-(napthylaminomethylene)cyclohexanones [12].

In fact, some important evidence could support this mechanism: i) extremely ready *o*-migration has been observed in the conversion of 1-(2-naphthylaminomethyl)-2-naphthol, **VII**, into 2-amino-2'-hydroxy-1,1'-dinaphthylmethane, **VIII**, which takes place in nearly quantitative yield in boiling benzene and the latter changes readily into dibenz[*a,j*]acridines, **IX**, (Scheme 6) [13]; ii) the rate of the reaction in a protic solvent is more rapid than in aprotic solvent [ethanol (~2 hours) *vs.* benzene (~20 hours)]; iii) when α-naphthylamine and dimedone were refluxed in ethanol or benzene, were isolated the com-



Scheme 5



Scheme 6

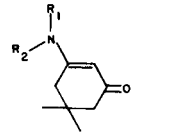
Table 4

Physical, Analytical and Spectral Data for Compounds **VI**

Compound No.	R	Mp °C	Yield %	Molecular Formula	Analyses, % C	H	Spectral Data
a [6]	-H	189-190	46.0	$C_{25}H_{21}NO$	85.44 (85.40)	6.02 (6.00)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.35 (m, 1H), 7.85-7.05 (m, 10H), 3.4 (s, 2H), 2.57 (s, 2H), 1.2 (s, 6H); ms: M^+ at m/z 351
b	*o*-Cl	178-180	54.0	$C_{25}H_{20}ClNO$	77.81 (77.78)	5.22 (5.20)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.36 (m, 1H), 7.9-7.05 (m, 9H), 3.36 (s, 2H), 2.56 (s, 2H), 1.2 (s, 6H); ms: M^+ at m/z 385
c	*o*-OMe	155-157	77.0	$C_{26}H_{23}NO_2$	81.86 (81.80)	6.07 (6.0)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.34 (m, 1H), 7.85-6.9 (m, 9H), 3.62 (s, 3H), 3.55 (s, 2H), 2.55 (s, 2H), 1.2 (s, 6H); ms: M^+ at m/z 381.
d [6]	*o*-Me	169-171	77.0	$C_{26}H_{23}NO$	85.44 (85.41)	6.34 (6.30)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.42 (m, 1H), 7.9-6.9 (m, 9H), 3.37 (s, 2H), 2.57 (s, 2H), 1.8 (s, 3H), 1.17 (s, 3H); ms: M^+ at m/z 365
e	*p*-Cl	224-226	78.0	$C_{25}H_{20}ClNO$	77.81 (77.78)	5.22 (5.20)	ir (chloroform): 1700 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.37 (m, 1H), 7.9-7.05 (m, 9H), 3.36 (s, 2H), 2.56 (s, 2H), 1.2 (s, 6H); ms: M^+ at m/z 385
f	*p*-Br	226-228	62.0	$C_{25}H_{20}BrNO$	69.77 (69.73)	4.68 (4.65)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.4 (m, 1H), 7.9-7.0 (m, 9H), 3.4 (s, 2H), 2.57 (s, 2H), 1.17 (s, 6H); ms: M^+ at m/z 429
g [6]	*p*-NO_2	263-265	65.0	$C_{25}H_{20}N_2O_3$	75.73 (75.68)	5.08 (5.0)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.37 (m, 1H), 7.0-8.5 (m, 9H), 3.4 (s, 2H), 2.57 (s, 2H), 1.17 (s, 6H); ms: M^+ at m/z 396
h [6]	*p*-OMe	232-235	99.0	$C_{26}H_{23}NO_2$	81.86 (81.80)	6.07 (5.98)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.35 (m, 1H), 7.85-7.0 (m, 9H), 3.87 (s, 3H), 3.35 (s, 2H), 2.55 (s, 2H), 1.17 (s, 6H); ms: M^+ at m/z 381
i	*p*-Me	219-221	76.0	$C_{26}H_{23}NO$	85.44 (85.40)	6.34 (6.30)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.85 (m, 1H), 7.8-7.0 (m, 9H), 3.35 (s, 2H), 2.55 (s, 2H), 2.45 (s, 3H), 1.2 (s, 6H); ms: M^+ at m/z 365
j	*p*-NH_2	255-257	94.0	$C_{25}H_{22}N_2O$	81.93 (81.88)	6.05 (5.97)	ir (chloroform): 1690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.35 (m, 1H), 7.85-6.65 (m, 11H), 3.35 (s, 2H), 2.55 (s, 2H), 1.18 (s, 6H); ms: M^+ at m/z 366

[6] Prepared by I. Lielbriedis and collaborators.

pounds **X** and **XI** (Scheme 7), and their structures were deduced by ir, ms and ^1H nmr data [14]. However, when a mixture of **X** or **XI** and benzaldehyde in ethanol was refluxed 48 hours, no reaction was observed. In contrast, the reaction of benzaldehyde with α-naphthylamine in ethanol or benzene gave the intermediate **XII** which could not be isolated pure because it decomposed on purification process. Nevertheless, the crude product showed an absorption band at 1630 cm^{-1} (-C=N-) and its ^1H nmr, a singlet at δ 8.45 (-C*H*=N).



X R_1 = α-naphthyl R_2 = H

XI R_1 = H R_2 = α-naphthyl

Scheme 7

Further investigation of this mechanism and other anomalous products on the reaction of dimedone with β-arylidennaphthylamines are presently being carried out.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a Nicolet FT-55X spectrophotometer. The ^1H nmr spectra were recorded on a Varian FT-80 spectrometer operating at 80 MHz, in deuteriochloroform solution containing tetramethylsilane as the internal standard with chemical shifts (δ) expressed downfield from TMS. Mass spectra were obtained with a Hewlett Packard 59854-A quadropole mass spectrometer.

Crystallography.

X-Ray Analysis Data for 7-Phenyl-10,10-dimethyl-8,9,10,11-tetrahydrobenz[c]acridin-8-one, **VIa**.

The molecular formula is $C_{25}H_{21}NO$, Mω = 351, monoclinic, space group $P2_1/n$, Z = 4, a = 11.926(6), b = 9.167(4), c = 18.011(5) Å, β = 98.26(3)°, V = 1948.6(2) Å^3, Dx = 1.196 g cm^{-3}, μ(MoKα) = 0.67 cm^{-1}; crystal size *ca.* 0.66 x 0.4 x 0.32 mm (pale-orange).

The cell dimensions and intensities were measured on a Nicolet R3m automatic four-circle diffractometer with graphite-monochromated

MoKα radiation (λ = 0.71069 Å). A total of 3449 reflections were collected up to $2\theta = 50°$ of which 2620 independent reflections corrected by Lorentz and polarization effects but no absorptions correction with (Io) ≥ 1.73σ(Io) were used for structure determination and refinement.

The structure was solved by direct methods and refined by the block-diagonal least squares method with anisotropic temperature factor for non-H atoms. The final R was 0.053. Atomic scattering factors from International Tables for X-ray Crystallography [15]. All calculations were carried out on a NOVA 4S computer using the SHELXTL program system [16].

Reaction of (*o*- and *p*-*R*)-Benzaldehydes, α-Naphthylamine and Dimedone. Synthesis of 7-(*o*- and *p*-*R*-Phenyl)-10,10-dimethyl-7,8,9,10,-11,12-hexahydrobenz[*c*]acridin-8-ones **Va-j**.

General Procedure.

A) With Ethanol as the Solvent [6].

A mixture of 0.01 mole (1.06 g) of benzaldehyde and 0.01 mole (1.43 g) of α-naphthylamine in ethanol (15 ml) was stirred under reflux for 15 minutes. Then 0.01 mole (1.4 g) of dimedone in 15 ml of ethanol was added, and the mixture heated for 2 hours. The reaction mixture was then allowed to cool. The precipitated product was filtered off and recrystallized from dimethylformamide-dioxane to yield 2.04 g (58%) of **Va**, mp 266° (lit 254° [6]). The physical and spectral data for synthesized compounds, **Va-j**, are recorded in Table 1.

B) With Benzene as the Solvent (in this work).

A mixture of dimedone (0.01 mole, 1.4 g), α-naphthylamine (0.01 mole, 1.43 g) and benzaldehyde (0.01 mole, 1.06 g) in 15 ml of benzene was refluxed for 20 hours under a Dean-Stark trap. The reaction mixture was then allowed to cool. The precipitated product was filtered off and recrystallized from acetone-hexane to yield 1 g (28%) of **Va**, mp 266°.

Oxidation of 7-(*o*- and *p*-*R*-Phenyl)-10,10-dimethyl-7,8,9,10,11,12-hexahydrobenz[*c*]acridin-8-ones **Va-j**. Synthesis of 7-(*o*- and *p*-*R*-Phenyl)-10,10-dimethyl-8,9,10,11-tetrahydrobenz[*c*]acridin-8-ones **VIa-j**.

General Procedure.

One ml of a 20% solution of chromic anhydride in acetic acid was added dropwise to a solution of 7-phenylbenz[c]acridin-8-one, **Va**, (0.03 g, 8 x 10^{-5} mole), acetic acid (5 ml) and chloroform (15 ml). The reaction mixture was stirred at room temperature for 10 minutes. It was treated with cold water (10 ml) and then extracted with diethyl ether (5 x 20 ml). The resulting solution was washed with a 10% aqueous sodium bicarbonate (5 x 20 ml), water (5 x 20 ml), dried over anhydrous sodium sulfate and concentrated (rotatory evaporator) to afford a slightly yellow solid. Crystallization of this material from acetone-hexane gave 0.014 g (46%) of **VIa**, mp 189-190°.

The physical, analytical and spectral data for the synthesized compounds, **VIa-j**, are recorded on Table 4.

5,5-Dimethyl-3-(*N*-naphthylamino)cyclohex-2-enones **X** and **XI**.

Dimedone (0.277 g, 2 x 10^{-4} mole), α-naphthylamine (0.285 g, 2 x 10^{-4} mole) in benzene (15 ml) were treated for 20 hours under reflux with a Dean-Stark separator to remove water produced. The reaction mixture was concentrated (rotatory evaporator) to afford a slightly yellow oil. Alumina tlc showed the presence of two compounds. Chromatography on alumina utilizing a mixture of hexane-ethyl acetate (1:1) as eluent gave in succession **X** (13 x 10^{-3} g, 3%) as slightly yellow crystals, mp 180-182° (from hexane), and **XI** (0.170 g, 32%) as white crystals, mp 179-181° (from acetone). The respective ir, ^{1}H nmr and ms of **X** and **XI** were indistinguishable: ir (chloroform): ν cm^{-1} 3420 (-NH-), 1600 (enaminone-CO); ^{1}H nmr (deuteriochloroform): δ ppm 7.0-7.9 (m, 8H, N*H* and Ar), 5.0 (s, 1H, C_3-H), 2.4 (s, 2H, C_4-H), 2.11 (s, 2H, C_6-H), 1.0 (s, 6H, $2CH_3$); ms: m/z 265 (M^+).

Benzylideneamino-1-naphthalene **XII**.

Benzaldehyde (0.11 g, 1.0 x 10^{-3} mole) was added to an ethanolic solution (4 ml) of α-naphthylamine (0.15 g, 1.0 x 10^{-3} mole) and the yellow solution was boiled under reflux for 2.5 hours and cooled. The reaction mixture was concentrated (rotatory evaporator) to afford a yellow oil; ir (neat): ν cm^{-1} 1630 (-C=N); ^{1}H nmr (deuteriochloroform): δ ppm 8.45 (s, 1H, C*H*=N-), 6.85-8.4 (m, 12H, Ar).

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[1] Author to whom correspondence should be addressed.

[2] Contribution No. 891 from Instituto de Química, UNAM.

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