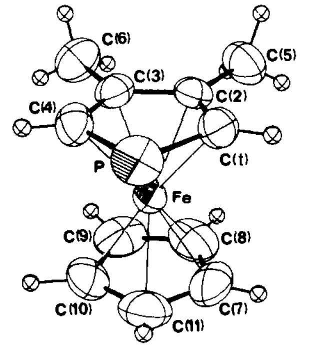
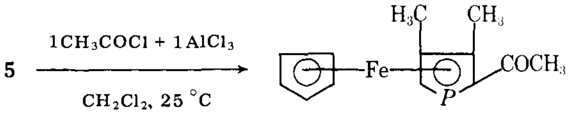


Figure 1. Structure of the phosphaferrocene **5** showing the 50% probability ellipsoids. Selected bond distances (in Å) are: C(1)-C(2), 1.408 (7); C(2)-C(3), 1.414 (6); C(3)-C(4), 1.403 (7); P-C(1), 1.758 (5); P-C(4), 1.768 (5); C(2)-C(5), 1.503 (8); C(3)-C(6), 1.516 (8); C(7)-C(8), 1.378 (12); C(8)-C(9), 1.411 (9); C(9)-C(10), 1.412 (10); C(10)-C(11), 1.393 (10); C(11)-C(7), 1.399 (10); Fe-P, 2.276 (1); -C(1), 2.064 (4); -C(2), 2.046 (4); -C(3), 2.040 (4); -C(4), 2.051 (4); -C(7), 2.046 (6); -C(8), 2.036 (7); -C(9), 2.027 (6); -C(10), 2.039 (5); -C(11), 2.045 (4).

5.25 (overlapping d of m, $J_{H-P} \sim 6$ Hz, Hβ); **5** δ 2.17 (s, CH_3), 3.71 (d, $J_{H-P} = 36$ Hz, Hα), 4.13 (s, C_5H_5). Mass spectra (70 eV, 40 °C; main peaks only): **4** *m/e* 204 (I = 100%, M), 139 (I = 13%, M-C_5H_5), 121 (I = 14%, M-C_4H_4P), 56 (I = 14%, Fe); **5** *m/e* 232 (I = 100%, M), 166 (I = 17%, M-C_5H_6), 121 (I = 8%, M-C_6H_8P), 56 (I = 10%, Fe).

Preliminary experiments have shown that **5** can be selectively acetylated on the phospholyl moiety:



6

The site of acylation was unambiguously established on the basis of the ^1H NMR spectrum of **6**: δ 2.18 (s, $CH_3\beta'$), 2.28 (d, $J_{H-P} \sim 2.6$ Hz, $COCH_3$), 2.43 (s, $CH_3\beta$), 4.03 (d, J_{H-P} = 36 Hz, 1 H, CHP), 4.13 (s, 5 H, C_5H_5).

The chemical data thus clearly suggest a π-aromatic nature for the phospholyl ligand. This nature was unequivocally proved by the x-ray study of **5**.

Suitable crystals of **5** were obtained by vacuum sublimation at 40 °C. They belong to the monoclinic system, space group $P2_1/c-C_{2h}{}^5$) with a = 12.292 (4) Å, b = 10.824 (3) Å, c = 7.831 (2) Å, β = 91,60 (4) °, Z = 4, and ρ_c = 1,48 g/cm^3.

Diffraction data were collected in a $\theta/2\theta$ scan mode using a Picker diffractometer and monochromated Mo Kα radiation. The structure was solved by direct methods[7] and refined to convergence using 1279 reflections having $I \geqslant 3\sigma(I)$. The value for the conventional agreement factor $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ at the present stage of refinement is 0.041.

The structure (Figure 1) consists of discrete molecules in which an iron atom is sandwiched between a π bonded cyclopentadienyl ring and a π bonded phospholyl group so as to attain an eclipsed conformation.

The phospholyl ligand is not strictly planar; the phosphorus atom lies out of the strictly planar four-membered carbon moiety by 0.041 (2) Å away from the iron atom. Selected geometric details are given in the caption of Figure 1.

The planar cyclopentadienyl ring and the planar four-membered carbon moiety $C_4(P)$ of the phospholyl are nearly parallel, the dihedral angle is 3.18°. The iron atom is located somewhat closer to the $C_4(P)$ plane: Fe···$C_4(P)$ = 1.625 (1) Å whereas Fe···C_5H_5 = 1.655 (1) Å.

Acknowledgment. One of us (F.M.) thanks Mrs. Maillet for technical assistance.

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(6) The chromatographed products still contain minute amounts of ferrocene. They can be purified further by recrystallization in methanol at low temperature.
(7) Program MULTAN, P. Main, MM Woolfson, and G. Germain.
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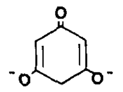
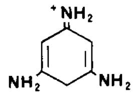
The Dependence of Phenol–Dienone Tautomerism upon the Hydrogen Bonding Characteristics of the Solvent: 3,5-Dipyrrolidinophenol

Sir:

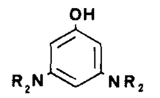
The observation that the dianion of phloroglucinol exists predominately as the cyclohexa-2,5-dienone (**1**),[1] and the monoprotonated form of 1,3,5-triaminobenzene as the analogous form **2**[2] suggests the intriguing possibility that appropriately substituted benzenes may exist preferentially as such a structure in a nonionic state. In the course of his extensive investigations of polyamino benzenes, Effenberger examined a series of 3,5-diaminophenols, **3a–c**, with this point in mind.[3]



1

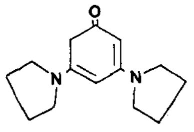


2



a $R_2 = (CH_2)_4$
b $R_2 = (CH_2)_5$
c $R = CH_3$

3



4

However, ^1H NMR spectra of these materials in dimethyl sulfoxide solution showed only aromatic forms present. Strikingly, the ultraviolet absorption reported for 3,5-dipyrrolidinophenol, **3a**, showed a maximum at 370 nm, with an extinction coefficient of 3050 L mol^{-1} cm^{-1} in methanol.[3] We show here that this absorption is characteristic of a cyclohexa-2,4-dienone form, **4**, which may predominate in solvents of appropriate hydrogen-bonding character.

The ultraviolet absorption spectra of **3a** in three solvents are shown in Figure 1. The absorption in dimethyl sulfoxide is that of a phenol, corresponding to the form shown by the ^1H NMR spectrum, but that in water shows a maximum at 375 nm (ϵ = 15 300). As it seemed reasonable to speculate that it is the ability of water to donate a hydrogen bond which stabilizes the carbonyl group of the dienone form, a solvent was sought which retains this ability, while being capable of dissolving enough of **3a** to allow study by NMR spectra. Trifluoroethanol proved to be suitable.[4]

The addition of trifluoroethanol to a deuteriochloroform solution of **3a** caused increasing amounts of olefinic absorption

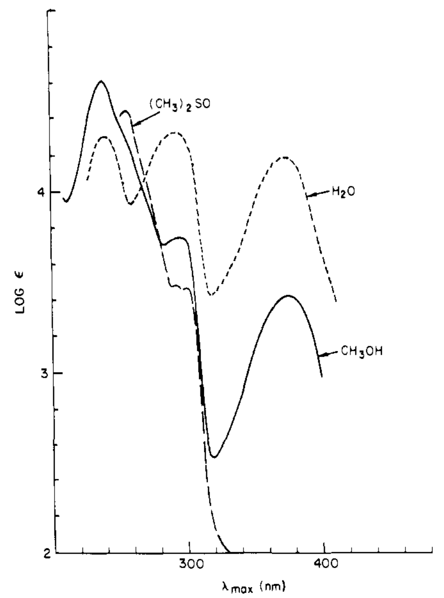


Figure 1. The ultraviolet absorption spectra of **3a** in three solvents.

Table I

Solvent	α^a	β^a	$\alpha - \beta$	E	K
tert-Butyl alcohol	0.44	0.95	−0.51	353	0.021
Isopropyl alcohol	0.68	0.92	−0.24	435	0.026
n-Butyl alcohol	0.71	0.85	−0.14	704	0.043
Ethyl alcohol	0.85	0.77	0.08	948	0.059
Methyl alcohol	0.99	0.62	0.37	2600	0.18
Ethylene glycol	0.79	0.51	0.28	3580	0.27
Water	1.02	0.14	0.88	15300	9.0

[a] Reference 5.

to appear in the ^{1}H NMR spectrum; in 0.2 M CF_3CD_2OH–$CDCl_3$ (10:1) solution only absorption characteristic of the cyclohexa-2,4-dienone **4** could be detected in the ^{1}H NMR spectrum: two broadened singlets at 5.12 and 4.74 ppm, with a methylene singlet superimposed on the broad multiplet of the pyrrolidine rings. In the ^{13}C spectrum, a carbonyl appeared at 183.1 ppm, with four olefinic carbons (164.3, 157.9, 90.7, and 84.7), and a methylene carbon (38.3) among the pyrrolidine signals (48.6, 2C, 48.0 (2C), and 25.1 (4C)). The ultraviolet absorption (λ (max) 370 nm, ϵ 16 000 L mol^{-1} cm^{-1}) and infrared spectrum (1600 cm^{-1}) in this solvent mixture are well suited to **4**.

Recent studies by Taft and Kamlett[5] have provided parameters characterizing the ability of a solvent to donate hydrogen bonds (the hydrogen bond donor (HBD) acidity, α) and to accept hydrogen bonds (the hydrogen bond acceptor (HBA) basicity, β), of an extensive series of solvents. It seems here that each of these two abilities stabilizes one of the two forms, producing competitive effects. We were therefore interested in seven solvents for which both α and β values have been reported. These values and their differences are listed in Table I with the extinction coefficients observed for **3a**, and the corresponding equilibrium constants.[6] Evidently, for **3a** ⇌ **4**,

$$\ln K = -[(G_p - G_c) - (G_\alpha - G_\beta)]/RT$$

where G_p and G_c represent the free energies of the phenolic and carbonyl forms, respectively, in the absence of hydrogen bonding, and G_α and G_β represent the energies lost in the formation of hydrogen bonds in which the hydrogen is donated and received by the solvent, respectively. Although both the extinction coefficient of **4** and the quantity $G_p - G_c$ must vary somewhat in this series of solvents,[7] the correlation coefficient between ln K and $\alpha - \beta$ is 0.95.[8]

Previous studies have shown the importance of intermolecular hydrogen bonding in stabilizing phenols,[9] but a quantitative estimate of the competitive effect observed here has apparently not been reported.[10-12]

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(6) $K = E(\text{obsd})/E(4)/(1 - E(\text{obsd})/(4)$; $E(4)$ is taken as 17 000, from the extinction coefficient observed in trifluoroethanol and the appearance in the ^{13}C spectrum of peaks which apparently represent approximately 5% of the 2,5 dienone form. The predominance of the 2,5-dienone forms of the ions **1** and **2** apparently reflects the superior charge separation of this form.

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(8) Linear regression provides the relation: $\ln K = -2.5 + 4.3(\alpha - \beta)$; the intercept corresponds to $(G_p - G_c) = 1.5$ kcal.

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(10) Crystallographic examination of **3a** indicates that it exists exclusively as the phenol in solid form. R. J. Highet and J. V. Silverton, to be submitted for publication.

(11) Linear regression was performed by MLAB. Cf. G. Knott, "MLAB, an On-line Modeling Laboratory", 4th ed, National Institutes of Health, Bethesda, Maryland, 1974.

(12) We are indebted to a referee for the observation that the correlation confirms that hydrogen bonding in the dienone is primarily by solvent to oxygen. The competitive hydrogen bonding to the amine nitrogen, which would destabilize the dienone by lessening >NC═CC═O resonance, is evidently not significant.

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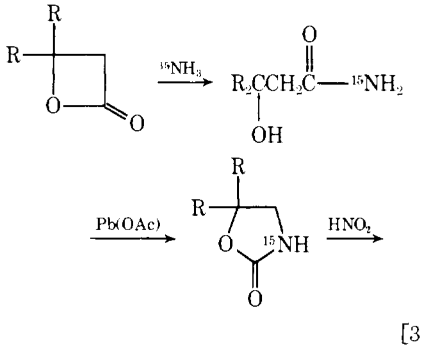
Pathways from Nitrosooxazolidones to Vinyl Azides

Sir:

Reactions of 5,5-dialkyl-*N*-nitrosooxazolidones (**1**) with base and a variety of nucleophiles have been studied.[1-5] The formation of vinyl iodides, azides, isothiocyanates, phosphonates, and ethers was explained by assuming that the vinyl cation (**5**) reacts with nucleophiles.[2] Our interest in azo coupling by aliphatic diazonium ions[6] induced us to reinvestigate the reaction of **1** with azide. We report here on the dissection of various mechanistic pathways from **1** to vinyl azides.

[3-^{15}N]-**1** was prepared as shown in Scheme I.[7] Reaction

Scheme I



[3-^{15}N]-**1a**, R = CH_3
b, R,R = $(CH_2)_5$