Experimental and Theoretical Studies on Physicochemical Properties of Novel Six-membered Cyclic α-Monocarbonyl Azo-compounds

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The preparation and physicochemical properties of a novel six-membered α-monocarbonyl azo-compound are reported. Low-temperature oxidation of 4,4-diaryl-3,4-dihydrophthalazin-1(2*H*)-ones (**2**) with lead tetra-acetate (LTA) in the presence of triethylamine in CH_2Cl_2 afforded 4,4-diaryl-phthalazin-1(4*H*)-ones (**3**). Molecular orbital (MO) calculations on the model compound (**8**) of (**3**) disclosed on comparison with the corresponding azo-compound (**7**) and the α,α′-dicarbonyl azo-compound (**9**) that the FMO properties of (**8**) are markedly different from that of (**9**). Thus, (**8**) should be a poor dienophile unlike (**9**), and analyses of the bond population indicated that (**8**) would undergo ready nitrogen extrusion as well as (**7**) and indeed, (**3**) was stable only below −60 °C. The MO calculations also indicated inherent 1,2-migration of the 4-substituent to the N(3) atom. 1,2-Aryl migration of (**3**) in acidic CH_2Cl_2 solution results in the formation of 3,4-diaryl-1-oxidophthalazinium betaine derivatives (**13**).

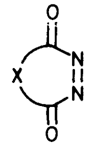
Variables such as ring size and polar substituents in azo-compounds markedly affect their physical properties and chemical reactivities. For instance, several cyclic α,α′-dicarbonyl azo-compounds (A) are known to serve as dienophiles in the Diels–Alder reaction[1] and cyclic azo-compounds including polycyclic ones (B) in general give rise to nitrogen extrusion thermally or photochemically to give diradical species. The thermal or photochemical extrusion of molecular nitrogen from the corresponding azo-compounds provides an effective and convenient method for generating carbon–carbon bonds, through which various cyclic molecules, including highly strained, sterically crowded, fluxional structures, have been synthesised.[2]

In contrast, relatively little work has been carried out on cyclic α-monocarbonyl azo-compounds (C) which bear both functions of the azo-compounds (A) and (B). The only systems investigated are 3-indazolone[3] and 3-pyrazolones.[4] Six-membered cyclic α-monocarbonyl azo-compounds were unknown prior to our preliminary publication.[5]

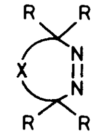
The rearrangement of phthalazin-1(4*H*)-one to phthalazin-1(2*H*)-one readily occurs unless blocked by 4,4-disubstitution.† For this reason, phthalazin-1(4*H*)-one is an underinvestigated molecule. We have reported that heating Crystal Violet Lactone (CVL) (**1a**) and its analogues with hydrazine hydrate afforded 4,4-diaryl-3,4-dihydrophthalazin-1(2*H*)-ones (**2**),[7] from which phthalazin-1(4*H*)-ones (**3**) are formally obtainable by oxidation (Scheme 1).

As part of our continuing work on the physicochemical study of leuco-triarylmethane dyes, we have examined the oxidation of (**2**). Among various oxidants available for the oxidation of hydrazino and hydrazide group, lead tetra-acetate (LTA) in methylene dichloride (CH_2Cl_2) in the presence of triethylamine was found to be effective for the oxidation of (**2**).

In this paper, we describe the formation of one such series of 4,4-diarylphthalazin-1(4*H*)-ones (**3**) by low-temperature LTA oxidation and their novel acid-catalysed rearrangements. We also discuss the electronic structure and chemical reactivity of (**3**) and related molecules based on molecular orbital calculations.



(A)



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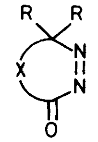
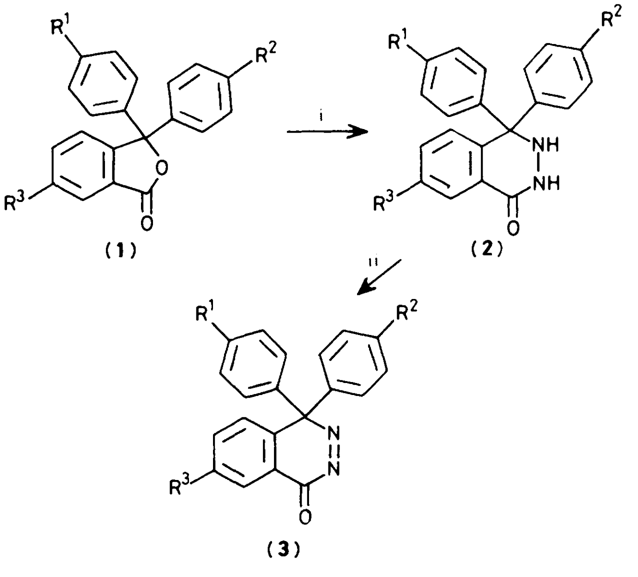


(C)



a ; $R^1 = R^2 = R^3 = NMe_2$
b ; $R^1 = R^2 = NMe_2$, $R^3 = H$
e ; $R^1 = NMe_2$, $R^2 = R^3 = H$

Scheme 1. *Reagents:* i, $NH_2NH_2{\cdot}H_2O$; ii, oxidation

Results and Discussion

(1) *Preparation and Characterisation of* 4,4-*Diarylphthalazin-*1(4H)-*ones* (**3**).—Low-temperature oxidation (−78 °C) of (**2**)

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† Phthalazin-1(4*H*)-one has been reported as part of an equilibrium mixture with phthalazin-1(2*H*)-one.[6] This must be misleading, since the procedure described is a well known method for the synthesis of phthalazin-1(2*H*)-ones. In fact, we have re-examined a similar reaction and have detected no evidence for the formation of phthalazin-1(4*H*)-one.

Table 1. I.r. absorptions of compounds (**3**) in CH_2Cl_2 at -80 °C

Compound (**3**)	$\nu_{C=O}/cm^{-1}$
b; $R^1 = R^2 = NMe_2$, $R^3 = H$	1 715
c; $R^1 = NMe_2$, $R^2 = OMe$, $R^3 = H$	1 717
d; $R^1 = NMe_2$, $R^2 = Me$, $R^3 = H$	1 718
e; $R^1 = NMe_2$, $R^2 = R^3 = H$	1 712
f; $R^1 = R^2 = OMe$, $R^3 = H$	1 718

with LTA in the presence of triethylamine in CH_2Cl_2 yielded a deeply coloured solution. The product was assigned structure (**3**) on the basis of the method of synthesis, the spectral properties (i.r.), and the ensuing chemical reactions. Products (**3**) are stable only below -60 °C at least overnight and probably longer, as determined by the evolution of molecular nitrogen and discharge of the colour at higher temperatures.

The reaction mixture, therefore, was concentrated to half the initial volume at -78 °C and the i.r. spectrum of the solution thus obtained was recorded at -80 °C. The i.r. spectra are summarised in Table 1, and show a strong carbonyl stretching band at 1 715—1 720 cm^{-1}.

In five-membered cyclic compounds, replacement of the carbon double bond by an azo-function causes an increase in the carbonyl stretching frequency of *ca.* 50 cm^{-1} as deduced by comparison of the 1 790 cm^{-1} band in 3-indazolone[3a] with the 1 737 cm^{-1} in inden-1-one.[8] Thus, the carbonyl stretching frequency observed is entirely consistent with the assigned structure (**3**) on the basis of its comparison with that, 1 665 cm^{-1}, in carbon analogues such as naphthalen-1(4*H*)-one.[9]

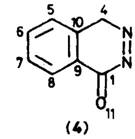
We note that the yield of (**3**) varied with the substituent at the *para*-position of the 4-phenyl ring. This is probably due to the vast difference in solubility of (**2**) in CH_2Cl_2, since it is highly unlikely that a substituent in this position could affect the rate of oxidation sterically or electronically.

(2) *Molecular Orbital* (*MO*) *Calculations.*—Molecular orbital calculations on various phthalazinones and related molecules were carried out by the semiempirical MINDO/3 method.[10] Since the geometry of phthalazinone derivatives is not known, we assumed for simplicity a structure in which the ring skeleton is planar (C_s symmetry) and the benzene ring is a regular hexagon with C–C bond distances of 1.40 Å and C–H bond distances of 1.08 Å. For other geometrical parameters, optimisation was carried out with standard bond lengths and bond angles[11] as a trial geometry. For the other molecules examined, full optimisation within C_s symmetry was undertaken starting from a trial geometry with standard bond lengths and angles. We do believe that these approximations do not significantly influence the main feature of the computed molecular orbital quantities.

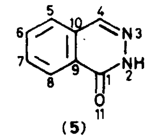
(a) *MO considerations on isomerisation of phthalazin*-1(4H)-*one* (**4**) *to phthalazin*-1(2H)-*one* (**5**). The inherent propensity for isomerisation (1,3-hydrogen shift) of (**4**) to (**5**) was evaluated theoretically. The computed frontier molecular orbital (FMO) energies and nodal properties of (**4**) and (**5**) are shown in Figure 1, together with those of (**6**) (*vide infra*).

The highest occupied molecular orbital (HOMO) of (**4**) was shown to be a σ-orbital (A' symmetry) localised on the azo-function and is characteristic of azo-compounds in general. The next highest occupied orbital (NHOMO) of (**4**) is largely polarised on the aromatic portion. On the other hand, the HOMO of (**5**) is a π-orbital (A'' symmetry) which is polarised on the azo-group, demonstrating the vast difference in electronic structure between (**4**) and (**5**).

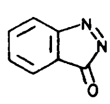
The computed total energy difference between two isomers is 6.9 kcal mol^{-1}, demonstrating that (**5**) is thermally more stable



(**4**)



(**5**)



(**6**)

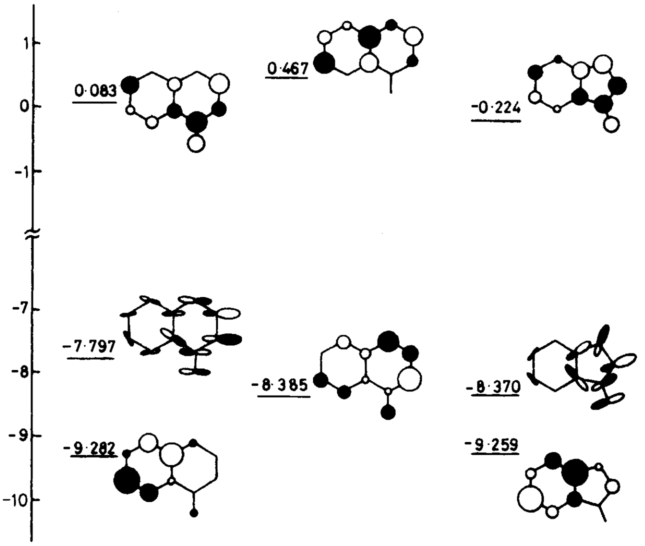
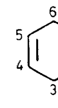


Figure 1. Frontier molecular orbital energies and nodal properties of (**4**)—(**6**) calculated by the MINDO/3 method

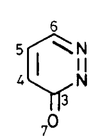
than (**4**). In addition, comparison of the heat of formation (Δ*H*) between the two isomers also justified such an assumption [Δ*H* 1.64 kcal mol^{-1} for (**4**) and 8.57 kcal mol^{-1} for (**5**)]. All these results imply that (**4**) tends to isomerise to (**5**), which also occurs in the case of pyridazinones.

(b) *Molecular orbital considerations on tendency towards nitrogen elimination and Diels–Alder reaction.* A variety of theoretical calculations on relatively simple azo-compounds have thus far been reported.[12] However, the effect of an α-carbonyl function on the electronic structure of cyclic azo-compounds has not yet been theoretically investigated. Therefore, MO calculable quantities of the pyridazine derivatives (**7**)—(**9**) were compared to gain some insight into the differences in their chemical features.

The higher-lying occupied and lower-lying unoccupied molecular orbital energies and nodal properties are shown in Figure 2. It is immediately seen that the MO properties of (**9**) are markedly different from those of (**7**) and (**8**); the molecular orbitals of (**9**) pertaining to the azo function are low in energy relative to those of (**7**) and (**8**) due to the introduction of two carbonyl groups. One of the most striking features of (**9**) is that the LUMO ($\psi_{21}{}^*$) is the in-plane *n*-orbital of the azo-function with an antibonding combination which has the large lobe outside the ring, whereas the same type of molecular orbital is the HOMO (ψ_{16} and ψ_{18}) in both (**7**) and (**8**), and the relative energy order of the orbital properties is the same as those calculated with azoalkanes.[12] Although vacant orbitals calculated by LCAO-SCF scheme are 'virtual' orbitals, it is abundantly documented in the literature that the relative energy differences in low-lying vacant orbitals have been successfully used as indices for the interpretation of the chemical reactivities involving such orbitals. Thus, it is evident that (**9**) should act as the most reactive dienophile in a Diels–Alder reaction with a normal electron demand, and the origin of the high reactivity



(7)



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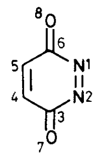

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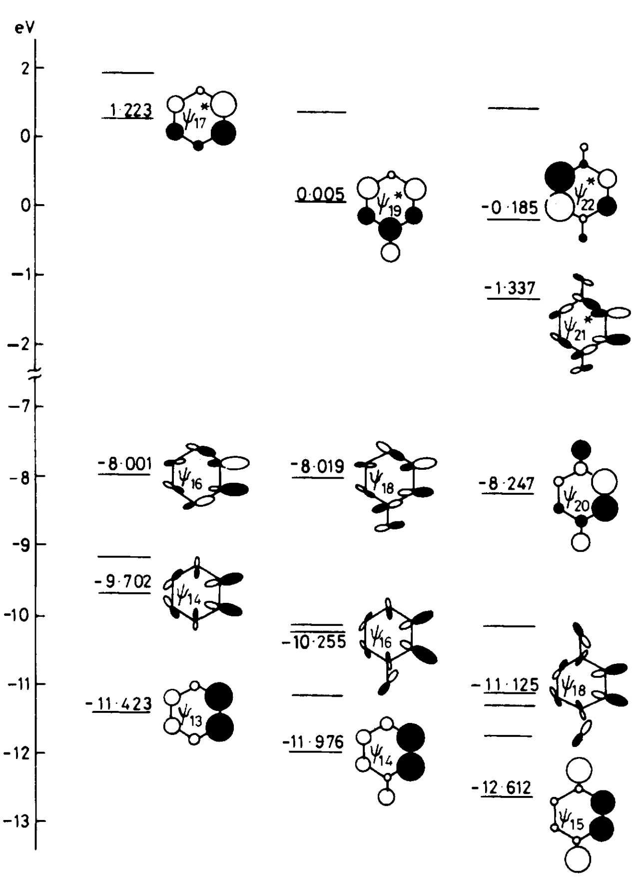
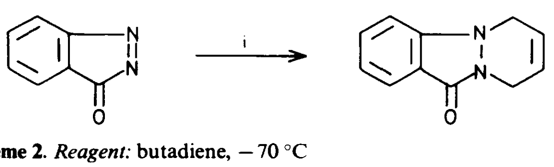
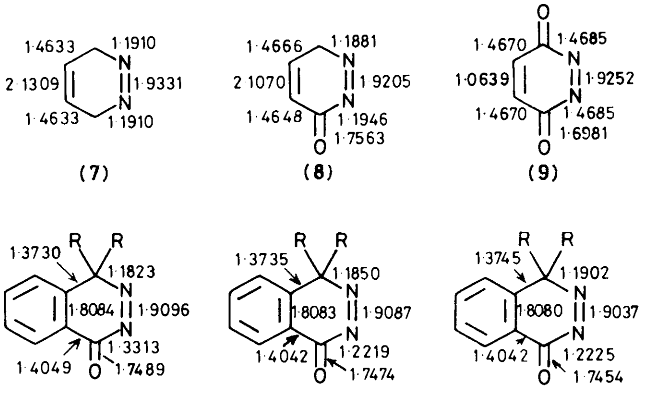


Figure 2. The higher-lying occupied and lower-lying unoccupied molecular orbital energies and nodal properties of (7)—(9) calculated by the MINDO/3 method



Scheme 2. *Reagent:* butadiene, −70 °C



(7) (8) (9)

(10) R = CH═CHCN (11) R = CH═CH$_2$ (12) R = CH═CHNH$_2$

Atomic bond populations of (7)—(12)

can be ascribed to the presence and dominant role of this unique low-lying LUMO (ψ_{21}*) based on frontier molecular orbital theory, the validity of which has been now proven for problems in all types of cycloaddition. If the lowest vacant π-orbital (ψ_{22}*) of (9) plays an important role in the Diels–Alder reaction, the C(4)–C(5) ethylenic double bond would be the reactive site due to the larger coefficient, which is in disagreement with experimental fact.

And also, the transition state for such a reaction of (9) should be different from that involved with an ethylenic dienophile where it is widely accepted that the transition state is of 'stacking-type' geometry. The geometry of the transition state involved in (9) can be considered to be such that the two interacting planar molecules (diene and dienophile) are perpendicular to each other. In the light of unreactivity of (7) as a dienophile in the Diels–Alder reaction, (8) should also be unreactive due to the relatively high LUMO energy and the similar nodal properties.

It is known that five-membered cyclic α-monocarbonyl azo-compounds such as 3-indazolone (6) react at −10 °C with cyclopentadiene or butadiene instantaneously on mixing as determined by colour discharge of the deep red solution.[3a]

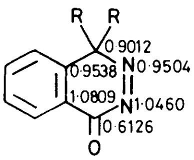
Here, it is interesting to compare the molecular orbital properties of (6), which were shown in Figure 1, with those of (4) and (9). As shown in Figure 1, the LUMO of reactive dienophile, (6) has π-character, unlike (9), but is lower in energy than either the LUMO of (4) or the lowest vacant π-orbital of (9). Thus, in the case of (6), the low-lying π-type LUMO would be responsible for the high reactivity as a dienophile.

The atomic bond populations[13] of (7)—(9) calculated from the MINDO/3 wavefunctions are shown above. The magnitude of the C(6)–N(1) [≡ C(3)–N(2)] bond in (7) is much smaller than that of (9), and that of C(6)–N(1) bond of (9) is the largest. In (8) which contains both functions of (7) and (9), the magnitude of N(1)–C(6) is nearly equal to that in (7). If the feasibility of the nitrogen elimination is correlated with the bond strengths of the ground states, thermal nitrogen extrusion of (7) occurs readily while it is least likely for (9), in accord with the experimental facts. Thus, it can be suggested that the thermal nitrogen elimination of (8), if it occurs, would be initiated by N(1)–C(6) bond cleavage. Also, in view of the experimental fact that the rate of thermal nitrogen elimination of (3) increased with the ability of the substituent to stabilise the carbocation centre at C(4), thermal nitrogen elimination of (3) is initiated by the ionic cleavage of the N(3)–C(4) bond, followed by the C(1)–N(2) bond.

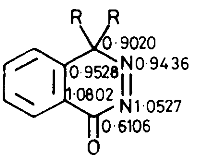
(c) *Substituent effect at* C(4) *of six-membered α-monocarbonyl azo-compounds.* In order to assess the effect of the polar substituent at C(4) of phthalazin-1(4*H*)-one (3), MO calculations on the model compounds (10)—(12) were also performed.

The differences in the atomic bond populations among them are small, and the atomic bond population of N(3)–C(4) is the smallest irrespective of the nature of the substituent. Therefore, nitrogen elimination of these compounds may be caused by N(3)–C(4) bond cleavage and the ease of nitrogen elimination of (3) is correlated with electronic features of N(3) and C(4).

The π-electron densities of each phthalazinone ring atom of (10)—(12) are shown. Inspection of the π-electron densities demonstrates that the N(3) and C(4) atoms in every compound are electron-deficient and the magnitude of the polarity between N(3) and C(4) of (10)—(12) increases in that order. The electron-donating substituent at C(4) of the phthalazinone increases the magnitude of the π-electron charge transfer from N(3) and C(1) to N(2) and O(11), and the electron-withdrawing substituent decreases it.



(10)



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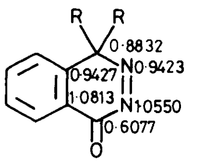


(12)

π-Electron densities of (**10**)—(**12**)

Table 2. Substituent effect on nitrogen elimination of (**3**)

Compound (**3**)	First-order rate constant in CH_2Cl_2 (−50 °C) k/s^{-1}	$\Sigma\sigma^+$
b; $R^1 = R^2 = NMe_2$, $R^3 = H$	$2.3 \pm 0.2 \times 10^{-3}$	−3.40
c; $R^1 = NMe_2$, $R^2 = OMe$, $R^3 = H$	$1.7 \pm 0.2 \times 10^{-3}$	−2.48
d; $R^1 = NMe_2$, $R^2 = Me$, $R^3 = H$	$1.4 \pm 0.1 \times 10^{-3}$	−2.01
e; $R^1 = NMe_2$, $R^2 = R^3 = H$	$1.2 \pm 0.1 \times 10^{-3}$	−1.70

Table 3. The 1,2-aryl migration of (**3**) in CH_2Cl_2–TFA

	Product (%)		Products from nitrogen elimination	
Substrate	(**13**)	(**13′**)	(%)	$\Sigma\sigma^+$
(**3b**)	8.7		91.3	−3.40
(**3c**)	22.8	10.7	66.5	−2.48
(**3d**)	44.3	0	55.7	−2.01
(**3e**)	55.8	0	44.2	−1.70
(**3f**)	56.3		43.7	−1.56

These results imply that nitrogen extrusion in the phthalazinone is caused by N(3) attracting the σ-electrons of the N(3)–C(4) bond. The electron-donating substituent at C(4) increases the rate of nitrogen elimination.

(3) *Chemical Properties of Phthalazin-*1(4H)*-ones* (**3**).—(a) *Substituent effects of the* 4-*aryl ring on nitrogen elimination of* (**3**). Cyclic azo-compounds can undergo nitrogen elimination thermally or photochemically. Some substrates decompose spontaneously, and others are moderately or even extremely resistant to nitrogen elimination. However, the effect of a polar substituent α to the azo-group on nitrogen elimination of cyclic α-monocarbonyl azo-compounds has not yet been investigated.

We have measured the rate of nitrogen elimination on one series of 4,4-diarylphthalazin-1(4*H*)-ones (**3**) in CH_2Cl_2 at − 50 °C. The results obtained are summarised in Table 2, and a plot of log *k* against the sum of Brown–Okamoto σ^+ values $(\Sigma\sigma^+)$[14] shows a good linear relationship as shown in Figure 3.

Apparently, the *para*-substituent of the 4-aryl group affects the rate of the nitrogen elimination; the rate increases as the gross magnitude of the electron-donating nature of the substituents increases.

(b) *Attempted Diels–Alder reactions of* (**3**). Diels–Alder reactions of (**3**) were attempted with butadiene and many other dienophiles at −70 °C, since compound (**3**) is stable in CH_2Cl_2 only below −60 °C. We obtained, however, no detectable adducts in such reactions.

The difficulty in the formation of the Diels–Alder adduct of (**3**) could be ascribed to the unfavourite molecular orbital properties as discussed for (**8**) previously as well as the steric effect of two bulky 4-aryl groups in (**3**).

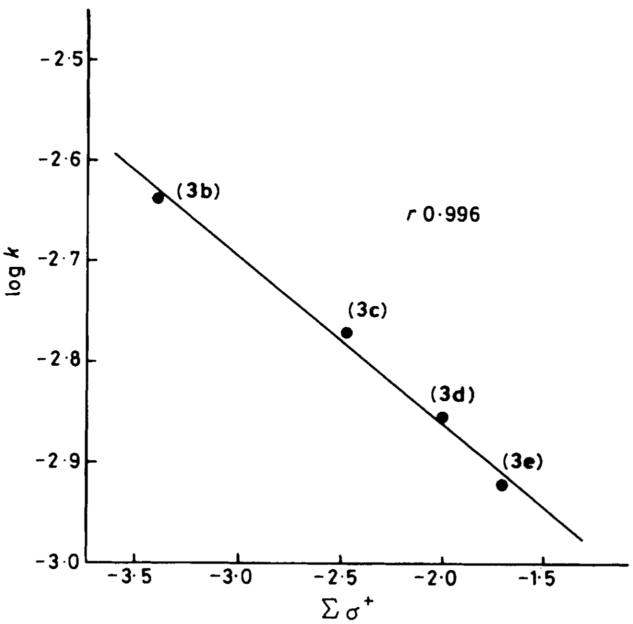
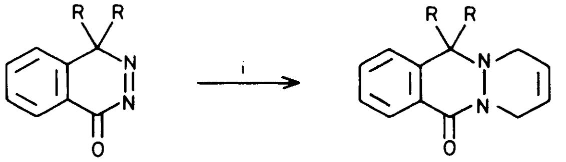


Figure 3. Plot of log *k* against $\Sigma\sigma^+$



Scheme 3. *Reagent:* i, butadiene, −70 °C

(c) 1,2-*Aryl shift; betaine formation.* As shown previously, the LUMO coefficient of N(3) of (**4**) is large, and this is indicative of the inherent 1,2-migratory aptitude of the adjacent aryl group, if it proceeds along the line derived from the frontier orbital theory. It can be expected that preferential protonation would occur at the site of the carbonyl oxygen atom and result in a further lowering of the LUMO energy to a large extent. Efficient 1,2-aryl migration, therefore, could be furnished in a strongly acidic medium using 'hard acid'.

With a view to examining this possibility, trifluoroacetic acid (TFA)–CH_2Cl_2 (1:2) solution* was added to each CH_2Cl_2 solution containing (**3b**—**f**) at −80 °C. The resulting solution was gradually warmed up to room temperature, and there were obtained 3,4-diaryl-1-oxidophthalazinium betaine derivatives (**13**) and/or (**13′**) in each reaction in addition to other products resulting from nitrogen elimination. These results were summarised in Table 3.

The special feature of these results is that the betaine formation appears to be inversely proportional to the ease of nitrogen extrusion, *i.e.* the instability of the 4,4-diarylphthalazin-1(4*H*)-ones (**3**).

Thus, 1,2-aryl migration occurs competitively at about the temperature at which nitrogen elimination occurs. This was also confirmed by the following experiment; when the solution of (**3b**) with added TFA was allowed to stand at −78 °C overnight and then quenched with sodium methoxide at low temperature, no detectable betaine was obtained, confirming that 1,2-aryl migration does not occur at so low a temperature. In fact, a plot of the yield of betaine formation as a function of the sum of

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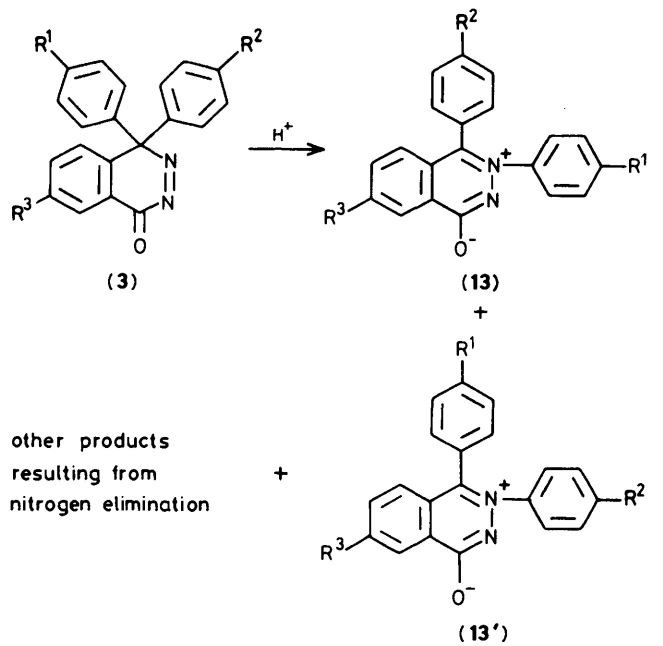
* This ratio was chosen in order not to freeze out the acid even at − 80 °C.



(3)

(13)

(13′)

Scheme 4.

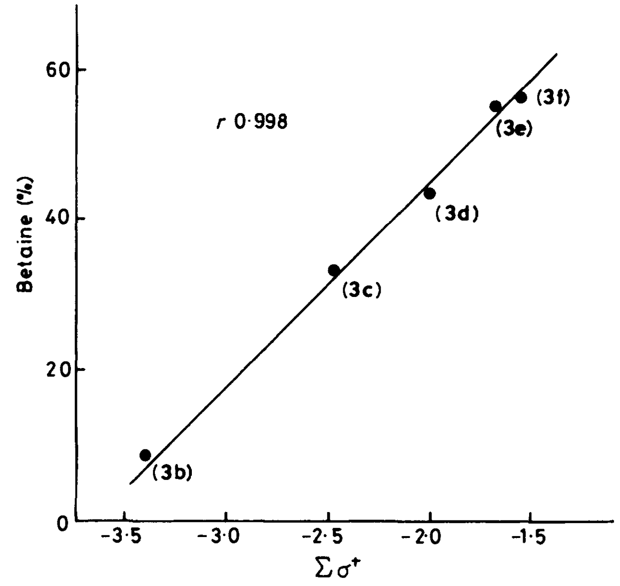


Figure 4. Plot of betaine formation against $\Sigma\sigma^+$

Brown–Okamoto σ^+ values ($\Sigma\sigma^+$) showed the linear relation in Figure 4.

Further, extrapolation of Figure 4 indicated that even if the 'saturation effect' was taken into consideration[15,16] (the effect of multiple substitution is not strictly additive), one may not be able to obtain the betaine from 4,4-diarylphthalazin-1(4*H*)-one (**3a**) which bears a *p*-dimethylamino substituent on all three aromatic rings ($\Sigma\sigma^+$ 5.1).

Although several 4,4-disubstituted naphthalen-1(4*H*)-ones have been shown to undergo acid-catalysed rearrangement to phenol derivatives,[17] no structurally related heterocyclic dienones have yet been shown to undergo an analogous rearrangement, as far as we are aware.

The magnitude of substituent effect for the relative migratory aptitude reported herein appears to be parallel to those shown in univalent nitrenium ions ($\mathrm{C{=}N^+}$) or nitrenes ($\mathrm{C{-}\underset{..}{\ddot{N}}}$).[18] It thus appears likely that this novel type of betaine formation could involve the divalent nitrenium ions ($-\overset{+}{\mathrm{N}}-$) shown in Scheme 4.

The divalent nitrenium ions, which are isoelectronic with carbenes, have been confirmed under solvolytic conditions by the pioneering studies of Gassmann and his co-workers.[19] Our results reported herein, *i.e.* betaine formation from (**3**) on protonation by strong acid, represent the first evidence for divalent nitrenium ion formation by a route other than solvolysis.

Experimental

Preparation and I.r. Spectra of 4,4-*Diarylphthalazin*-1(4H)-*ones* (**3**).—A solution of LTA (0.98 g, 0.0022 mol) in anhydrous CH_2Cl_2 (10 ml) was added to a solution of a 4,4-diaryl-3,4-dihydrophthalazin-1(2*H*)-one (**2**) (0.002 mol) and triethylamine (1.01 g, 0.001 mol) in anhydrous CH_2Cl_2 (40 ml) at −80 °C during 30 min. The mixture was stirred for an additional 3 h at this temperature, and the reaction mixture was concentrated to half the initial volume at −80 °C under reduced pressure. The i.r. spectra of the supernatant liquids were recorded on a JASCO DS-403G grating i.r. spectrophotometer at −80 °C. A KBr cell in an Oxord DN-704 cooling unit cooled with liquid nitrogen was used.

1,2-*Aryl Shift of the* 4,4-*Diarylphthalazin*-1(4H)-*one*. (**3**)—A solution of LTA (2.22 g, 0.005 mol) in anhydrous CH_2Cl_2 (30 ml) was added to a solution of a 4,4-diaryl-3,4-dihydrophthalazin-1(2*H*)-one (**2**) (*ca.* 0.005 mol) in anhydrous CH_2Cl_2 (200 ml) at −80 °C during 30 min. The mixture was stirred for an additional 3 h at this temperature. A solution of TFA–CH_2Cl_2 (1 : 2) (30 ml) was then added at −80 °C. After warming to room temperature, the solution was washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on alumina, and the product was identified. Experimental details for the formation of (**13b—f**) *via* (**3b—f**), and the physicochemical data for compounds (**13b—f**), are given in Supplementary Publication No. SUP 23992 (7 pp.).*

Kinetic Measurements of Nitrogen Elimination of 4,4-*Diarylphthalazin*-1(4H)-*ones* (**3**).—The apparatus consisted of a 200 ml flask with stirring capable of causing vigorous agitation of the mixture immersed in an acetone-bath maintained at the desired temperature (±0.5 °C). The flask was fitted with a glass tube, containing a stopcock-regulated support for the sample vial. The glass tube was connected by Tygon tubing to a gas burette.

In the flask was placed a solution of a 4,4-diaryl-3,4-dihydrophthalazin-1(2*H*)-one (**2**) (0.0015 mol) in anhydrous CH_2Cl_2 (100 ml) at −80 °C. LTA (0.67 g, 0.0015 ml) was added to the solution. A solution of tartaric acid (0.68 g, 0.0045 mol) in MeOH–CH_2Cl_2 (1 : 1; 20 ml) was added. The temperature of the mixture was raised to −50 °C (±0.5 °C). The rate of nitrogen evolution was measured by the displacement of water in the gas burette. Several minutes were required for the reaction mixture to regain thermal equilibrium, so pressure readings were not started until 5—10 min had elapsed. For results, see Table 2.

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* For details of Supplementary Publications see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 2.*, 1984, Issue 1.

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