

like bonding of the piperidine-derived radicals in III is somewhat exceptional.¹⁸

Trace quantities of the three compounds were dissolved in aqueous glycine-hydrochloric acid or glycine-NaOH buffers (ionic strength 0.1, pH values of 2.6 and 10.8, respectively). Although we report here on spectra from two carefully prepared aqueous buffered solutions, other spectra showed no sensitivity to buffers of different composition, ionic strength, or to the absence of buffer in solutions of reasonable acidic or basic pH. The carboxyl groups of biradicals I and III ionize completely ($-\text{COO}^-$) at basic pH but not at acid pH. Conversely, the dimethylamine group of II is ionized at acid pH.

First-derivative esr spectra (Figure 1) were taken in a Varian E-3 spectrometer equipped with temperature controller. The esr spectra of mononitroxide radicals exhibit three lines which arise through hyperfine interaction with the abundant ^{14}N nuclei.¹⁴⁻¹⁷ For short correlation times, $\tau_c \sim 10^{-11}$ sec, the lines have equal peak heights, while longer correlation times bring about departures from equality.^{16,17} Nitroxide biradicals exhibit a five-line esr spectrum with relative intensity 1:2:3:2:1 when the spin-spin exchange interaction (measured in frequency units) is large in comparison with the hyperfine frequency. Intermediate strengths of exchange interaction lead to spectra intermediate between these limiting cases.^{1,8} Thus the esr spectra reflect intramolecular pairwise spin exchange by the presence of the second and fourth weaker, broader lines. Our findings may be summarized by the following statement: *ionization augments the spin exchange in biradicals I and II, but decreases the exchange in biradical III.*

Examination of CPK space-filling models of biradicals I-III, with particular attention to the conformational changes which may accompany electrostatic repulsion of the ionic charges, suggests the probabilities of the conformations favoring direct overlap and provides the basis for the following interpretation of our findings.

When biradicals I and II are predominantly un-ionized, spin exchange is partly hindered because conformations in which the ionizable groups are proximal, and the nitroxide groups are distal, contribute appreciably to the partition function. In doubly ionized biradicals I and II, where the charged groups are mutually repelled, the aforementioned conformations become less likely, and thus the probability of spin exchange encounters of the nitroxide subunits increases. The pH effect is smaller in II than in I because the separation between the ionizable extremities of II is larger than between those of I.

The mutual repulsion of the *ionized* carboxylic groups of III constrains the planes of the nitroxide-bearing piperidine rings to be parallel, at a distance of 7.6 Å. Under this condition of constraint, only the *cis* conformation, in which parallel planes of the rings are juxtaposed, may give rise to exchange. The observation of no exchange (Figure 1f) indicates to us that at the 7.6-Å distance the overlap of the peak radial densities of the unpaired π orbitals is too small to permit observable spin exchange. At acid pH, when III is predominantly un-ionized, the rings are no longer constrained to be

(18) A. Rassat and P. Rey, *Bull. Soc. Chim. Fr.*, 816 (1967);

parallel and conformations in which the nitroxide-bearing extremities of the rings are in close contact become likely (Figure 1e).

Deeper understanding of the relation between direct exchange and molecular geometry would be achieved by computer simulation of biradical conformations in the spirit of the work of Levinthal, *et al.*¹⁹

We have in progress measurements to determine the electrostatic energy of the doubly ionized biradicals by determining the temperature dependence of the spin exchange.

With this information it should be possible to use appropriately constructed biradicals to measure conformational changes of molecules and membranes to which they are suitably coupled.^{10,17}

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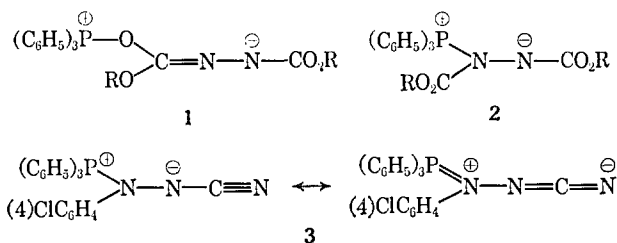
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Structure and Cycloaddition of a Quasi 1,3 Dipole from Triphenylphosphine and 4-Chlorobenzene Diazocyanide

Sir:

Structures 1^{1-3} and 2^4 have been proposed for the betaine derived from triphenylphosphine and azodicarboxylic ester. Recently we found the cycloaddition reactions of this quasi 1,3 dipole to be reconcilable only with 2^5 . We now demonstrate structure 3 for an analogous, somewhat more stable, betaine from triphenylphosphine and 4-chlorobenzene *anti*-diazocyanide.

Combination of the components in dry ether led to the precipitation of pale yellow crystals (93%, decomposes above 80°) which analyzed correctly for 3 . The stretching frequency of the cyanamide anion was found at 2098 cm^{-1} (KBr); the ^{31}P chemical shift, -32.2 ppm (benzene; 85% H_3PO_4 external standard), suggests a phosphonium ion. The betaine 3 is stable for a few hours at 20° in the crystalline state; in solution it deteriorates rapidly.



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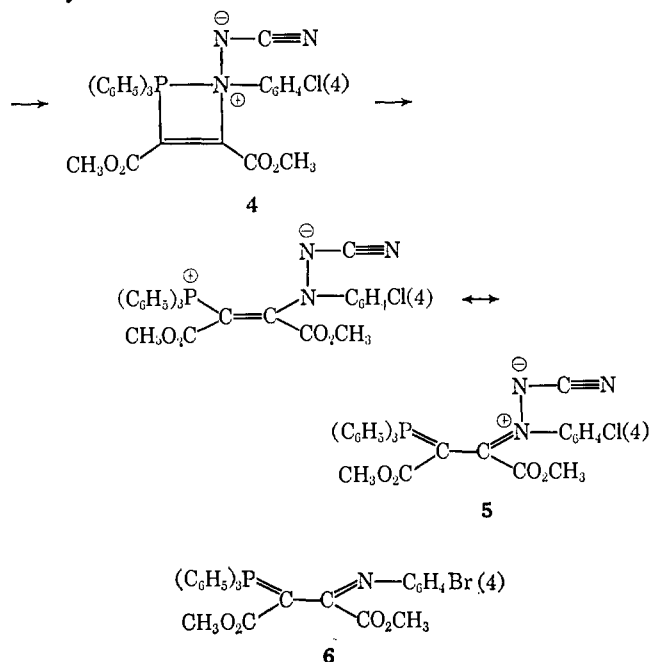
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(5) E. Brunn and R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, 8, 513 (1969).

Dimethyl acetylenedicarboxylate reacts with **3** to give an orange-red 1:1 adduct in 63% yield⁶ (mp 199–206 dec); ³¹P nmr –16.7 ppm (CHCl₃). The ir frequency at 2130 cm⁻¹ (st, KBr) is attributable to a cumulated double bond system. Of the two ester bands at 1728 and 1657 cm⁻¹, the latter reveals strong electron-releasing conjugation. Structure **5** is the result of an X-ray analysis. The *cis* arrangement of P and N functions suggests an initial 2 + 2 cycloaddition⁷ of the imminophosphorane **3** to give **4** which is followed by P–N bond cleavage to form the zwitterion **5**. The analogy with the formation of **6** from N-(4-bromophenyl)iminophosphorane and dimethyl acetylenedicarboxylate^{8,9} is obvious; structure **6** was elucidated by X-ray diffraction as well.^{10,11}



X-Ray intensity data from a single crystal of **5** were collected with an automatic diffractometer with Cu K α radiation (λ 1.5418 Å) using the θ - 2θ scan technique. The material crystallized in the triclinic system, space group P $\bar{1}$, with cell parameters $a = 11.864$ Å, $b = 12.582$ Å, $c = 11.672$ Å, $\alpha = 110.2^\circ$, $\beta = 117.7^\circ$, and $\gamma = 68.5^\circ$, and two molecules in the unit cell. The symbolic addition procedure¹² for phase determination led directly to the structure. Least-squares refinement with isotropic thermal parameters has resulted in an R factor of 14%. A difference map indicates strong anisotropic motion at the C-1 atom and the peripheral atoms of the phenyl rings. Refinement with 5000 independent reflections and anisotropic thermal parameters is in progress.

The bond lengths (Figure 1) are generally the ones expected for the resonance hybrid **5**. The P–C distance of 1.75 Å corresponds to 1.70 Å in **6**.¹¹ There is a twist of 33° between the bonding planes of the two

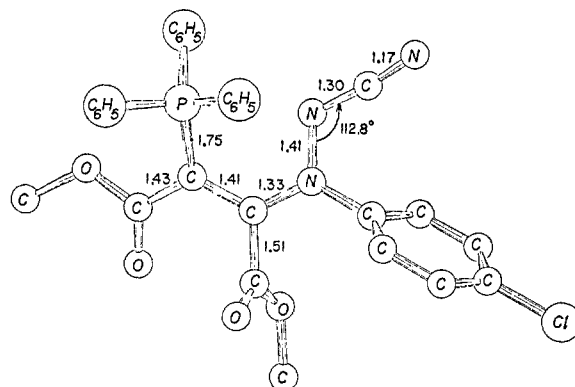


Figure 1. Perspective drawing of structure **5**.

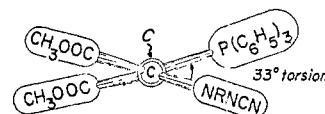
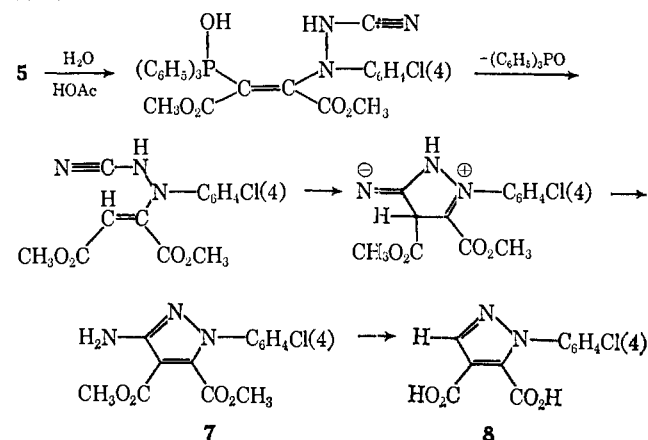


Figure 2.

central carbon atoms of the maleic ester moiety (Figure 2). The C=N⁺ length of 1.33 Å may be compared with 1.32 Å in diazomethane.¹³ The CN bonds of the cyanamide anion part (1.17 and 1.30 Å) are not much different from the values 1.18 and 1.33 Å found for cyanamide itself.¹⁴

Hot 90% acetic acid hydrolyzed **5** to the pyrazole derivative **7** (mp 123–124°, 44% yield). Deamination and ester hydrolysis transformed **7** into 1-(4-chlorophenyl)pyrazole-2,3-dicarboxylic acid (**8**, 79%, mp 194–195° dec) which was independently synthesized.

Scheme I



Originally, the nature of the hydrolysis product **7** obscured rather than clarified the structure of **5**. A rationalization of the deep-seated change is given in Scheme I.

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