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SIX-MEMBERED CYCLIC α-MONOCARBONYL AZO-COMPOUNDS; A NOVEL REARRANGEMENT OF 4,4-DISUBSTITUTED 1(4H)-PHTHALAZINONE TO 3,4-DISUBSTITUTED-1-OXIDOPHTHALAZINIUM BETAINE

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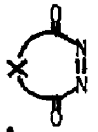
Sammary: The characterization (IR) and evaluation of the reactivity (MO calculation) on one series of six-memebered cyclic α-monocarbonyl azo-compound are presented. A competitive process involving a novel acid catalyzed rearrangement and the nitrogen extrusion is also described.

Several cyclic α,α'-dicarbonyl azo-compounds, A, are well known to serve as excellent dienophiles in the Diels-Alder reaction[1] and cyclic azo-compounds, B, in general, undergo the nitrogen extrusion thermally or photochemically to give rise to diradical species, providing an important method for generating carbon-carbon bonds, through which various size cyclic molecules have been sythesized. In contrast, relatively little is known of cyclic α-monocarbonyl azo-compounds, C. The only well-investigated systems are 3-indazolone, 1[2] and 3-pyrazolones, 2[3], and six-membered cyclic α-monocarbonyl azo-compound is not yet known[4], although one such compound i.e. 4,4-disubstituted-1(4H)-phthalazinone, 3a, has been postulated in our previous communication for the intermediacy of the formation of 4,4-disubstituted-3,4-dihydro-1(2H)-phthalazinone, 4a, t the azulenone derivative.[6] And also, several 4,4-disubstituted-1(4H)-naphthalenones have been shown to undergo the acid-catalyzed rearrangement to phenol derivative[7] and no structurally relat heterocyclic dienones have yet been shown to undergo an analogous rearrangement.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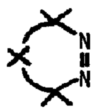
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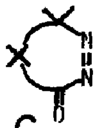
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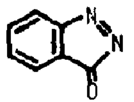
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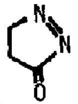
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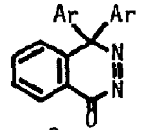
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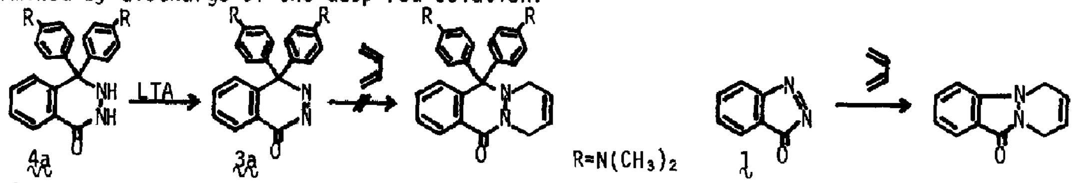
In view of currently increasing interest in the reaction of cyclic azo-compounds and the diradical species derived from such compounds, it would be of interest to explore the nature and reactivity of six-membered α-monocarbonyl azo-compound, which bears the both partial moiety of th above azo-compounds, A and B, and would be an essentially new class heterocyclic molecule. We wish to report here the characterization of one such series of 4,4-diaryl-1(4H)-phthalazinone, 3, and the acid catalyzed rearrangement involved in 3, resulting in the novel formation of 3,4-diary 1-oxidophthalazinium betaine.

Low temperature oxidation (-78°) of 4a[8] with lead tetraacetate in the presence of triethylamin in methylene chloride yielded a deeply colored solution, which after the precipitated solid was filtered off was concentrated to about half volume at -78°. The infrared spectrum of the soluti thus obtained showed at -80° the strong carbonyl stretching band at 1715 cm^{-1}, which is entirely consistent with the assigned structure, 3a, on the basis of its comparison with that (1665 cm^{-1}) o the carbon analog; 1(4H)-naphthalenone.[9,10]

The compound 3a in methylene chloride is stable below -50° at least overnight and probably longer. Treatment of 3a with butadiene and other various kinds of dienes at -70° overnight gav no detectable adducts in the reaction thus far investigated. This is a sharp contrast to the similar treatment of 3-indazolone 1, which reacts with butadiene instanteneously on mixing as determined by discharge of the deep red solution.[2]



4a 3a R=N(CH$_3$)$_2$ 1

Among several possible factors for this difficulty in the formation of the Diels-Alder adduct to assess the influence of the structural change between the two systems, we have carried out th MO calculations on 3-indazolone, 1, and 1(4H)-phthalazinone, 5, by CNDO/2 method.[12] The frontie molecular orbital coefficients and energies (Figure 1), and the total atom charges (Figrue 2) ar shown.

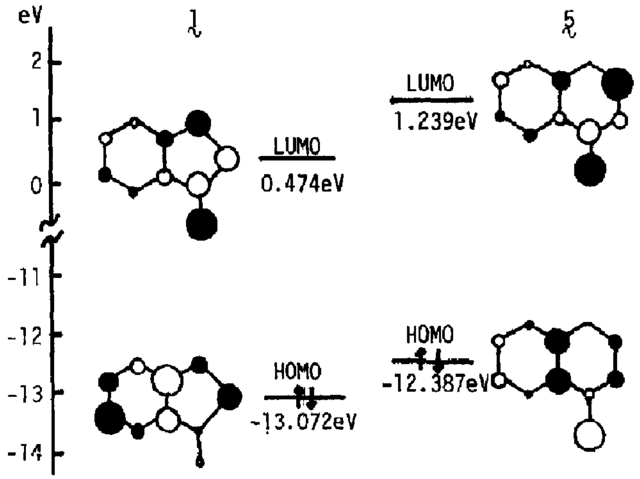


Figure 1. Energy levels and FMO coefficients by CNDO/2

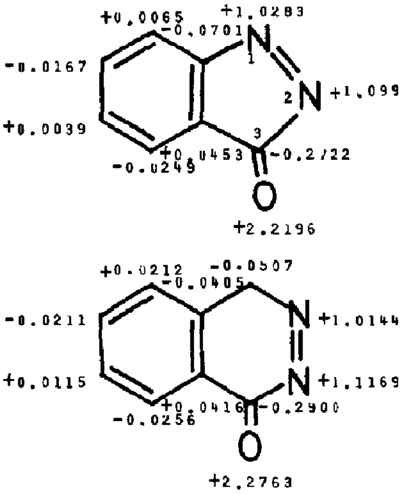
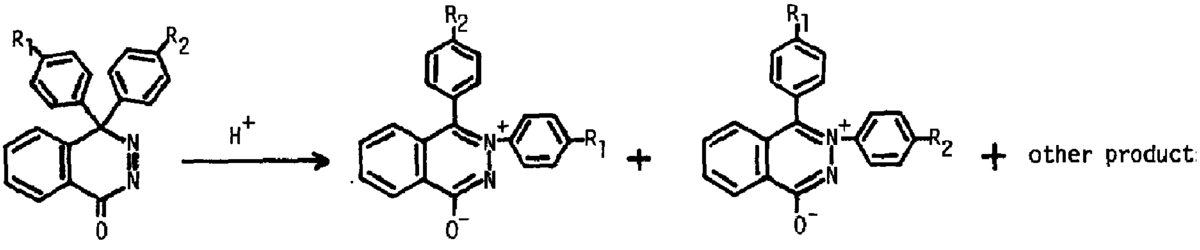


Figure 2. Total Atom Charge

Inspection of Figure 1 demonstrates that although LUMO of the both substrate is very low-lyin in energy, the LUMO energy level of 1 is further lower than that of 5 by 0.765 eV, and thus 1 should be of greater dienophilicity, since the predominant frontier molecular orbital interactio in a Diels-Alder reaction with normal electron demand involves the LUMO of dienophile. The dif ence in magnitude of LUMO coefficients at the azo function of 5 ($C_3^2-C_2^2=0.129$) is greater than the same difference for 1 ($C_1^2-C_2^2=0.045$) so that the Diels-Alder reactions of 5 should be more regioselective than those of 1.

Furthermore, the large LUMO coefficient at N_3 on 5 is indicative of the inherent 1,2-migrator aptitude of the adjacent aryl group. In view of the distribution of the calculated total atom charges on 5 shown in Figure 2, one might expect that preferential protonation would occur at th site of the carbonyl oxygen atom, resulting in a lowering of its LUMO energy to a large extent. The efficient 1,2-aryl migration, therefore, could be furnished in strong acidic media.

With a view to examining such a possibility, TFA-CH_2Cl_2(1:2) solution was added at -78° to each solution containing **3a** and several other derivatives, **3b-d**, prepared from the corresponding **4**[8] in a similar manner as for **3a**. The resulting solution was slowly warmed up to room temperature, and there were obtained 3,4-diaryl-1-oxidophthalazinium betaine derivatives, **6** and **7**, in each reaction in addition to other products resulted from its nitrogen elimination,[6,13] providing a new synthetic method for these betaine derivatives. The structures of **6** and **7** rest on their respecti spectral properties[14] and the results of these reactions are summarized in Table I.



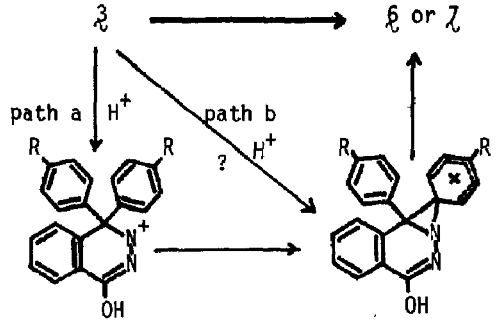
3 **6** **7**

Table I

Substrate	Product Ratio %		products from nitrogen elimination
	6	**7**	
3a: $R_1=R_2=N(CH_3)_2$	8.7	—	91.3
3b: $R_1=N(CH_3)_2$, $R_2=OCH_3$	22.8	10.7	66.5
3c: $R_1=N(CH_3)_2$, $R_2=H$	55.8	0	49.2
3d: $R_1=R_2=OCH_3$	56.3	—	43.7

The special feature of these results is that the yield of the betaine formation seems to be inversely proportional to ease of the nitrogen extrusion, i.e. instability of the starting 1(4H)-phthalazinones, indicating that 1,2-aryl migration occurs competitively around the temperature where the nitrogen elimination also occurs. In fact, when the solution of **3a** with an addition of TFA was allowed to stand at -78° for a prolonged period (overnight) and then quenched with sodium methoxide at low temperature, no detectable betaine was obtained, confirming that 1,2-aryl migrati does not occur at so low a temperature under the reaction condition used. The substituent effect for the relative migratory aptitude, therefore, should not be compared to each other among reactio based on the yield of the betaine formation, but can be done in one molecule based on the ratio of the two betaine formation, as in the case of **3b** and **3c**, which seems to be parallel to those shown in the univalent nitrenium ions ($C{=}N^+$) or nitrenes ($C\text{-}\ddot{N}$).[16] It thus appears likely that the beta formation could involve the divalent nitrogen cation species; nitrenium ions, although from the present data it is not conclusively evident whether such a divalent nitrenium ion actually occurs as a discrete entity (path a) or its formation is prevented by migration in concert with the protonation (path b).

The divalent nitrenium ions, which are isoelectronic with carbene species, have received only a very limited investigation, although the pioneering studies of Gassmann and co-workers about a decade ago provided its elegant confirmation under a solvolytic condition.[17] Further studies on such interesting mechanistic implications are in progress.



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4. In the literature, one example of such compounds, i.e. 1(4H)-phthalazinone, has been repor depicting as an equibrium mixture with 1(2H)-phthalazinone.[5] Such a depiction, however, must be misleading, since the procedure described is the common and conventional method fo the synthesis of 1(2H)-phthalazinones, and even though it should be formed during the reac it must isomerize to 1(2H)-phthalazinone with great ease.
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10. Replacement of the carbon double bond by azo function causes an increase in the carbonyl stretching frequency of about 50 cm^{-1} as deduced by the comparison of 3-indazolone (1790 with 1-indenone (1737 cm^{-1})[11].
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12. The standard bond lengths were used for the calculation parameters. The detailed geometr employed will be presented in a full paper.
13. Focussing our attentions on the betaine formation, we defer the discussions of the structu identification on these compounds, which will be reported in a full paper.
14. Each elemental analysis and mass spectrum confirms that the product is an isomer of **3**. A in agreement with the structure **6** and **7**, each product shows absence of carbonyl absorptic in the IR spectrum between 1610-2000 cm^{-1} as well as the absence of -NH or OH absorption i the 3100-3600 cm^{-1} region. The UV spectra show absorptions characteristic of phthalazini betaines.[15]
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