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Syntheses of Some Novel Optical Brightener Kernels via 1,3-Dipolar Cycloaddition Reactions

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ABSTRACT

1,3-Dipolar cycloaddition reactions of 3-phenylphthalazinium-1-olate with various dipolarophiles which lead to some potential optical brightener structures are described. The cycloadducts obtained from vinyl ethers exhibited the Price effect, whereas N-vinyl carbazole adduct displayed atropisomerism.

INTRODUCTION

To impart whiteness to textile materials use is often made of colourless substances fluorescing in the blue or violet part of the spectrum. The additive combination of the blue rays of fluorescence and yellow rays reflected by the material produces the sensation of a very bright white colour.[1] These optical brighteners[2] usually contain heterocycles such as coumarins, 2-quinolones, 2-pyrazolines, naphthalimides, pyrazoles, etc.,[2–5] and fall into two classes, viz. the basic skeleton of the optical brightener contains the heterocycle, or the heterocycle is added to a fluorescent conjugated system to increase and shift its absorption bathochromically.[6]

In this present work, 1,3-dipolar cycloaddition reactions of 3-phenylphthalazinium-1-olate with various acetylenic and olefinic dipolarophiles, giving potential optical brightener systems, are described. These adducts usually either display fluorescent properties of the above type or can be modified to give more potentially useful systems.

The first examples of phthalazinium-1-olates were prepared in 1926 by

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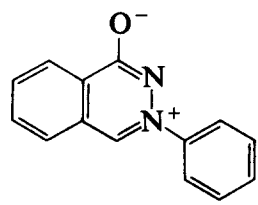
Rowe and co-workers by coupling 2-hydroxynaphthalene-1-sulphonic acid with diazotised anilines followed by treatment with acid.[7] These studies were developed to give a large number of 3-aryl derivatives,[8-11] and subsequently other alternative routes to the synthesis of 3-arylphthalazinium-1-olates were described.[12-14] Katritzky and co-workers were the first to report the 1,3-dipolar cycloadditions of 3-phenylphthalazinium-1-olate with olefinic and acetylenic dipolarophiles.[14]

RESULTS AND DISCUSSION

The synthesis of 3-phenylphthalazinium-1-olate **1** was carried out by the method described by Dennis *et al.*[14] The betaine was reacted with various acetylenic and olefinic dipolarophiles.



1

Acetylenic dipolarophiles

Dimethylacetylene in 1,2-dichloroethane when reacted with **1** gave the cycloadduct **2** in 45% yield. The structure of the product was established by ^{1}H n.m.r. (Table 1), i.r. (6-membered lactam ν(C=O) at 1715 cm^{-1}) and elemental analysis.

The phthalazinium betaine **1** and 1-butyne-3-ol under reflux gave the cycloadduct **3**. The i.r. spectrum showed an OH stretching band (centered at 3300 cm^{-1}) and a conjugated carbonyl group (ν(C=O) 1715 cm^{-1}). The ^{1}H n.m.r. spectrum exhibited two sharp singlets. These were assigned as H_4 (5·50 ppm) and H_{10} (6·40 ppm) (Table 1). From the same reaction mixture, another compound was isolated. The i.r. showed a diffuse OH band (centered at 3320 cm^{-1}) and a strong carbonyl band (at 1715 cm^{-1}). ^{1}H n.m.r. analysis was consistent with structure **4** (Table 1). Dennis *et al.* reported similar rearrangements of some cycloadducts of 3-phenylphthalazinium-1-olate[14] and proposed a 'criss-cross' cyclisation mechanism for the formation of this type of compound.[15]

Acetylene ethoxide and **1** reacted to give the cycloadduct **5** in 60% yield. The i.r. spectrum displayed a strong carbonyl band (1710 cm^{-1}, $CHCl_3$). The ^{1}H n.m.r. singlet at δ5·50 was assigned to H_4 (see Table 1).

TABLE 1

^{1}H N.M.R. Data (60 MHz) for Compounds **2–5**[a]

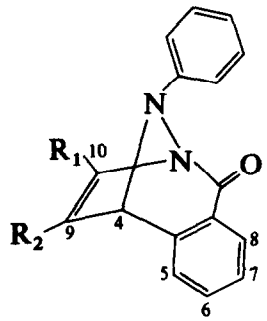
(a) Chemical shifts

Proton	**2**[c]	**3**[b]	**4**[c]	**5**[b]
4	5·60[d]	5·50[d]	—	5·50[d]
5	7·00–8·40[l]	7·00–8·30[l]	7·20–8·30[l]	7·00–8·40[l]
6	7·00–8·40[l]	7·00–8·30[l]	7·20–8·30[l]	7·00–8·40[l]
7	7·00–8·40[l]	7·00–8·30[l]	7·20–8·30[l]	7·00–8·40[l]
8	7·00–8·40[l]	7·00–8·30[l]	7·20–8·30[l]	7·00–8·40[l]
8b	—	—	6·40[d]	—
10	—	6·40[d]	—	7·00–8·40[l]
1′	—	2·40–2·90[k]	2·80[k]	4·57[j]
2′	—	0·70–1·60[f]	1·22[h]	1·47[h]
Ph	7·00–8·40[l]	7·00–8·30[l]	7·20–8·30[l]	7·00–8·40[l]
9-Me	1·50[d]	—	—	—
10-Me	2·10[d]	—	—	—
OH	—	4·20[e]	1·90–3·00[l]	—

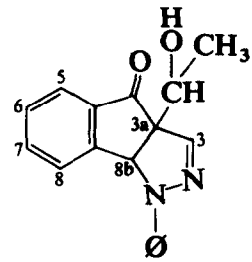
(b) Coupling constants

Proton	**2**	**3**	**3**	**4**
J(1′, 2′)	—	1·5	10·0	n
J(1′, OH)	—	3·5	—	n

[a] ppm relative to TMS as internal standard.
[b] In CCl_4.
[c] In $CDCl_3$.
[d] Singlet.
[e] Doublet.
[f] Triplet of doublets.
[g] Doublet of doublets.
[h] Triplets.
[i] Pseudo triplet.
[j] Quartet.
[k] Multiplet.
[l] Overlaps.
[m] Broad.
[n] Not measurable.
Coupling constants in Hz.



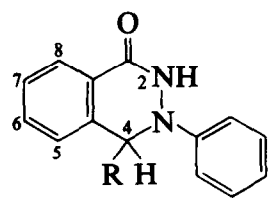
2 R_1: CH_3, R_2: CH_3
3 R_1: H, R_2: $CH(OH)CH_3$
5 R_1: H, R_2: OCH_2CH_3



4

Olefinic dipolarophiles

The phthalazinium betaine **1** failed to give any cycloadduct with allylamine. Instead, the dipolarophile underwent nucleophilic addition to the betaine to yield compound **6**. The i.r. spectrum of this showed overlapped N–H stretchings centered at 3290 cm^{-1} and a strong band at 1705 cm^{-1} (lactam C=O). The proton assignments tabulated in Table 2 were confirmed by spin decoupling experiments. To prevent the nucleophilic attack of allylamine, the amino group was protected by acetylation, but the resultant olefinic compound showed no dipolarophilic activity towards **1**.



6 R = $NHCH_2CH$: CH_2
7 R = CH_2CH: CHCN

Allyl alcohol and allyl cyanide failed to give any cycloadduct but the latter compound gave compound **7** in low yield. Presumably, the formation of **7** occurred by attack of the anion **9** which was generated in the reaction medium by basic impurities.

$$\underset{\mathbf{8}}{H_2C{=}CHCHCN} \longrightarrow \underset{\mathbf{9}}{H_2CHC{=}CHCN}$$

The phthalazinium betaine **1** and propargyl alcohol yielded an unexpected cycloadduct **10**. The structure of this was established by i.r. (v(OH) 3500 cm^{-1}, v(acetylenic C—H) 3300 cm^{-1}, v(C≡C) 2140 cm^{-1}, v(CO) 1735 cm^{-1} in $CHCl_3$), ^1H n.m.r. and elemental analysis (Tables 2 and

TABLE 2

^{1}H N.M.R. Data (60 MHz) for Compounds **6**, **7** and **10**

(a) Chemical shifts

Proton	**6**[b]	**7**[c]	**10**[c]
2	5·50[d]	1·30[d]	—
4	6·40–7·50[l]	5·10[g]	4·60–5·20[l]
5	6·40–8·60[l]	6·70–8·60[l]	6·50–8·50[l]
6	6·40–8·60[l]	6·70–8·60[l]	6·50–8·50[l]
7	6·40–8·60[l]	6·70–8·60[l]	6·50–8·50[l]
8	6·40–8·60[l]	6·70–8·60[l]	6·50–8·50[l]
9n	—	—	0·80–3·20[l]
9x	—	—	0·80–3·20[l]
1′	2·20[d]	2·40–3·80[k]	4·60[g]
1″	—	—	0·80–3·20[l]
2′	2·90[i]	6·70–8·60[l]	—
3′	6·40–8·60[l]	5·70–8·00[e]	2·50[d]
4′a	4·90[l]	—	—
4′b	5·03[l]	—	—
Ph	6·40–8·60[l]	6·70–8·60[l]	6·50–8·50[l]

(b) Coupling constants

J(1′, 1′)	—	—	9·0
J(1′, 3′)	—	—	1·0
J(5, 6)	n	n	n
J(2′, 2′)	5·0	—	—
J(3′, 2′)	3·0	n	—
J(4, 1′)	—	5·5	—

[a] ppm relative to TMS as internal standard.
[b] In CCl_4.
[c] In $CDCl_3$.
[d] Singlet.
[e] Doublet.
[f] Triplet of doublets.
[g] Doublet of doublets.
[h] Triplets.
[i] Pseudo triplet.
[j] Quartet.
[k] Multiplet.
[l] Overlaps.
[m] Broad.
[n] Not measurable.
Coupling constants in Hz.

TABLE 3
^{1}H N.M.R. Data (60 MHz) for Compounds **13–16**

(a) Chemical shifts

Proton	**13**[c]	**14 A**[c]	**14 B**[c]	**15 A**[b]	**15 B**[b]	**16 A**[c]	**16 B**[c]
4	5·10[e]	5·10[g]	3·75[l]	4·95[g]	3·80[l]	4·10[g]	4·10[g]
9n	3·40–2·60[i]	2·57[i]	2·70[k]	2·30[i]	2·80[g]	2·40–3·80[l]	2·40–3·80[l]
9x	3·40–2·60[i]	2·57[i]	3·80[k]	2·30[i]	3·62[g]	2·40–3·80[l]	5·10[k]
10	6·60[g]	5·40[g]	6·08[g]	5·30[e]	6·10[g]	6·20[g]	5·55[g]
Ar	6·5–8·5[l]	6·8–8·5[l]	6·8–8·5[l]	6·6–8·6[l]	6·4–8·6[l]	6·4–8·6[l]	6·4–8·6[l]
1′	—	3·70–4·25 [j]	4·52[j]	3·60[k], 4·20[k]	4·52[h]	—	—
2′	2·10[d,m]	1·80[h]	1·40[h]	1·80–0·40[l]	0·80–2·20[l]	—	—
3′	—	—	—	1·80–0·40[l]	0·80–2·20[l]	—	—
4′	—	—	—	0·75[l]	0·80[l]	—	—

(b) Coupling constants

J(1′, 2′)	—	3·5	3·5	n	3·5	—	—
J(4, 9n)	—	2·0	1·0	2·0	n	n	n
J(4, 9x)	3·5	3·0	n	3·5	n	n	n
J(9x, 9n)	10·0	5·0	10·0	8·0	n	n	n
J(10, 9x)	4·5	0·5	6·5	n	4·0	n	n
J(10, 9n)	1·5	2·5	3·5	n	7·0	n	n

[a] ppm relative to TMS as internal standard.
[b] In CCl_4.
[c] In $CDCl_3$.
[d] Singlet.
[e] Doublet.
[f] Triplet of doublets.
[g] Doublet of doublets.
[h] Triplets.
[i] Pseudo triplet.
[j] Quartet.
[k] Multiplet.
[l] Overlaps.
[m] Broad.
[n] Not measurable.
A and **B** stand for the conformers of the same compound.
Coupling constants in Hz.

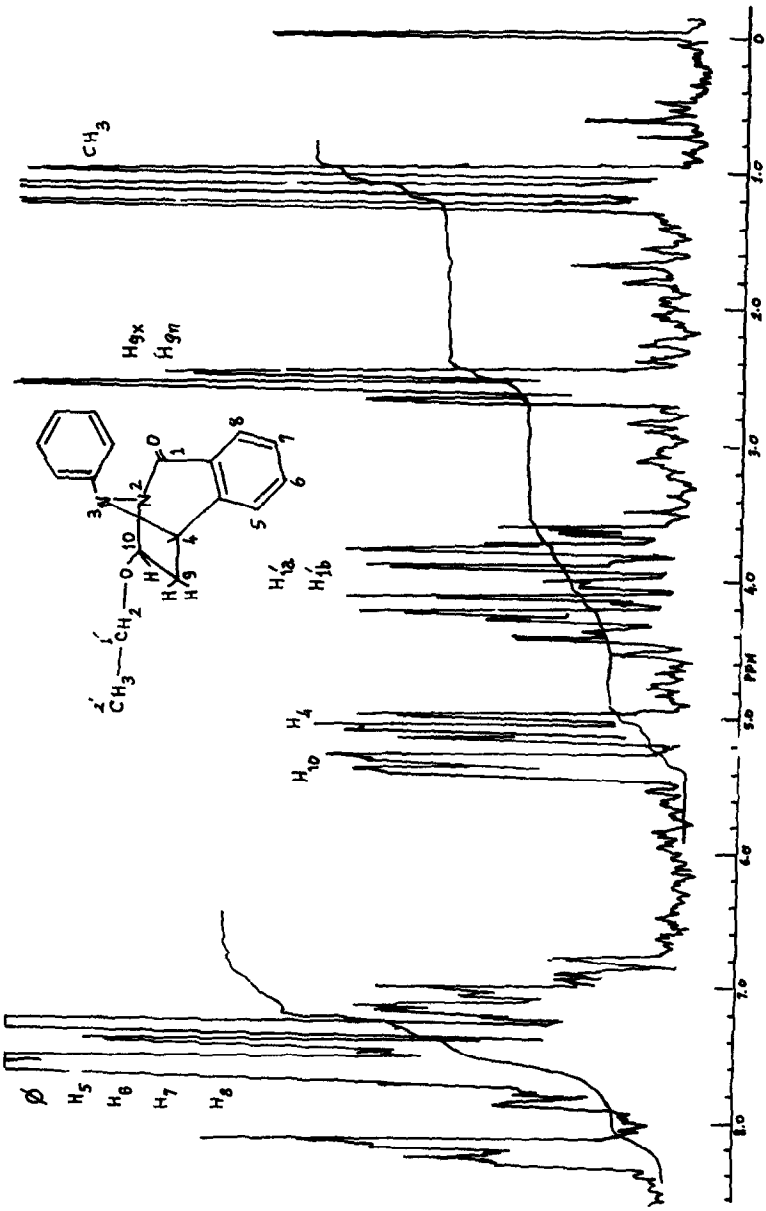


Fig. 1. The ^{1}H n.m.r. spectrum of compound 14.

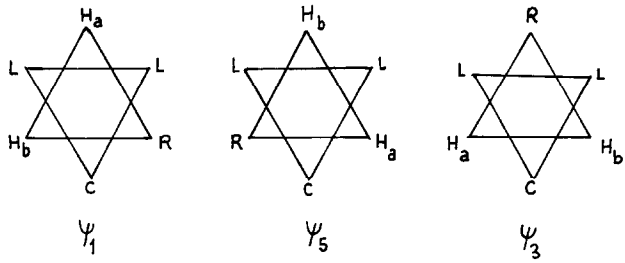


Fig. 2. Three possible conformers of compound **14**.

5). These results indicate that in the reaction medium used, a hyperconjugated acetylenic dipolarophile, i.e. propargyl alcohol, was converted to an electron-rich olefinic dipolarophile **12** which should cycloadd more rapidly across the olefinic bond than the triple bond.

$$\underset{\mathbf{11}}{2HC\equiv CCH_2OH} \longrightarrow \underset{\mathbf{12}}{H_2C{=}C(CH_2OH)(OCH_2C\equiv CH)}$$

The betaine **1** when reacted with vinyl acetate yielded the 10-exo adduct **13** in 46% yield. The i.r. spectrum showed two carbonyl groups, viz. saturated ester (1735 cm^{-1}) and lactam (1675 cm^{-1}). The ^1H n.m.r. spectrum exhibited a low field doublet of doublets at 6·6 ppm assigned to H-10. The bridgehead proton appeared at 5·10 ppm as a doublet (Table 3). All the assignments were confirmed by double irradiation experiments.

Ethyl vinyl ether reacted with the betaine **1** in a sealed tube to give the cycloadduct **14**. The carbonyl band appeared at 1710 cm^{-1} in the i.r. spectrum. The ^1H n.m.r. spectrum recorded in $CDCl_3$ is shown in Fig. 1. The complex splitting pattern of methylenic protons of the ethyl group is in accord with the observation of Price,[17] according to which each free electron pair, being in the skew position relative to a proton, shifts the ^1H n.m.r. signal of this proton about 1·7 ppm to the lower field.[18] Three possible conformers of the cycloadduct **14** about the etheric linkage are shown in Fig. 2, where L, R and C stand for the lone pair, methyl and the cycloadduct skeleton respectively. Conformers indicated by ψ_1 and ψ_5 should produce two sets of AB spectra. Each of them should consist of eight lines equally coupling with methyl protons. Conformer ψ_3 should exhibit a four-lined A_2 spectrum. In the absence of field effects ψ_1 and ψ_5 are interrelated through a C_2 operation.[19] Hence eight lines instead of 16 may be expected (indistinguishable H_a**1**, H_b**5** and H_b**1**, H_a**5**). Presumably, some of the lines overlap to produce fewer than the expected 20 lines for the methylene protons. The spectrum of the same n.m.r. sample recorded a month later showed the complete decay of conformers ψ_1 and ψ_5 into ψ_3 (Fig. 3).

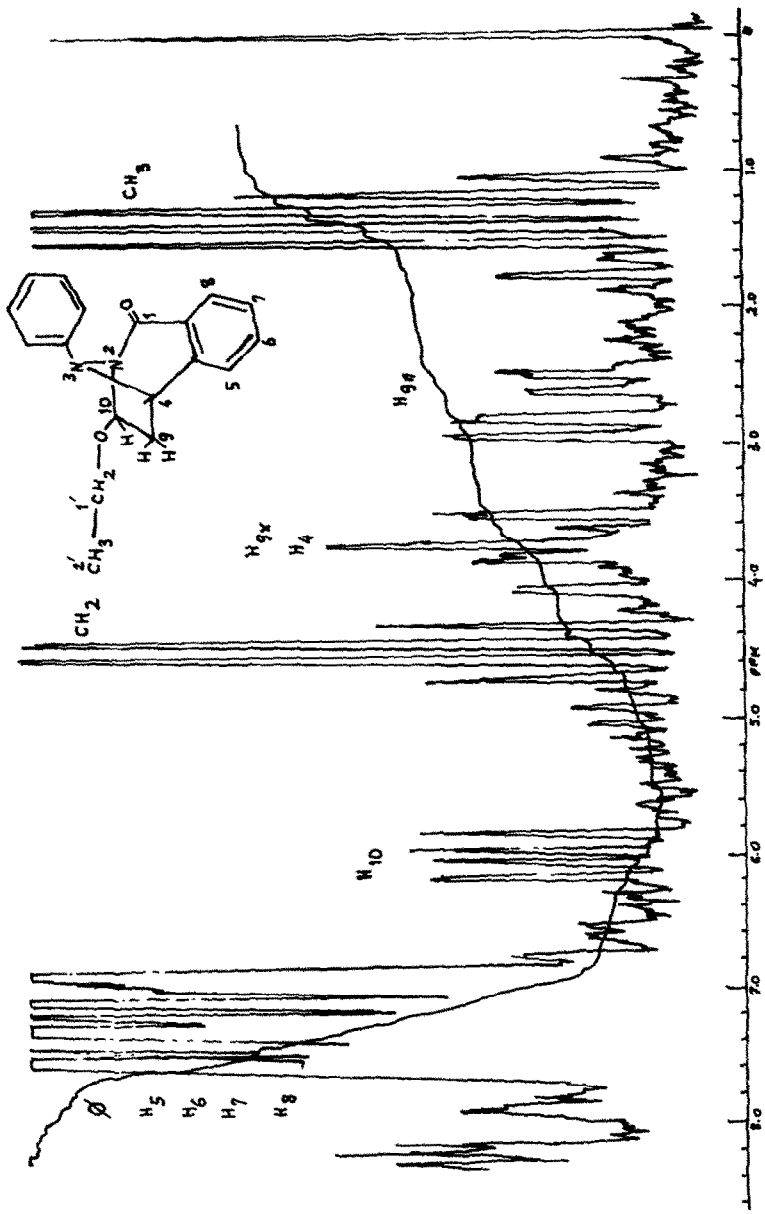


Fig. 3. The ^{1}H n.m.r. spectrum of compound **14** a month later.

Therefore, the cycloadduct **14** exhibits a restricted rotation about the etheric bond, resulting in sufficiently long-lived rotational isomers. The observed spectrum is then a superimposition of these components. Table 3 tabulates ^{1}H n.m.r. data of the adduct **14**.

The phthalazinium betaine **1** reacted with butyl vinyl ether and gave the cycloadduct **15**, which again decayed into its most stable form on standing as with the adduct **14**.

Another electron-rich olefin, N-vinyl carbazole, reacted with 3-phenylphthalazinium-1-olate (**1**) to yield the cycloadduct **16**. The ^{1}H n.m.r.

TABLE 4

^{1}H N.M.R. Data (60 MHz) for Compounds **17–21**

(a) Chemical shifts

Proton	**17**[b]	**18**[b]	**19**[b]	**20**[c]	**21**[b]
4	6·20[k]	5·60[k]	5·40[e]	5·28[e]	6·60[d]
9x	5·40[k]	3·50[k]	3·10[g]	3·00[f]	—
9n	3·40–4·00[l]	—	—	—	5·40[l]
10x	—	—	2·40[g]	1·8[g]	3·10[e]
10n	—	—	2·00[g]	3·0[f]	3·50[k]
Ar	7·00–8·40[k]	6·80–8·40[k]	6·40–8·00[k]	6·80–8·60[k]	6·70–8·70[k]
CH_2	3·40–4·00[l]	1·40–3·00[k]	—	4·0[k]	4·10[d]
CH_3	1·20[h]	—	0·50–1·40[k]	—	—
OH	—	—	—	—	5·40[l]

(b) Coupling constants

J(4, 9)	—	—	7·0	8·0	—
J(10x, 9)	—	—	10·0	—	—
J(10n, 9)	—	—	3·0	7·0	—
J(10n, 10x)	—	—	13·0	14·0	7·0

[a] ppm relative to TMS as internal standard.
[b] In CCl_4.
[c] In $CDCl_3$.
[d] Singlet.
[e] Doublet.
[f] Triplet of doublets.
[g] Doublet of doublets.
[h] Triplets.
[i] Pseudo triplet.
[j] Quartet.
[k] Multiplet.
[l] Overlaps.
[m] Broad.
[n] Not measurable.
Coupling constants in Hz.

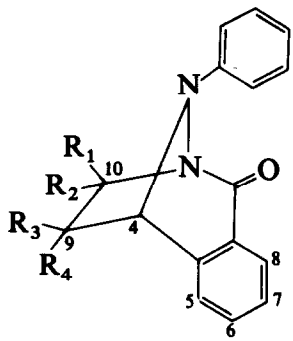
spectrum showed a complex pattern, again implying the presence of certain conformers. However, the periodically recorded ^1H n.m.r. spectra of the same sample revealed that components of the mixture were stable at room temperature even for 2 months. It was also observed that the spectrum was insensitive to temperature changes ($\pm 35°C$). Extensive double irradiation and shift reagent experiments were carried out to elucidate the structure **16**. Moreover, it was found that the sample was a two-component rotamer mixture having mole fractions of 0·572 and 0·428 respectively (within the sensitivity limits of the instrument). The atropisomerism[20] exhibited by the cycloadduct **16** arises from the steric effects between the carbazole moiety and the phenyl substituent or the lone pair of the bridge nitrogen atom.

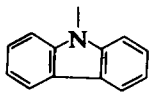
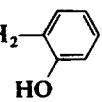
The phthalazinium betaine **1** reacted with 1-bromo vinyl ethyl ether to give **17**. The i.r. spectrum showed a strong lactam carbonyl band at 1705 cm^{-1} ($CHCl_3$). The ^1H n.m.r. spectrum (CCl_4) exhibited a doublet of doublets for H_4 (δ6·2) (Table 4). 1-Pyrrolidino-1-cyclopentene, when reacted with **1**, yielded **18**. The structure elucidation was based on the spectral analysis. The lactam carbonyl occurred at 1690 cm^{-1} ($CHCl_3$). In the ^1H n.m.r. spectrum H_4 appeared as a doublet at δ5·6 (Table 4). On the other hand, 3,3-dimethyl-1-butene and allyl bromide, when reacted with **1**, produced the 9-endo-substituted cycloadducts **19** and **20** respectively. The i.r. spectra of these compounds in chloroform displayed lactam carbonyl stretching at 1710 and 1700 cm^{-1} respectively. The ^1H n.m.r. data are tabulated in Table 4. 2-Allyl phenol and the phthalazinium betaine gave a 9-exo adduct (**21**). The structure possesses a lactam carbonyl at 1720 cm^{-1} ($CHCl_3$). The ^1H n.m.r. spectrum (CCl_4) exhibited a sharp singlet for H_4.

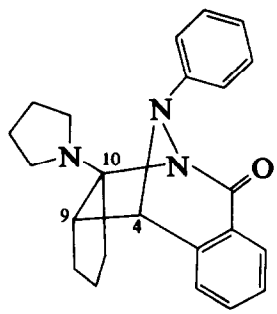
3-Phenylphthalazinium-1-olate **1** failed to give any cycloadduct with N-vinylpyrrolidone, N-vinylsuccinimide, 4-vinylpyridine, 2-vinylpyridine and α-methylstyrene. Electron-deficient dipolarophiles, e.g. ethyl acrylate, methyl vinyl ketone and a hyperconjugated dipolarophile, viz. 2-methyl-2-butene under the applied reaction conditions, also gave no cycloadduct.

Further transformations

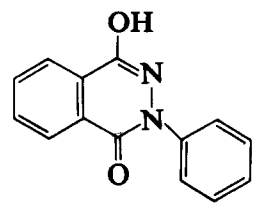
The cycloadduct **13** was hydrolysed in aqueous ethanol solution containing 0·12M NaOH, in order to obtain compound **22**. Instead, compound **23** was isolated. Its i.r. spectrum showed a broad band centered at 3420 cm^{-1} (v(OH)) and strong bands at 1600–1570 cm^{-1} (lactam and aromatic stretchings). The ^1H n.m.r. spectrum recorded in $CDCl_3$ showed a sharp singlet at δ9·38 (intramolecularly hydrogen bonded OH) and overlapped multiplets in the region of δ7·90–8·25 (aromatic protons). The same compound was also obtained in the ethanolic ammonium hydroxide solution of cycloadduct **13**. Compound **23** has m.p. 209–210°C (lit. 210–211).



10 R_1: CH_2OH	R_2: $OCH_2C{\equiv}CH$	R_3: H	R_4: H
13 R_1: $OCOCH_3$	R_2: H	R_3: H	R_4: H
14 R_1: OCH_2CH_3	R_2: H	R_3: H	R_4: H
15 R_1: OC_4H_9	R_2: H	R_3: H	R_4: H
16 R_1: 	R_2: H	R_3: H	R_4: H
17 $R_{1(2)}$: OCH_2CH_3	$R_{2(1)}$: Br	R_3: H	R_4: H
19 R_1: H	R_2: H	R_3: H	R_4: $C(CH_3)_3$
20 R_1: H	R_2: H	R_3: H	R_4: CH_2Br
21 R_1: H	R_2: H	R_3: 	R_4: H
22 $R_{1(2)}$: OH	$R_{2(1)}$: H	R_3: H	R_4: H
24 R_1: H	R_2: OCH_2CH_3	R_3: H	R_4: H



18



23

Its formation probably occurred through acyl or alkyl cleavage of the ester bond to form **22**, which then underwent a solvolytic chain cleavage.[21] Rowe *et al.* demonstrated a similar type of cleavage of 1-hydroxy-3-aryl-3,4-dihydrophthalazine-4-acetic acid.[22]

Ethanolysis of compound **13** produced **24**, which is the stereoisomer of the cycloadduct **14**. The ^1H n.m.r. spectrum of the 7-endo isomer **24** did not show any indication of a hindered rotation about the etheric linkage.

EXPERIMENTAL

The melting points were determined with a Reichert apparatus. The spectra were recorded with a Beckman 18A grating i.r. spectrophotometer, a Varian T-60A n.m.r. spectrometer, a Hitachi Perkin–Elmer RMU6E mass spectrophotometer and a Cary 17D UV spectrophotometer. Compounds were purified by preparative thick layer chromatography on Kieselgel GF 254 or HF 254 + 366, until they were observed as single spots on t.l.c.

Some of the characteristic syntheses are described below; others are given in Table 5.

3,4-Dihydro-9,10-dimethyl-3-phenyl-2,4-ethanophthalazin-1(2H)-one **2**. 3-Phenylphthalazinium-1-olate (0·18 g, 0·0008 mol), dimethylacetylene (3 ml), 1,2-dichloroethane (3 ml) and hydroquinone (a few crystals) were heated in a Carius tube at 60°C for 14 days. The crude product was filtered. The filtrate was evaporated *in vacuo* and chromatographed on silica gel ($CCl_4/CHCl_3$, 3:2). The eluate gave the *cycloadduct* **2** (0·1 g, 45%) as canary yellow prisms, m.p. 151–153°C (pet. ether–EtOH, 5:1) (found: C, 78·50; H, 5·65; N, 10·08%. $C_{18}H_{16}N_2O$ requires C, 78·26; H, 5·79; N, 10·14%); ν_{max} (nujol) 1715 cm^{-1} (α,β-unsaturated C=O); λ_{max} (EtOH) 295 nm (log ε 3·56), 277 nm (log ε 3·76), 248 nm (log ε 3·79), 217 nm (log ε 3·45); *m/e* 276.

3,4-Dihydro-9-(1-hydroxyethyl)-3-phenyl-2,4-ethenophthalazine-1(2H)-one **3** *and 3a,8b-dihydro-3a-(1'-hydroxyethyl)-1-phenylindeno(1,2,-c)pyrazol-4(1H)-one* **4**. The betaine **1** (0·42 g, 0·0019 mol) was dissolved in 1-butyne-3-ol (10 ml) and a few crystals of hydroquinone added. The mixture was refluxed for 5 days. The filtrate was evaporated under vacuum and chromatographed on silica gel ($CHCl_3$). The eluate gave **3** (0·175 g, 30%) as yellow prisms, m.p. 179–181°C (pet. ether–EtOH, 5:1) (found: C, 73·65; H, 5·33; N, 9·62%. $C_{18}H_{16}N_2O_2$ requires C, 73·97; H, 5·47; N, 9·58%); ν_{max} (CCl_4) 3300 cm^{-1} (OH), 1715 cm^{-1} (C=O); λ_{max} (EtOH) 254 nm (log ε 4·48); *m/e* 292. The eluate also gave the isomeric compound **4** (0·117 g, 20%) as yellow prisms, m.p. 163–165°C (pet. ether–EtOH, 5:1) (found: C, 73·87; H, 5·50; N, 9·48%); ν_{max} (CCl_4) 3320 cm^{-1} (OH), 1715 cm^{-1} (C=O); λ_{max} (EtOH) 255 nm (log ε 4·49); *m/e* 292.

3,4-Dihydro-10-exo-ethoxy-3-phenyl-2,4-ethanophthalazin-1(2H)-one **14**. The betaine **1** (0·212 g, 0·001 mol), ethyl vinyl ether (3 ml), 1,2-dichloroethane (5 ml) and a few crystals of hydroquinone were heated in a sealed tube at 60°C for 13 days. The filtrate was evaporated under vacuum and purified by prep. t.l.c. (CCl_4). The eluate gave **14** (0·196 g, 70%) as white prisms, m.p.

TABLE 5
Some Characteristics of Compounds **5–21**

Comp. no.	*Dipolarophile*[a]	*Solvent*	*Rxn time*[b]	*% Yield*	*m.p. (°C)*	λ_{max} *(log ε)*[d]
5	Acetylene ethoxide	—	4	60	160–161	215 (4·32)
6	Allylamine	—	7	65	64–66	224 (3·78)
						246 (3·57)
7	Allyl cyanide	—	13	40	172–174	222 (4·40)
10	Propargyl alcohol	—	6	45	[e]	257 (3·51)
13	Vinyl acetate	—	11	46	122–123	213 (3·82)
						227 (3·50)
						247 (3·70)
15	Vinyl butyl ether (7·5 ml)	1,2-Dichloroethane (4 ml)	9	62	[e]	246 (3·31)
						281 (3·66)
						294 (3·51)
16	N-Vinyl carbazole (0·212 g)	1,2-Dichloroethane (20 ml)	13	38	178–180	225 (3·96)
						247 (3·76)
						259 (3·63)

17	1-Bromovinyl ethyl ether (2 ml)	1·2-Dichloroethane (15 ml)	5	41	150–151	213 (3·83) 231 (3·77)
18	1-Pyrrolidino-1-cyclopentene (10 ml)	—	3	44	89–91	222 (3·69) 245 (3·70) 256 (3·69) 277 (3·80)
19	3,3-Dimethyl-1-butene (1 ml)	1,2-Dichloroethane (15 ml)	12	28	56–57	230 (3·80) 248 (3·81) 254 (3·81) 277 (3·80)
20	Allylbromide	—	7	65	208–209	213 (4·35)
21	2-Allyl phenol (7 ml)	1,2-Dichloroethane	8	57	42–44	230 (4·13)

[a] 0·5 g betaine was used.
[b] Days.
[c] Crystallised in pet. ether–EtOH (5:1).
[d] In EtOH.
[e] Resisted crystallisation.

104–106°C (pet. ether–EtOH, 5:1) (found: C, 73·38; H, 6·19; N, 9·62%. $C_{18}H_{18}N_2O_2$ requires C, 73·46; H, 6·12; N, 9·52%); ν_{max} ($CHCl_3$) 1710 cm^{-1} (C=O); λ_{max} (EtOH) 223 nm (log ε 3·72), 246 nm (log ε 3·55); *m/e* 294.

REFERENCES

1. Sadov, F., Korchagin, M. & Matetsky, A., *Chemical Technology of Fibrous Materials.* Mir Publishers, Moscow, 1978.
2. Dorlass, A., Schellhammer, C. & Schroeder, J., *Angew. Chem. Int. Ed.*, **14** (1975) 665.
3. Peterson, S., *Angew. Chem.*, **61** (1949) 17.
4. Sarkar, A. K., *Fluorescent Whitening Agents.* Merrow Pub. Co. Ltd, Watford, 1971.
5. Goldin, H. & Venkataraman, K., *The Chemistry of Synthetic Dyes*, Vol. 5. Academic Press, New York, 1971.
6. Wheelock, C. E., *J. Am. Chem. Soc.*, **81** (1959) 1348.
7. Rowe, F. M., Levin, E., Burns, A. C., Davies, J. S. H. & Tepper, W., *J. Chem. Soc.* (1926) 690.
8. Rowe, F. M. & Levin, E., *J. Chem. Soc.* (1928) 2550.
9. Rowe, F. M. & Dunbar, C., *J. Chem. Soc.* (1932) 473.
10. Rowe, F. M. & Twitchett, H. J., *J. Chem. Soc.* (1936) 1704.
11. Peters, A. T., Rowe, F. M. & Brodrick, C. I., *J. Chem. Soc.* (1948) 1249.
12. Lund, H., *Tetrahedron Lett.* (1965) 3973.
13. Lund, H., *Collect. Czech. Chem. Commun.*, **30** (1965) 4237.
14. Dennis, N., Katritzky, A. R. & Ramaiah, M., *J. Chem. Soc. Perkin*, **I** (1976) 2281.
15. Katritzky, A. R. & Boulton, A. J., *Advances in Heterocyclic Chemistry*, Vol. 26. Academic Press, London, 1980, p. 1.
16. Shostakovskii, M. F., Bogdanov, A. V. & Plotnikova, G. I., *Russ. Chem. Rev.*, **33** (1964) 66–77.
17. Price, C. C., *Tetrahedron Lett.*, **47** (1971) 4527.
18. Potapov, V. M., *Stereochemistry.* Mir Publishers, Moscow, 1978.
19. Pople, J. A., Schreider, W. G. & Bernstein, H. J., *High Resolution Nuclear Magnetic Resonanace.* McGraw-Hill, New York, 1959.
20. March, J., *Advanced Organic Chemistry.* McGraw-Hill, New York, 1968.
21. Fuson, R. C., *Reactions of Organic Compounds.* John Wiley, New York, 1962.
22. Castle, R. N., *Heterocyclic Compounds*, Vol. 27. John Wiley, New York, 1973.