Cyclic Acylimines and Cyclic Carbinolamides I. 2-Azaphenalones (1,2).

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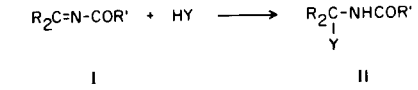
2-Azaphenalone hydrochloride (VI), 2-methyl-1-azaphenalonium chloride (XIV), 3-phenyl-2-azaphenalone (XVIII) and 3-phenyl-2-methyl-2-azaphenalonium chloride (XXI) were synthesized and their chemical and physical properties were studied. At room temperature they add weak nucleophiles (*e.g.*, alcohols, amides) as well as compounds possessing active methylene groups. The methanol addition products (*e.g.*, V) reacted thermally or in the presence of an acid catalyst with nucleophiles to give products identical with those obtained from the azaphenalone hydrochlorides.

Open chain *N*-acylimines (I) are reactive compounds (3-6). They easily add weak nucleophiles such as alcohols and amides to give addition products (II):



I II

The driving force in the addition reactions is probably the gain in the resonance energy of the amide group. The hybridization of the unshared pair of electrons on the nitrogen changes from sp^2 in the acylimine to sp^3-like, in the addition product. In cyclic systems, because of hindrance of rotation, the overlap of the lone pair of electrons on the nitrogen with the π electrons of the carbonyl groups should be less favourable and therefore the activity of cyclic acylimines, in addition reactions, should be even greater. The present investigation was aimed at the preparation of cyclic acylimines and the study of their chemical and physical properties. The azaphenalone system (VI) was chosen because it cannot tautomerize to an enamide (III), a migration that would occur if there are hydrogens on the carbon β to the amidic nitrogen (3,7,8).

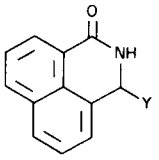
Ia III

3-Methoxy-2-azadihydrophenalone (V) was prepared from the pseudo methyl ester of 1,8-naphthaldehydic acid (IV) by amidation with methanolic ammonia followed by treatment with methanolic hydrogen chloride. The methoxy derivative showed a strong NH absorption at 3410 cm^{-1} and a carbonyl band at 1680 cm^{-1}, in the infrared. The NMR spectrum showed, apart from the aromatic absorptions, a doublet (1H) at δ 5.98 and a singlet (3H) at δ 3.02. Treatment of the methoxy azaphenalone (V) with thionyl chloride in a benzene suspension at room temperature afforded a yellow nonhygroscopic solid (VI) which did not dissolve in the ordinary organic solvents. The infrared spectrum of the azaphenalone hydrochloride (VI) showed a broad ammonium band at 2400 cm^{-1} and a carbonyl absorption at 1700 cm^{-1}. The NMR spectrum showed, in concentrated sulfuric acid, apart from the aromatic protons, only one singlet at δ 9.6 (1H).

The azaphenalone hydrochloride (VI) showed unusual chemical reactivity towards weak nucleophiles. It reacted rapidly with methanol and 2-propanol to give 3-methoxy and 3-(2-propoxy)azaphenalone (V, VII, R = $OCH(CH_3)_2$). It also reacted with amides (Table I) and with compounds possessing active methylene groups such as acetoacetate, cyanoacetate, acetone and acetophenone within 10 minutes to 24 hours to give addition products (VIII, Table II). These reactions were carried out at room temperature in a suspention or, in the cases of the liquid reagents, in the reagent itself as solvent. The disappearance of the insoluble hydrochloride indicated the termination of the reaction. Azaphenalone hydrochloride (VI) is a protonated acylimine, a type of compound that was suggested as an intermediate in the acid-catalyzed amidoalkylation of aromatic compounds or compounds possessing active methylene groups (9). The azaphenalone hydrochloride reacted with 2,3-dimethylbutadiene, in a benzene suspension, to give a Diels-Alder type of product (IX) and sodium borohydride reduced the carbon-nitrogen double bond of VI to give naphthalimidine (XII). The methanol addition product (V) can be substituted for the hydrochloride (VI) in some reactions. It reacted thermally with ethanol or 2-propanol to give the corresponding 3-ethoxy and 3-(2-propoxy)azaphenalones (VII, Y = OEt; $OCH(CH_3)_2$). It reacted with phenylmagnesium bromide to give 3-phenylazaphenalone (XI) and was reduced with sodium borohydride to the naphthalimidine (XII).

TABLE I

Addition of Nucleophiles to Azaphenalone Hydrochloride (VI)

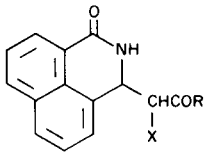


Y	Yield %	M.p.		Formula	Analyses Calcd. C	H	N	Found C	H	N
OCH_3	95	175-176	(a)	$C_{13}H_{11}NO_2$	73.22	5.20	6.57	73.14	5.25	7.00
OC_2H_5	98	168	(b)	$C_{14}H_{13}NO_2$	73.99	5.77	6.16	74.21	5.70	5.95
$OCH(CH_3)$	97	163.5	(c)	$C_{15}H_{15}NO_2$	74.66	6.27	5.81	74.61	6.32	5.98
$S\text{-}C_7H_7$	53	172-173 dec.	(d)	$C_{19}H_{15}NOS$	74.70	4.91	4.58	-	-	4.41
$N\text{-}C_5H_{10}$	96	218-219	(e)	$C_{17}H_{18}N_2O$	76.66	6.81	10.52	76.49	6.75	11.02
$HNCOC_6H_5$	63	264-265	(f)	$C_{19}H_{14}N_2O_2$	75.48	4.67	9.27	75.24	4.68	9.00
$HNCO_2C_7H_7$	78	223-224	(f)	$C_{20}H_{16}N_2O_3$	72.28	4.85	8.43	72.00	4.82	8.58

(a) Crystallized from methanol. (b) Crystallized from ethanol. (c) Crystallized from 2-propanol. (d) Crystallized from benzene. (e) Crystallized from acetone. (f) Crystallized from ethyl acetate.

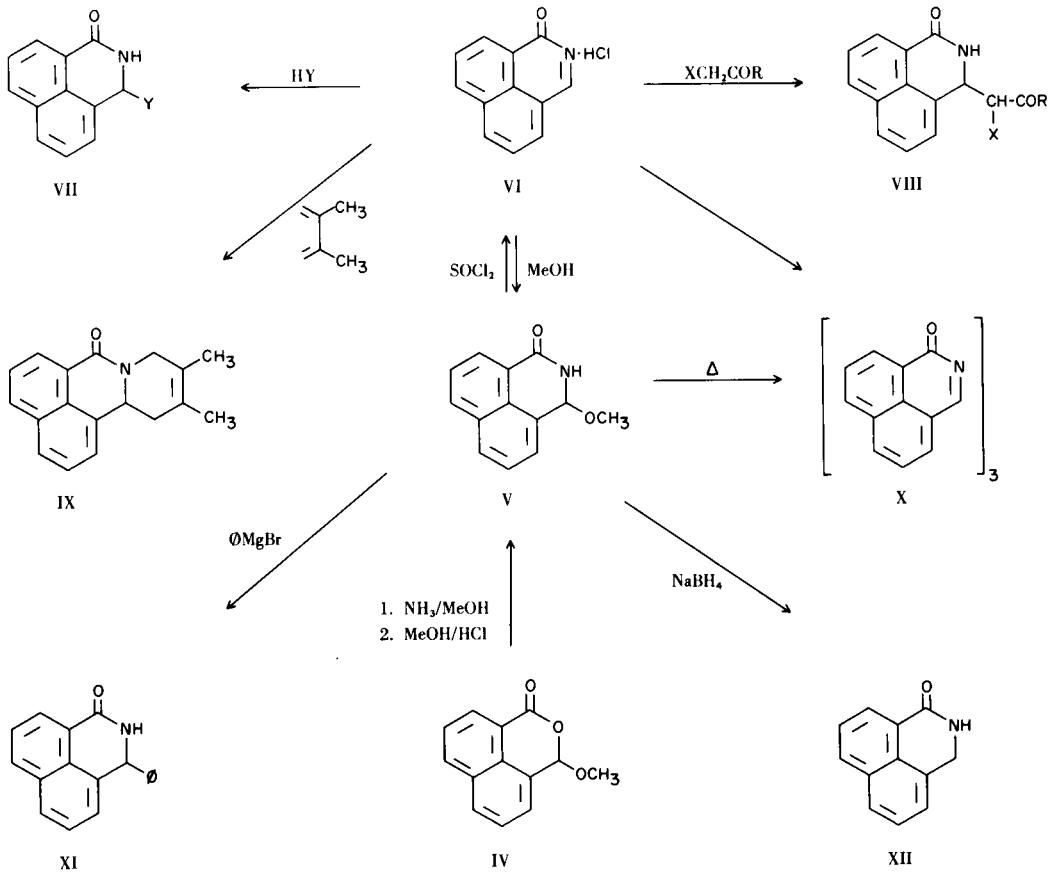
TABLE II

Addition of Active Methylene Compounds to Azaphenalone Hydrochloride



X	R	Yield	M.p.		Formula	Analyses Calcd. C	H	N	Found C	H	N
CH_3CO	CH_3	93	297 dec.	(a)	$C_{17}H_{15}NO_3$	72.58	5.37	4.98	72.47	5.22	5.26
CH_3CO	OC_2H_5	90	134-135	(b)	$C_{18}H_{17}NO_4$	69.44	5,50	4.50	69.23	5.55	4.86
CN	OC_2H_5	75	191-192	(c)	$C_{17}H_{14}N_2O_3$	69.37	4.80	9.52	68.91	4.83	9.99
H	CH_3	98	140-141	(a)	$C_{15}H_{13}NO_2$	75.30	5.48	5.85	74.88	5.50	5.96
H	C_6H_5	99	175-176	(a)	$C_{20}H_{15}NO_2$	79.71	5.02	4.65	79.79	5.28	5.02
$(CH_2)_4$		97	163-164	(d)	$C_{18}H_{17}NO_2$	77.39	6.13	5.01	76.56	6.35	5.20
$COCH_2(CH_3)_2CH_2$		94	254-255	(e)	$C_{20}H_{19}NO_3$	74.74	5.96	4.36	74.34	6.08	4.44

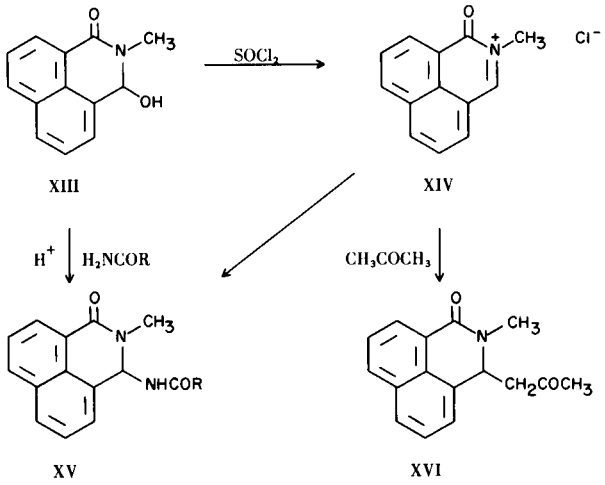
(a) Crystallized from acetone. (b) Crystallized from benzene-hexane. (c) Crystallized from acetone-hexane. (d) Crystallized from carbontetrachloride-hexane. (e) Crystallized from methanol-acetone.



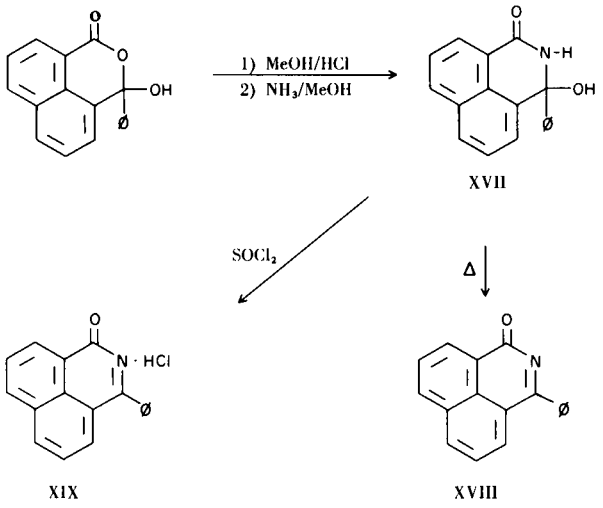
Attempts to obtain the free 2-azaphenalone from the hydrochloride (VI), or thermally from the 3-methoxy-2-azaphenalone (V) led to the isolation of an insoluble white solid (m.p. 336° dec.). This product is probably a symmetrical triazine (X). The infrared spectrum showed a carbonyl band at 1660 cm^{-1} and did not show any NH absorptions (tertiary amide). It depolymerized in concentrated sulfuric acid to give the same UV and NMR spectra as the azaphenalone hydrochloride.

In addition to the azaphenalone hydrochloride (VI), 2-methyl-2-azaphenalonium chloride (XIV) was prepared from the pseudo ester of 1,8-naphthaldehydic acid (IV) and methylamine and subsequent treatment of the carbinolamide (XIII) with thionyl chloride.

2-Methyl-2-azaphenalonium chloride is sensitive to oxidation, and was converted on standing at room temperature to *N*-methylnaphthalimide. It did, however, show the same marked reactivity as the parent compound (VI) towards weak nucleophiles. It added benzamide, benzylcarbamate and acetone to give products XV (R = C_6H_5; C_7H_7) and XVI. The 3-hydroxy-2-azaphenalone (XIII) was found to react in boiling benzene and in the presence of naphthalenesulfonic acid with the nucleophiles described above, to give the same addition product.

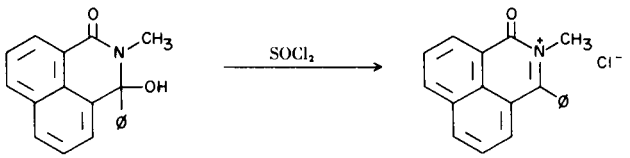


3-Phenyl-2-azaphenalone (XVIII) and its hydrochloride (XIX) were prepared from 1-benzoyl-8-naphthalenecarboxylic acid by the sequence of reactions described above:



XVII XIX XVIII

The 3-phenyl-2-azaphenalone (XVIII), due to conjugation and steric effects, was much less reactive towards weak nucleophiles. It reacted with methanol or ethanol only at reflux temperature, but did not react with benzamide, acetone or even phenylmagnesium bromide. The hydrochloride (XIX) and its *N*-methylated derivative (XXI), which was prepared by the same sequence of reactions, were found to be somewhat more reactive than the free 3-phenyl-2-azaphenalone. They added methanol at room temperature and were reduced with sodium borohydride to the corresponding naphthalimidine derivatives.



XX XXI

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were measured in chloroform solutions and NMR spectra in deuteriochloroform (unless otherwise indicated).

3-Methoxy-2-azadihydrophenalone (V).

The pseudo methyl ester (10) of 1,8-naphthaldehydic acid (IV, 10 g.) was suspended in methanol (200 ml.). The suspension was cooled in an ice-water bath and saturated with ammonia. The starting material went into solution and at the end of the reaction (0.5 hour) the product started to precipitate. The hydroxylactam which was obtained after the removal of the solvent and excess ammonia, was re-suspended in methanol (400 ml.) and 10 ml. of methanolic hydrogen chloride was added. The mixture was stirred for half an hour, and the precipitate was filtered, washed with cold methanol and dried in a dessicator over potassium hydroxide. The solid, which is very sensitive to acids, was crystallized from methanol. It melted at 175-176°, yield 9 g. (80%). The methoxylactam showed a strong NH band at 3410 cm^{-1} and a CO absorption at 1680 cm^{-1} in the infrared. The NMR spectrum showed aromatic protons at δ 7.2-8.3, a doublet (1H) at δ 5.98 and a sharp singlet (3H) at δ 3.02; mass spectrum m/e 213.

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.14; H, 5.25; N, 7.00.

An analytical sample of the intermediate hydroxylactam was obtained by crystallization from acetone, m.p. 334° (dec.).

Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.18; H, 4.36; N, 7.05.

2-Azaphenalone Hydrochloride (VI).

To a suspension of the methoxy derivative described above (V, 0.5 g.) in dry benzene (10 ml.) there was added an excess of thionyl chloride (0.5 g.). The methoxy derivative went into solution and a yellow precipitate was formed immediately. The yellow suspension was stirred for half an hour, the solid was filtered through a sinter glass funnel and was washed with dry benzene. It was dried in a dessicator over potassium hydroxide. The hydrochloride decomposed slowly on heating above 100°, yield 0.5 g. (97%).

The hydrochloride showed (potassium bromide) an ammonium band at 2360 cm^{-1} (broad), two bands in the triple bond region at 2120 and 1990 cm^{-1} and a doublet in the carbonyl region at 1710 and 1695 cm^{-1}. The ultra-violet spectrum (concentrated sulfuric acid) showed absorptions at 440 mμ (log ε, 4.11), 419 mμ (log ε, 4.11), 310 mμ (log ε, 3.35) and 234 mμ (log ε, 4.28). In the NMR (concentrated sulfuric acid) apart from the aromatic protons (δ 8.0-9.2) only one sharp singlet (1H) appeared at δ 9.6. The mass spectrum showed an m/e peak of 181 (M-HCL).

Anal. Calcd. for $C_{12}H_8ClNO$: N, 6.45; Cl, 1636. Found: N, 6.47; Cl, 15.60.

Addition of Nucleophilic Reagents to the Azaphenalone Hydrochloride (VII). General Procedure.

The hydrochloride (VI, 0.215 g., 1 mmole) was suspended in dry benzene (5 ml.) or anhydrous ether (10 ml.). To the well stirred suspension there was added 1 mole of the nucleophile. Stirring was continued until the insoluble hydrochloride dissolved (1 minute to 5 hours). The product which precipitated on the addition of hexane (20 ml.) was filtered and crystallized from the proper solvent (Table I). In the case of the alcohols the reagent itself was used as the solvent for the reaction. All the products showed NH absorptions at 3400 cm^{-1} and CO absorption at 1650-1670 cm^{-1} in the infrared.

Addition of Active Methylene Compounds to Azaphenalone Hydrochloride (VI). General Procedure.

The azaphenalone hydrochloride (VI, 0.215 g., 1 mmole) was added to an excess of the reagent (5 ml.). Stirring was continued until the disappearance of the hydrochloride (0.5-3.0 hours). The product which precipitated on the addition of ether was filtered and crystallized (Table II). In the case of dimedone the reaction was carried out in dry ether (10 ml.) for 6 hours. Satisfactory infrared and NMR spectra have been obtained for the new compounds mentioned in Table II.

The Reaction of 2-Azaphenalone Hydrochloride with 2,3-Dimethylbutadiene (IX).

A suspension of the hydrochloride (0.5 g.), 2,3-dimethylbutadiene (0.5 g.) in dry benzene (10 ml.) was stirred at room temperature for 5 days. The solution was filtered and evaporated to dryness. It was chromatographed over basic alumina (10 g.) and eluted with benzene to give 0.22 g. (32%) of a crystalline pro-

duct which melted at 126-127° after crystallization from hexane. The product showed CO absorption at 1650 cm^{-1} in the infrared. The NMR spectrum showed a singlet at δ 2.30 (2H), δ 3.42 (1H), δ 5.01 (1H), and δ 8.30 (1H), a triplet at δ 5.0 (1H) and a multiplet at δ 7.20-7.95 (5H); mass spectrum m/e 263.

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.95; H, 6.84; N, 5.26.

2-Azadihydrophenalone (XII).

To a suspension of the azaphenalone hydrochloride (VI, 0.084 g.) in dry glyme (5 ml.), there was added excess sodium borohydride (0.06 g.). After the disappearance of the yellow colour (20 minutes) the suspension was distributed between ethyl acetate and aqueous hydrochloric acid (3%). The organic layer was washed with water, dried over magnesium sulfate and evaporated to dryness. The residue melted at 207-208° after crystallization from benzene, yield 0.063 g. (88%). It showed NH absorption at 3420 cm^{-1} and CO absorption at 1675 cm^{-1} in the infrared. The NMR spectrum showed (dimethylsulfoxide-d_6 a singlet at δ 4.58 (2H) and a multiplet at δ 7.1-7.9 (7H); mass spectrum m/e 183.

Anal. Calcd. for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.47; H, 4.83; N, 7.21.

Tri-2-azaphenalone (X).

A solution of 3-methoxy-2-azadihydrophenalone (V, 0.5 g.) in toluene (15 ml.) was refluxed for 1 hour. The cooled mixture was filtered to give 0.425 g. (100%) of a solid which was insoluble in organic solvent, m.p. 336°. It showed CO absorption at 1665 cm^{-1} and no NH absorption in the infrared. The NMR and UV spectrum, in concentrated sulfuric acid, were identical with the spectrum of the monomeric hydrochloride described above (VI).

The same insoluble material was obtained from the hydrochloride either thermally by heating *in vacuo* (0.1 mm) at 130° for 1 hour, or by stirring a suspension of the hydrochloride in t-butanol overnight.

The Thermal Reaction of 3-Methoxy-2-azaphenalone (V) with Ethanol and 2-Propanol.

A solution of the methoxyazaphenalone (V, 0.1 g.) in absolute ethanol (50 ml.) was refluxed for 18 hours. The residue obtained after the removal of the ethanol was identical with the 3-ethoxy-2-azadihydrophenol (Table I), through mixed melting point, infrared, and NMR spectra; mass spectrum, m/e 227 ($C_{14}H_{13}NO_2$).

Refluxing a solution of the methoxy derivative (V, 0.46 g.) in 2-propanol (10 ml.) for 20 hours exchanged the methoxy for the 2-propoxy group. The yield was 0.41 g. (79%); m.p. 164°. This product was identical with 3-(2-propoxy)-2-azadihydrophenalone (Table I).

3-Phenyl-2-azadihydrophenalone (XI).

To a solution of phenylmagnesium bromide which was prepared from magnesium (0.46 g.) and bromobenzene (2.96 g.), in dry ether (50 ml.) there was added 3-methoxyaqaphenalone (V, 0.525 g.) suspended in ether (50 ml.). The mixture was stirred overnight, aqueous ammonium chloride was added and the aqueous layer was extracted twice with ethyl acetate. The residue obtained after the removal of the solvent was crystallized from benzene to give 0.28 g. (44%) of 3-phenyl-2-azadihydrophenalone, m.p. 252-254° dec. It showed NH absorption at 3470 cm^{-1} and a CO absorption at 1670 cm^{-1} in the infrared; mass spectrum, m/e 259.

Anal. Calcd. for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.54; H, 5.38; N, 4.89.

2-Methyl-2-hydroxy-2-azadihydrophenalone (XIII).

The pseudo methyl ester of 1,8-naphthaldehydic acid (6.6 g.) was dissolved in methanolic methylamine solution (200 ml., 7%), and the solution was left at room temperature for 48 hours. The solvent and excess methylamine were removed *in vacuo*, and the residue was dissolved in ethyl acetate and washed twice with water. The ethyl acetate solution was dried over magnesium sulfate and evaporated to dryness. The solid residue was crystallized from benzene, m.p. 152-153°, yield 6.8 g. (100%). It showed OH absorptions at 3570 and 3300 cm^{-1} and CO absorption at 1650 cm^{-1}. The NMR spectrum showed singlets at δ 3.22 (3H) and δ 6.0 (1H), a broad peak at δ 4.1 (1H) and a multiplet at δ 7.2 (6H); mass spectrum m/e 312.

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.22; N, 6.57. Found: C, 73.97; H, 5.31; N, 6.55.

2-Methyl-2-azaphenalonium Chloride (XIV).

To a suspension of 2-methyl-3-hydroxy-2-azadihydrophenalone (XII, 1.0 g.) in dry cyclohexane (10. ml.) there was added, with stirring, excess thionyl chloride (1.0 ml.). A yellow precipitate formed immediately. The suspension was centrifuged and the solvent was decanted. Cyclohexane was added, the suspension was stirred again, centrifuged and the solvent again decanted. The yellow solid was dried in the desiccator over potassium hydroxide. The hydrochloride is very unstable and decomposed on standing. It melted at 160-161° dec., yield 0.9 g. (90%). It showed CO absorption at 1710 cm^{-1} in the infrared. The NMR spectrum showed (concentrated sulfuric acid) singlets at δ 4.15 (2H) and δ 9.75 and multiplets at δ 8.1-8.4 (2H) and δ 8.80-9.20 (4H); mass spectrum, m/e 196 (M-HCl); UV λ max (concentrated sulfuric acid), 441 (log ε, 4.29), 417 (log ε, 4.25), 313 (log ε, 3.54), 232 mμ (log ε, 4.36).

Anal. Calcd. for $C_{13}H_{10}ClNO$: Cl, 1530. Found: Cl, 14.60.

The Reaction of XIV with Benzamide.

A suspension of the chloride (0.147 g.), benzamide (0.080 g.) in dry ether (5 ml.) was stirred for 1 hour. The solid product was filtered and crystallized from benzene, m.p. 262-263°, yeild 0.12 g. (60%). It showed NH absorptions at 3430, 3290 and 1490 cm^{-1}, and CO absorptions at 1660 and 1650 cm^{-1} in the infrared; mass spectrum, m/e 316.

Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 76.60; H, 5.10; N, 8.70.

The chloride (XIV) reacted similarly with benzyl carbamate and phenyl acetamide to give crystalline products which melted at 198-199° (66%) and 253-254° (81%), respectively.

Anal. Calcd. for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 73.04; H, 5.29; N, 7.89.

Anal. Calcd. for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.22; H, 5.48; N, 8.55.

The Reaction of XIV with Acetone.

The chloride (0.188 g.) was added to dry acetone (2.0 ml.) and the solution was stirred for 10 minutes. The acetone solution was distributed between ethyl acetate and water, the organic layer was separated and washed with water. It was dried over magnesium sulfate and evaporated to dryness. The residue was crystallized from benzene-hexane, m.p. 124-125°, yield 0.147 (71%). It showed CO absorptions at 1718 and 1650 cm^{-1} in the infrared; the NMR spectrum showed singlets at δ 1.99 (3H), δ 3.24 (3H), quartets at δ 2.8-3.0 (2H), δ 5.45 (1H) and a multiplet at δ 7.3-8.3

(5H); mass spectrum m/e 253.

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 76.20; H, 6.00; N, 5.34.

The same product was obtained in 90% yield by reacting the 2-methyl-3-hydroxy-2-azadihydrophenalone in boiling acetone, in the presence of a catalytic amount of β-naphthalene sulfonic acid, for 1 hour. The hydroxy derivative also reacted in boiling benzene, in the presence of β-naphthalene sulfonic acid, with benzamide and and benzylcarbamate within 1 hour to give the corresponding 3-benzamido and 3-carbobenzoxyamino-2-methyl-2-azadihydrophenalones described above.

2-Methyl-2-azadihydrophenalone.

The chloride (XIV) was reduced in glyme as described above for the azaphenalone hydrochloride (VI). The crude product was chromatographed twice, once on silica gel and once over basic alumina. The solid product which did show the characteristic infrared and NMR spectra was very unstable. It was oxidized on standing with 48 hours to the methylimide.

3-Hydroxy-3-phenyl-2-azadihydrophenalone (XVII).

A methanolic solution of methyl 8-benzoyl-1-naphthoate (11) (12.3 g. in 200 ml.) was saturated with dry ammonia at 0° for 30 minutes. The solution was left at room temperature for 48 hours. The methanol and excess ammonia was removed *in vacuo* and the residue was triturated with ethyl acetate and filtered. The crystalline product melted at 185°, yield 9.9 g. (85%). The product is sensitive to acid and heat; an analytical sample was obtained by crystallization from ethyl acetate. It showed OH absorption at 3570 cm^{-1}, NH absorption at 3380 cm^{-1} and CO absorption at 1660 cm^{-1} in the infrared.

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.16; H, 4.70; N, 5.47.

3-Phenyl-2-azaphenalone (XVIII).

A solution of the 3-hydroxy derivative described above (XVII, 0.5 g.) in toluene (20 ml.) was refluxed for 10 hours and the water formed was removed by azeotropic distillation. The yellow crystalline product which separated on cooling was filtered. The yield was 0.5 g. (100%); m.p. 208-209°. It showed CO absorption at 1670 cm^{-1} and C=N absorption at 1640 cm^{-1} in the infrared. The NMR spectrum showed aromatic protons in the δ 7.1-8.7 region; mass spectrum, m/e 257.

Anal. Calcd. for $C_{18}H_{11}NO$: C, 84.03; H, 4.31; N, 5.44. Found: C, 83.73; H, 4.27; N, 5.47.

3-Phenyl-2-azaphenalone Hydrochloride (XIX).

This compound was obtained from the hydroxy derivative by treatment with thionyl chloride in a benzene suspension as described above for the preparation of the 2-methylazaphenalonium chloride. It showed CO absorption at 1720 and C=N absorption at 1710 cm^{-1} in the infrared (potassium bromide); mass spectrum m/e 257 (M-HCl).

Anal. Calcd. for $C_{18}H_{12}ClNO$: N, 4.76; Cl, 12.10. Found: N, 4.75; Cl, 1272.

3-Methoxy-3-phenyl-2-azaphenalone.

A solution of the 3-phenyl-2-azaphenalone (XVIII, 0.115 g.) in methanol (5 ml.) was refluxed for 15 minutes. The methanol was removed under reduced pressure and the residue was crystallized from methylene chloride-hexane, m.p. 180-181° dec. The yield was quantitative.

The same product was obtained from the hydrochloride (XIX) and methanol. In this case the reaction was instantaneous at room temperature. The mixture was distributed between ether and water, the ether was dried and evaporated, and the residue was crystallized as above. It showed NH absorption at 3380 cm^{-1} and CO absorption at 1665 cm^{-1}. The NMR spectrum showed the methoxy singlet at δ 3.03 (3H); mass spectrum, m/e 289.

Anal. Calcd. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.52; H, 5.33; N, 4.63.

3-Phenyl-2-azadihydrophenalone.

To a solution of 3-phenyl-2-azaphenalone (0.138 g.) in glyme (15 ml.) there was added excess sodium borohydride (0.4 g.). The yellow colour disappeared after stirring for 10 minutes. The suspension was distributed between chloroform and 3% hydrochloric acid. The two layers were separated, the chloroform solution was dried and evaporated. The residue was crystallized from benzene, m.p. 252-253°, yield 0.070 g. (52%). It was identical through mixed melting point and infrared spectra with the product described above (XI).

2-Methyl-3-hydroxy-3-phenyl-2-azadihydrophenalone (XX).

A suspension of methyl 8-benzoyl-1-naphthoate (6.3 g.) in methanolic methylamine (80 ml. of a 26% solution) was stirred for 16 hours. The methanol and excess methylamine was removed *in vacuo*, and the residue was crystallized from methanol. It melted at 231-232°, yield 6.3 g. (100%). It showed OH absorptions at 3570 and 3300 cm^{-1} and CO absorption at 1645 cm^{-1}; mass spectrum, m/e 289.

Anal. Calcd. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.22; N, 4.84. Found: C, 78.57; H, 5.20; N, 4.83.

2-Methyl-3-phenyl-2-azaphenalonium Chloride (XXI).

To a suspension of the hydroxy derivative described above (XX, 1.4 g.) in dry benzene (60 ml.) there was added an excess of thionyl chloride (2.0 ml.). The suspension was stirred for half an hour, and the yellow solid was filtered through a sintered glass and dried in a desiccator over potassium hydroxide. It melted at 195-196°, yield 1.5 g. (97%). It showed CO absorption at 1728 cm^{-1} in the infrared (potassium bromide). The NMR spectrum (concentrated sulfuric acid) showed a singlet at δ 3.88 (3H) and multiplets at δ 7.50-8.42 (7H) and δ 8.80-9.25 (4H); mass spectrum m/e 272 (M-Cl).

Anal. Calcd. for $C_{19}H_{14}ClNO$: N, 4.55; Cl, 11.50. Found: N, 4.34; Cl, 10.91.

2-Methyl-3-methoxy-3-phenyl-2-azadihydrophenalone.

The 2-methyl-3-phenyl-2-azaphenalonium chloride (XXI, 0.243 g.) was dissolved in dry methanol (10 ml.). The solution was neutralized with sodium methylate and distributed between ethyl acetate and water. The ethyl acetate solution was dried and evaporated to dryness. The residue was crystallized from hexane and melted at 152-153°, yield 0.25 g. (100%). It showed CO absorption at 1650 cm^{-1} in the infrared; mass spectrum, m/e 303.

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.34; H, 6.05; N, 4.24.

2-Methyl-3-phenyl-2-azadihydrophenalone.

The 2-methyl-3-phenyl-2-azaphenalonium chloride described above (0.44 g.) was added in small portions to a cold suspension of excess sodium borohydride (0.47 g.) in dry glyme (20 ml.) over a period of 10 minutes. The suspension was distributed between ethyl acetate and 3% hydrochloric acid. The ethyl acetate solution was dried over magnesium sulfate and evaporated to dryness. The residue was crystallized from methanol and melted at 150-151°, yield 0.21 g. (54%). It showed CO absorption at 1650 cm^{-1} in

the infrared. The NMR spectrum showed singlets at δ 3.07 (3H), δ5.88 (1H) and δ 7.26 (5H), a quartet at δ 8.49 (1H) and a multiplet at δ 7.40-8.10 (5H); mass spectrum m/e 273.

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.02; H, 5.56; N, 5.05.

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