Heterocyclic Mesomeric Betaines. Part 1. Synthesis and Cycloaddition Reactions of Hetero Derivatives of the Phenalenide Anion

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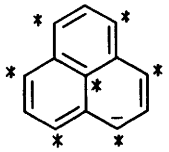
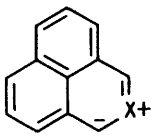
Conjugated heterocyclic mesomeric betaines (**9**; R = Ph, Me, and H) which are isoconjugate with the alternant phenalen-1-ide anion (**1**) have been synthesized. 8-Aminoquinoline and α-halogeno ketones yield the salts (**10**). These salts and triethylamine yield the conjugated heterocyclic mesomeric betaines (**9**) which cannot be isolated, but have been characterized by 1,3-dipolar cycloaddition with acetylenic and olefinic dipolarophiles. Dehydrogenation of some of the cycloadducts (**11**), (**15**), and (**16**) yield the corresponding conjugated cyclazine derivatives (**12**), (**17**), and (**18**). Hydrolysis of the esters (**17**) and (**18**) followed by thermal decarboxylation yields the novel cyclazines (**21**).

The new classification of heterocyclic mesomeric betaines which we have proposed [1] emphasizes the isoconjugate relation of 16 classes of heterocyclic mesomeric betaines to alternant and non-alternant hydrocarbon anions and dianions. The phenalen-1-ide anion (**1**) is an alternant system and we now report on the synthesis and the chemistry of conjugated mesomeric betaines which are isoconjugate with this tricyclic anion (**1**). These conjugated heterocyclic mesomeric betaines can be regarded as being formally derived from the phenalen-1-ide anion (**1**) by hetero substitution at unstarred positions [1] of the anion.

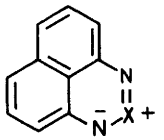
Several conjugated heterocyclic mesomeric betaines isoconjugate with the phenalen-1-ide anion (**1**) are known, such as the 1*H*-2-azaphenalen-2-ium-1-ides (**2**),[2,3] the 1*H*-2λ⁴-thiaphenalen-2-ylium-1-ides (**3**),[2,4–6] the 1*H*-1,2,3-triazaphenalen-2-ium-1-ides (**4**),[7–20] and the 1*H*-1,3-diaza-2λ⁴-thiaphenalen-2-ylium-1-ides (**5**).[21–25] The synthesis of the 1*H*-1,3-diaza-2λ⁴-selenaphenalen-2-ylium-1-ides (**6**) has been claimed,[26] although recent attempts to repeat this synthesis were unsuccessful.[27]



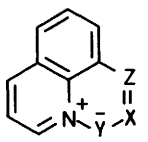
(**1**)



(**2**) X = NR
(**3**) X = S



(**4**) X = NR
(**5**) X = S
(**6**) X = Se



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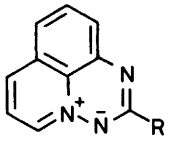

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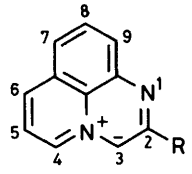
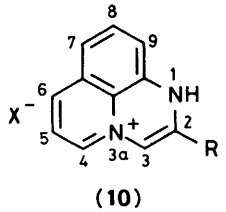


(**9**)



(**10**)

In formulae (**9**) and (**10**): **a**, R = Ph; **b**, R = Me; **c**, R = H

Our interest in conjugated heterocyclic mesomeric betaines isoconjugate with the alternant phenalen-1-ide anion (**1**) is associated with structures which conform to the general formula (**7**) in which the atoms or groups X, Y, and Z are selected from suitably substituted carbon or nitrogen atoms. Recently, the synthesis of the 1*H*-1,3,3aλ⁵-triazaphenalen-3a-ium-3-ides (**8**; R = H and Me) has been achieved and their 1,3-dipolar cycloaddition reactions with dimethyl acetylenedicarboxylate has been reported.[28–30] We now describe the synthesis and the cycloaddition reactions of 1,3aλ⁵-diazaphenalen-3a-ium-3-ides (**9**).

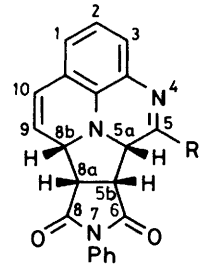
Synthesis and Chemistry of the Conjugated Heterocyclic Mesomeric Betaines (**9a**), (**9b**), *and* (**9c**).—Reaction of 8-aminoquinoline with phenacyl bromide in boiling acetone solution afforded maroon needles of 2-phenyl-1*H*-1,3aλ⁵-diazaphenalen-3a-ium bromide (**10a**; X = Br) (24%). The ^{1}H n.m.r. spectrum of this salt (**10a**; X = Br) showed 12 aromatic protons (δ 8.16—6.97), one of which was a singlet (δ 7.08). The salt was, therefore, assigned the structure (**10a**; X = Br) to replace the incorrect alternative tautomeric imine structure assigned by Kanemasa, Kobira, and Kajigaeshi.[31] Treatment of the bromide (**10a**; X = Br) with perchloric acid gave the corresponding perchlorate (**10a**; X = ClO_4) [$\lambda_{max.}$ (EtOH) 512 nm (ε 5 000)].

Similarly, the salts (**10b**; X = ClO_4) (15%) and (**10c**; X = ClO_4) (86%) were obtained as amorphous red solids. The u.v. and visible spectra of the salts (**10b**) and (**10c**) (X = ClO_4) are similar to those of the salt (**10a**; X = ClO_4).

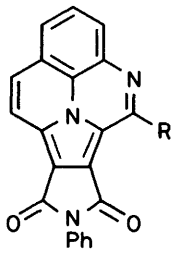
2-*Phenyl*-1H-1,3aλ⁵-*diazaphenalen*-3a-*ium*-3-*ide* (**9a**).—When the salt (**10a**; X = Br) was treated with triethylamine, a deep green colour was generated which is attributed to the formation of the conjugated heterocyclic mesomeric betaine (**9a**). Although this heterocycle (**9a**) could not be isolated, its existence was demonstrated by trapping with various 1,3-dipolarophiles.

In the following experiments, the mesomeric betaine (**9a**) was always generated and allowed to react directly. Reaction of 2-phenyl-1*H*-1,3aλ⁵-diazaphenalen-3a-ium-3-ide (**9a**) with *N*-phenylmaleimide in acetonitrile solution at room temperature gave the 1,3-dipolar cycloadduct (**11a**) (76%). The *endo*-stereochemistry (**11a**) was assigned on the basis of the coupling constants between the protons at positions 5a and 5b and between the protons at positions 8a and 8b. The coupling

constants were also estimated using a version ($J = 10\cos^2\theta$)[32] of the Karplus relationship.[33] The coupling constants $J_{5a,5b}$ and $J_{8a,8b}$ were determined to be 9 and 7 Hz, respectively. This is in agreement with the calculated values of 10 and 10 Hz based upon the stereochemistry of the *endo*-stereoisomer (**11a**). In the alternative *exo*-stereoisomer, the corresponding coupling constants are estimated to be *ca.* 2 Hz.



(11)



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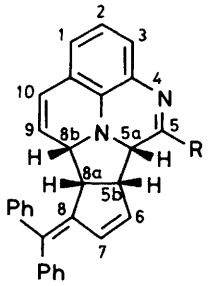

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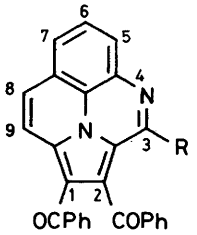

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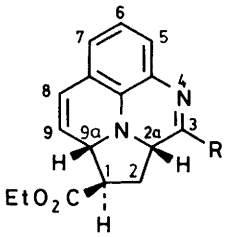

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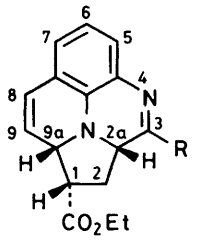


(16)

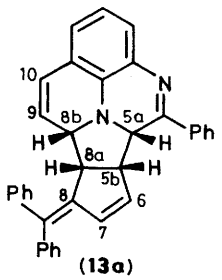
In formulae (**11**)—(**16**): **a**, R = Ph; **b**, R = Me; **c**, R = H

When the cycloadduct (**11a**) was heated in boiling acetonitrile solution in the presence of triethylamine, dehydrogenation occurred and the tetradehydro derivative, 5,7-diphenyl-7*H*-4,7,10c-triazapentaleno[1,2,3-*cd*]phenalene-6,8-dione (**12a**) (34%) was obtained. The constitution (**12a**) was fully supported by its mode of formation and its spectroscopic properties.

Reaction of the conjugated heterocyclic mesomeric betaine (**9a**) with 6,6-diphenylfulvene in boiling acetonitrile solution gave a single cycloadduct which was shown to have the structure (**13a**) (81%). The regio- and diastereo-selectivity of this cycloaddition were determined by ^{1}H n.m.r. spectroscopy in association with double irradiation studies. The assignments in the ^{1}H n.m.r. spectrum of compound (**13a**) are shown in Table 1.

Irradiation of the signal (δ 3.79) established that the proton associated with this signal was coupled to the protons that are associated with the signals at δ 5.65, 4.49, and 4.19. This signal (δ 3.79) can be assigned to 5b-H and the doublet (δ 4.49) can be assigned to 5a-H. Furthermore, this doublet (δ 4.49) collapsed

Table 1. The ^{1}H n.m.r. spectrum of (5aα,5bα,8aα,8bα)-8-diphenylmethylene-5-phenyl-5a,5b,8a,8b-tetrahydro-5a*H*-4,10a-diazapentaleno[1,2,3-*cd*]phenalene (**13a**)



(13a)

Proton position	Chemical shift (δ)	Multiplicity	Coupling constant (*J*)
5a	4.49	d	$J_{5a,5b}$ 7 Hz
5b	3.79	tt	$J_{5a,5b}$ 7 Hz, $J_{5b,6}$ 2 Hz, $J_{5b,7}$ 2 Hz, $J_{5b,8a}$ 7 Hz
6	5.65	dd	$J_{6,7}$ 6 Hz, $J_{5b,6}$ 2 Hz
7	6.04	dd	$J_{5b,7}$ 2 Hz, $J_{6,7}$ 6 Hz
8a	4.19	t	$J_{5b,8a}$ 7 Hz, $J_{8a,8b}$ 7 Hz
8b	4.05	ddd	$J_{8a,8b}$ 7 Hz, $J_{8b,9}$ 5 Hz, $J_{8b,10}$ 1 Hz
9	4.90	dd	$J_{8b,9}$ 5 Hz, $J_{9,10}$ 9 Hz
10	6.37	dd	$J_{9,10}$ 9 Hz, $J_{8b,10}$ 1 Hz
ArH	6.6—7.6, 16H	m	—
	8.09, 2H	m	—

to a singlet when 5b-H (δ 3.79) was irradiated. This established the regioselectivity of the cycloaddition with 6,6-diphenylfulvene because in the regioisomeric structure [*cf.* (**13a**)] the signal (δ 3.79) would have to be assigned to 8a-H and its irradiation would not have caused the observed collapse of the doublet (δ 4.49) to a singlet.

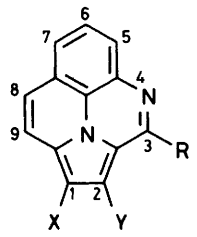
The *endo*-stereochemistry of the cycloadduct (**13a**) cannot be firmly assigned but the *endo*-structure was favoured on the basis of the coupling constants $J_{5a,5b}$ [7 Hz (calc. 7 Hz)], $J_{8a,8b}$ [7 Hz (calc. 8 Hz)], $J_{5b,8a}$ [7 Hz (calc. 10 Hz)], and $J_{5b,6}$ [2 Hz (calc. 2.5 Hz)]. The corresponding calculated values (7, 5, 10, and 4 Hz) for the *exo*-diastereoisomer are in less satisfactory agreement with the observed values. The mass spectrum of compound (**13a**) did not show a molecular ion, but displayed a base peak at *m/z* 470 ($M^{+\bullet}$ − 4H) corresponding to the aromatization of the cycloadduct (**13a**).

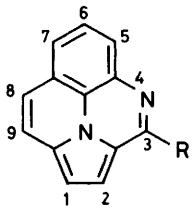
When the conjugated heterocyclic mesomeric betaine (**9a**) was treated with dibenzoylacetylene in boiling acetonitrile solution in the presence of sulphur, the tetradehydro derivative, 1,2-dibenzoyl-3-phenyl-4,9b-diazacyclopenta[*cd*]phenalene, with the fully conjugated structure (**14a**) (10%) was obtained directly. The ^{1}H n.m.r. spectrum of this product (**14a**) showed only aromatic protons and the mass spectrum displayed a molecular ion (*m/z* 476).

Addition of ethyl acrylate to the conjugated heterocyclic mesomeric betaine (**9a**) occurred at room temperature in acetonitrile solution giving a mixture of the diastereoisomers (**15a**) and (**16a**) in the ratio 2:7. These two (C-1)-epimers (**15a**) and (**16a**) were separated by preparative thick layer chromatography giving the cycloadduct (**15a**) (11%), m.p. 88—90 °C, and the cycloadduct (**16a**) (37%), m.p. 185—186 °C. The regioselectivity of the transformation (**9a**) ⟶ (**15a**) + (**16a**) was apparent from the ^{1}H n.m.r. spectra of the products. In the cycloadduct (**15a**), 2a-H was observed as a double doublet (δ 4.55; *J* 8 and 10 Hz). In the alternative regioisomer, whose formation was not observed, 2a-H would be expected to be associated with a doublet. Similarly, in the cycloadduct (**16a**) 2a-H was observed as a double doublet (δ 4.43; *J* 6 and 11 Hz).

The assignment of the *endo*-(**15a**)- and *exo*-(**16a**)-stereochemistries was based upon the interpretation of the chemical shifts of the ethoxycarbonyl protons. In the cycloadduct, m.p. 88—90 °C, the diastereotopic methylene protons of the ethyl ester are observed as a multiplet (δ 4.22) and the methyl protons as a triplet (δ 1.29, *J* 8 Hz). The isomer, m.p. 185—186 °C, shows signals for the methylene protons (δ 3.85) and the methyl protons (δ 0.92). The protons of the ethyl substituent can be expected to appear at higher field in the *endo*-(**16a**) diastereoisomer due to the positive shielding provided by the appositely placed benzene ring. Thus, the cycloadduct, m.p. 185—186 °C, is assigned the *endo* configuration (**16a**) and the cycloadduct, m.p. 88—89 °C, is assigned the *exo* configuration (**15a**). Neither of the cycloadducts (**15a**) and (**16a**) showed a molecular ion in their mass spectrum (*m/z* 344), but both isomers exhibited a base peak at *m/z* 340 ($M^{+\bullet}$ − 4H), corresponding to aromatization.

When the cycloadduct (**16a**) was heated in acetonitrile solution in the presence of triethylamine, dehydrogenation occurred giving the diazacyclopenta[*cd*]phenalene (**17a**) (80%). In boiling acetonitrile solution, the conjugated heterocyclic mesomeric betaine (**9a**) reacted with ethyl acrylate in the presence of sulphur giving a mixture of two isomeric diazacyclopenta[*cd*]phenalenes (**17a**) and (**18a**) in the ratio 5:1





(**17**) X = CO_2Et, Y = H

(**18**) X = H, Y = CO_2Et

(**19**) X = CO_2H, Y = H

(**20**) X = H, Y = CO_2H

(**21**)

In formulae (**17**)—(**21**): **a**, R = Ph, **b**, R = Me; **c**, R = H

(51%). This mixture was separated by high pressure liquid chromatography. The compound (**17a**) was identical with the dehydrogenation product obtained from the cycloadduct (**16a**). It appears that at higher temperatures the reaction of the conjugated heterocyclic mesomeric betaine (**9a**) with ethyl acrylate is not regioselective, so two cycloadducts are formed and these two regioisomers are then transformed into their tetradehydro derivatives (**17a**) and (**18a**). Further evidence for the regioselectivity of 1,3-dipolar cycloaddition between the conjugated heterocyclic mesomeric betaine (**9a**) and ethyl acrylate was demonstrated when the reaction was initially carried out at room temperature and the reaction mixture then heated under reflux to effect dehydrogenation of the primary cycloadduct. Under these conditions, only one dehydrogenated cycloadduct (**17a**) could be detected as a product. Enhanced regioselectivity at the lower temperature is due to a more efficient kinetic distinction between the formation of regioisomers at the lower temperature.

Regioselectivity was also observed when ethyl propiolate was used as a 1,3-dipolarophile. Reaction of conjugated heterocyclic mesomeric betaine (**9a**) with ethyl propiolate at room temperature gave only the dehydrogenated cycloadduct (**17a**) (49%). Presumably, under these conditions, the initially formed cycloadduct undergoes a facile dehydrogenation giving the conjugated product (**17a**).

2-*Methyl*-1H-1,3aλ^5-*diazaphenalen*-3a-*ium*-3-*ide* (**9b**).—Similarly, the conjugated heterocyclic mesomeric betaine (**9b**) was generated by treatment of the salt (**10b**; X = ClO_4) with triethylamine in the presence of the appropriate 1,3-dipolarophile. Reaction with *N*-phenylmaleimide in acetonitrile at room temperature afforded the cycloadduct (**11b**) (72%). The *endo*-stereochemistry of this cycloadduct (**11b**) was established by ^{1}H n.m.r. spectroscopy in the manner described for the cycloadduct (**11a**). In particular, the observed coupling constants $J_{5a,5b}$ 8 Hz and $J_{8a,8b}$ 8 Hz are consistent with the *endo*-stereochemistry (**11b**).

The conjugated heterocyclic mesomeric betaine (**9b**) and dibenzoylacetylene in the presence of sulphur in boiling acetonitrile gave 1,2-dibenzoyl-3-methyl-4,9b-diazacyclopenta-[*cd*]phenalene (**14b**) (20%). This product (**14b**), which was formed by dehydrogenation of the primary cycloadduct, showed in its ^{1}H n.m.r. spectrum 13 aromatic protons (δ 7.92—7.20) and a 3 H singlet (δ 2.62) assignable to the 3-methyl group. The mass spectrum showed a molecular ion (*m/z* 414).

When the conjugated heterocyclic mesomeric betaine (**9b**) was treated with ethyl acrylate at room temperature, only the dehydrogenated cycloadduct (**17b**) was isolated in very low yield (1%). However, examination of the ^{1}H n.m.r. spectrum of the total crude reaction product clearly indicated the presence of the primary adduct (**16b**) (Table 2). These observations suggest a regiospecific 1,3-dipolar cycloaddition of ethyl acrylate to the conjugated heterocyclic mesomeric betaine (**9b**) in a manner analogous to that observed for the conjugated heterocyclic mesomeric betaine (**9a**). The chemical shifts of the ethyl protons in the cycloadduct (**16b**) (OCH_2CH_3, δ 3.85) and (OCH_2CH_3, δ 0.97) are remarkably similar to the corresponding protons (OCH_2CH_3, δ 3.85) and (OCH_2CH_3, δ 0.92) in the cycloadduct (**16a**). On this basis, the *endo*-stereochemistry of cycloadduct (**16b**) was assigned. Further evidence for the regiospecificity of the 1,3-dipolar cycloaddition followed by dehydrogenation (**9b**) ⟶ (**17b**) was provided by the observation that when the conjugated heterocyclic mesomeric betaine (**9b**) was treated with ethyl acrylate at room temperature and the mixture subsequently heated under reflux, then only compound (**17b**) (48%) was isolated. Similarly, reaction of the conjugated heterocyclic mesomeric betaine (**9b**) with ethyl acrylate and sulphur in boiling acetonitrile solution gave only compound (**17b**) (57%). This last result is in contrast with the behaviour of the conjugated heterocyclic mesomeric betaine (**9a**) which gave a mixture of the isomers (**17a**) and (**18a**) (5:1) under these conditions.

When the conjugated heterocyclic mesomeric betaine (**9b**) was treated with ethyl propiolate in methanol solution, compound (**17b**) (20%) was the only product isolated.

1H-1,3aλ^5-*Diazaphenalen*-3a-*ium*-3-*ide* (**9c**).—The conjugated heterocyclic mesomeric betaine (**9c**) was generated from the salt (**10c**) by treatment with triethylamine. Reaction with *N*-phenylmaleimide afforded the *endo*-cycloadduct (**11c**) (17%) whose structure was determined by comparison of its spectroscopic properties with those of the compounds (**11a**) and (**11b**). With dibenzoylacetylene and sulphur in boiling acetonitrile solution, 1,2-dibenzoyl-4,9b-diazacyclopenta[*cd*]phenalene (**14c**) (12%) was isolated. In addition to 15 aromatic protons (δ 8.00—7.10) observed in the ^{1}H n.m.r. spectrum of compound (**14c**), a 1 H singlet (δ 9.20) was assigned to 3-H.

Cycloaddition of ethyl acrylate to the conjugated heterocyclic mesomeric betaine (**9c**) at room temperature was regiospecific giving ethyl-4,9b-diazacyclopenta[*cd*]phenalene-1-carboxylate (**17c**) (35%) as the only isolated product: examination of the crude reaction mixture by ^{1}H n.m.r. spectroscopy clearly demonstrated the presence of the primary cycloadduct (**16c**) (Table 2). The ^{1}H n.m.r. spectrum of the tetradehydro derivative

(**17c**) showed two 1 H singlets (δ 8.86 and 7.58) and signals due to five additional aromatic protons (δ 7.60—8.04). Reaction of the conjugated heterocyclic mesomeric betaine (**9c**) with ethyl acrylate and sulphur in boiling acetonitrile gave a mixture (33%) of the isomers (**17c**) and (**18c**) in the ratio 10:1. This mixture was separated by high pressure liquid chromatography giving the compound (**17c**), m.p. 130—132 °C, and its regioisomer (**18c**), m.p. 126—129 °C. Compound (**17c**) was also formed (12%) by the reaction of the conjugated heterocyclic mesomeric betaine (**9c**) with ethyl propiolate at room temperature.

During our investigation,[34] two preliminary reports[31] of the generation of the 1*H*-1,3aλ^5-diazaphenalen-3a-ium-3-ides (**9a**) and (**9b**) and their trapping as cycloadducts were published. These preparations of various cycloadducts used different dipolarophiles from those described here and their results are complementary to ours. We wish to replace the incorrect structures proposed[31] for the salts (**10a**) and (**10b**).

Photolysis of 1-quinolin-8-yltriazoles has been recently reported as an interesting novel route to two derivatives of the heterocyclic mesomeric betaine (**9**).[35]

Preparation of the 4,9b-*Diazacyclopenta*[cd]*phenalenes* (**21a—c**).—Hydrolysis of the ethyl esters (**17**) and (**18**) and decarboxylation of the resulting carboxylic acids (**19**) and (**20**) have completed an interesting synthesis of the novel cyclazines (**21a—c**). Thus, alkaline hydrolysis of a mixture of the esters (**17a**) and (**18a**) and thermal decarboxylation of the resulting mixture of acids (**19a**) and (**20a**) afforded 3-phenyl-4,9b-diazacyclopenta[*cd*]phenalene (**21a**) (39%) as an orange solid, m.p. 139—142 °C. The ^{1}H n.m.r. spectrum of compound (**21a**) showed two doublets (δ 7.47, *J* 5 Hz) and (δ 7.16, *J* 5 Hz) which were attributed to 1-H and 2-H. The mass spectrum of compound (**21a**) showed a molecular ion (*m/z* 268).

In a similar manner, compounds (**21b**) and (**21c**) were synthesized from the corresponding esters and their structures were fully supported by their ^{1}H n.m.r. spectra and mass spectra.

Regioselectivity of Cycloadditions.—We have examined the observed regioselectivity (**9c**) ⟶ (**16c**) of the cycloaddition of the conjugated heterocyclic mesomeric betaine (**9c**) with ethyl acrylate using the FMO method.[36,37] The regioselectivity of cycloadditions of conjugated heterocyclic mesomeric betaines isoconjugate with odd alternant hydrocarbon anions and electron deficient olefinic dipolarophiles is controlled by the HOMO (mesomeric betaine) – LUMO (dipolarophile) interaction.[38] Accordingly, we have calculated the FMO energies and the coefficients at positions 3 and 4 of the conjugated heterocyclic mesomeric betaine (**9c**) using the CNDO/2 method[39] (Table 4). The geometry chosen for the conjugated heterocyclic mesomeric betaine (**9c**) in this calculation was a regular tricycle with all C–C and C–N and C–N bond lengths 1.40 Å, and all C–H bond lengths 1.09 Å. The FMO energies and coefficients for acrylates have already been reported.[40] The kinetically preferred transition state can be identified by the interaction at sites associated with the largest coefficients of the HOMO (mesomeric betaine) and the largest coefficients of the LUMO (dipolarophile). This demonstrates that the

Table 2. ^{1}H N.m.r. spectral data for cycloadducts (**11**)

	(**11a**)	(**11b**)	(**11c**)
ArH	8.02, 2 H, m	7.22, 3 H, m	7.23, 3 H, m
	7.1—7.6, 7 H, m	7.14, 1 H, d[g]	7.18, 1 H, dd[l]
	6.2—6.9, 3 H, m	6.8—6.5, 3 H, m	6.80, 1 H, dd[m]
	6.40, 2 H, m	6.41, 2 H, m	6.70, 1 H, d[j]
10-H	*a*	*a*	6.55, d[n]
9-H	6.09, dd[b,c]	6.01, dd[c,h]	6.00, dd[c,n]
8b-H	4.52, dd[c,d]	4.36, dd[c,i]	4.33, dd[c,i]
8a-H	3.55, dd[d,e]	3.60, t[j]	3.39, t[i,o]
5b-H	3.79, t[e,f]	3.40, t[j]	3.55, t[o,k]
5a-H	4.92, d[f]	4.12, d[k]	4.20, dd[k,p]
5-H	—	—	8.04, d[p]
5-Me	—	2.40, s	—

[a] 10-H Is located with the aromatic signals. [b] $J_{10,9}$ 11 Hz. [c] $J_{9,8b}$ 5 Hz. [d] $J_{8b,8a}$ 7 Hz. [e] $J_{8a,5b}$ 9 Hz. [f] $J_{5b,5a}$ 9 Hz. [g] *J* 10 Hz. [h] $J_{10,9}$ 8 Hz. [i] $J_{8b,8a}$ 8 Hz. [j] *J* 8 Hz. [k] $J_{5b,5a}$ 8 Hz. [l] *J* 8 and 2 Hz. [m] *J* 7 and 2 Hz. [n] $J_{10,9}$ 10 Hz. [o] $J_{8a,5b}$ 8 Hz. [p] $J_{5a,5}$ 4 Hz.

Table 4. Calculated FMO energies and coefficients

	(**9c**)		$H_2C{=}CHCO_2R$[40]	
	HOMO	LUMO	HOMO	LUMO
E/eV	−8.681	0.354	−14.069 4	2.728 9
C-1′	—	—	0.296 2	0.429 3
C-2′	—	—	0.379 7	0.619 1
C-3	−0.590	0.325	—	—
C-4	0.386	0.321	—	—

Table 3. ^{1}H N.m.r. spectral data for the cycloadducts (**15**) and (**16**)

	(**15a**)	(**16a**)	(**16b**)	(**16c**)
ArH	8.04, 2 H, m	8.03, 2 H, m		
	7.45, 3 H, m	7.4—7.7, 3 H, m	7.01, 1 H, d[c]	7.01, 1 H, dd[l]
	7.27, 1 H, d[a]	7.28, 1 H, d[c]	6.68, 1 H, d[c]	6.35—6.85, 3 H, m
	6.83, 1 H, dd[b]	6.5—6.8, 3 H, m	6.55, 1 H, d[c]	
	6.71, 1 H, t[c]			
1-H	2.79, m	3.03, m	2.97, m	2.96, m
2-H	2.50, m	2.37, m	2.03, m	2.20, m[m]
	1.93, m	2.20, m	2.26, m	
2a-H	4.55, dd[d]	4.43, dd[h]	3.85, m	3.91, m
3-H	—	—	—	7.77, d[n]
3-Me	—	—	2.16, s	—
8-H	6.51, d[e]	*i*	6.45, d[e]	*i*
9-H	6.00, dd[e,f]	5.83, dd[f,j]	5.75, dd[e,f]	5.76, dd[e,f]
9a-H	4.07, dd[f,g]	4.28, dd[f,k]	4.22, dd[f,g]	4.21, m
OCH_2CH_3	4.22, m	3.85, m	3.85, m	3.91, m
OCH_2CH_3	1.29, t[c]	0.92, t[c]	0.97, t[c]	0.96, t[c]

[a] *J* 9 Hz. [b] *J* 8 and 2 Hz. [c] *J* 8 Hz. [d] *J* 10 and 8 Hz. [e] $J_{9,8}$ 10 Hz. [f] $J_{9a,9}$ 5 Hz. [g] $J_{9a,1}$ 8 Hz. [h] *J* 11 and 6 Hz. [i] 8-H Is located with the aromatic signals. [j] $J_{9,8}$ 11 Hz. [k] $J_{9a,1}$ 9 Hz. [l] *J* 8 and 1.5 Hz. [m] One 2-H proton was located beneath the signal associated with Et_3N. [n] $J_{3,2a}$ 3 Hz.

transition state for the cycloaddition between the conjugated heterocyclic mesomeric betaine (**9c**) and ethyl acrylate giving the cycloadduct (**16c**) is preferred. This conclusion is consistent with the experimentally observed regioselectivity (**9c**) ⟶ (**16c**).

Experimental

M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. Evaporation refers to evaporation under diminished pressure. Light petroleum refers to the fraction, b.p. 40—60 °C, unless otherwise stated.

Merck Kieselgel-CG_{254} (type 60) coated on glass plates was used for analytical (thin layer) and preparative (thick layer) chromatography. During fractionation by thick layer chromatography, appropriate fractions were combined on the basis of their t.l.c. behaviour.

Low resolution mass spectra were determined with an A.E.I. MS-12 or a Kratos MS-25 mass spectrometer. High resolution mass spectra were determined with an A.E.I. MS-9 or a Kratos MS-80 mass spectrometer.

U.v. and visible spectra were measured for solutions in ethanol (spectroscopic grade) with a Perkin-Elmer 402 u.v.-visible spectrophotometer.

Unless otherwise stated, i.r. spectra were measured for solutions in chloroform with a Perkin-Elmer 157G grating i.r. spectrophotometer.

Unless otherwise stated, ^{1}H n.m.r. spectra were recorded either with a Perkin-Elmer R-34 (220 MHz) or with a Bruker WH-400 (400 MHz) spectrometer in deuteriochloroform solution, with tetramethylsilane as internal standard.

^{13}C N.m.r. spectra (25 MHz) were recorded using a Jeol PFT-100 spectrometer with an EC-100 computer. Chemical shifts were initially determined from proton decoupled spectra and multiplicities due to C–H coupling were determined from off-centre resonance decoupled spectra.

When substances are stated to be identical, their identity has been established by comparison of, where appropriate, m.p. and mixed m.p., i.r. spectra, ^{1}H n.m.r. spectra, and t.l.c. behaviour.

*2-Phenyl-*1H*-1,3a*λ^5*-diazaphenalen-*3a*-ium Bromide* (**10a**; X = Br) *and Perchlorate* (**10a**; X = ClO_4).—A solution of 8-aminoquinoline[41] (2.8 g) and phenacyl bromide (4.0 g) in acetone (30 ml) was heated under reflux (16 h). After cooling, the solvent was decanted from the residue. The residual syrup was washed with boiling chloroform (2 × 20 ml) to give a red solid. Recrystallization from ethanol gave *2-phenyl-*1H*-1,3a*λ^5*-diazaphenalen-*3a*-ium bromide* (**10a**; X = Br) (1.5 g, 24%) as maroon needles, m.p. 287 °C (decomp.) (with softening at 280 °C) (lit.,[31] 276—279 °C), $\nu_{max.}$(KBr) 3 400, 1 640, 1 615, 1 580, 1 480, 820, and 770 cm^{-1}; δ(CD_3OD) 8.16 (1 H, d, *J* 6 Hz), 7.98 (1 H, d, *J* 8 Hz), 7.70 (2 H, m), 7.6—7.2 (5 H, m), 7.18 (1 H, d, *J* 8 Hz), 7.08 (1 H, s, 3-H), and 6.97 (1 H, d, *J* 8 Hz).

Compound (**10a**; X = Br) (40 mg) was dissolved in warm acetic acid (2 ml) and perchloric acid (60%; 20 drops) was added to the cooled solution. The mixture was diluted with ether (20 ml) and after 1.5 h at room temperature the red precipitate was collected and washed with ether. Recrystallization from methanol gave *2-phenyl-*1H*-1,3a*λ^5*-diazaphenalen-*3a*-ium perchlorate* (**10a**; X = ClO_4) (34 mg, 80%) as maroon needles, m.p. 277—279 °C (Found: C, 59.1; H, 4.0; Cl, 10.2; N, 8.2. $C_{17}H_{13}ClN_2O_4$ requires C, 59.2; H, 3.8; Cl, 10.3; N, 8.1%); $\lambda_{max.}$ 381, 397, and 512 nm (ε 2 990, 2 830, and 4 780).

*2-Methyl-*1H*-1,3a*λ^5*-diazaphenalen-*3a*-ium Perchlorate* (**10b**; X = ClO_4).—A solution of 8-aminoquinoline[41] (3.0 g) and chloroacetone (1.8 ml) in acetone (30 ml) was heated under reflux (18 h) and cooled. The precipitate was collected and washed with hot chloroform (20 ml). The residue (0.74 g) was dissolved in warm acetic acid (5 ml), perchloric acid (60%, 3 ml) was added to the cooled solution, and the mixture diluted with ether (40 ml) to yield a solid (0.9 g, 15%). This was dissolved in hot acetonitrile, and the solution filtered and diluted with ether to precipitate *2-methyl-*1H*-1,3a*λ^5*-diazaphenalen-*3a*-ium perchlorate* (**10b**; X = ClO_4) as an amorphous solid, m.p. >300 °C (Found: C, 51.2; H, 3.9; Cl, 12.7; N, 10.2. $C_{12}H_{11}ClN_2O_4$ requires C, 51.0; H, 3.9; Cl, 12.5; N, 10.0%); $\lambda_{max.}$ 377, 395, and 495 nm (ε 1 880, 2 090, and 3 230); $\nu_{max.}$(KBr) 3 000, 1 650, 1 610, 1 420, 1 140, 1 110, 1 080, and 820 cm^{-1}; δ[$(CD_3)_2SO$], 10.53 (1 H, br s, 1-H), 8.05 (1 H, d, *J* 6 Hz), 7.96 (1 H, d, *J* 8 Hz), 7.3—7.4 (2 H, m), 7.11 (1 H, d, *J* 8 Hz), 6.69 (2 H, m), and 1.90 (3 H, s, C-CH_3); *m/z* 182 ($M^{+\bullet}$ − $HClO_4$).

1H*-1,3a*λ^5*-Diazaphenalen-*3a*-ium Perchlorate* (**10c**; X = ClO_4).—A solution of 8-aminoquinoline[41] (1.0 g) and chloroacetaldehyde (50% in water) (2.0 ml) in methanol (10 ml) was heated under reflux (18 h). The cooled solution was filtered and evaporated to give a maroon residue (2.0 g) which was dissolved in warm acetic acid (12 ml) and filtered. Perchloric acid (60%; 5 ml) was added to the cooled solution, followed by ether (70 ml). The precipitate was collected and washed with ether (taking care that air was not sucked through the solid) to yield 1,3aλ^5*-diazaphenalen-*3a*-ium perchlorate* (**10c**; X = ClO_4) (1.60 g, 86%) as an amorphous solid, m.p. >300 °C (with softening and darkening at *ca.* 200 °C) [Found: *m/z* 168.0681. $C_{11}H_8N_2^+$ (M − $HClO_4$) requires *m/z* 168.0688]; $\lambda_{max.}$ 378, 395, and 504 nm (ε 1 780, 1 780, and 2 050); $\nu_{max.}$(KBr) 3 430, 1 660, 1 615, 1 365, 1 140, 1 115, and 1 090 cm^{-1}; δ[$(CD_3)_2SO$] 10.45 (1 H, br d, *J* 6 Hz, 1-H), 8.11 (1 H, d, *J* 5 Hz), 8.00 (1 H, d, *J* 8 Hz), 7.32 (2 H, m), 7.09 (1 H, d, *J* 8 Hz), 6.92 (1 H, t, *J* 6 Hz), 6.74 (1 H, d, *J* 6 Hz), and 6.70 (1 H, d, *J* 8 Hz).

1,3-*Dipolar Cycloadditions of* 2-*Phenyl-*1H*-1,3a*λ^5*-diazaphenalen-*3a*-ium-*3*-ide* (**9a**): *Formation of Cycloadducts* (**11a**), (**13a**), (**15a**), *and* (**16a**) *and Tetradehydro Derivatives* (**14a**), (**17a**), *and* (**18a**).

General Method.—To a solution of the dipolarophile and triethylamine in acetonitrile (5—10 ml) either at room temperature or at the boiling point (80 °C) was added the salt (**10a**; X = Br) in portions with stirring. In some cases sulphur was added to promote dehydrogenation. The solvent was evaporated and the product was isolated by preparative thick layer chromatography on silica gel.

(a) *With* N*-phenylmaleimide.* The salt (**10a**; X = Br) (140 mg), triethylamine (0.1 ml), and *N*-phenylmaleimide (120 mg) at room temperature gave (5aα,5bα,8aα,8bα)-5,7-*diphenyl-*5a,5b,8a,8b-*tetrahydro-*7H-4,7,10a-*triazapentaleno*[1,2,3-cd]-*phenalene-*6,8-*dione* (**11a**) (136 mg, 76%) (eluant; ether–light petroleum, 2:1) as yellow needles, m.p. 212—215 °C (from ethanol) [Found: C, 77.4; H, 4.6; N, 10.0; *m/z* 413 (*M* − 4H). $C_{27}H_{19}N_3O_2$ requires C, 77.7; H, 4.6; N, 10.1%; *M*, 417]; $\nu_{max.}$(KBr) 1 710, 1 380, and 1 170 cm^{-1}; δ (Table 2).

(b) *With* 6,6*-diphenylfulvene.* The salt (**10a**; X = Br) (171 mg) triethylamine (0.5 ml), and 6,6-diphenylfulvene (185 mg) at 80 °C (45 min) gave (5aα,5bα,8aα,8bα)-5-*phenyl-*8-*diphenylmethylene-*5a,5b,8a,8b-*tetrahydro-*5aH-4,10a-*diazapentaleno*[1,2,3-cd]*phenalene* (**13a**) (201 mg, 81%) (eluant; ether–light petroleum, 1:2) as pale yellow needles, m.p. 167—171 °C (from ethanol) [Found: *m/z* 470.1786. $C_{35}H_{22}N_2$ (M − 4H) requires *m/z* 470.1783]; $\nu_{max.}$ 1 600, 1 480, 1 460, 1 445, 1 360, and 1 300 cm^{-1}; δ (Table 1).

(c) *With dibenzoylacetylene.* The salt (**10a**; X = Br) (143 mg), triethylamine (0.2 ml), dibenzoylacetylene (108 mg), and sulphur (34 mg) at 80 °C (30 min) gave 1,2-*dibenzoyl-*3-*phenyl-*

4,9b-*diazacyclopenta*[cd]*phenalene* (**14a**) (21 mg, 10%) (eluant; ether–light petroleum, 1:1) as yellow needles, m.p. 220—222 °C (from ethanol) (Found: $M^{+\bullet}$, 476.1521. $C_{33}H_{20}N_2O_2$ requires *M*, 476.1525); $\nu_{max.}$ 1 670, 1 600, 1 405, and 1 350 cm^{-1}; δ 8.03 (1 H, dd, *J* 8 and 2 Hz) and 7.1—7.8 (19 H, m).

(d) *With ethyl acrylate.* (i) The salt (**10a**; X = Br) (200 mg), triethylamine (0.3 ml), and ethyl acrylate (0.3 ml) at room temperature (5 min) gave a mixture (ratio 2:7 by ^1H n.m.r. spectroscopy) of *ethyl* (1α,2aα,9aα)-3-*phenyl*-1,2,3a,9a-*tetrahydro*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**15a**) and *ethyl* (1α,2aβ,9aβ)-3-*phenyl*-1,2,3a,9a-*tetrahydro*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**16a**). Fractionation of this mixture (eluant; ether–light petroleum, 1:1) gave compound (**15a**) (23 mg, 11%) as yellow rhombs, m.p. 88—90 °C (from butyl alcohol) [Found: *m/z* 340.1212. $C_{22}H_{16}N_2O_2$ (*M* − 4H) requires *m/z* 340.1212]; $\nu_{max.}$ 1 730 cm^{-1}; δ (Table 3); and compound (**16a**) (78 mg, 37%) as yellow needles, m.p. 185—186 °C (from ethanol) [Found: C, 76.6; H, 5.8; N, 8.0%; *m/z* 340 (*M* − 4H) $C_{22}H_{20}N_2O_2$ requires C, 76.7; H, 5.9; N, 8.1%; *M*, 344]; $\nu_{max.}$(KBr) 2 920, 1 710, 1 415, 1 230, and 1 210 cm^{-1}; δ (Table 3).

(ii) The salt (**10a**; X = Br) (0.10 g), triethylamine (0.10 ml), ethyl acrylate (0.10 ml), and sulphur (45 mg) at 80 °C (3 h) gave a mixture (ratio 5:1 by ^1H n.m.r. spectroscopy) of *ethyl* 3-*phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**17a**) and *ethyl* 3-*phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene*-2-*carboxylate* (**18a**) [combined yield (53 mg, 51%)] (eluant; ether–light petroleum, 1:1). This mixture was fractionated by high pressure liquid chromatography [Spherisorb 14μ column; ethyl acetate–light petroleum (b.p. 60—80 °C), 18:82] to give compound (**17a**) as yellow needles, m.p. 183—185 °C (from acetonitrile) (Found: C, 77.4; H, 4.7; N, 7.9%; $M^{+\bullet}$, 340. $C_{22}H_{16}N_2O_2$ requires C, 77.6; H, 4.8; N, 8.2%; *M*, 340); $\nu_{max.}$ 1 690 cm^{-1}; δ 8.00—8.13 (4 H, m), 7.91 (1 H, dd, *J* 2 and 8 Hz), 7.70 (1 H, s, 2-H), 7.50—7.65 (5 H, m), 4.44 (2 H, q, *J* 8 Hz, OCH_2CH_3), and 1.45 (3 H, t, *J* 8 Hz, OCH_2CH_3); and compound (**18a**) as yellow needles, m.p. 175—176 °C (from ethanol) (Found: $M^{+\bullet}$, 340.1215. $C_{22}H_{16}N_2O_2$ requires *M*, 340.1212); $\nu_{max.}$ 1 710 cm^{-1}; δ 7.95 (1 H, dd, *J* 1 and 8 Hz), 7.78 (2 H, m), 7.65 (1 H, t, *J* 8 Hz), 7.59 (1 H, dd, *J* 8 and 11 Hz), 7.53 (3 H, m), 7.48 (2 H, d, *J* 3 Hz), 7.37 (1 H, s, 1-H), 3.83 (2 H, q, *J* 8 Hz, OCH_2CH_3), and 0.88 (3 H, t, *J* 8 Hz, OCH_2CH_3).

(iii) The salt (**10a**; X = Br) (0.10 g), triethylamine (0.15 ml), and ethyl acrylate (0.15 ml) at room temperature, followed by boiling at 80 °C (1 h) afforded only compound (**17a**) (by ^1H n.m.r. spectroscopy): the isomer (**18a**) could not be detected.

(e) *With ethyl propiolate.* Triethylamine (0.10 ml) was added dropwise to a solution of the salt (**10a**; X = Br) (0.10 g) and ethyl propiolate (0.15 ml) in methanol (5 ml) at room temperature. After 5 min the solvent was removed and the residue was fractionated by preparative thick layer chromatography (eluant; ether–light petroleum, 1:1) to give compound (**17a**) (51 mg, 49%), identical with an authentic sample.

1,3-*Dipolar Cycloadditions of* 2-*Methyl*-1H,1,3aλ^5-*diazaphenalen*-3a-*ylium*-3-*ide* (**9b**): *Formation of Cycloadducts* (**11b**) *and* (**16b**) *and the Tetradehydro Derivatives* (**14b**) *and* (**17b**)

General Method.—The general method described for the cycloadditions of the heterocyclic mesomeric betaine (**9a**) was used.

(a) *With* N-*phenylmaleimide.* The salt (**10b**; X = ClO_4) (23 mg), triethylamine (0.05 ml), and *N*-phenylmaleimide (40 mg) at room temperature gave (5aα,5bα,8aα,8bα)-5-*methyl*-7-*phenyl*-5a,5b,8a,8b-*tetrahydro*-7H-4,7,10c-*triazapentaleno*[1,2,3-cd]-*phenalene*-6,8-*dione* (**11b**) (21 mg, 72%) (eluant; ether–ethyl acetate, 2:1) as cream needles, m.p. 165—168 °C (from ethanol) [Found: *m/z* 351.1002. $C_{22}H_{13}N_3O_2$ (*M* − 4H) requires *m/z* 351.1008]; $\nu_{max.}$ 1 715 and 1 380 cm^{-1}; δ (Table 2).

(b) *With dibenzoylacetylene.* The salt (**10b**; X = ClO_4) (0.10 g), triethylamine (0.10 ml), dibenzoylacetylene (0.09 g), and sulphur (0.05 g) at 80 °C (1 h) gave 1,2-*dibenzoyl*-3-*methyl*-4,9b-*diazacyclopenta*[cd]*phenalene* (**14b**) (30 mg, 20%) (eluant; ether–light petroleum, 1:1) as yellow needles, m.p. 206—207 °C (from ethanol) (Found: $M^{+\bullet}$, 414.1354. $C_{28}H_{18}N_2O_2$ requires *M*, 414.1368); $\nu_{max.}$ 1 650 cm^{-1}; δ 7.92 (1 H, dd, *J* 2 and 8 Hz), 7.65—7.76 (3 H, m), 7.40—7.55 (6 H, m), 7.20—7.35 (5 H, m), and 2.62 (3 H, s, 3-CH_3).

(c) *With ethyl acrylate.* (i) The salt (**10b**; X = ClO_4) (0.20 g), triethylamine (0.10 ml), and ethyl acrylate (0.10 ml) gave the cycloadduct (**16b**); δ (Table 3). Attempted isolation of compound (**16b**) failed (eluant; ether) and only compound (**17b**) (15 mg, 1%), identical with an authentic sample prepared below, was isolated.

(ii) The salt (**10b**; X = ClO_4) (0.10 g), triethylamine (0.10 ml), ethyl acrylate (0.10 ml), and sulphur (0.03 g) at 80 °C (1 h) gave *ethyl* 3-*methyl*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**17b**) (56 mg, 57%) (eluant; ether) as yellow needles, m.p. 140—143 °C (from ethyl acetate) (Found: $M^{+\bullet}$, 278.1053. $C_{17}H_{14}N_2O_2$ requires *M*, 278.1055); $\nu_{max.}$ 1 695 and 1 090 cm^{-1}; δ 7.98 (1 H, d, *J* 10 Hz), 7.78 (1 H, d, *J* 9 Hz), 7.48—7.62 (4 H, m), 4.45 (2 H, q, *J* 7 Hz, OCH_2CH_3), 2.70 (3 H, s, 3-CH_3), and 1.46 (3 H, t, *J* 7 Hz, OCH_2CH_3).

(iii) The salt (**10b**; X = ClO_4) (0.20 g), triethylamine (0.10 ml), and ethyl acrylate (0.10 ml) were mixed at room temperature. Cycloaddition occurred immediately and then sulphur (0.03 g) was added. Boiling of the mixture at 80 °C (30 min) gave only compound (**17b**) (94 mg, 48%), identical with an authentic sample.

(d) *With ethyl propiolate.* To a suspension of the salt (**10b**; X = ClO_4) (0.10 g) in methanol (5 ml) was added 1.5 ml of a solution of ethyl propiolate (0.15 ml) in methanol (5 ml). Triethylamine (0.08 ml) was then added with stirring. The mixture was stirred (45 min) at room temperature, sulphur (0.03 mg) was added, and the mixture was heated (0.5 h) under reflux, cooled, and evaporated. Fractionation of the residue (eluant; ether) gave compound (**17b**) (21 mg, 20%), identical with an authentic sample.

1,3-*Dipolar Cycloadditions of* 1H-1,3aλ^5-*Diazaphenalen*-3a-*ium*-3-*ide* (**9c**): *Formation of Cycloadducts* (**11c**) *and* (**16c**) *and Tetradehydro Derivatives* (**14c**), (**17c**), *and* (**18c**)

General Method.—The general method described for the cycloaddition reactions of heterocyclic mesomeric betaine (**9a**) was used.

(a) *With* N-*phenylmaleimide.* The salt (**10c**; X = ClO_4) (127 mg), triethylamine (0.20 ml), and *N*-phenylmaleimide (133 mg) at room temperature gave (5aα,5bα,8aα,8bα)-7-*phenyl*-5a,5b,8a,8b-*tetrahydro*-7H-4,7,10c-*triazapentaleno*[1,2,3-cd]-*phenalene*-6,8-*dione* (**11c**) (28 mg, 17% (eluant; ether–ethyl acetate, 1:2) as orange needles, m.p. >300 °C (with softening at *ca.* 200 °C) (from ethanol) [Found: *m/z* 337.0851. $C_{21}H_{11}N_3O_2$ (*M* − 4H) requires *m/z* 337.0851]; $\nu_{max.}$ 1 715, 1 460, 1 380, and 1 170 cm^{-1}; δ (Table 2).

(b) *With dibenzoylacetylene.* The salt (**10c**; X = ClO_4) (137 mg), triethylamine (0.20 ml), dibenzoylacetylene (0.11 g), and sulphur (0.04 mg) at 80 °C (1 h) gave 1,2-*dibenzoyl*-4,9b-*diazacyclopenta*[cd]*phenalene* (**14c**) (24 mg, 12%) (eluant; ether–light petroleum, 1:1) as yellow needles, m.p. 254—259 °C (from ethanol) (Found: $M^{+\bullet}$, 400.1208. $C_{27}H_{16}N_2O_2$ requires *M*, 400.1212); $\nu_{max.}$ 1 650, 1 600, 1 400, and 1 380 cm^{-1}; δ 9.20 (1 H, s, 3-H), 8.00 (1 H, dd, *J* 2 and 7 Hz), 7.88 (1 H, d, *J* 10 Hz), 7.75—7.80 (2 H, m), 7.30—7.45 (6 H, m), and 7.10—7.22 (5 H, m).

(c) *With ethyl acrylate.* (i) The salt (**10c**; X = ClO_4) (97 mg), triethylamine (0.10 ml), and ethyl acrylate (0.10 ml) gave the cycloadduct (**16c**); δ (Table 3). Attempted isolation of compound (**16c**) failed (eluant; ether–light petroleum, 1:1) and only compound (**17c**) (33 mg, 35%) was isolated.

(ii) The salt (**10c**; X = ClO_4) (152 mg), triethylamine (0.10 ml), ethyl acrylate (0.10 ml), and sulphur (0.04 g) at 80 °C (3 h) gave a mixture (ratio 10:1 by ^1H n.m.r. spectroscopy) of *ethyl* 4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**17c**) and *ethyl* 4,9b-*diazacyclopenta*[cd]*phenalene*-2-*carboxylate* (**18c**) [combined yield (50 mg, 33%)] (eluant; ether–light petroleum, 1:1). This mixture was fractionated by high pressure liquid chromatography [Spherisorb 14μ column; ethyl acetate–light petroleum (b.p. 60—80 °C), 35:65] to give compound (**17c**) as a yellow solid, m.p. 130—132 °C (Found: $M^{+\bullet}$, 264.0909. $C_{16}H_{12}N_2O_2$ requires M, 264.0899); $\nu_{max.}$ 1 710, 1 410, and 1 140 cm^{-1}; δ 8.86 (1 H, s, 2-H or 3-H), 8.04 (1 H, d, J 9 Hz), 7.85 (1 H, dd, J 2 and 8 Hz), 7.60—7.66 (3 H, m), 7.58 (1 H, s, 3-H or 2-H), 4.45 (2 H, q, J 7 Hz, OCH_2CH_3), and 1.46 (3 H, t, J 7 Hz, OCH_2CH_3); and compound (**18c**) as a yellow solid, m.p. 126—129 °C (Found: $M^{+\bullet}$, 264.0898. $C_{16}H_{12}N_2O_2$ requires M, 264.0899); $\nu_{max.}$ 1 715 and 1 150 cm^{-1}; δ 9.46 (1 H, s, 1-H or 3-H), 7.91 (1 H, dd, J 1 and 8 Hz), 7.66 (1 H, t, J 8 Hz), 7.58 (1 H, dd, J 1 and 7 Hz), 7.42 (2 H, d, J 4 Hz), 7.38 (1 H, s, 3-H or 1-H), 4.66 (2 H, q, J 7 Hz, OCH_2CH_3), and 1.45 (3 H, t, J 7 Hz, OCH_2CH_3).

(d) *With ethyl propiolate.* To a stirred suspension of the salt (**10c**; X = ClO_4) (0.10 g) in methanol (10 ml) at room temperature was added ethyl propiolate (0.15 ml) and then triethylamine (0.20 ml). The mixture was kept for 1.5 h and then filtered and evaporated. The residue was fractionated by preparative thick layer chromatography (eluant; ether–light petroleum, 1:1), and then refractionated (eluant; ether–pentane, 2:1) to give compound (**17c**) (12 mg, 12%) identical with an authentic sample.

5,7-*Diphenyl*-7H-4,7,10c-*triazapentaleno*[1,2,3-cd]*phenalene*-6,8-*dione* (**12a**).—A solution of the cycloadduct (**11a**) (43 mg) and triethylamine (0.2 ml) in acetonitrile (5 ml) was heated under reflux (6.5 days). 5,7-*Diphenyl*-7H-4,7,10c-*triazapentaleno*[1,2,3-cd]*phenalene*-6,8-*dione* (**12a**) crystallized from the cooled reaction mixture as a buff solid (15 mg; 34%), m.p. 280—282 °C (Found: $M^{+\bullet}$, 413.1164. $C_{27}H_{15}N_3O_2$ requires M, 413.1179); $\nu_{max.}$ 1 760, 1 615, 1 355, and 905 cm^{-1}; δ 8.14 (1 H, dd, J 2 and 8 Hz), 8.02 (2 H, m), 7.78—7.90 (4 H, m), 7.60 (3 H, m), and 7.36—7.50 (5 H, m).

Ethyl 3-*Phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**17a**).—A solution of the cycloadduct (**16a**) (30 mg) and triethylamine (0.05 ml) in acetonitrile (4 ml) was heated under reflux (24 h). The yellow solid which crystallized from the cooled reaction mixture was collected and recrystallized from acetonitrile to give *ethyl* 3-*phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene*-1-*carboxylate* (**17a**) (24 mg, 80%) as yellow needles, m.p. 183—185 °C, identical with an authentic sample.

3-*Phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene* (**21a**), 3-*Methyl*-4,9b-*diazacyclopenta*[cd]*phenalene* (**21b**), *and* 4,9b-*Diazacyclopenta*[cd]*phenalene* (**21c**)

General Method.—A mixture of the compounds (**17**) and (**18**) in methanolic potassium hydroxide was heated under reflux for 3 h and then cooled and evaporated. The residue was treated with 25% hydrochloric acid, cooled, and the acids (**19**) and (**20**) collected. This mixture of acids was thermally decarboxylated by heating in a Pyrex glass tube with a Bunsen burner flame. Some of the product sublimed, but the total reaction mixture was extracted with methanol, filtered, and evaporated to give the corresponding 4,9b-diazacyclopenta[*cd*]phenalene. The product was purified by filtration down a short alumina column (Hopkin and Williams, neutral) and elution with chloroform. The following compounds were obtained by this method. (*a*) 3-*Phenyl*-4,9b-*diazacyclopenta*[cd]*phenalene* (**21a**) (39%), m.p. 139—142 °C (Found: $M^{+\bullet}$, 268.0987. $C_{19}H_{12}N_2$ requires M, 268.1000); $\lambda_{max.}$ 355 and 372 nm (ε 7 890 and 8 500); $\nu_{max.}$ 1 695 and 1 410 cm^{-1}; δ (CD_3OD) 8.01 (2 H, dd, J 2 and 8 Hz), 7.54—7.74 (8 H, m), 7.47 (1 H, d, $J_{1,2}$ 5 Hz, 1-H or 2-H), and 7.16 (1 H, d, $J_{1,2}$ 5 Hz, 1-H or 2-H).

(b) 3-*Methyl*-4,9b-*diazacyclopenta*[cd]*phenalene* (**21b**) (44%), m.p. 207—210 °C (decomp.) (Found: $M^{+\bullet}$, 206.0858. $C_{14}H_{10}N_2$ requires M, 206.0839); $\lambda_{max.}$ 342, 358, 427, 452, and 478 nm (ε 9 780, 12 150, 3 400, 3 400, and 1 910); $\nu_{max.}$ 1 340 cm^{-1}; δ (CD_3OD) 7.52 (1 H, d, $J_{1,2}$ 5 Hz, 1-H or 2-H), 7.30—7.50 (5 H, m), 7.05 (1 H, d, $J_{1,2}$ 5 Hz, 1-H or 2-H), and 2.70 (3 H, s, 3-CH_3).

(c) 4,9b-*Diazacyclopenta*[cd]*phenalene* (**21c**) (50%), m.p. 169—172 °C (with sublimation before melting) (Found: $M^{+\bullet}$, 192.0697. $C_{13}H_8N_2$ requires M, 192.0688); $\lambda_{max.}$ 343, 359, 441, 467, and 496 nm (ε 6 400, 8 180, 2 560, 2 580, and 1 530); $\nu_{max.}$ 2 980, 1 585, and 1 340 cm^{-1}; δ (CD_3OD), 8.92 (1 H, s, 3-H), 7.80—7.60 (6 H, m), and 7.30 (1 H, d, $J_{1,2}$ 6 Hz, 1-H or 2-H).

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