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Structures of Some Condensation Products of α-Dicarbonyl Compounds and Tris(amino)phosphines in Solution

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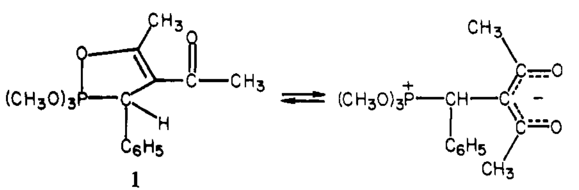
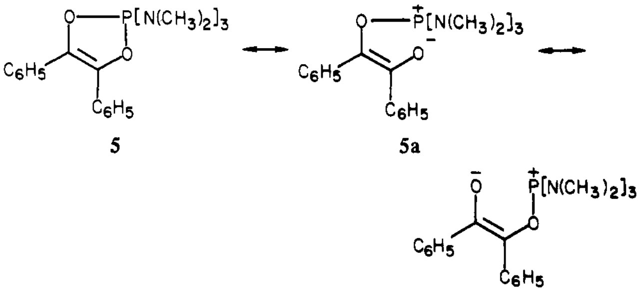
Abstract: Several condensation products of tris(amino)phosphines and α-dicarbonyl compounds have been studied by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The condensation product of tris(dimethylamino)phosphine and benzil has been shown to be pentacoordinated. The same phosphine and diethyl ketomalonate gave an adduct which undergoes facile ionization above room temperature to a zwitterion. The adduct between tris(dimethylamino)phosphine and phenanthrenequinone is also pentacoordinated. Several other pentacoordinated mixed aminooxyphosphoranes were also studied.

The condensation of trivalent phosphorus compounds with α-dicarbonyl compounds and α,β-unsaturated carbonyl compounds has been shown to be a general route to a wide variety of pentacoordinated phosphorus compounds, many of which have been the subject of structural investigations.[1] It has also been shown that these substances often ionize on heating; the equilibrium between **1** and **2** can be observed by ^{1}H NMR above 155 °C.[1d,e]



1 2

A series of compounds has been prepared by condensation of a number of tris(amino)phosphines with α-dicarbonyl compounds.[1d,2] The structures of these substances have been examined by ^{31}P NMR spectroscopy. The chemical shifts of these materials vary from ca. 42 ppm upfield of 85% phosphoric acid, reported then as positive but now as negative, to ca. 39 ppm downfield. Interestingly only one compound, **5**, formed from tris(dimethylamino)phosphine (**3**) and benzil (**4**) exhibited an intermediate absorption at δ -13 in methylene chloride. This shift was found to be both solvent and concentration dependent. In hexane the absorption was found at δ -30.2.



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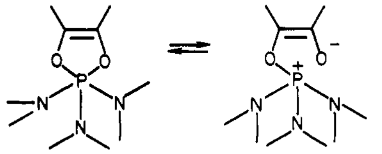
It was suggested,[1d,2a] and quite reasonably so, that those substances which absorb at the maximum values upfield from 85% phosphoric acid are phosphoranes **6**, perhaps in rapid equilibrium with a small amount of zwitterion **7**. Conversely those substances whose resonances were found far downfield were assigned structures **7**, with the proviso that they might be in rapid equilibrium with a small amount of **6**. Finally the benzil-tris(dimethylamino)phosphine condensation product, **5**, was regarded as a rapidly equilibrating mixture of **6** and **7** when the solvent was methylene chloride. In hexane, **6** was suggested as being by far the major component. In no case were separate resonances observed for **6** and **7** and thus the equilibration must be rapid on the ^{31}P NMR time scale. In the extreme case of upfield and downfield shifts, one component might be present in such a small amount that it cannot be detected.



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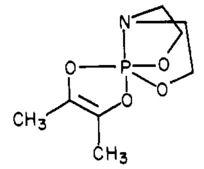

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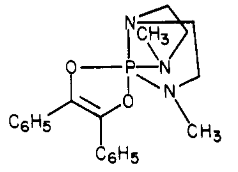

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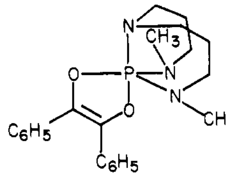

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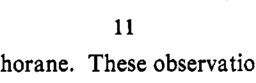

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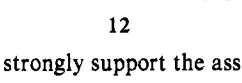

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More recently compounds, **8**, **9**, and **10**[3] have been prepared and their variable-temperature ^{1}H and ^{13}C NMR spectra have been recorded. Compounds **8** and **10** undergo intramolecular ligand reorganization at room temperature while **9** is rigid on the NMR time scale. The ^{31}P NMR chemical shift of **8** was found to be δ -3, which is at quite a low field for a phosphorane. The coupling constants between phosphorus and the olefinic carbons of the ring and the methyl group carbons are virtually identical with those of **11**, a substance which is well-characterized as a phosphorane. These observations strongly support the assigned

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[1] (a) Emsley, J.; Hall, C. D. "The Chemistry of Phosphorus"; Wiley: New York, 1976; Chapter 6. (b) Sheldrick, W. S. *Top. Curr. Chem.* **1978**, *73*, 1–49. (c) Luckenbach, R. "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements"; G. Thieme: Stuttgart, 1973. (d) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168. (e) Westheimer, F. H. *Ibid.* **1968**, *1*, 70. (f) Holmes, R. R. *Ibid.* **1979**, *12*, 257.

[2] (a) Ramirez, F.; Patwardhan, A. V.; Kugler, H. J.; Smith, C. P. *Tetrahedron* **1968**, *24*, 2275. (b) *J. Am. Chem. Soc.* **1967**, *89*, 6276, 6283. (c) Ramirez, F.; Gulati, A. S.; Smith, C. P. *J. Org. Chem.* **1968**, *33*, 13. (d) Ramirez, F.; Patwardhan, A. V.; Smith, C. P. *J. Am. Chem. Soc.* **1965**, *87*, 4973. (e) Burgada, R. *C. R. Hebd. Seances Acad. Sci.* **1964**, *258*, 4789

[3] (a) Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Huang, C.; Tseng, K. *J. Am. Chem. Soc.* **1980**, *102*, 5073. (b) *Ibid.*, in press.

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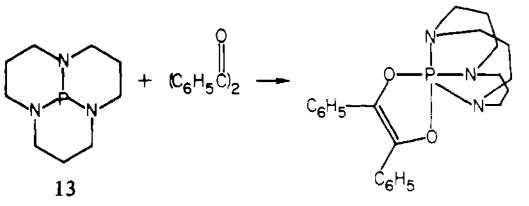
structure. The ^{31}P NMR chemical shifts of **9**, δ −30.6, and **10**, δ −37.1, suggest that they are phosphoranes. The couplings between phosphorus and the olefinic carbons of the ring as well as the ipso carbons of the benzene rings were found to be very similar, within ca. 2 Hz, to those found for **12**, a material which is pentacoordinated. With the ^{13}C NMR spectra of **12** as a reference it seemed of interest to probe the structures of other phosphorus compounds derived from α-dicarbonyl compounds and various tris(amino)phosphines.

Results and Discussion

The condensation product, **5**, of **3** and **4** was the first compound investigated. This material in hexane has a single resonance in its ^{31}P NMR spectrum at δ −30.5, which is essentially the same as reported by Ramirez et al.[2a] The ^{13}C NMR spectrum shows that the olefinic carbons are equivalent, δ 134.16 ($J_{POC} < 1$ Hz) and the ipso carbons of the benzene rings are also equivalent, δ 133.05 ($J_{POCC} = 11.6$ Hz). For comparison, the same two pairs of carbons of **12** are found at δ 133.73 ($J_{POC} = 2.1$ Hz) and δ 131.35 ($J_{POCC} = 13$ Hz). The ortho, meta, and para carbons of **5** were found as single resonances and the methyl group carbons bonded to nitrogen were found as a simple doublet. These data are in accord with a phosphorane structure for **5** and they require that **5** be undergoing rapid intramolecular ligand reorganization. A hexane solution of **5** at −75 °C gave a ^{13}C NMR spectrum in which there was no change in the resonances for the olefinic and ipso carbons. The lack of change shows that intramolecular reorganization continues unabated.

The ^{13}C NMR spectrum of **5** in deuterated methylene chloride also shows equivalent olefinic and ipso carbons at δ 136.42 ($J_{POC} < 2$Hz) and δ 135.35 ($J_{POCC} = 8.8$ Hz). The ortho, meta, and para carbons are found as single resonances and the carbons of the methyl groups bonded to nitrogen resonate as a simple doublet. The observation of a single phosphorus resonance, POC and POCC coupling, and equivalent pairs of carbons is clearly explainable by a rapid intramolecular reorganization process. There seems to be no need to invoke ionization other than as a means of explaining the change in the ^{31}P NMR chemical shift when the solvent is changed from hexane, δ −30 to methylene chloride, δ −12.8. The change can be equally well explained by considering that there are greater contributions by **5a** and **5b** to the resonance hybrid in the more polar medium. Greater contributions by these two cause a deshielding of phosphorus and thus a downfield shift in the resonance. Greater contributions also lengthen the P–O bonds and this leads to less steric congestion about phosphorus which may well be appreciable.[1b] It is also interesting to note that the POC and POCC coupling constants change with solvent. In particular the POCC coupling constant becomes smaller in changing from hexane to methylene chloride. This finding is in agreement with a more loosely bound substance. The original explanation[2a] that ionization is responsible for the change in chemical shifts of **5** is not acceptable because of the observation of POC and POCC coupling and because of the great similarity of the ^{13}C NMR spectrum to that of **12**. Coupling is lost in an exchanging system when $1/\Upsilon_e > J$, where Υ_e is the lifetime at a particular site and J is the coupling constant in Hz.[4] Using the data from the variable-temperature ^{13}C NMR studies on **9** and **10**, one finds that the $\Delta\nu$ for the olefinic carbons under the conditions of no exchange is 97 Hz for **10** and 68 Hz for **9**. When $\Upsilon_e\Delta\nu \approx 1/2\pi$, then the spin multiplets become averaged out.[5] This equation yields 0.001 64 s for Υ_e for **10** and 0.002 34 s for Υ_e for **9**, with $1/\Upsilon_e = 610$ s^{-1} for **10** and $1/\Upsilon_e = 427$ s^{-1} for **9**. These values are far larger than J, which in **5** is <2 Hz. Of course, this calculation assumes that a rigid **5** would have olefinic carbons whose chemical shift differences are comparable to that of **9** and **10**. There seems to be no reason for expecting any dramatic change in these values.

Condensation of the novel macrocyclic phosphine **13**[6] with benzil afforded a product **14**. This material is also assigned the structure

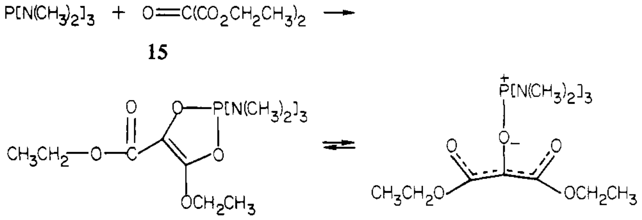


13 **14**

of a phosphorane on the basis of its ^{31}P chemical shift in methylene chloride, δ −37, and its ^{13}C NMR spectrum. The olefinic carbons are found as a singlet and the ipso carbons as a doublet, $J_{POCC} = 10.8$ Hz. All of the other potentially equivalent carbons are found to be so. At −75 °C the ^{13}C NMR spectrum of **14** still shows equivalent olefinic and ipso carbons. The other resonances were broader than at room temperature. There was no splitting into absorptions for nonequivalent carbons.

Compounds **5**, **10**, and **14** all undergo intramolecular ligand reorganization at room temperature. Only **10** is slowed sufficiently at low temperatures so that separate resonances for the various carbons are observed ($\Delta G^{\ddagger} = 13$ kcal/mol, coalescence temperature −7 °C). The most likely reason for these differences is due to the ability of the lone pair of electrons on nitrogen to interact with phosphorus. When the nitrogen occupies an equatorial position and the pair of electrons is in a p orbital which lies in the equatorial belt, maximum overlap occurs.[7] In the case of **10**, this interaction can be maximized; the nitrogens can adopt sp^2 hybridization and the lone pair in a p orbital can interact with phosphorus with little disturbance to the rest of the molecule. The same is not true for **14**; the introduction of the extra ring forces the nitrogens toward sp^3 hydridization and thus there is much less effective overlap between the orbital(s) on phosphorus and nitrogen. In compound **5**, two of the dimethylamino groups must be locked in the preferred conformation before effective overlap can occur. This leads to a negative entropy change and probably increasing steric interactions. It is interesting to note that no such steric interactions exist in **10**.

Compound **16** was first prepared by Burgada,[2e] who formulated



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16 **17**

it as being pentacoordinated. Subsequently Ramirez and coworkers[2d] investigated the ^{31}P NMR spectrum of this substance and they found a resonance at δ +38.2. On the basis of this observation they formulated the material as having the structure **17**. These two extreme structures can be distinguished by ^{1}H and ^{13}C NMR spectroscopy. This material has been prepared again and it has one resonance at δ +38.5 in its ^{31}P NMR spectrum, which is in agreement with that previously recorded. The ^{1}H NMR spectrum at 40 °C and 60 MHz showed equivalent methyl group protons at δ 1.26 ($J_{HCCH} = 7$ Hz) and equivalent methylene group protons at δ 4.22 ($J_{HCCH} = 7$ Hz). The hydrogens of the methyl groups bonded to nitrogen are found at δ 2.90 ($J_{PNCH} = 10$ Hz). The ^{1}H NMR spectrum at 30 °C and 80 MHz is very different in that the resonances for the methyl group and methylene group hydrogens are found as broad featureless absorptions centered at δ 1.2 and 4.2. The hydrogens of the methyl groups bonded to nitrogen are found as a doublet at δ 2.83 ($J_{PNCH} = 10$

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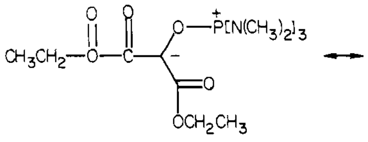
(4) Abragam, A. "The Principles of Nuclear Magnetisim"; Clarendon Press: London, 1961; Chapter 8, p 308.

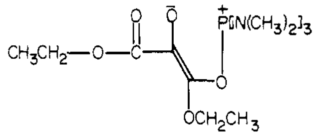
(5) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High Resolution Nuclear Magnetic Resonance"; McGraw-Hill, New York, 1959; Chapter 5, p 100.

(6) Atkins, T. J. *Tetrahedron Lett.* **1978**, 4331.

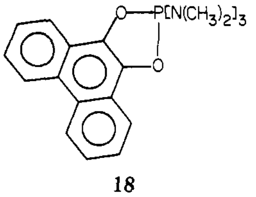
(7) Muetterties, E. L.; Meakin, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 5674.

Hz). These latter results suggest an exchange process with a coalescence temperature at 80 MHz of ca. 30 °C. This conclusion is fully supported by variable-temperature ^{13}C NMR studies. The ^{13}C NMR spectrum at 29 °C has a relatively broad resonance at δ 14.9, which is assigned to the methyl group carbons of the ethyl groups. The resonance for the carbons of the methyl groups bonded to nitrogen is a sharp doublet, δ 36.9 (J_{PNC} = 4.0 Hz). There are two broad resonances at δ 56.7 and 57.7. These are assigned to nonequivalent methylene group carbons of the ethyl groups. Two other broad absorptions are found at δ 105 and 166. The spectrum at −7 °C has two resonances at δ 14.8 and 15.0 for nonequivalent carbons of the methyl groups of the ethyl groups. The carbons of the methyl groups bonded to nitrogen absorb at δ 36.9 as a sharp doublet (J_{PNC} = 3.9 Hz). Two distinct resonances are found at δ 56.8 and 57.8 and these are assigned to nonequivalent carbons of the methylene groups of the ethyl groups. Finally, three resonances are found at δ 103.3 (J_{POC} = 5 Hz), 162.6, and 165.9. A very similar spectrum was obtained at −35 °C. The spectrum at 50 °C could be only partially obtained because of decomposition of the adduct. A single resonance was observed at δ 14.2, a doublet at δ 36.4 (J_{PNC} = 3.5 Hz), a singlet at δ 56.8, and a broad resonance at δ 104. These data are fully accomodated by assigning structure **16** to the adduct at room temperature and below, with the proviso that it is undergoing rapid intramolecular ligand reorganization. In **16** there are exactly the number of nonequivalent carbons that were found in the −7 °C spectrum. The two resonances at δ 162.6 and 165.9 are due to the carbonyl carbon and the carbon bearing two oxygens. The remaining resonance at δ 103.3 is assigned to the olefinic carbon bearing one oxygen. An inspection of the contributors to the hybrid shows that in one of them, **16a**, a negative charge is placed on this carbon and thus the shielding can be accounted for. Above room temperature, ionization to **17** becomes rapid on the ^1H and ^{13}C NMR time scales, and thus the various hydrogens and carbons become equivalent. This behavior is entirely analogous to that found for **1** ⇄ **2** except that it occurs at a lower temperature. In the case of **16** ⇄ **17** the ΔG^* is 16 kcal/mol with the coalescence temperature 29 °C. The $\Delta\nu$ was taken from the carbons of the methyl groups of the ethyl groups at −35 °C. The downfield shift of the ^{31}P resonance of **16** indicates a high positive charge on phosphorus. That this is nearly a unit positive charge is strongly indicated by the finding that $[(CH_3)_2N]_3P^+OC_2H_5 + BF_4^-$ has δ +36.1.


16a


16b

The product of the reaction of phenanthrenequinone, compound **18**, was found to have a ^{31}P chemical shift at δ +38.6 in methylene chloride. On the basis of this shift it was assigned a zwitterionic structure analogous to **7**.[2b,d] A rapid equilibrium between **7** and a small amount of **6** was not excluded. Compound **19** has the pentacoordinated structure illustrated and its ^{13}C NMR spectrum has been used to compare to those of **18** and **20**. Both **20**, and **21** have now been prepared and their ^{31}P resonances are found at δ −28.9 and −29.4, respectively. The ^{13}C NMR spectrum of **21** has not been recorded because of its extreme insolubility. The ^{13}C NMR spectrum of **20** has a doublet at δ 135.7 (J_{POC} = 0.8 Hz), which is assigned to equivalent olefinic carbons. For comparison, **19** has a doublet at δ 134.5 (J_{POC} = 5.5 Hz). The ipso carbons adjacent to the olefinic carbons of **20** are found as a doublet at δ 122.8 Hz (J_{POCC} = 10.7 Hz) and those of **19** are found at δ 121.9 (J_{POCC} = 13.4 Hz). The remaining pairs of carbons of both **19** and **20** are equivalent and thus rapid intramolecular ligand reorganization is indicated in both cases. Compound **20** is too insoluble for variable-temperature ^{13}C NMR measurements. There seems to be every reason for assigning the pentacoordinated structures illustrated to **20** and **21**.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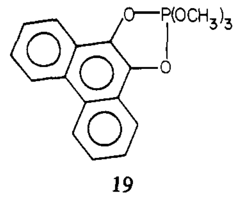
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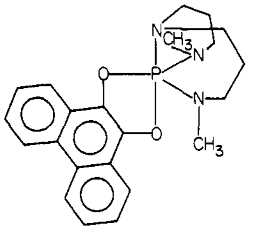
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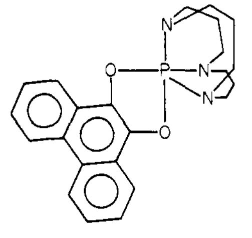
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The ^{13}C NMR spectrum of **18** is quite different from that of **19**. There is a doublet at δ 142.6 (J_{POC} = 3.6 Hz), which is assigned to the olefinic carbons on the basis of both its chemical shift and a gated decoupling experiment which led to little change in the ^{13}C NMR resonance. This result suggests that there is long-range coupling to no more than one proton, which is what is expected for the olefinic carbons. A doublet is found at δ 132.8 (J_{POCC} = 1.3 Hz) and this is assigned to the ipso carbons which are bonded to the olefinic carbons. Five other aromatic resonances are present and there is a doublet for equivalent methyl group carbons bonded to nitrogen at δ 37.2 (J_{PNC} = 4.2 Hz). These data demand that some mechanism must be available which allows the various pairs of carbons to become equivalent and this must occur without loss of POC and POCC coupling. It is also necessary to explain the considerable differences in the spectra of **18** and **19**. The most logical explanation is that **18** is a highly polar pentacoordinated molecule in which contributors analogous to **16a** and **16b** are major. Furthermore, rapid intramolecular ligand reorganization must be occurring at room temperature. The wide difference in the ^{31}P chemical shifts and the ^{13}C NMR spectra of **18** and **20** is most likely due to steric congestion in **18**, which is relieved by lengthening of the P–O bonds. The ^{13}C NMR spectrum of **18** at 50 °C showed little change over that at ambient temperature. The doublet at δ 142.6 was somewhat sharper. Evidently rapid ionization is not taking place at this temperature.

The fact that **18** has more ionic character than **10** is undoubtedly due to the fact that the phenanthrene backbone can more effectively delocalize the negative charge than can the stilbene backbone in **10**. Rotation of the phenyl groups out of the plane occurs as a means of decreasing steric interaction between them and this, of course, leads to less delocalization. The wide difference in coupling constants found for **20** and **18** supports the concept of a much looser structure for **18** which leads to considerable attenuation of coupling.

The results of this study serve to further quantify the nature of the bonding in a number of pentacoordinated phosphorus compounds. It is very clear that **11**, **12**, and **19** are true phosphoranes as evidenced by their ^{31}P NMR chemical shifts. This conclusion was reached very early in studies of phosphoranes.[1d] The strong POC and POCC couplings are also strongly in favor of these structural assignments. The structures of the mixed aminooxyphosphoranes that have been studied in this report are also pentacoordinated in the main. The ^{31}P NMR chemical shifts, the ^{13}C NMR chemical shifts, and the magnitude of POC and POCC couplings show that in the extreme these structures possess a considerable amount of ionic character. Shifts toward an ionic structure occur when increased delocalization can take place and when there is a relief of steric strain.

Experimental Section

^{1}H NMR spectra were run on Varian Model A-60A, T-60, and FT-80 spectrometers. All chemical shifts are reported in ppm relative to internal tetramethylsilane. ^{13}C and ^{31}P NMR were run on a Varian Model FT-80 spectrometer equipped with a 10-mm, variable-temperature broad-band probe. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), $-\delta$ upfield. ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane (internal).

Preparation of 10. The procedure of Ramirez[2a] was followed. The ^{13}C NMR spectrum of **10** in hexane has a doublet at δ 134.16 ($J_{POC} <$ 1 Hz, olefinic carbons), a doublet at δ 133.05 (J_{POCC} = 11.6 Hz, ipso carbons), a doublet at δ 42.05 (J_{PNC} = 4.3 Hz, carbons of methyl groups attached to nitrogen), two resonances at δ 128.12 and 126.50 (ortho and meta or meta and ortho), and a resonance at δ 126.91 which is due to the para carbon. In deuterated methylene chloride the resonances are found at δ 136.42 ($J_{POC} <$ 1 Hz), 135.35 (J_{POCC} = 8.8 Hz), 40.03 (J_{PNC} = 2.0 Hz), 128.16 and 126.22 (ortho and meta or meta and ortho), and 126.46 (para).

Preparation of 16. The method of Burgada[2e] was followed and the material was purified by recrystallization from tetrahydrofuran. The ^{1}H, ^{13}C, and ^{31}P NMR spectral data are reported in the text. These spectra were all obtained in deuterated chloroform.

Preparation of 18. The procedure of Ramirez[2b] was followed. The ^{13}C NMR spectrum in deuterated methylene chloride has a doublet at δ 37.17 (J_{PNC} = 4.2 Hz), which is assigned to methyl group carbons bonded to nitrogen, aromatic resonances at δ 120.17, 121.36, 122.21, 124.94, and 125.56, a doublet at δ 132.81 (J_{POCC} = 1.3 Hz), and another doublet at δ 142.59 (J_{POC} = 3.6 Hz).

Preparation of 14. Under nitrogen 0.420 g (2 mmol) of benzil in 2 mL of deuterated methylene chloride was added slowly to a stirred solution of 0.398 g (2 mmol) of **13** in 2 mL of deuterated methylene chloride at 10 °C. After the addition, 5 min, the mixture was allowed to warm to room temperature. The ^{1}H NMR spectrum at 60 MHz has an absorption at δ 1.40–2.40, which is assigned to $\mathrm{PNCH_2C}H_2$ hydrogens, another at δ 2.40–3.50, which is assigned to $\mathrm{PNC}H_2\mathrm{CH_2}$ hydrogens, and an absorption at δ 7.10–7.70 for aromatic hydrogens. The ratio of the areas was 3:6:5. The ^{31}P NMR spectrum had one absorption at δ -36.8. The ^{13}C NMR spectrum had a doublet at δ 24.77 (J_{PNCC} = 6.2 Hz); another doublet was found at δ 51.36 (J_{PNC} = 2.9 Hz). Two aromatic resonances were found at δ 126.39 and 128.27 (ortho and meta or meta and ortho) and another was found at δ 127.08 (para). The ipso carbons absorb at δ 131.56 (J_{POCC} = 10.8 Hz) and the olefinic carbons are found at δ 132.78.

Preparation of 21. To a stirred suspension of 0.416 g (2 mmol) of phenanthrenequinone in 2 mL of -benzene-d_6 was added 0.398 g (2 mmol) of **13** in 2 mL of benzene-d_6 under nitrogen at -10 °C. After the addition was completed a gray-green precipitate had formed. The reaction mixture was centrifuged and the supernatant liquid showed an absorption at δ -29.4.

Preparation of 20. The same procedure was used as for the preparation of **21** except deuterated chloroform was the solvent. The ^{31}P NMR resonance was found at δ -28.9. The ^{13}C NMR spectrum had a singlet at δ 24.92 ($\mathrm{PNCH_2}C\mathrm{H_2}$), a doublet at δ 39.95 (J_{PNCH_3} = 2.8 Hz), a doublet at δ 48.15 (J_{PNC} = 4.8 Hz), and a singlet at δ 50.75. The last two absorptions are assigned to carbons bonded to nitrogen. The olefinic carbons were found at δ 135.67 (J_{POC} = 0.8 Hz), and the carbons adjacent absorb at δ 122.77 (J_{POCC} = 10.7 Hz). Finally there were resonances at δ 120.20 (J = 0.6 Hz), 122.97, 123.30, and 125.60.

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Ipso Nitration. Solvolytic Behavior of 1,4-Dimethyl-4-nitrocyclohexadienyl Acetate and 1,4-Dimethyl-4-nitrocyclohexadienol

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Abstract: The solvolytic rearomatizations of the *E* and *Z* isomers of 1,4-dimethyl-4-nitrocyclohexadienyl acetate (**1**) have been examined in aqueous ethanol and in sulfuric acid solutions. Solvolysis of **1** in aqueous ethanol involves the elimination of nitrous acid and the migration of the acetoxyl group to yield 2,5-dimethylphenyl acetate. The kinetic behavior of this solvolytic reaction parallels that of the secondary adduct 4-nitro-3,4,5-trimethylcyclohexadienyl acetate (**2**). No kinetic isotope effects were detected when 1,4-dimethyl-4-nitrocyclohexadienyl-*2,3,5,6*-d_4 acetate (**1**-d_4) or 1,4-dimethyl-4-nitrocyclohexadienyl-*Me*-d_6 (**1**-d_6) were used as substrates. The collected data suggest a rate-limiting loss of nitrite ion from **1** followed by migration of the acetoxyl group and proton loss. The behavior of the *E* and *Z* isomers of 1,4-dimethyl-4-nitrocyclohexadienol (**3**) in aqueous ethanol differs from that of **1** in several ways. The major product of solvolysis is 2,4-dimethylphenol. The rates of solvolysis of the stereoisomers of **3** do not differ appreciably one from the other, and the spectral yield is only 30–40% of that anticipated. These differences are taken to reflect a rate-limiting migration in the solvolysis of **3** rather than a rate–limiting loss of nitrate ion. Solvolysis of **1** in greater than 77% sulfuric acid gives 1,4-dimethyl-2-nitrobenzene in quantitative yield. The yield of nitro aromatic falls off smoothly as the acid concentration is lowered toward 50%. Within the 70–50% acid range, the yield of side-chain substitution products appears to increase, hold roughly constant, and then decrease. Larger yields of nitro aromatic and smaller yields of side-chain substitution product are found when **1**-d_6 is used as a reactant. The solvolyses in strong acids are discussed in terms of re-formation of the ipso ion and subsequent partitioning.

This paper deals with the solvolytic rearomatization of 1,4-dimethyl-4-nitrocyclohexadienyl acetate (**1**).[1] Earlier we reported some studies of the solvolytic behavior of 4-nitro-3,4,5-trimethylcyclohexadienyl acetate (**2**), the ipso adduct formed by formal 1,4-addition of nitronium acetate to 1,2,3-trimethylbenzene.[2] We found that this secondary nitrocyclohexadienyl acetate lost the elements of nitrous acid in aqueous ethanol to give 5-acetoxy-1,2,3-trimethylbenzene and lost the elements of acetic acid in strong sulfuric acid solutions to give 4-nitro-1,2,3-trimethylbenzene. It seemed useful to compare the solvolytic be-

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(2) Banwell, T.; Morse, C. S.; Myhre, P. C.; Vollmar, A. *J. Am. Chem. Soc.* **1977**, *99*, 3042.

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