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1-OXIDO-3-PHENYLPHTHALAZINIUM: CYCLOADDITIONS AND NOVEL REARRANGEMENTS [1]

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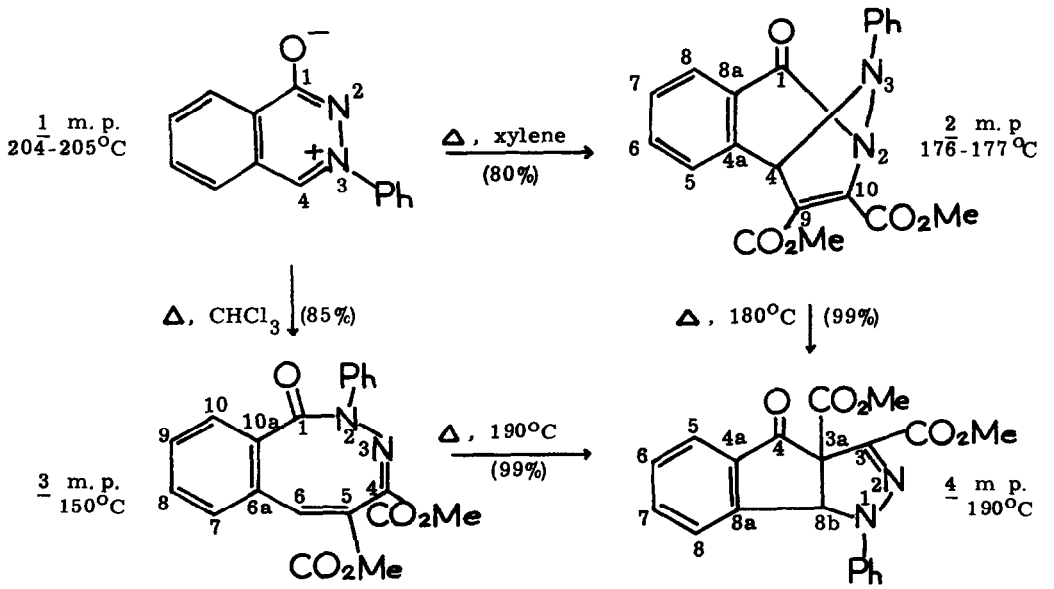
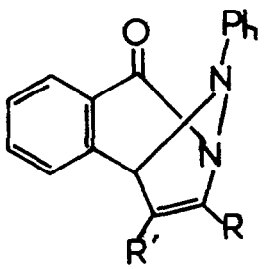
3-Methyl-1-oxidophthalazinium undergoes 1,3-dipolar addition with acetylenes[2] similar to those given by 1-substituted-3-oxidopyridiniums.[3] We have now unravelled the more complex behaviour of 1-oxido-3-phenylphthalazinium (1). Betaine 1 yields normal adducts[4] with styrene and diphenylacetylene. However, whereas betaine 1 with dimethyl acetylenedicarboxylate gives the normal adduct 2 by refluxing in xylene, use of chloroform as solvent affords the ring expanded product 3. On heating in the absence of solvent, both 2 and 3 are converted to a third isomer 4, at a temperature of 180°C.



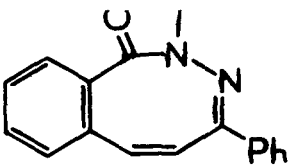
The structures 2 3 and 4 were elucidated by spectral methods. Adduct 2 shows $\nu C{=}O$ at 1715 cm^{-1} (amide) and 1755 cm^{-1} (unsaturated ester) with the bridgehead proton at δ6.26. By contrast, adduct 3 discloses unsaturated ester $\nu C{=}O$ at 1730 cm^{-1} together with amide $\nu C{=}O$ at 1650 cm^{-1}, and the 1H singlet has moved downfield to δ8.24. Adduct 4 disclosed three distinct carbonyl absorptions: saturated ester (1750 cm^{-1}) unsaturated ester (1735 cm^{-1}) and ketone (1705 cm^{-1}), together with the bridgehead proton singlet at δ6.28.

Reaction of betaine 1 with phenylacetylene gave, in refluxing o-dichlorobenzene, the two normal cycloadducts 5 and 6; however, in refluxing xylene, 5 (10%) was produced with the abnormal product 7 (75%). Adduct 5 showed $\nu C{=}O$ at 1710 cm^{-1} with an AB pattern in the NMR spectra at δ6.02 and 4.74, J 9 Hz. Adduct 6 disclosed $\nu C{=}O$ 1715, with two 1H singlets at δ6.75 and 5.70. The diazocine 7, the structure of which is secured by X-ray analysis (Fig. 1), has the amide $\nu C{=}O$ at 1650 cm^{-1} with an AB pattern one half of which was visible at δ6.60, J 11 Hz; the other proton originally at ca. δ8.0 became visible with J 11 Hz when $Pr(fod)_3$ was added to the solution. On sublimation, at 200°C, diazocine 7 gives a second tricyclic derivative 8, characterised by its X-ray analysis (Fig. 2).



5 R = Ph, R' = H

6 R = H, R' = Ph



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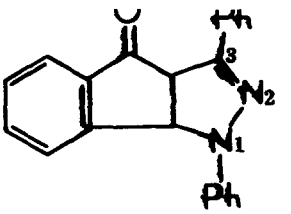

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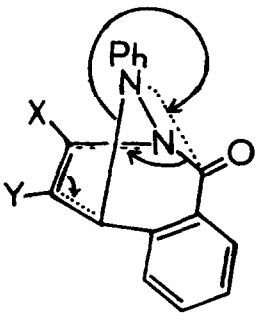
3a, 8b-Dihydro-1, 3-diphenylindeno[1, 2-c]pyrazol-4-(1H)-one (8) is monoclinic, space group $P2_1/c$, Z = 4; at -40°C, a = 11.017 (3), b = 9.386 (2), c = 16.222 (2) Å, β = 107.16(1)°. The N(1)-N(2) and N(2)-C(3) bond lengths of 1.373 Å and 1.304 Å respectively, are indicative of extensive conjugation in the phenyl-N(1)-N(2)-C(3)-phenyl moiety.

Further confirmatory evidence for our structures is afforded by various transformation products. Thus 4 on catalytic hydrogenation gives a dihydro derivative, whereas 7 forms a tetrahydro compound, both of which show the expected IR and NMR spectral characteristics.[5]

The diazocines 3 and 7 are formally analogues of benzocyclooctatetraene, the X-ray determination shows that the eight-membered ring has the 'tub' conformation[6] and the C(1)-N(2) bond possesses some double bond character owing to conjugation with the carbonyl group. 2, 4-Diphenyl-2, 3-benzodiazocin-1(2H)-one (7) is triclinic, space group

PI, Z = 2; at -40°C, a = 9.753 (2), b = 11.116 (4), c = 9.202 (2) Å, α = 113.12 (2), β = 103.23 (2), γ = 102.07 (2)°.[7]

The mechanisms of these rearrangements are not yet clear. The formation of isomeric cycloadducts by heating in different solvents may be merely a consequence of the different refluxing temperatures. The diazocines 3 and 7 could be formed from the normal cycloadducts 2 & 5 by electrocyclic reactions of type 9; this would be similar to the mechanism postulated by Padwa et al.[8] for the conversion of adduct 10 into the azocine 11. The formation of the abnormal tricyclic derivatives 4 and 8 could then be explained by 1,3-acyl shifts in 2 and 5 respectively. However, another possibility is that adducts of type 2, 3 and 4 are interconverted via species 12 which by a 1,2-shift of the acyl group can yield 2, by electrocyclic ring opening can yield 3, and by 1,3-shift of the acyl group can give 4.



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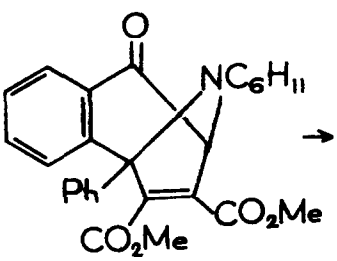
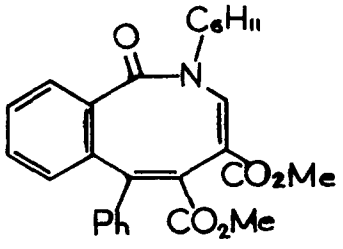
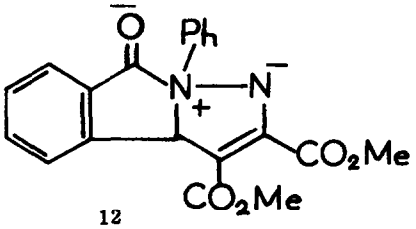




10 11



12

Rearrangements 2 → 4 and 3 → 4 are indicative of the rich chemistry of conjugated heterocyclic medium rings, an area which we are actively pursuing.

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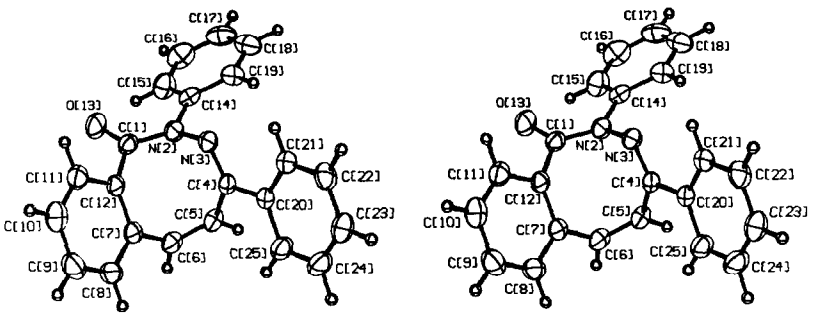

FIGURE 1. Stereodrawing of a molecule of 2,4-diphenyl-2,3-benzodiazocin-1(2H)-one, compound 7, with the atom-numbering scheme.

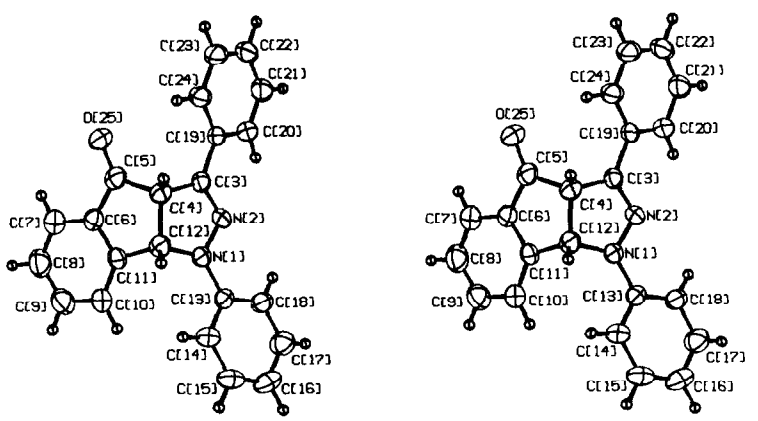

FIGURE 2. Stereodrawing of a molecule of 3a,8b-dihydro-1,3-diphenylindeno[1,2-c]-pyrazol-4(1H)-one, compound 8, with the atom-numbering scheme.