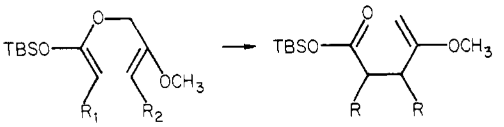
Table III. ^{1}H NMR Spectral Data for Compound A (6)

chemical shift[a]	mult[b]	coupling constant, Hz	assignment
1.37, 1.41, 1.63, 1.66	s		CH_3
3.57	t	$J_{6,6'} = J_{5,6} = 8$	$H_{6'}$
4.06	dd	$J_{5,6} = 6$	H_6
4.46	dt	$J_{4,5} = 8$	H_5
5.17	dd	$J_{3,4} = 13$	H_4
5.49	s		H_2
6.54	d		H_3

[a] Chemical shifts are in parts per million from Me_4Si. [b] s = singlet, d = doublet, t = triplet, dd = doublet of doublets, and dt = doublet of triplets.

rangement of 10 would seem to be an unlikely possibility except that some Claisen rearrangements are known to occur readily at room temperature (eq 2).[6]



(2)

TBS = t-Bu$(CH_3)_2$Si, $R_1 = (CH_2)_2CH_3$, $R_2 = (CH_2)_5CH_3$

The photochemical reaction mixture was analyzed at various stages of conversion to determine if the aldehyde 10 was being formed; however, no indication of this intermediate was obtained. This finding did not exclude the presence of 10 since it is possible that it reacts sufficiently rapidly (either photochemically or thermally) that it fails to accumulate in the reaction mixture.

Although it is not possible to rigorously exclude the intermediacy of the aldehyde 10, one piece of information, the formation of a single product from photolysis of 2, does argue against it. The carbonyl oxygen in 10a should react with C_2 essentially equally well from either side of the unsaturated five-membered ring; that is, 10a should react to give a mixture of diastereomers. In contrast, the oxacarbene 8 could yield a single product if the diradical 7 cyclized to 8 more rapidly than it assumed a conformation which would allow bonding of the carbonyl oxygen with C_2 in such a manner to invert the C_2 configuration. Thus, the explanation which seems in best accord with all the information is that the configuration at C_2 in the photoproduct 6 is the same as the starting material (2) and that the rapidly reacting oxacarbene 8 is an intermediate in the reaction.

Experimental Section

General Procedures. ^{1}H NMR spectra were run on a Varian T-60 spectrometer and a Varian HR-300 spectrometer. ^{13}C NMR spectra were obtained from a Varian XL-100 spectrometer. All NMR spectra were run in deuteriochloroform. IR spectra were measured in carbon tetrachloride on a Beckman Acculab I spectrophotometer. Chemical-ionization mass spectra were obtained from a Finnigan 1015-D mass spectrometer at 150 eV with methane as the reagent gas.

Photolysis of 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-3-hexulofuranose (2). 1,2:5,6-Di-*O*-isopropylidene-α-D-*ribo*-3-hexulofuranose[1] (2; 0.99 g, 3.8 mmol) in 350 mL of benzene was purged with nitrogen for 2 h and then irradiated through a Pyrex filter for 35 h with a Hanovia 450-W, medium-pressure, mercury lamp. The solvent was removed under reduced pressure, and the dark-brown residue was chromatographed on a 2.5 × 20 cm column of 200–325-mesh silica gel slurry packed in 1:9 ether–pentane. The effluent from the column was monitored with an ISCO-UA2 ultraviolet analyzer. The only significant amount of material (0.37 g, compound A) eluted from the column came through in the first 400 mL of solvent (1:9 ether–pentane). Increasing the percentage of ether in the solvent and eluting the column with more polar solvents did not result in the isolation of significant amounts of any other material. Compound A was a colorless syrup which was homogeneous by TLC (silica gel) and GC (OV-17) analyses.

The mass, ^{13}C NMR, and ^{1}H NMR spectra are given in Tables I–III, respectively. The IR spectrum of A contained a sharp absorption at 1810 cm^{-1}, characteristic of a lactone, and a doublet at 1675 and 1660 cm^{-1}, characteristic of an enol ether.[7] The use of this spectral information to assign structure 6 to compound A is described in detail in the Results and Discussion.

Photolysis of 2 also was conducted with *tert*-butyl alcohol as the solvent. The result was the same as when benzene was the irradiation solvent.

Acknowledgment. Appreciation is expressed to Professor J. Houser of the University of Akron for his generous assistance in obtaining the 300-MHz ^{1}H NMR spectrum of compound 6.

Registry No. 1, 582-52-5; 2, 2847-00-9; 6, 78549-99-2.

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Does the 2-Pyridyl Cation Behave Like an Aryne?[1]

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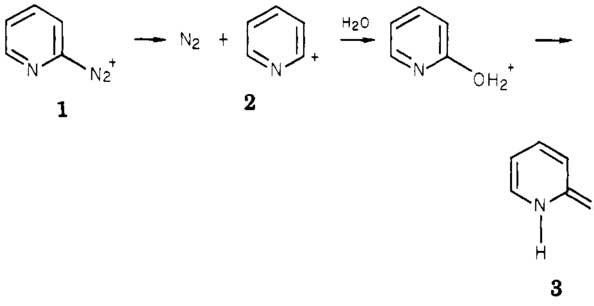
Received April 22, 1981

2-Pyridinediazonium ion (1) is known to undergo replacement of its diazonio group by nucleophiles with great ease.[3] Although the replacement reaction might be thought to occur by the S_NAr mechanism, with activation by the ring nitrogen atom,[3] both analogy with corresponding reactions in the benzene series[4] and the fact that the diazonio group of 2-pyridinediazonium ion is replaced very rapidly even by such weak nucleophiles as water[5] at pH 2 and fluoride ion in HF solution[6] suggest the S_N1 mechanism of eq 1.



(1)

If this representation is correct, the high rate of the dinitrogen-detachment step is perhaps associated with resonance stabilization, 2a ↔ 2b, within the 2-pyridyl

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[1] Research supported in part by the National Science Foundation.

[2] On research leave from Panjab University, Chandigarh, India, 1980–81.

[3] Smith, D. M. In "Rodd's Chemistry of Carbon Compounds", 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1976; Vol. IV, Part F, p 124.

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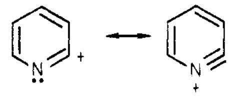
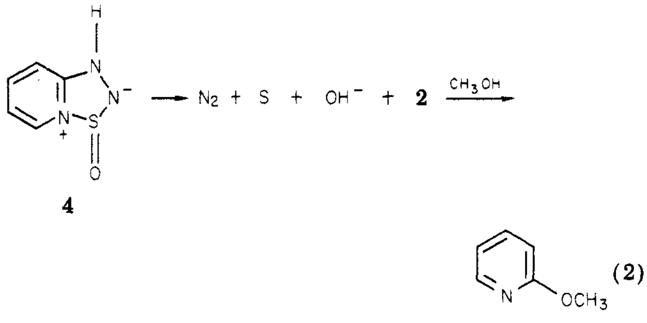
[5] Kalatzis, E. *J. Chem. Soc. B* **1967**, 273.



2a 2b

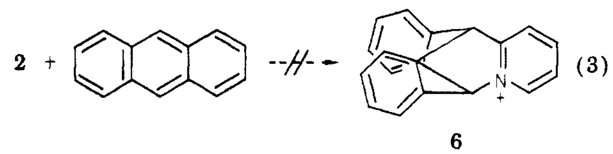
cation. In 1962, the arynelike character of structure **2b** was pointed out independently by Lewis and Cooper[7] and by Kauffmann and Boettcher.[8] **2b** is isoelectronic with benzyne. However, to our knowledge no efforts have been made to observe uniquely arynelike behavior by the presumed intermediate **2**. Of two prominent modes of reaction of arynes, combination with nucleophiles could be attributed to aryl cation structure **2a**, but certain types of cycloaddition would be indicative of **2b**-like character in the intermediate.

We sought to generate **2** in the presence of anthracene and furan, both of which are known to add benzyne in Diels–Alder fashion.[9] Our early efforts to effect "aprotic" diazotization[10] of 2-aminopyridine in CH_2Cl_2 solution containing also furan were unsuccessful: much 2-aminopyridine was recovered, and no well-defined product was formed. We therefore turned attention to thermolysis of the interesting heterocycle **4**, after Kauffmann and Marhan,[11] as a means to generate **2**. These workers showed that **4** reacts in boiling chloroform containing methanol, or better in boiling methanol, to form 2-methoxypyridine (**5**) in yield as high as 36%. They suggested that a tautomer of **4** decomposes as shown in eq 2 to produce **2**, which then captures methanol and releases a proton to form **5**.



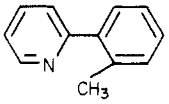
4 5

We investigated the thermolysis of **4** in the presence of anthracene in boiling toluene. Our anticipation was that if **2** is truly formed as an intermediate and if it behaves as an aryne as suggested by structure **2b**, the intermediate would add to anthracene to form azoniatriptycene cation **6**, as shown in eq 3. **6** is a known species, having been



6

prepared by cycloaddition of benzyne to the acridizinium ion.[12] In the event, we could find no product with properties such as one would expect of **6**, nor did we find any 9-(2-pyridyl)anthracene (which is readily formed by thermolysis of **6**[12]) as a product. However, we did obtain two 2-pyridyltoluenes, **7** and **8**, each in 19% yield.



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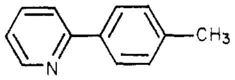
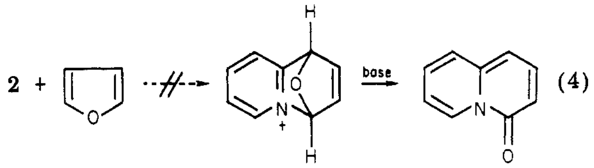


8

Products **7** and **8** can be regarded as resulting from normal electrophilic substitution in toluene with **2** acting as electrophile.[13] One might alternatively imagine them to result from cycloaddition of **2**, behaving as an aryne,[9] to toluene with ensuing ring opening of the initial adducts. Two arguments against this alternative interpretation are, first, that it offers no explanation of why the meta isomer of **7** and **8** was not formed, and, second, that if the reaction occurred via cycloaddition, anthracene should have reacted preferentially because it is much more reactive than a monocyclic aromatic hydrocarbon as a diene in cycloaddition reactions.

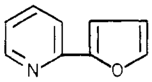
Viewing the formation of **7** and **8** as electrophilic substitution, we inquire why substitution occurred in toluene but not in anthracene. The relative rates of reaction of **2** with these two hydrocarbons would be governed by the respective rate constants and concentrations. In our experiment, toluene (ca. 7.4 M) was in about 15-fold excess over anthracene (ca. 0.5 M). Although the 9-position of anthracene is very reactive with some electrophiles, in some cases it is not so reactive; thus hydrodetrimethylsilylation is actually faster at the 2- or 4-position of toluene than at the 9-position of anthracene.[14] The experimental result is thus consistent with other knowledge of aromatic electrophilic substitution reactivity.

If **2** had arynelike reactivity, it would be expected to add to furan as shown in eq 4, and it would be expected that

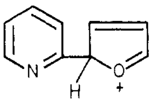


9 10

subsequent ring opening would occur as shown. We effected decomposition of **4** in furan at 110 °C. In the resulting mixture, we found nothing with the properties of **10**, a known compound.[15] However, we did obtain 2-(2-pyridyl)furan (**11**) in 30% yield. The formation of **11** can be interpreted as a normal electrophilic substitution wherein **2** acts upon furan to form σ-adduct **12**, which then loses a proton. It should be noted, though, that spontaneous ring opening of conceivable cycloadduct **9** would also furnish **12**. The obtaining of **11** rather than **10** is therefore



11



12

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not definitive of mechanism.

In summary, we have not obtained any evidence that the 2-pyridyl cation participates in arynelike cycloaddition as might be expected from canonical structure **2b**. We have obtained products that appear to result from normal aromatic electrophilic substitution reactions.

Experimental Section

1,2,3,5-Thiatriazolo[5.4-*a*]pyridine 3-oxide (4) was prepared from 2-pyridylhydrazine following the method of Kauffmann and Marhan.[11]

Reaction of 4 in Toluene Containing Anthracene. A solution of 4 (1.0 g, 6.4 mmol) and anthracene (3.45 g, 19.4 mmol) in 30 mL of toluene was heated at reflux for 2 h. The solid that separated on cooling was collected and identified as anthracene on the basis of its melting point and mixture melting point with an authentic sample. The filtrate was extracted thrice with small portions of dilute aqueous HCl. The combined aqueous layer was washed once with diethyl ether, neutralized by addition of $NaHCO_3$, and extracted with diethyl ether. The dried ether extract was concentrated by evaporation at reduced pressure and the residue was examined by GC/MS with use of a Finnigan 4000 system. Of three major peaks, two had molecular mass 169 and were similar in fragmentation pattern. The third had base peak *m/e* 220; a product with the same mass spectrum was also obtained from reaction of 4 with furan (see below); it follows that the third product is derived strictly from 4.

One of the species of mass 169 was recognized to be 2-(*p*-tolyl)pyridine (**8**) by comparison of its GLC retention time and mass spectrum with those of an authentic sample (from Aldrich Chemical Co.); mass spectrum, *m/e* 169, 168, 167, 154, 141, 120. The other product of mass 169 was isolated by preparative GLC on a 10% UC W-98 on Chromosorb P column and was identified as 2-(*o*-tolyl)pyridine (**7**); mass spectrum, *m/e* 169, 168, 167, 154, 141, 120; NMR ($CDCl_3$) δ 2.37 (s, 3 H), 7.14–7.90 (m, 7 H), 8.51–8.74 (m, 1 H); picrate, mp 140–142 °C (lit.[16] mp 143 °C). The yields of **7** and **8** were 19% each.

The third major peak had the following mass spectrum: *m/e* 220 (base peak), 187, 156, 155, 78. Inasmuch as 4 has molecular mass 155, components from at least two molecules of 4 must be represented in this species. One possibility is di-2-pyridyl sulfone (mass 220). The peak at *m/e* 78 is probably the 2-pyridyl cation, at 156 di-2-pyridyl radical cation, at 155 the same less one protium, and at 187 the mass 220 species less O_2H.

An attempt to effect reaction of 4 with anthracene at reflux in benzene for 1 h was unsuccessful; only unreacted 4 and anthracene could be found in the cooled mixture.

Reaction of 4 in Furan. A mixture of 4 (0.60 g) with furan (5 mL) was sealed in a glass tube and heated for 2 h at 110 °C. The contents of the cooled tube were decanted, and the dark, sticky material adhering to the wall of the tube was removed by two washings with diethyl ether. The combined decantate and extracts were evaporated, leaving a dark, oily material which was examined by GC/MS. Three major components were revealed; one had parent peak *m/e* 145 and is discussed below; a second had *m/e* 172, 171, 156, 144, 118, 95, 79, 78, and is perhaps di-2-pyridyl ether; the third had parent peak *m/e* 220 and mass spectrum identical with that of the species formed from reaction of 4 with anthracene and toluene as discussed above. By preparative GLC on 10% UC W-98 on Chromosorb B, 2-(2-pyridyl)furan (**11**) was isolated; mass spectrum, *m/e* 145, 117, 116, 90, 89, 78; NMR ($CDCl_3$) δ 8.73–8.46 (m, 1 H), 7.50–7.83 (m, 3 H), 6.84–7.23 (m, 2 H), 6.50–6.63 (m, 1 H); IR (film) 1575, 1560, 1450, 1420, 1275, 1145, 1110, 980, 750 cm^{-1}; picrate mp 172–174 °C. The NMR spectrum and picrate melting point agree with those in literature data[17] for **11**. The IR and picrate melting point are different than those reported[15] for **10**. The yield of **11** by GLC was 30%.

Attempted Diazotization of 2-Aminopyridine. 2-Aminopyridine (0.011 mol) was recovered unchanged from exposure to 3-methylbutyl nitrite (0.01 mol) in a solvent of furan (0.033 mol) and CH_2Cl_2 (10 mL) for 30 min at reflux. Diazotization likewise failed to occur when acetic acid (0.011 mol) was present as well as the other species mentioned. A mixture of 2-aminopyridine (4.2 g), 3-methylbutyl nitrite (5.6 g), furan (27.2 g), trifluoroacetic acid (10.0 g), and CH_2Cl_2 (about 75 mL) was heated at reflux for 1 h; besides much 2-aminopyridine, isolated as its picrate (mp 213–215 °C), there was obtained 1.1 g of an oily material lacking characteristics of either **10** or **11**. We did not try to employ the aprotic diazotization procedure of Doyle and Bryker.[18]

Registry No. 2, 35895-92-2; **4**, 78715-82-9; **5**, 1628-89-3; **7**, 10273-89-9; **8**, 4467-06-5; **11**, 55484-03-2; furan, 110-00-9; toluene, 108-88-3.

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Mono- and Polyanhydride Formation by Reaction of 2,2,4,4,6,6-Hexachlorotriazatriphosphorine with Carboxylic Acid Salts under Mild Conditions

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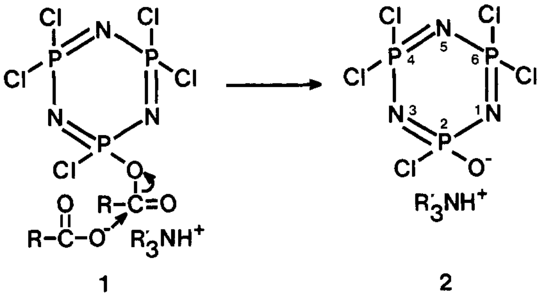
Received March 17, 1981

In the last decade several convenient uses of 2,2,4,4,6,6-hexachlorotriazatriphosphorine ($N_3P_3Cl_6$) in organic syntheses have been reported.[1-4] Moreover, $N_3P_3Cl_6$ has been extensively used for activating carboxylic acid in amide syntheses.[5-8] In this paper we report the reaction of $N_3P_3Cl_6$ with carboxilic acids neutralized by a tertiary amine. When the reaction was performed in organic solvents, at low temperature, a fast and quantitative formation of carboxylic acid anhydride was observed; consequently, $N_3P_3Cl_6$ was converted into the trialkylammonium salt of 2-hydroxy-2,4,4,6,6-pentachlorotriazatriphosphorine, a new cyclophosphazene derivative (**2**). The probable mechanism of reaction involves a compound of type **1** as an active intermediate that can undergo a nucleophilic attack by the carboxylate anion to form an anhydride. Our findings are consistent with the following



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