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BASE-CATALYZED REACTIONS OF QUATERNARY SALTS OF 2- AND 4-AZAFLUORENES

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Armit and Robinson's work [1] on the conversion of 7,8-methylenedioxy-5-methyl-11-phenylindeno[3,2-b]quinolinium monomethyl sulfate when treated with aqueous alcoholic potassium hydroxide to 7,8-methylenedioxy-5-methyl-11-phenyl-5H-indeno[3,2-b]quinoline was one of the sources of the chemistry of pseudoazulenes [2], isoelectronic analogs of azulene, for whose structure a mesomeric form with Kekulé and dipolar structures has been suggested [1, 3].

The isomeric azafluorenes are of particular interest for the synthesis of pseudoazulenes. Treibs and Beger [3] have theoretically examined N-alkyl-substituted 1H(2H,3H,4H)-indenopyridines, which correspond to the four isomeric azafluorenes. However, since the discovery of pseudoazulenes only one compound of this type has been prepared from azafluorenes — 1,2,3-trimethyl-9-phenyl-2H-indeno[2,1-c]pyridine (black acicular crystals with mp 212-216°C) [4]. The lack of simple methods for the synthesis of azafluorenes has retarded the development of this area of the chemistry of nitrogen heterocycles.

Azafluorenes are also of interest for the synthesis of azafluorenium ylides. The chemistry of pyridinium ylides has now been thoroughly studied [5]. However, little is known of the chemistry of azafluorenium ylides. Quaternary salts of azafluorenes are converted under alkaline conditions to azafluorenium ylides and nitrogen-containing pseudoazulenes. Whether compounds of the first or second type are formed depends on the nature of the cation, which is involved in the formation of the quaternary salt.

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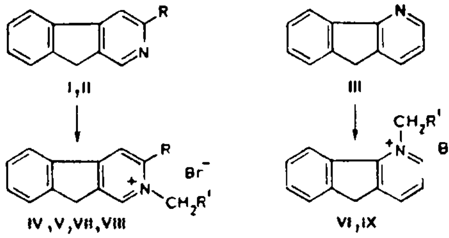
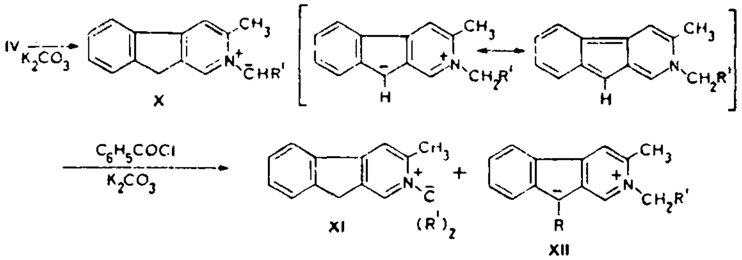
We have used the accessible 3-methyl-2-azafluorene (I) [6], 2-azafluorene (II) [7], and 4-azafluorene (III) [8] to prepare the bromides [9, 10] containing the N-phenacyl [compounds (IV)-(VI)] and N-benzyl groups [compounds (VII)-(IX)] and have examined their base-catalyzed reactions.



I,IV,VII $R=CH_3$; II,V,VIII $R=H$ IV-VI $R'=COC_6H_5$; VII-IX $R'=C_6H_5$

When these salts are treated with aqueous potassium carbonate or triethylamine (conditions for the formation of pyridinium ylides), the proton can be abstracted from the methylene group of the N-phenacyl (N-benzyl) radical, the 9-methylene group, or the C_3 methyl group [salts (IV) and (VII)]. The signals of the protons of the 9-methylene group and of the phenacyl radical disappear from the PMR spectrum 10 min after addition of CD_3ONa to a solution of salt (IV) in CD_3OD [salt (IVa)], while the signals of the other protons persist in their entirety (Table 1). The IR spectrum of salt (IV) in the medium- and low-frequency regions is identical before and after deuteration. Consequently, we may expect that both azafluorenium ylides and pseudoazulene-type systems can be formed from N-phenacylazafluorenium salts. After treatment of salt (IV) with aqueous potassium carbonate and purification of the reaction products on aluminum oxide we isolated 3-methyl-2-azafluorenium benzoylmethylide (X) (reddish orange powder melting at 142°C with decomposition), which was unaffected by storage in the solid state for about a month at —10°C, darkened at room temperature over a period of 1-2 h, and was also rapidly affected in chloroform solution. In acids its color became pale yellow. The PMR spectrum (Table 1) of ylide (X) recorded in CF_3COOH and CF_3COOD showed a reduction in the integrated intensity of the signal at δ 6.35 ppm (assigned after [11]), from 2H to 1H, implying the respective protonation and deuteration of the benzoylmethylide group.



That treatment of quaternary salt (IV) with potassium carbonate solution forms in addition to ylide (X) an indenopyridinium zwitterion (its mesomeric pseudoazulene form is also shown in the reaction scheme) is demonstrated by the benzoylation of the reaction products. We isolated two compounds — the benzoylation product of ylide (X), 3-methyl-2-azafluorenium dibenzoylmethylide (XI) (a stable bright yellow substance with mp 227-227.5°C) and the benzoylation product of the indenopyridinium zwitterion, N-phenacyl-3-methyl-9-benzoylindeno-[2,3-c]pyridinium hydroxide inner salts (XII) (dark violet crystals with a metallic luster, mp 191-192°C). Indenopyridinium (XII) seems capable of existing in several modifications; in one of the runs it was isolated as a red powder with mp 215-217°C (decomposition).

The peaks of the molecular ions (M^+) with m/e 403* in the mass spectra of compounds (XI) (4.5%) and (XII) (9%) support their elemental compositions. In the spectra of both compounds the peaks of the 385 ions (100 and 54%) correspond to M^+ of the substitutionally isomeric indenoindolizines (M_1^+), which are probably formed by elimination of an H_2O molecule when the sample is heated in the ion source. The isomeric nature of compounds (XI) and (XII) is supported by the subsequent decomposition of the M_1^+ ion (parentheses enclose the intensity in % of the base peak for compounds (XI) and (XII), respectively): $[M_1 - C_6H_5]^+$ 308 (73 and 0), $[M_1 - (C_6H_5CO - H)]^+$ 281 (44 and 66), $[M_1 - C_6H_5CO]^+$ 280 (37 and 100), $C_6H_5C{\equiv}O^+$ 105 (37 and

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*Here and subsequently the ions are specified by the mass/charge ratio.

TABLE 1. Spectral Properties of Quaternary Azafluorenium Salts (IV)-(IX), Azafluorenium Ylides (X), (XI), Indenopyridiniums (XII), (XVII), (XIX), (XXI), 1,8-Diaza-1H,8H-fluoreno[9,9*a*,1-*a*,b]fluoranthenes (XVIII), (XX), and Their Analog (XXII)

Compound	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm					
		solvent, ethanol	3-R (3-CH_3, s, 3H; 3-H, d, 1H)	9-H s 2H (1H)	N^+—CH_2, s 2H (N^+—CHD, s 1H)	1-H, s 1H	other aromatic protons
II		$CDCl_3$, HMDS CF_3COOH, TMS	8,54; $J=5$ Hz 8,00 (superim. d)	3,88 3,82		8,71 8,22 (superim. d)	6,9—7,8, m, 7,81, d, 1H (5-H); 7,2—7,6, m 4H
IV	246 (4,18), 310 (4,40), 450 (3,22)	CD_3OD, HMDS	2,70	4,17	6,37	8,82	8,4, s, 1H (4-H); 8,08, br. d, 2H (2×H-ortho to CO); 7,4—7,7, m, 7H
IVa		CD_3OD+CD_3ONa, TMS	2,68	—	—	8,81	8,4, s, 1H (4-H); 8,06 br. d, 2H (2×H-ortho to CO); 7,4—7,7, m, 7H
V	210 (4,65), 328 (4,20)	CD_3OD, HMDS	8,57	4,04	6,30	8,73	8,17, br. d, 2H (2×H-ortho to CO); 7,2—8,0, m
VI	210 (4,66), 290 (4,00), 330 (4,14)	CF_3COOH, TMS	8,65, br. d 2H (3-H+5-H)	4,35	6,81	—	8,25, br. d, 2H (2×H-ortho to CO); 7,3—8,0, m
VII	207 (4,49), 310 (4,25), 460 (3,12)	CF_3COOH, TMS	2,73	4,27	5,77	8,75	8,17, s, 1H (4-H); 7,3—8,1, m
VIII	205 (4,28), 300 (3,59)	CF_3COOH, TMS	8,67	4,21	5,75	8,78	7,4—8,3, m
IX	208 (4,59), 294 (4,38)	CF_3COOH, TMS	8,70	4,35	6,44	8,20 d	8,45, d, 1H (5-H); 7,2—8,0, m
X		CF_3COOH, TMS CF_3COOD, TMS	2,87 2,87	4,32 4,32	6,35 (6,34)	8,69 8,71	7,5—8,5, m, 10H 7,5—8,5, m, 10H

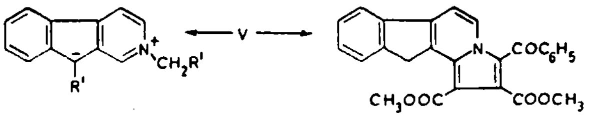
XI	222 (4,70), 300 (4,96)	$CDCl_3$, HMDS CF_3COOH, TMS CF_3COOD, TMS	2,73 2,78 2,78	3,93 4,17 4,15	— — —	8,46 8,65 8,67	6,70—8,1, m 7,2—8,2, m 7,1—8,3, m
XII	205 (5,13), 248 (5,01), 286 (5,11), 340 (4,53), 370 (4,49), 508 (4,12)	$CDCl_3$, HMDS CF_3COOH, TMS CF_3COOD, TMS	2,27 2,83 2,80	— (6,45) —	— 6,24 6,22	9,31 8,60 8,57	6,8—8,0, m 7,4—8,3, m, 15H 7,4—8,3, m, 15H
XVII	210 (4,64), 265 (4,71), 283 (4,59), 336 (4,19), 370 (4,19), 490 (4,00)	$CDCl_3$, HMDS	2,55	—	5,43	9,55	6,7—8,2, m
XVIII	208 (4,77), 280 (4,80), 391 (3,85), 504 (3,88), 674 (4,69)	$CDCl_3$, HMDS	2,80	—	5, 5,2 d, $J_{AB}=16$ Hz	—	6,8—7,6, m
XIX	206 (4,76), 226 (4,66), 286 (4,78), 338 (4,35), 370 (4,35), 500 (4,19)	CF_3COOH, TMS	8,65, br. d, 2H (3-H+5-H)	(6,33)	5,65	—	7,2—8,3, m
XX	206 (4,82), 280 (4,78), 500 (3,66), 660 (4,57)	—					
XXI	206 (5,63), 240 (5,61), 302 (5,60), 351 (5,64), 378 (5,40), 520 (4,19)	$CDCl_3$, TMS	8,75	—	5,77	—	6,7—7,9, m
XXII	212 (4,56), 246 (4,28), 291 (4,06), 330 (4,27), 377 (3,86), 615 (4,23)	$CDCl_3$, HMDS	—	—	6,45, s, 4H	—	6,7—7,5, m; 8,0, m, 2H (4-H and 11-H); 8,7, d, 2H (2-H and 9-H)

51), and $[C_6H_5]^+$ 77 (26 and 44). The appearance in the mass spectrum of compound (XI) of the fragment $[M - C_6H_5CO]^+$, 298 (10%), which is not present in the spectrum of compound (XII), is apparently due to its ylide structure.

In the IR spectrum of compound (XI) the 1635 cm^{-1} band belongs to the carbonyl group of the dibenzoylmethylide fragment, while the very intense broad band at 1500 cm^{-1} represents the ylide linkage (assigned by analogy with [12]). In the IR spectrum of compound (XII) the phenacyl carbonyl group is responsible for the 1692 cm^{-1} band. The anomalously high intensity of the bands in the 1600-1480 cm^{-1} region is apparently caused by the low-frequency shift of the stretching band of the carbonyl group of the C_9 substituent resulting from its conjugation with the azafluorene system and reduction in the C═O bond order.

The two-proton singlet of the C_9 methylene group of ylide (XI) remains unchanged in $CDCl_3$, CF_3COOH, and CF_3COOD (Table 1). The diamagnetic shift (δ 8.46 ppm) of the α-proton of ylide (XI) relative to its position in salt (IV) (δ 8.82 ppm) in $CDCl_3$ can provide indirect support for the ylide structure of (XI) (as in [13]) with two equivalent carbonyl groups. The PMR spectrum of compound (XII) lacks the signals of the C_9 proton when recorded in $CDCl_3$ but contains a one-proton singlet at 6.45 ppm when recorded in CF_3COOH (protonation at the C_9 atom), which is not present in CF_3COOD solution. These results confirm that the indenopyridinium zwitterion is benzoylated at the C_9 atom and that the anionic center is localized at this position (by analogy with [14]).

Treatment of N-phenacyl-2-azafluorenium bromide (V) with benzoyl chloride in the presence of triethylamine forms N-phenacyl-9-benzoylindeno[2,3-c]pyridinium hydroxide inner salts (XIII) as reddish crimson crystals.

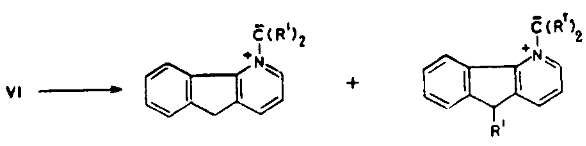


XIII XIV

The mass spectrum of zwitterion (XIII) supports its structure. It contains the M^+ peak, 389 (18), and also the fragment ions $[M - C_6H_5]^+$ 312 (15), $[M - C_6H_5CO]^+$ 284 (14), $[M - C_6H_5COCH_2]^+$ 270 (12), $[M - C_6H_5CO, - C_6H_5CO]^+$ 179 (7), $[M - C_6H_5COCH, - (C_6H_5CO - H)]^+$ 167 (14), $C_6H_5C\equiv O^+$ 105 (100), and $[C_6H_5]^+$ 77 (70). The IR spectrum of compound (XIII), like that of indenopyridinium (XII), contains the phenacyl carbonyl band at 1690 cm^{-1}, and also a group of bands in the 1600-1480 cm^{-1} and 1310-1215 cm^{-1} regions, which are due to the carbonyl of the C_9 benzoyl group.

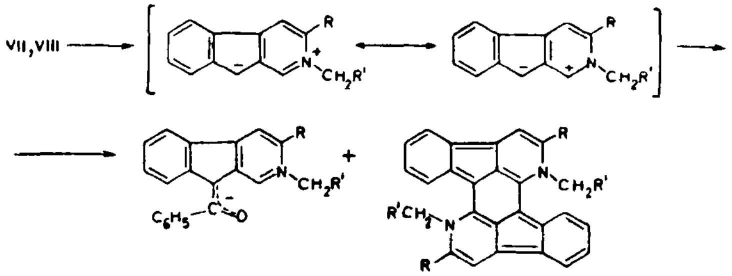
Apparently treatment of salt (V) with triethylamine also forms 2-azafluorenium benzoylmethylide; this is supported by the formation of 3-benzoyl-1,2-bis(methoxycarbonyl)indeno-[1,2-g]indolizine (XIV) when this salt reacts with dimethyl acetylenedicarboxylate.

The mass spectrum together with PMR and IR spectra imply that the interaction of salt (VI) with benzoyl chloride in the presence of triethylamine forms a mixture of 4-azafluorenium dibenzoylmethylide (XV) and 9-benzoyl-4-azafluorenium dibenzoylmethylide (XVI).



XV XVI

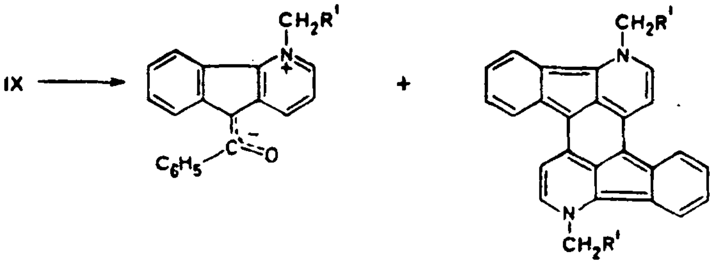
We established by benzoylating the azafluorenium salts (VII) and (VIII) in the presence of triethylamine that deprotonation takes place at the 9-methylene group and not at the benzyl radical. We prepared N-benzyl-3-methyl-9-benzoylindeno[2,3-c]pyridinium hydroxide inner salt (XVII) and 2,9-dimethyl-1,8-dibenzyl-1,8-diaza-1H,8H-fluoroeno[9,9a,1-a,b]fluoranthene (XVIII) from bromide (VII), and their analogs, (XIX) and (XX), respectively (which do not contain methyl groups), from bromide (VIII). Benzoyl derivatives (XVII) and (XIX), like their analog (XIII), are reddish crimson, while compounds (XVIII) and (XX) are blue. Compounds (XVIII) and (XX) seem to be formed by intermolecular 1,3-dipolar cycloaddition of one of the mesomeric forms of the N-benzylindenopyridinium zwitterion and subsequent dehydrogenation (like the reaction of the ylides described in [15]). In the PMR spectrum of compound (XVIII) (Table 1) the methylene protons of the symmetrical N-benzyl groups are anisochronous and give an AB spectrum with ν_{AB} = 24.8 Hz and J_{AB} = 16 Hz. This inequivalence could be due either to the nonplanar asymmetric structure of the molecule or to the inhibition of the rotation of the benzyl groups by steric interactions set up by the C_7 and C_{14} protons.



XVII,XIX XVIII,XX

XVII,XVIII R = CH₃ ; XIX,XX R = H

In the same way we prepared N-benzyl-9-benzoylindeno[1,2-b]pyridinium hydroxide inner salt (XXI) and 3,10-dibenzyl-3,10-diaza-3H,10H-fluoreno[9,9a,1-a,b]fluoranthene (XXII) from bromide (IX).



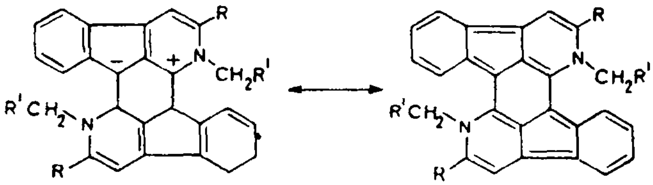
XXI XXII

Benzoyl derivative (XXI) is reddish crimson, while compound (XXII) is blue.

The IR spectra of indenopyridiniums (XVII), (XIX), and (XXI) resemble those of compounds (XXI) and (XIII), which supports their structural similarity. The PMR and UV parameters of the synthetic compounds are summarized in Table 1.

Quaternary salts (IV)-(IX) are mainly characterized by two short-wavelength UV bands at 205-210 nm (log ε 4.15-4.59) and 290-330 nm (log ε 4.00-4.40) (Table 1). Salts (IV) and (VII) also show absorption in the visible region of the spectrum [λ_{max} 450 (log ε 3.22) and 460 nm (3.12) respectively], which is due to the partial deprotonation in alcoholic solution of the methylene group of the phenacyl (benzyl) radical and the generation of the ylide structure [12]. Addition of triethylamine to alcoholic solutions of these salts causes an increase in the intensity of these bands, implying further deprotonation.

The UV spectra of zwitterions (XII), (XVII), (XIX), and (XXI) are more complex than those of the corresponding salts. All the spectra have absorption in the 490-520 nm region (log ε 4.0-4.19); when acid is slowly added to these zwitterions, this long-wavelength band is hypsochromically shifted by 90 nm, increasing in intensity, as protonation of the anionic benzoyl center at the C_9 atom takes place. There is an equivalent band in the 500 nm region in the UV spectra of compounds (XVIII) and (XX). These spectra also have a band with λ_{max} 660-674 nm, which is typical of pseudoazulenes [4].



a XVIII, XX b

These results to some extent support both the zwitterionic structure (a) and the structure comprising two pseudoazulene fragments (b) for compounds (XVIII) and (XX). The UV spectrum of compound (XXII), in which by comparison with compounds (XVIII) and (XX) there are no steric hindrances to the formation of structure (b) set up by the substituents, contains only one long-wavelength absorption maximum with λ_{max} at 615 nm (log ε 4.23).

We thank A. A. Fomichev for discussion of the PMR spectra of compounds (XV)-(XXII).

EXPERIMENTAL

Spectra were recorded with: IR: a UR-20 with KBr, NaCl, and LiF prisms, as KBr tablets for (XVII), (XXI), and as Vaseline oil mulls; UV: a Specord UV-vis; PMR: Varian HA-100D for (XII), Tesla BS-487C for (II), (IV)-(XI), (XV), and (XVI), and a Bruker WP-80 for (XVII)-(XXII) with hexamethyldisiloxane (HMDS) and tetramethylsilane (TMS) as internal standards. The mass spectra were derived on an MX-1303 with direct sample insertion into the ion source, ionizing voltage 70 V, at detection temperatures 100°C for (V), (VII), (VIII), (XIV), and (XXI), 120°C for (XIII), (XV)-(XVII), and (XIX), 130°C for (IX) and (XVIII), 140°C for (XI) and (XX), and 160°C for (XII) and (XXII). Aluminum oxide (grade II) was used for chromatography.

N-Phenacyl-2-azafluorenium Bromide (V). A solution of 2-azafluorene (II) (0.5 g, 2.9 mmole) and bromoacetophenone (0.6 g, 3 mmole) in acetone (10 ml) was refluxed for 1 h 30 min. The resulting crystals were washed with hot acetone and dried to give salt (V) (0.9 g, 90%), mp 190-192°C. IR spectrum: 1700 (CO), 1640 cm^{-1} (C—C$_{arom}$). Found: N 3.7%. $C_{20}H_{16}BrNO$. Calculated: N 3.0%.

Compounds (VII)-(IX) were prepared in the same way from azafluorenes (I)-(III) and benzyl bromide. Bromide (VII), yield 90%, had mp 226-228°C (from alcohol). Found: Br 23.0; N 3.7; [M — HBr]$^+$ 271. $C_{20}H_{18}BrN$. Calculated: Br 22.7; N 4.0%; [M — HBr] 271; M 352. Bromide (VIII), yield 99%, had mp 222-224°C (from absolute alcohol). Found: Br 23.2; N 4.1%; [M — HBr]$^+$ 257. $C_{19}H_{16}BrN$. Calculated: Br 23.6; N 4.2%; [M — HBr]$^+$ 257. Bromide (IX), yield 90% had mp 207-208°C (from alcohol). Found: N 3.8%; [M — HBr]$^+$ 257. $C_{19}H_{16}BrN$. Calculated: N 4.2%; [M — HBr] 257.

3-Methyl-2-azafluorenium Benzoylmethylide (X). Bromide (IV) (mp 225-226.5°C; 1.24 g, 3 mmole), water (5 ml), and 40% potassium carbonate solution (3.4 ml) were shaken for 10 min in a stream of helium. The resulting crystals were dissolved in chloroform (20 ml) and the solution was filtered through a layer of aluminum oxide. The solvent was removed under vacuum without heating. The residue (0.48 g) was triturated with ether to give benzoylmethylide (X) (0.37 g, 38%) as reddish orange crystals decomposing at 142°C. Found: N 4.9%; [M — H_2O]$^+$ 281. $C_{21}H_{17}NO$. Calculated: N 4.7%; [M — H_2O] 281.

3-Methyl-2-azafluorenium Dibenzoylmethylide (XI) and N-Phenacyl-3-methyl-9-benzoylindeno-[2,3-c]pyridinium Hydroxide Inner Salt (XII). A chloroform solution of ylide (X) (1 g, 3.3 mmole, calculated from salt (IV) used in the reaction) was shaken for 10 min with a solution of benzoyl chloride (0.5 g, 3.5 mmole) in chloroform (5 ml) and 40% potassium carbonate solution (3 ml). The color changed from reddish orange to dark cherry. The chloroform solution was filtered through a layer of aluminum oxide and dried over magnesium sulfate. The residue after evaporation of the chloroform was crystallized from benzene to give the compound (0.91 g) as violet crystals. This substance (0.6 g) was refluxed in benzene and the insoluble residue was separated. The benzene solution deposited compound (XII) (0.2 g, 13%), dark violet plates with a metallic luster, mp 191-192°C (from benzene). Found: N 2.7%; [M — H_2O]$^+$ 385. $C_{28}H_{21}NO_2$. Calculated: N 3.5%; [M — H_2O] 385. The benzene-insoluble residue was crystallized from alcohol to give dibenzoylmethylide (XI) (0.31 g, 20%), bright yellow crystals, mp 227-227.5°C. Found: C 83.1; H 5.1; N 3.8%; [M — H_2O]$^+$ 385; M 403. $C_{28}H_{21}NO_2$. Calculated: C 83.4; H 5.2; N 3.5%; [M — H_2O] 385; M 403.

In an analogous run compound (XII) was chromatographed twice on a column (elution with ethyl acetate) and then crystallized from benzene—alcohol (5:1) as a red powder with mp 215-217°C (decomposition). IR spectrum: 1692, 1605, 1595, 1575, 1555, 1522, and 1485 cm^{-1}. Found: C 83.5; H 5.1; N 2.8%; M$^+$ 403. $C_{28}H_{21}NO_2$. Calculated: C 83.4; H 5.2; N 3.5%; M 403.

N-Phenacyl-9-benzoylindeno[2,3-c]pyridinium Hydroxide Inner Salt (XIII). To a suspension of salt (V) (0.7 g, 1.9 mmole) and benzoyl chloride (0.28 g, 2 mmole) in chloroform (10 ml) was added triethylamine (0.4 g, 4 mmole). The mixture was vigorously stirred for 1 h. The chloroform solution was washed with water, and then chromatographed on a column (Al_2O_3, 20 g, 12 × 3 cm, elution by chloroform). Two fractions were collected; each was rechromatographed on a column (Al_2O_3, 7.0 g, 5 × 1.5 cm, elution by chloroform—benzene, 1:3). After removal of the solvent the residue was triturated under absolute ether and dried to give indenopyridinium zwitterion (XIII) (15 mg), a reddish crimson powder, mp 114°C (decomposition), R$_f$ 0.14 (ethanol—chloroform, 1:20). IR spectrum: 1690 (phenacyl CO), 1630, 1600, 1500-1580, 1490, 1310, and 1215 cm^{-1}. Found: N 3.7%; M$^+$ 389. $C_{27}H_{19}NO_2$. Calculated: N 3.6%; M 389.

3-Benzoyl-1,2-bis(methoxycarbonyl)indeno[1,2-g]indolizine (XIV). To a suspension of salt (V) (0.62 g, 1.63 mmole) in chloroform (10 ml) were successively added dimethyl acetylenedicarboxylate (0.49 g, 3.5 mmole) and triethylamine (0.49 g, 4.9 mmole). The dark green mixture was vigorously stirred at 40°C for 3 h and then washed with water. The chloroform solution was chromatographed on a column (26 × 2 cm, Al_2O_3, 80 g, elution by benzene—chloroform, 3:1, and then by chloroform). The first fraction of the eluate (a yellow solution) gave indolizine (XIV) (0.15 g, 21.7%), yellow crystals, mp 236-238°C (washed with hot benzene), R_f 0.7 (chloroform—ethyl acetate, 3:1), sparingly soluble in benzene, chloroform, methanol, ethanol, acetonitrile, and acetic acid. IR spectrum: 1725 (two $COOCH_3$), 1695 (C_6H_5CO), 1600 ($C—C_{arom}$), group of bands at 700-770 cm^{-1} ($C—H_{arom}$). Found: C 73.0; H 5.1; N 3.8%; M^+ 425 (30%). $C_{26}H_{17}NO_5$. Calculated: C 73.4; H 4.5; N 3.3%; M 425. The second fraction (a dark green solution) gave a green powder (0.15 g, 21.1%), which was identified by chromatography as a mixture of indolizine (XIV) and a green substance of unknown structure with R_f 0.6, which could not be purified by preparative thin-layer chromatography.

4-Azafluorenium Dibenzoylmethylide (XV) and 9-Benzoyl-4-azafluorenium Dibenzoylmethylide (XVI). Following the synthesis of compounds (XI) and (XII), salt (VI) (mp 220-221°C; 1.1 g, 3 mmole) [10], benzoyl chloride (0.42 g, 3 mmole), and 20% potassium carbonate solution (5 ml) in chloroform (10 ml) gave a dark blue powder (0.45 g). Column chromatography (Al_2O_3, 16 g, 10 × 2 cm, elution with chloroform) gave a mixture (0.26 g, 22%) of ylides (XV) and (XVI), as reddish brown crystals, mp 189-190°C (from benzene). IR spectrum: 1739 [CO in $C(COC_6H_5)_2$], 1600, 1559, 1324, and 1223 (COC_6H_5 on C_9), 1523 and 1495 cm^{-1} $(\rangle\overset{+}{N}-\overset{-}{C}\langle)$. PMR spectrum ($CDCl_3$, TMS): 8.62 (d, 1H, 3-H), 8.1 (d, 1H, 5-H), 6.9-8.2 (m, H_{arom}), 4.1 (s, ~1H, 9-H). UV spectrum, λ_{max} (log ε): 204 (5.68), 235 (5.51), 290 (5.24), 364 (5.24), and 520 nm (4.06). The mass spectra were consistent with the structures of compounds (XV) and (XVI): M_1^+ 389 (31), M_2^+ 493 (8); fragment ions respectively: $[M - C_6H_5]^+$ 312 (6.2) and 416 (1.6), $[M - C_6H_5CO]^+$, 284 (6.5) and 388 (17), $C_6H_5C{\equiv}\overset{+}{O}$, 105 (100), $[C_6H_5]^+$, 77 (45). Found: C 82.4; H 5.7; N 3.8%. Calculated: XV — $C_{27}H_{19}NO_2$; C 83.3; H 4.9; N 3.6%; M 389; XVI — $C_{34}H_{23}NO_3$; C 82.7; H 4.7; N 2.8%; M 493.

N-Benzyl-3-methyl-9-benzoylindeno[2,3-c]pyridinium Hydroxide Inner Salt (XVII) and 2,9-Dimethyl-1,8-dibenzyl-1,8-diaza-1H,8H-fluoreno[9,9a,1-a,b]fluoranthene (XVIII). Salt (VII) (1 g, 2.8 mmole), benzoyl chloride (0.4 g, 2.8 mmole), and triethylamine (0.4 g, 4 mmole) in chloroform (10 ml) were vigorously stirred for 30 min, and then shaken with water. The dark blue chloroform solution was immediately chromatographed (Al_2O_3, 80 g, 20 × 3 cm, elution with benzene—chloroform, 1:1, and then with chloroform). Compound (XVII) (0.15 g, 13.5%) was isolated first, reddish crimson crystals, mp 215-216.5°C (from benzene). Mass spectrum: M^+ 375 (54), $[M - CO]^+$ 347 (4.3), $[M - C_7H_6]^+$ 285 (18), $[M - C_6H_5CH_2]^+$ 284 (2.0), $[M - (C_6H_5CO—H)]^+$ 271 (22), $[M - C_6H_5CO]^+$ 270 (35), $[M - CO, - C_6H_5CH_2]^+$ 256 (14), 181 (38), 180 (60), $C_6H_5C{\equiv}\overset{+}{O}$, 105 (100), $[C_6H_5CH_2]^+$ 91 (49), $[C_6H_5]^+$ 77 (23). IR spectrum: 1616, group of bands, 1530-1450, 1318, 1223 cm^{-1}. Found: N 4.1%. $C_{27}H_{21}NO$. Calculated: N 3.8%; M 375. The chloroform eluate gave compound (XVIII) (0.33 g, 44%), dark blue crystals, mp 264°C (decomposition). Mass spectrum: M^+ 538 (95), M^{2+} 269 (18), $[M - C_7H_6]^+$ 448 (95), $[M - C_6H_5CH_2]^+$ 447 (100), $[M - C_7H_6, - C_6H_5]^+$ 371 (7), $[M - C_6H_5CH_2, - C_6H_5]^+$ 370 (12), $[M - C_6H_5CH_2, —C_6H_5CH_2]^+$ 356 (11) $[C_6H_5CH_2]^+$ 91 (39). Found: N 5.5%. $C_{40}H_{30}N_2$. Calculated: N 5.2%; M 538.

N-Benzyl-9-benzoylindeno[2,3-c]pyridinium Hydroxide Inner Salt (XIX) and 1,8-Dibenzyl-1,8-diaza-1H,8H-fluoreno[9,9a,1-a,b]fluoranthene (XX). Following the synthesis of compounds (XVII) and (XVIII), salt (VIII) (0.6 g, 1.8 mmole), benzoyl chloride (0.25 g, 1.8 mmole), and triethylamine (0.35 g, 3.5 mmole) in chloroform (10 ml) gave after chromatography (20 × 3 cm column, Al_2O_3, 80 g) compound (XIX) (0.4 g, 62.5%), bright reddish crimson crystals, mp 227-229°C (from benzene), R_f 0.16 (chloroform). Mass spectrum: M^+ 361 (100), $[M - C_6H_4]^+$ 285 (5), $[M - C_6H_5]^+$ 284 (6.5), $[M - C_7H_6]^+$ 271 (3.2), $[M - C_6H_5CH_2]^+$ 270 (3.2), $[M - C_6H_5CH_2, —CO]^+$ 242 (45), $[M - C_6H_5CH_2, —C_6H_5CO]^+$ 165 (4.5), $C_6H_5C{\equiv}O^+$ 105 (11), $[C_6H_5CH_2]^+$ 91 (41). IR spectrum: 1605, 1580, 1550, 1500, 1320, and 1220 cm^{-1}. Found: C 86.6; H 5.5; N 4.4%. $C_{26}H_{19}NO$. Calculated: C 86.4; H 5.3; N 3.9%; M 361. Then compound (XX) (0.005 g, 1%) was isolated, dark blue crystals, mp 152-154°C (refluxed three times in benzene), R_f 0.06 (chloroform) or 0.28 (chloroform—alcohol, 20:1). Mass spectrum: M^+ 510 (7), $[M - C_7H_6]^+$ 420 (2.5), $[M - C_6H_5CH_2]^+$ 419 (3.8), $[C_6H_5CH_2]^+$ 91 (100). $C_{38}H_{26}N_2$. Calculated: M 510.

N-Benzyl-9-benzoylindeno[1,2-b]pyridinium Hydroxide Inner Salt (XXI) and 3,10-Dibenzyl-3,10-diaza-3H,10H-fluoreno[9,9a,1-a,b]fluoranthene (XXII). The reaction of salt (IX) (1 g, 3 mmole), benzoyl chloride (0.42 g, 3 mmole), triethylamine (0.6 g, 6 mmole), and chloroform (10 ml) was carried out in the same way. Chromatography (elution with chloroform and chloroform–alcohol, 20:1) of the reaction products gave compound (XXI) (0.37 g, 35%), bright reddish crimson crystals, mp 217-218°C (from benzene). Mass spectrum: M^+ 361 (100), $[M - C_6H_5]^+$ 284 (1.7), $[M - C_7H_6]^+$ 271 (4.3), $[M - C_6H_5CH_2]^+$ 270 (2.7), $[M - C_6H_5CO]^+$ 256 (4), $[M - C_6H_5CH_2, -CO]^+$ 242 (99), 166 (3.5), 165 (7.3), 164 (6.1), $C_6H_5C{\equiv}O^+$ 105 (44), $[C_6H_5CH_2]^+$ 91 (81), $[C_6H_6]^+$ 78 (32), $[C_6H_5]^+$ 77 (17). IR spectrum: 1608, 1590, 1565, 1530, 1465, 1435, 1315, and 1235 cm^{-1}. Found: C 86.6; H 5.3; N 4.0%. $C_{26}H_{19}NO$. Calculated: C 86.4; H 5.3; N 3.9%; M 361. Then dark lilac crystals (0.35 g, 35%) were isolated, rechromatography of which gave compound (XXII), dark blue crystals, mp 201-204°C (from alcohol with ether). Mass spectrum: M^+ 510 (30), $[M - C_7H_6]^+$ 420 (100), $[M - C_6H_5CH_2]^+$ 419 (78), $[M - C_7H_6, -C_6H_5]^+$ 343 (8), $[M - C_6H_5CH_2, -C_6H_5]^+$ 342 (12), $[M - C_7H_5, -C_6H_5]^+$ 341 (10), $[C_6H_5CH_2]^+$ 91 (76). Found: N 5.4%. $C_{38}H_{26}N_2$. Calculated: N 5.5%; M 510.

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