Synthesis of 3,4-Diazacyclopentadienone System

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Summary The synthesis of the new ring system, 2,5-diphenyl-3,4-diazacyclopentadienone (**1**) has been achieved; it exhibits strongly electron-deficient behaviour in its formation of addition products with alkenes, alkadienes, and phosphines and in its oxidation of hydrogen chloride.

THREE of the four possible diaza-substituted cyclopentadienone systems are known.[1] The fourth, 3,4-diazacyclopentadienone is known only as the electronically dissimilar *N*-oxides such as (**2**) and (**3**).[2] Attempts[2] to reduce (**2**) to (**1**) were unsuccessful.

We now report the synthesis of (**1**) in 85% yield by oxidation of 4-hydroxy-3,5-diphenylpyrazole[3] using lead dioxide in dry ether. It is a purple solid, m.p. 110° (decomp.), dark red in solution, λ_{max} (ether) 252 (ϵ 13,000), 335sh (400), and 433 nm (900). This electronic spectrum resembles the spectra of the cyclopentadienones (**4**)[4] and (**5**)[5]. In concentrated sulphuric acid, (**1**) and (**4**) absorb at 565 and 568 nm, respectively, and spectra run in sulphuric acid–acetonitrile exhibit, in both cases, isosbestic points indicating simple equilibria between the cyclopentadienones and their protonated forms. The i.r. spectrum of (**1**) in ether shows a strong carbonyl band at 1755 cm^{-1}, whereas in the solid phase (KBr disc or Nujol) the $C=O$ band at 1740 cm^{-1} is so weak that it is only just visible at normal concentrations. The possibility that the structure of (**1**) is modified in the solid state is discredited since solid (**1**) is purple like other cyclopentadienones. Therefore, it appears that the electronic environment in the crystal structure is such that during a vibration of the $C=O$ bond, the change in dipole moment is *ca.* zero and hence the intensity approaches zero.[6]† In solution, (**1**) decomposes rapidly even in the absence of light, and purification must be done by vacuum sublimation rather than crystallization.

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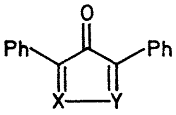
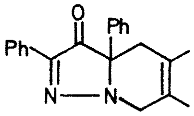
† This low intensity $C=O$ band should be Raman active. However, the Raman spectrum kindly run by Dr. M. Onyszchuk, Department of Chemistry, McGill University, Montreal was unsatisfactory owing to photodecomposition.

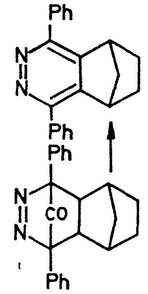
Chemical support for the structure assignment (**1**) was afforded by the preparation of solutions of (**1**) (identified by u.v. spectra) by two additional routes. Firstly, 4-hydroxy-3,5-diphenylpyrazole was oxidised to (**1**) by thionyl chloride or butyl nitrite, both reagents which have been used for an analogous oxidation by Büchi and Lukas.[7] Secondly, (**1**) is produced when 5-hydroxy-3,5-diphenylpyrazolin-4-one[3] is dehydrated with concentrated sulphuric acid.



	X	Y
(**1**)	N	N
(**2**)	N→O	N→O
(**3**)	N	N→O
(**4**)	C–Ph	C–Ph
(**5**)	C–C≡N	C–C≡N

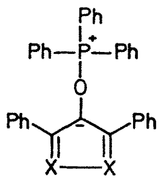


(**6**)



(**7**)

(**8**)



(**9**) X = C–C≡N

(**10**) X = N

In the Diels–Alder reaction, (**1**) adds to electron-rich dienes as a dienophile. An ether solution of (**1**) reacted with 2,3-dimethylbuta-1,3-diene at room temperature to give a 37% yield of (**6**), pale yellow crystals, m.p. 159—160°, ^{1}H n.m.r. (CDCl$_3$) δ 8·20 (m, 2H, aromatic protons near C=N), 7·40 (m, 8H, aromatic), 4·36 (m, 2H, C*H*$_2$–N) 2·70 (AB quartet, 2H, *J* 17 Hz, C–C*H*$_2$–C), 1·63 (m, 6H, C*H*$_3$), λ_{max} (95% EtOH) 270 (ε 17,200) 392 nm (8200), ν_{max} (Nujol) 1680 cm^{-1} (C=O). An analogous cyclopentadiene adduct was obtained as sticky crystals‡ (unstable in solution), ^{1}H n.m.r. (CCl$_4$) δ 8·2—7·0 (m, 10H, aromatic), 6·25 (m, 1H, *H*C=C), 5·91 (m, 1H, *H*C=C), 4·80 (m, 1H, C*H*–N), 3·58 (m, 1H, C$_3$C*H*), 1·95 (AB quartet, 2H, *J* 9 Hz, C*H*$_2$), ν_{max} (Nujol) 1720 cm^{-1} (C=O). These spectral data were considered to be adequate structural proof since they correlated well with the spectra of eight known compounds containing the same structural unit (N–N=CPh–C=O).[8] There have been a few reported[9] examples of 2,3-diazabuta-1,3-dienes undergoing Diels–Alder reactions as the diene component, but it was found that only very reactive dienophiles such as 4-phenyl-1,2,4-triazoline-3,5-dione and cyclobutadiene[10] were effective addends in those cases.

(**1**) also undergoes Diels–Alder additions with alkenes as exemplified by its reaction with norbornylene in dry ether at room temperature. The diazaterphenyl (**7**) is the product isolated (13% yield) which must have arisen by normal [4+2] cycloaddition to give the bridged carbonyl compound (**8**), which then aromatised by loss of carbon monoxide and hydrogen according to a route well-established in cyclopentadienone chemistry.[4] (**7**) exists as colourless flakes, m.p. 230·5—231·5°, ^{1}H n.m.r. (CDCl$_3$) δ 8·20—7·45 (m, 10H, aromatic), 3·73 (m, 2H, 2C*H*'s), 2·14 (m, 2H, C*H*$_2$), 1·63 (m, 4H, C*H*$_2$C*H*$_2$), λ_{max} (95% EtOH) 265 nm (ε 22,500). This reaction appears to be the first example of a 2,3-diazabuta-1,3-diene behaving as a dienophile in the Diels–Alder reaction.

One of the reasons for originating this research project was to discover reactive electron-deficient dienes which would react quickly with electron-rich dienophiles, but slowly with electron-deficient dienophiles according to Sauer's principle[11] of "inverse electron demand." (**1**) fits this description well since it readily reacts with norbornylene, whereas under the same conditions, tetracyanoethylene maleic anhydride, and acrylonitrile are unattacked. A carbocycle exhibiting similar electron-rich-behaviour to (**1**) is (**5**) which readily undergoes [4+2] cycloaddition with cyclohexene.[5]

There is a further resemblance between (**1**) and (**5**) in that both react rapidly with triphenylphosphine at room temperature. In the latter case the adduct (**9**) was isolated. In the former case, a solution of (**1**) in ether was rapidly decolourised by addition of triphenylphosphine, but work-up unexpectedly gave triphenylphosphine oxide and 4-hydroxy-3,5-diphenylpyrazole. These products are rationalized as originating from hydrolysis of the adduct (**10**) by traces of moisture.

Connected with the electron-deficient nature of (**1**) is its strong oxidising power. Extreme care had to be exerted to ensure that solvents were pure since the presence of ethanol or cyclohexene (or probably any other compound with a relatively labile hydrogen) caused (**1**) to be reduced to 4-hydroxy-3,5-diphenylpyrazole. An extreme example of the oxidising power of (**1**) is its ability to oxidise dry hydrogen chloride in ether solution to give molecular chlorine and a quantitative yield of 4-hydroxy-3,5-diphenylpyrazole hydrochloride.

We thank the National Research Council of Canada for financial support

(*Received, March 16th,* 1971; *Com.* 314.)

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‡ All new compounds reported in this communication had satisfactory elemental analysis with the exception of this compound which was not obtained completely pure.

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