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STUDIES OF ACENAPHTHENE DERIVATIVES—XXVIII[1]

THE REACTION OF 2-DIAZOACENAPHTHENONE WITH ANILS IN THE PRESENCE OF BORON TRIFLUORIDE

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Abstract—Reaction of 2-diazoacenaphthenone with anils in the presence of a catalytic amount of boron trifluoride etherate is reported. The diazoketone reacts with benzylidenanilines to afford a mixture of stereoisomers of spiro[acenaphthenone-2',4-imidazolidine], whose structures correspond to compounds derived from 1:2 adducts of the diazoketone and anils with the elimination of nitrogen. A pathway involving spiro-aziridine intermediates is proposed for their formation. Reaction of the diazoketone with α-alkylbenzylidenanilines however gives the corresponding acenaphtho[1,2-b]pyrroles, whose structures correspond to compounds arising from 1:1 adducts with the elimination of both nitrogen and water. The reaction of the tautomeric enamine form of the anil with a carbenoid intermediate generated from the diazoketone is suggested for pyrrole formation.

In earlier publications, we have shown that the reactions of 2-diazoacenaphthenone (1) with olefins[2] and with aroyl isocyanates[3] under mild conditions afforded spiro-cyclopropanes and spiro-oxazolidinones respectively. These reactions can be viewed as proceeding *via* a 1,3-cycloaddition of the diazomethane moiety of 1 to the unsaturated bonds, followed by the elimination of nitrogen and concurrent recyclization as shown in Scheme 1.

Thus, in the cycloaddition reaction not involving the ketocarbene, 1 behaves exclusively as a 1,3-dipole rather than as a 1,5-dipole.

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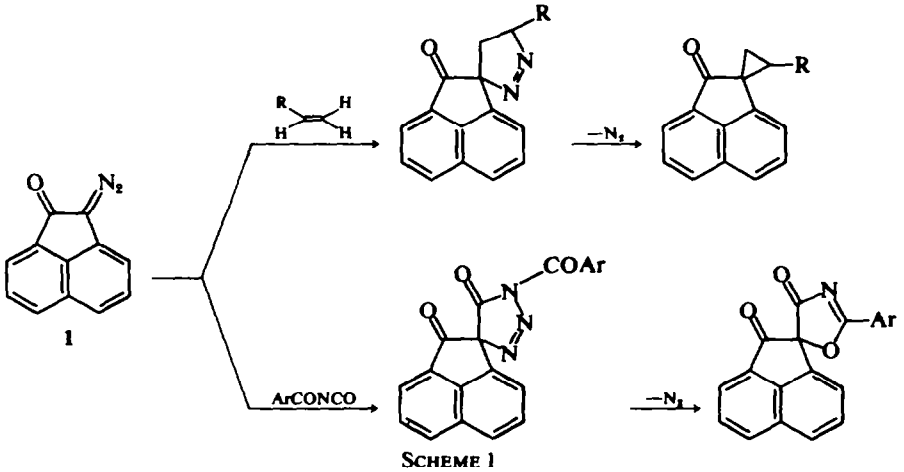
Although the addition of diazoalkanes to activated olefinic double bonds is a well known route to the preparation of pyrazolines,[4] few reports are available on the addition of diazoalkanes to carbon-nitrogen double bonds. Mustafa[5] observed the formation in small quantities of 1,2,3-triazolines by the 1,3-cycloaddition of diazomethane to anils, and solvent effects on the cycloaddition have been investigated by Kadaba.[6] However, there is little information about the reaction of α-diazoketones with anils. If the addition of 1 to anils would take place in a similar manner to olefins, spiro-aziridines would be the expected products. It thus seemed of interest to investigate the reaction of 1 with anils.



SCHEME 1

RESULTS AND DISCUSSION

Reaction with benzylidenanilines. 2-Diazoacenaphthenone (1) did not react with benzylidenanilines (2) upon prolonged reflux in benzene and was recovered in a quantitative yield.

When a benzene solution of 1 and *p*-chlorobenzylidene-*p*-chloroaniline (2a) was refluxed in the presence of catalytic amounts of boron-trifluoride etherate (BF_3-Et_2O) for 1 h, a crystalline compound 3a (m.p. 232–234°) was obtained in 33·8% yield, accompanied by trace amounts of 2,2'-diacenaphthylidene-1,1'-dioxide (biacenedione); 3a was determined to be a 1:1·5:1 mixture of three isomeric compounds, 3a-1 (m.p. 234–235°), 3a-2 (m.p. 241–242°) and 3a-3 (m.p. 273–274° dec), all as yellow prisms.

Microanalyses and molecular ion (M^+ *m/e* 666) of all three isomers fitted the molecular formula of a compound arising from the elimination of nitrogen from a 1:2 adduct of 1 and 2a. The IR spectra of 3a-1, 3a-2 and 3a-3 showed bands ascribable to $\nu_{C=O}$ at 1720, 1730 and 1732 cm^{-1} respectively and did not exhibit any ν_{NH} absorption.

The NMR spectrum of 3a showed three singlets at δ 5·43, 5·19 and 5·52 ppm in a 2:3:2 ratio; these singlets appeared as 1H in the spectra of pure samples of 3a-1, 3a-2 and 3a-3. Furthermore, the mass spectra of all the isomers were identical and displayed fragment peaks at *m/e* 415 (M^+-2a, 46·5%) and 290 (415⁺-Cl-  -N, 23%) besides a parent ion (M^+) at *m/e* 666. On the basis of these observations, it was deduced that 3a-1, 3a-2 and 3a-3 were stereoisomers of a 1,2,3,5-tetrakis(*p*-chlorophenyl)-spiro[acenaphthenone-2',4-imidazolidine], although their stereochemistry is not clear in the present stage.

Under similar conditions, 1 was reacted with benzylidenaniline (2b), *p*-methylbenzylidenaniline (2c) and *p*-chlorobenzylidene-*p*-toluidine (2d) to afford the corresponding spiro[acenaphthenone-2',4-imidazolidine] derivatives 3b, 3c and 3d. The NMR spectra indicated that 3b, 3c and 3d were also mixtures of stereoisomeric spiro-imidazolidines, but it was not possible to separate the respective isomers. The yields, physical properties and microanalyses of 3 are summarized in Table 1.

Hydrolysis of 3a and 3d with conc. HCl in refluxing EtOH gave the corresponding 2-ethoxy-2-(α-ethoxybenzyl)acenaphthenone 4a, and *p*-chloroaniline and *p*-toluidine respectively. Similar treatment of 3a in refluxing MeOH afforded 2-methoxy-2-(α-methoxybenzyl)acenaphthenone 4b and *p*-chloroaniline. The structures of 4a and 4b were confirmed by their spectral data and microanalyses.

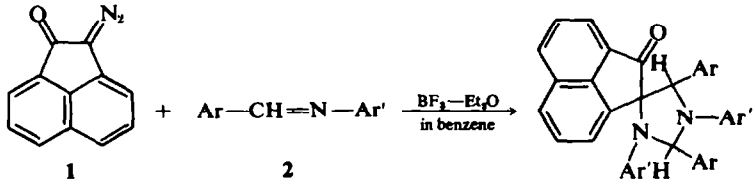
However on treatment of 3d with conc. HCl at room temp, acenaphthenequinone mono-*p*-toluimine (5), *p*-chlorobenzaldehyde and *p*-toluidine were formed in addition to trace amounts of anil 2d (Scheme 2). These facts also support the proposed structures for 3.

Reaction pathway. It is known that the decomposition of diazoalkanes and α-diazocarbonyl compounds is catalyzed by boron trihalides. In the case of CH_2N_2, the first step is without doubt coordination of the Lewis acid with the carbon atom, but there is some question about the subsequent steps leading to polymethylene.[7] On the other hand, it is considered that boron trihalide coordinates with the oxygen atom of the carbonyl group in α-diazoketones.[8]

Treatment of 1 with BF_3-Et_2O in benzene at room temp gave extremely unstable yellow crystals (possibly a complex) which could not be isolated† but when a benzene solution of anil 2a was refluxed with a catalytic amount of BF_3-Et_2O, 2a was recovered in 84% yield. Thus it appears that BF_3 reacts preferentially with 1 rather than with 2 in the reaction of 1 with 2 in the presence of BF_3-Et_2O.

We view the pathway for the formation of spiro[acenaphthenone-2',4-imidazolidine] derivatives 3 as depicted in Scheme 3. Although the postulation of C-bonded complex A is unusual, our previous results[2,3] suggested that the contribution of the mesomeric 1,5-dipolar form to the structure of 1 is small. The formation of a reactive species B (an "inverse ylid") may proceed either directly *via* A

†While decomposition of 1 with catalytic amounts of BF_3-Et_2O in refluxing benzene gave 2,2'-diphenyl-2,2'-dihydrodiacenaphthenylidene-1,1'-dione, with excess of BF_3-Et_2O 2-phenylacenaphthenone was obtained. However, reaction pathways are not clear.



1 2

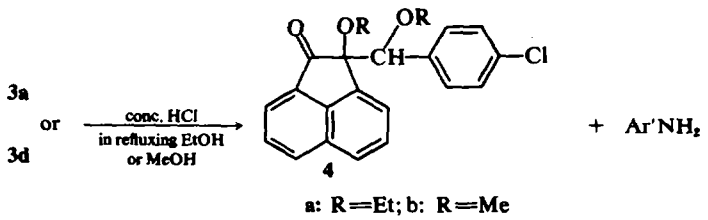
a: Ar=Ar'=*p*-ClC_6H_4; b: Ar=Ar'=Ph
c: Ar=*p*-$CH_3C_6H_4$, Ar'=Ph
d: Ar=*p*-ClC_6H_4, Ar'=*p*-$CH_3C_6H_4$

Table 1. Spiro[acenaphthenone-2',4-imidazolidines] 3

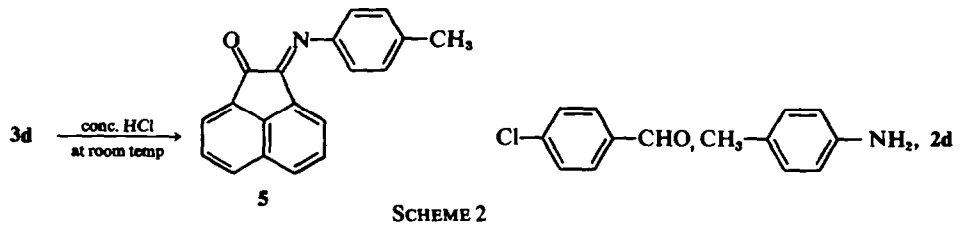
3[a]	Ar	Ar'	Reaction time (min)	Yield (%)	M.p. (°C)	IR ν_{CO} (cm^{-1})	NMR($CDCl_3$)[b] CH δ ppm (rel. ratio)	Microanalysis (%) Found (Calc.) C	H	N	M^+ (m/e)
3a-1	p-ClC_6H_4	p-ClC_6H_4	60	33·8	234–235	1720	5·43	68·80 (68·47)	3·47 (3·60)	4·08 (4·20)	666
3a-2	"	"			241–242	1730	5·19	68·71 (68·47)	3·58 (3·60)	4·16 (4·20)	666
3a-3	"	"			273–275 dec	1732	5·52	68·50 (68·47)	3·49 (3·60)	4·22 (4·20)	666
3b	C_6H_5	C_6H_5	40	30·8	248–248·5	1718	5·30(4) 5·60(1)	86·54 (86·33)	5·02 (5·34)	5·30 (5·30)	528
3c	p-$CH_3C_6H_4$	C_6H_5	10	31·4	136–138	1726	5·25(1) 5·40(2) 5·54(2)	86·59 (86·30)	5·62 (5·79)	4·78 (5·03)	556
3d	p-ClC_6H_4	p-$CH_3C_6H_4$	30	32·2	157–160	1728	5·22(5) 5·43(4) 5·51(1)	76·75 (76·80)	4·72 (4·80)	4·71 (4·48)	625

[a]Appearance: 3a-1–3a-3, yellow prisms; 3b, pale yellow prisms (MeOH); 3c, light yellow grains (EtOH-H_2O); 3d, yellow prisms (EtOH-H_2O).

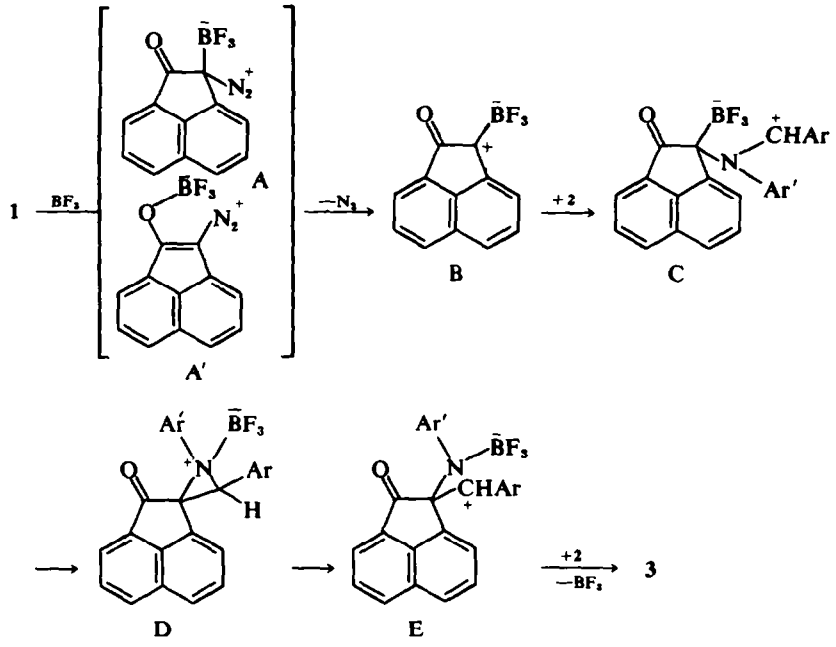
[b]Complicated signals appeared in the spectra, besides the singlets indicated in the Table: 3a-1, δ 5·85–8·1; 3a-2, 6·1–8·2; 3a-3, 6·1–8·2 (each 23H); 3b, 6·0–8·1 (27H), 3c, 1·7–2·5 (6H, CH_3), 5·8–8·3 (25H); 3d, 1·9–2·2 (6H, CH_3), 5·8–8·1 (23H).



a: R=Et; b: R=Me



SCHEME 2



SCHEME 3

or *via* an initial O-bonded complex A' which may then go to reactive species **B** as shown in Scheme 3. The reactive species **B** would then react with the nitrogen atom of anil **2** to yield betaine intermediate **C** which would cyclize to spiroaziridine **D**, followed by ring opening to 1,3-dipole **E**.[9] Cycloaddition of **E** to **2** would yield the final product **3**.

The proposed pathway involving aziridine intermediate **D** was supported by the following evidence. When a solution of diazoacetophenone (**6**) and anil **2b** in benzene containing a catalytic amount of BF_3-Et_2O was refluxed, compound **7b** ($C_{21}H_{17}NO$, M^+ *m/e* 299) whose molecular formula agreed with that of a compound arising from a 1 : 1 adduct with N_2 elimination, was obtained. On the basis of its spectral data, two structures, α- and β-anilinobenzylidenacetophenone **7b-1** and **7b-2** respectively are possible for **7b**. However, we found that product **7b** was different from authentic **7b-2**, prepared from dibenzoylmethane and aniline.[10] Consequently, **7b** was deduced to be α-anilinobenzylidenacetophenone (**7b-1**). Similarly, reaction of **6** with **2a** afforded α-*p*-chloroanilino-*p*-chlorobenzylidenacetophenone (**7a-1**).

$$PhCOCH_2COPh + PhNH_2 \rightarrow PhC(NHPh)=CHCOPh$$

7b-2

The pathway for the formation of **7-1** can be rationalized as depicted in Scheme 4. The 1,3-dipole G arising from aziridine intermediate F rearranges easily into stable product **7-1** with the elimination of BF_3 and concurrent hydrogen shift, because G has a hydrogen atom on the central carbon atom. In contrast, species E does not have a hydrogen atom at the 2-position and behaves as a real 1,3-dipole.

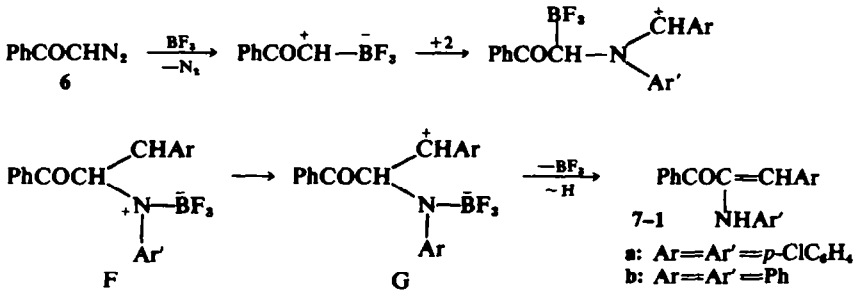
Reaction with α-alkylbenzylidenanilines. As mentioned above, the reaction of diazoketone **1** with benzylidenanilines (**2**) afforded a mixture of stereoisomeric spiro[acenaphthenone-2',4-imidazolidine] compounds **3**, whose stereochemistry could not be clarified. If diazoketone **1** reacts with α-alkylbenzylidenanilines (**8**) in a similar manner, it would be expected to form a 2,5-dialkyl-1,2,3,5-tetraaryl-spiro[acenaphthenone-2',4-imidazolidine] (**9**) whose stereochemistry would be easily elucidated when compared with those of 2,5-unsubstituted spiro compounds **3**.

Contrary to expectation, the reaction of **1** with α-methyl- (**8a**) and α-ethylbenzylidenaniline (**8b**) afforded compounds **10a** and **10b** whose molecular formulas agreed with those of compounds derived from the corresponding 1 : 1 adducts with the elimination of both nitrogen and water respectively. On the basis of their spectral data, these compounds were assigned as 1,2-diphenylacenaphtho[1,2-b]-pyrrole (**10a**) and 1,2-diphenyl-3-methylacenaphtho-[1,2-b]pyrrole (**10b**).

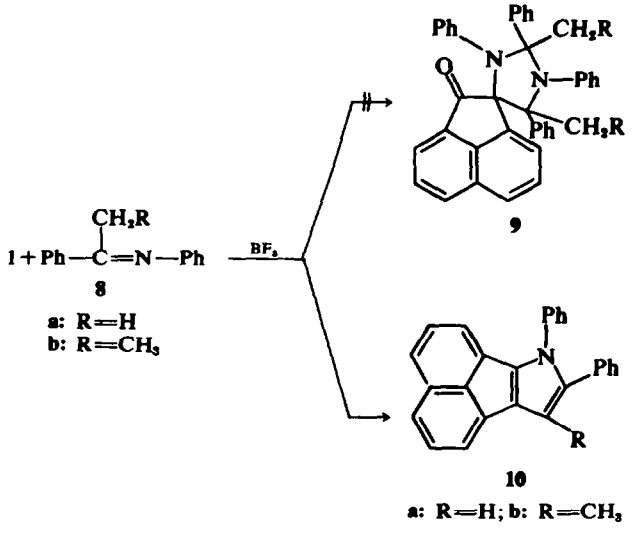
Although the exact pathway for the formation of **10** is not clear, we viewed the reaction as proceeding as shown in Scheme 5. It is well known[11] that α-alkylbenzylidenanilines (**8**) exist as their tautomeric enamines **8'**. Therefore, reactive species **B** would attack the β-carbon atom of enamines **8'** to form 1-hydroxy-2-(β-anilinostyryl)acenaphthylene I *via* betaine H with the elimination of BF_3 and concurrent hydrogen shift. Intermediate I would then cyclize to the final product **10**. In this case, an aziridine intermediate similar to D is not involved.

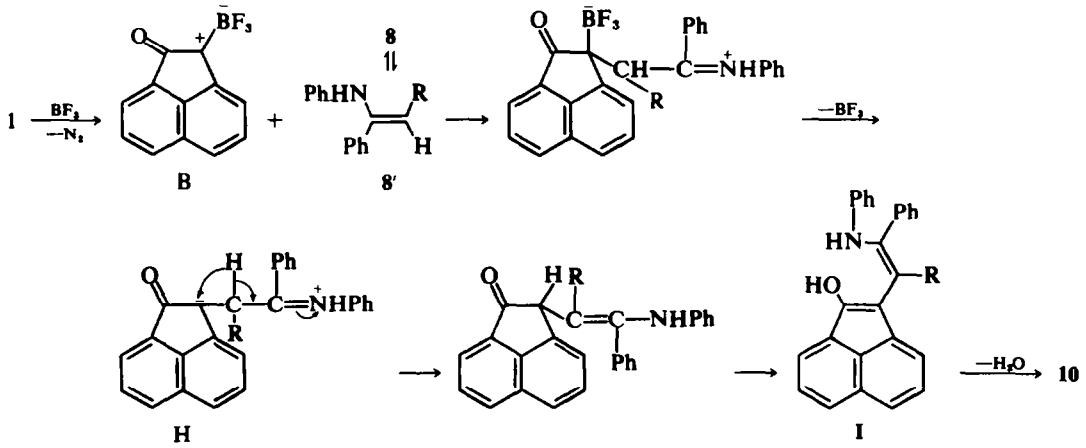
EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were measured as KBr discs and NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer (TMS as internal reference). Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer (direct inlet; 70 eV), and microanalyses were performed by Miss M. Akita of our laboratory.



SCHEME 4





SCHEME 5

2-Diazoacenaphthenone (1) was prepared by the reported method[12] and purified by chromatography on alumina, m.p. 93–94° (lit.,[12] m.p. 94°). Diazoacetophenone (6) was prepared by reaction of benzoyl chloride and CH_2N_2, m.p. 48–49° (lig.,[13] m.p. 49°). All anils were prepared by literature methods. *p*-Chlorobenzylidene-*p*-chloroaniline (**2a**), m.p. 109–110° (lit.,[6] m.p. 109–110·5°); benzylidenaniline (**2b**), m.p. 51–52° (lit.,[6] m.p. 52°); *p*-methylbenzylidenaniline (**2c**), b.p. 170–173°/14 mm (lit.,[14] b.p. 318°/760 mm); *p*-chlorobenzylidene-*p*-toluidine (**2d**), m.p. 124–125° (lit.,[15] m.p. 125°); α-methylbenzylidenaniline (**8a**), b.p. 175°/15 mm (lit.,[16] b.p. 170–180°/13 mm); α-ethylbenzylidenaniline (**8b**), b.p. 153°/5 mm (lit.,[17] b.p. 169°/11 mm). BF_3-Et_2O was purchased from Kishida Kagaku Co. (Osaka, Japan).

Decomposition of **1** *in the presence of* BF_3-Et_2O. (i) A solution of 400 mg (2 mmole) of **1** and 30 mg (0·2 mmole) of BF_3-Et_2O in 10 ml benzene was refluxed for 1 h. After cooling, the mixture was chromatographed on alumina to give 20 mg of *2,2'-diphenyl-2,2'-dihydrodiacenaphthylidene-1,1'-dione*, m.p. 245° dec, as colourless prisms. (Found: C, 89·02; H, 4·71. Calc. for $C_{36}H_{22}O_2$: C, 88·86; H, 4·56%). ν_{CO} 1720 cm^{-1}.

Further elution with $CHCl_3$ afforded trace amounts of biacendione, m.p. 294°, which was identical with the authentic sample prepared from acenaphthenequinone and acenaphthenone.

(ii) Similarly, treatment of 400 mg of **1** with 1·5 g (10 mmole) of BF_3-Et_2O in 20 ml of benzene gave 120 mg (27%) of 2-phenylacenaphthenone, m.p. 114–115° (lit.,[18] m.p. 115–116°), as colourless grains. (Found: C, 88·70; H, 5·15. Calc. for $C_{18}H_{12}O$: C, 88·50; H, 4·95%). ν_{CO} 1716 cm^{-1}. δ ppm ($CDCl_3$): 4·86 (1H, s, >CH), 7·5 (11H, m, aromatic protons).

Reaction of **1** with **2**. The general procedure is illustrated by the reaction of **1** with **2a**. A solution of 1·0 g (5 mmole) of **1** and 1·25 g (5 mmole) of **2a** in 30 ml of benzene was refluxed for 1 h with 80 mg of BF_3-Et_2O. After cooling, the mixture was concentrated to 20 ml *in vacuo* and chromatographed on alumina to give 1·16 g (33·8%) of a mixture of *spiro[acenaphthenone-2',4-imidazolidines]* **3a**, m.p. 232–234°, as yellow grains. (Found: C, 68·47; H, 3·62; N, 3·94. Calc. for $C_{38}H_{24}N_2OCl_4$: C, 68·47; H, 3·60; N, 4·20%). *m/e* (rel. intensity): 666 (trace), 417 (42·5), 416 (25), 415 (64·5), 291 (38), 290 (25), 289 (100).

Further elution with $CHCl_3$ afforded trace amounts of biacenedione, m.p. 294°.

Isolation of isomers from **3a** was carried out by chromatography on silica gel using cyclohexane-benzene as eluent. From the elution with cyclohexane-benzene (2:1 vol/vol), **3a-1** and **3a-2** were obtained, and **3a-3** was isolated from the elution with cyclohexane-benzene (1:1 vol/vol). All isomers were recrystallized from EtOH.

Similarly, reaction of **1** with anils **2b**, **2c** and **2d** afforded the corresponding *spiro[acenaphthenone-2',4-imidazolidine]* derivatives **3b**, **3c** and **3d**. The yields, physical properties and microanalyses are in Table 1.

Hydrolysis of **3a**. A solution of 400 mg of **3a** in 18 ml of EtOH was refluxed with 2 ml of conc. HCl for 5 h. After solvent was evaporated residue was poured into water and extracted with benzene (20 ml × 2). The extract was water-washed, dried (Na_2SO_4) and concentrated to about 10 ml. The resulting solution was chromatographed on alumina (benzene) to give crystals, which on crystallization from petrol gave 90 mg (39·7%) of *2-ethoxy-2-(α-ethoxy-p-chlorobenzyl)acenaphthenone* (**4a**), m.p. 139–140°, as colourless prisms. (Found: C, 72·49; H, 5·43. Calc. for $C_{23}H_{21}O_3Cl$: C, 72·54; H, 5·52%). ν_{CO} 1726 cm^{-1}. *m/e*: 379 (M^+), δ ppm (CCl_4): 0·80, 1·02 (each 3H, t, CH_3), 3·01, 3·23 (each 2H, q, CH_2), 4·87 (1H, s, >CH), 7·2–8·2 (9H, m, aromatic protons).

The aqueous layer was neutralized with K_2CO_3 aq. and benzene extracted. The benzene was evaporated to leave 70 mg (45·5%) of *p*-chloroaniline.

Similarly, a solution of 1·0 g of **3a** in 30 ml of MeOH was refluxed with 3 ml of conc. HCl for 5 h: 80 mg (15·6%) of *2-methoxy-2-(α-methoxy-p-chlorobenzyl)acenaphthenone* (**4b**), m.p. 193–194°, as colourless prisms and 290 mg (71%) of *p*-chloroaniline were obtained. (Found: C, 71·76; H, 4·83. Calc. for $C_{21}H_{17}O_3Cl$: C, 71·49; H, 4·82%). ν_{CO} 1732 cm^{-1}. δ ppm (CCl_4). 2·87, 3·0 (each 3H, s, CH_3), 4·74 (1H, s, >CH), 6·5–8·2 (10H, m, aromatic protons).

Hydrolysis of **3d**. A solution of 1·0 g of **3d** in 20 ml conc. HCl was stirred at room temp for 4 h. The precipitate was recrystallized from petrol (b.p. 42–60°) to give 220 mg (50·5%) of acenaphthenequinone mono-*p*-toluimine (**5**), m.p. 189–191°, as orange yellow prisms. This compound was identical with the authentic sample prepared from acenaphthenequinone and *p*-toluidine.

The filtrate was extracted with Et_2O and the extract evaporated to leave 90 mg (20%) of *p*-chlorobenzaldehyde. The aqueous layer was neutralized with Na_2CO_3 aq. to give 50 mg (29·2%) of *p*-toluidine and trace amounts of anil **2d**.

When a solution of 300 mg of **3d** in 18 ml of EtOH was refluxed with 2 ml conc. HCl for 2 h, 20 mg (11%) of **4a**, 60 mg (58%) of *p*-toluidine and 10 mg of acenaphthenequinone were obtained.

Reaction of **6** *with* **2b**. A solution of 1·46 g (10 mmole) of **6** and 1·81 g (10 mmole) of **2b** in 30 ml of benzene was refluxed with 80 mg of BF_3-Et_2O for 1 h. After concentration to 15 ml, the resulting solution was chromatographed on silica gel using benzene as eluent to give crystals. Recrystallization from petrol afforded 0·47 g (15·8%) of *α-anilinobenzylidenacetophenone* (**7b-1**), m.p. 84–86°, as yellow grains. (Found: C, 84·06; H, 5·60; N, 4·65. Calc. for $C_{21}H_{17}NO$: C, 84·06; H, 5·72; N, 4·68%). ν_{CO} 1625 cm^{-1}. *m/e* (rel. intensity): 299 (M^+, 27), 194 (12), 193 (14), 105 (84), 77 (100). δ ppm ($CDCl_3$): 12·2 (1H, NH).

Similarly, reaction of 2·72 g of **6** with 3·75 g of **2a** in the presence of 160 mg of BF_3-Et_2O in 60 ml of benzene afforded 1·78 g (26%) of *α-p-chloroanilino-p-chlorobenzylidenacetophenone* (**7a-1**), m.p. 160–161°, as yellow prisms. (Found: C, 68·84; H, 3·99; N, 3·67. Calc. for $C_{21}H_{15}NOCl_2$: C, 68·48; H, 4·08; N, 3·80%). ν_{CO} 1623 cm^{-1}. *m/e* (rel. intensity): 371 (10·6), 370 (21), 369 (55), 368 (76), 367 (89), 366 (92), 227 (42), 105 (100), 77 (98).

Preparation of β-anilinobenzylidenacetophenone (**7b-2**). A mixture of 1·12 g (5 mmole) of dibenzoylmethane and 0·58 g (6·2 mmole) of freshly distilled aniline was refluxed for 9 h. After cooling, the mixture was extracted with hot petrol (50 ml × 2) and the extract evaporated. The residue was chromatographed on alumina (benzene) to afford 820 mg (55%) of **7b-2**, m.p. 102–103° (lit.,[10] m.p. 102–103°).

Reaction of **1** *with* **8a**. A solution of 1·0 g (5 mmole) of **1** and 1·0 g (5 mmole) of **8a** in benzene (30 ml) was refluxed with 80 mg of BF_3-Et_2O for 8 h and concentrated to 15 ml. The resulting solution was chromatographed on alumina (benzene) to give crystals, which on recrystallization from EtOH afforded 730 mg (41%) of 1,2-*diphenylacenaphtho*[1,2-b]*pyrrole* (**10a**), m.p. 183–184°, as yellow prisms. (Found: C, 91·09; H, 4·73; N, 3·80. Calc. for $C_{26}H_{17}N$: C, 90·93; H, 4·99; N, 4·08%). δ ppm ($CDCl_3$): 6·7 (1H, s), 7·1–7·7 (16H, m, aromatic protons). *m/e*: 343 (M^+).

Similarly, reaction of **1** with **8b** in the presence of BF_3-Et_2O afforded 23% yield of 1,2-*diphenyl-3-methylacenaphtho*[1,2-b]*pyrrole* (**10b**), m.p. 152–153°, as orange needles (from EtOH). (Found: C, 90·70; H, 5·30; N, 3·66. Calc. for $C_{27}H_{19}N$: C, 90·72; H, 5·36; N, 3·92%). δ ppm ($CDCl_3$): 2·42 (3H, s, CH_3), 7·1–7·7 (16H, m, aromatic protons). *m/e*: 357 (M^+).

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