Recently, careful labeling studies and an independent synthesis provided strong evidence for the intermediacy of a 1,3-diazocine in the transformation of uracil–alkyne photoadducts to pyridones under strongly basic conditions.[14] Conclusions concerning a reaction in alkoxide solution may not be directly applicable to our rearrangement in strongly acidic medium; nevertheless, that study demonstrates the facility of valence isomerizations of the 1,3-diazocine system.

While we were not initially elated to observe the conversion of the exotic diazabiphenylene ring system, once constructed, to the more common isoquinoline system, we are now becoming interested in the valence isomerizations apparently available to its addition products, and we anticipate utilization of this reaction sequence that generates in situ a fluorescent product from a nonfluorescent precursor.

Acknowledgment. This work was supported by Research Grant GM-05829 from the National Institutes of Health.

Supplementary Material Available: Listing of physical and spectral data for compounds **1–6** (2 pages). Ordering information is given on any current masthead page.

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[13] The reaction appears to be first order in **5** and first order in trifluoroacetic acid with an obsesrved rate constant of ~0.015 $M^{-1} s^{-1}$ at 20 °C when the reaction is performed in CD_3OD and monitored by ^1H NMR. This is consistent with a preequilibrium involving protonation of **5** before the rate-determining step. The kinetics suggest that the reaction is specific acid catalyzed since as the acid is consumed (presumably by protonation of product) the reaction slows appropriately.

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1-Phenylphosphonin Oxide as an Unstable Valence Tautomer of 9-Phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene 9-Oxide

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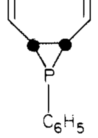
Received March 28, 1983

Scission of the 1,8-bond in bicyclo[6.1.0]nonatriene has been employed in the synthesis of cyclononatetraene;[1] the oxygen and nitrogen analogues (oxonin[2,3] and azonine[4]) have been prepared similarly. This conversion, however, has not been successful when a sulfide[5] or phosphine[6] group is present in the three-membered component of the bicyclic ring system. We have discovered that the 1,8-bond in the *P*-oxide (**2**) of 9-phenyl-9-phospha[6.1.0]-nona-2,4,6-triene[7] (**1**) has drastically reduced stability; rearrangement of **2** accompanies formation from **1** at −20 °C or above, and this has allowed us to observe the first monocyclic phosphonin oxide, of structure **3**.



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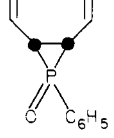

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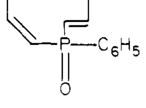
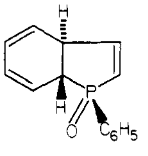


3

Phosphirane **1** was first oxidized by exposure for 12 h to a 5–10-fold excess of a 1:1 mixture of 30% H_2O_2 and methanol at 0 °C. This provided a product with $\delta(^{31}P)$ + 46.9 in about 95% purity, which was further purified by chromatography on alumina with elution by 10% methanol in benzene. The hygroscopic solid had a mass spectrum suggestive of either **2** or **3** (calcd and found for $M^+ - 1$ *m/e* 227.0625, base peak), but the ^{13}C NMR spectrum[8] eliminated both possibilities, especially by the presence of two different methine carbons, with one showing the characteristic large coupling for direct attachment to ^{31}P. The data suggested the product to possess one (**4**) of the 3a,7a-dihydrophosphindole oxide structures, and this was proved by rearrangement to the known[9] 2,3-dihydrophosphindole oxide **5** (10 h in 15% NaOH, 25 °C) and by air oxidation to the known[9] phosphindole oxide **6**. The formation of a 3a,7a-dihydrophosphindole derivative during oxidation of **1** can only be explained by assuming the intermediacy of a a phosphonin oxide, which undergoes intramolecular [4 + 2] cycloaddition. Since the 3a,7a-dihydrophosphindole oxide differed from the two known[10] forms with cis-fused rings ($\delta(^{31}P)$ + 61.9, +71.1), trans ring fusion was suspected and was confirmed by conducting partial epimerization (7.5% NaOH, 2 min at 25 °C) to the cis,cis isomer **7** with $\delta(^{31}P)$ +61.9. The trans ring fusion in **4** was also indicated by the H_{3a}–H_{7a} coupling constant (at 250 MHz), which was approximately 20 Hz in an ABX (X = ^{31}P) spectrum; this abnormally large value has been observed for trans protons in related systems (e.g., 20 Hz in *trans*-3a,7a-dihydroindene[11]). The cis isomer **7** had a H_{3a}–H_{7a} coupling of 12–14 Hz. The stereochemistry at phosphorus in **4** could not be directly determined but was revealed in the corresponding phosphine ($\delta(^{31}P)$ −16.4, formed with retention[12] using $C_6H_5SiH_3$; methiodide mp 105–115 °C dec, giving the correct C, H, P analyses). The magnitude of $^2J_{PH}$ in phosphines is related to the proximity of the lone pair on phosphorus to the proton on the sp^3 carbon.[13] The absence of ^{31}P coupling to H-7a (as observed in the H-coupled ^{31}P spectrum) suggests the *P*-phenyl and H-7a to have the cis arrangement shown in the corresponding phosphine oxide **4**.



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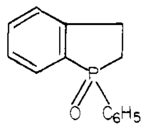

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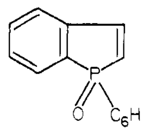

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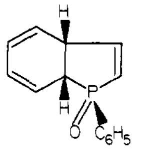

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The trans ring fusion in **4** implies that the initially formed phosphonin oxide precursor must have had the trans structure at the C-2,C-3 double bond (as in **3**) for the subsequent thermally induced [4 + 2] cycloaddition to be allowed by orbital symmetry considerations.[14] This is consistent with observations made in the cycloadditions with cyclononatetraene[1] and oxonin.[3] The trans double bond in **3** is also predicted by orbital symmetry conservation in the thermal opening of the cis-fused three-membered ring in

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[8] ^{13}C NMR ($CDCl_3$, 22.5 MHz, FT ^1H-decoupled, J_{PC} in parentheses) δ 42.6 (C-3a, 14.7), 46.7 (C-7a, 79.1), 122.0 (C-4 or C-7, s), 125.3 (C-4 or C-7, s), 126.0 (C-2, 87.9), 128.4 (C-5, s), 128.5 (phenyl meta, 11.7), 128.6 (phenyl ipso, 91.6), 129.1 (C-6, 12.2), 130.2 (phenyl ortho, 10.2), 131.8 (phenyl para, 2.9), 151.4 (C-3, 10.3); ^1H NMR ($CDCl_3$, 250 MHz, FT) δ 3.06–4.04 (H-3a and H-7a, five-line ABX m), 5.9–6.4 (H-4, H-5, H-6, and H-7, m), 6.43 (H-2, d of d, $^2J_{PH} = 25.9$, $^3J_{H\text{-}2,H\text{-}3} = 8.5$), 7.22 (H-3, d of d, $^3J_{PH} = 39.2$, $^3J_{H\text{-}2,H\text{-}3} = 8.5$), 7.33–7.84 ($C_6H_5$, m).

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2.[14] The thermal opening of the *cis*-fused three-membered ring in compounds of type **2** has been predicted[15] to give mono-*trans*-heteronins of type **3**.

1-Phenylphosphonin oxide (**3**) was then directly observed by low-temperature (−20 °C) ^{31}P NMR spectroscopy. A peak with $\delta(^{31}P)$ +16.2 was observed, which agrees well with the value of +17.2 found for 1-phenyldibenzo[*d*,*f*]phosphonin 1-oxide, the only other known oxide of a phosphonin.[16] Phosphonin oxide **3** has good stability at −17 °C, but at 24 °C it decays with a half-life of about 5 min with the formation of the [4 + 2] product **4**. This half-life is much shorter than that of *cis*^{4}-cyclononatetraene[16] ($t_{1/2}$ 50 min at 23 °C). The ^{13}C NMR spectrum was also taken on the reaction product while still at −20 °C but was too complex for full analysis. Confirming points for structure **3**, however, were the presence of downfield signals (δ ~154) typical of sp^2 carbons β to P=O and the absence of sp^3 carbons.

Oxidation of **1** by oxygen follows a different pathway and does not lead to **3**.

This technique is being used in the synthesis of other phosphonin oxides and may constitute a route to the still-unknown thionin oxide system.

Acknowledgment. We thank the National Science Foundation for financial support of this work through Grant CHE-7717876.

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Doubly Destabilized Carbocations. Unexpectedly High Reactivity in Formation of Carbocation Intermediates with Two Destabilizing Substituents

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Received May 12, 1983

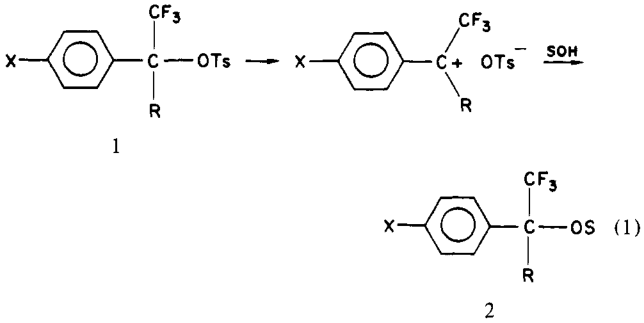
Carbocations bearing groups such as CF_3[1] and CN[2] may be termed electron deficient[3a] relative to hydrogen-substituted analogues and are destabilized[3b] in comparison to these species. Efforts to study carbocations substituted with two such groups have been inconclusive. Thus attempts to form long-lived carbocations bearing two α-CF_3 groups were not successful,[4] and although Astrologes and Martin[5] presented convincing evidence that the triflate corresponding to **1a** underwent methanolysis via a carbocation, the absence of suitable comparative data precluded a quantitative estimate of the rate deceleration.

We have now studied the reactivities of **1a–d**, which give the solvolytic rate constants reported in Table I, and which proceed with substitution by the solvent to give **2** as major products. The dependence of the rates of **1b** on the solvent polarity parameter Y_{OTs}[6] is $\log k = 0.76Y_{OTs} - 3.30$, and the rates of **1a–c** in CF_3CO_2H at 25 °C gave the relation $\log k = -10.7\sigma^+ - 8.65$. All these results support the mechanism of eq 1 with intervention of carbocation intermediates bearing two electron-withdrawing groups.

Table I. Solvolysis Rates of ROTs (**1**)[a]

ROTs	T, °C	solvent[c]	k_1, s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
1a	121.0	TFA	2.53×10^{-5}		
	111.5		1.20×10^{-5}		
	96.5		3.56×10^{-6}		
	25.0[b]		1.94×10^{-9}	22.4	−23.4
1b	25.0[b]	TFA	0.470	20.7	9.5
	19.1		0.235		
	12.7		9.50×10^{-2}		
	4.0		3.15×10^{-2}		
1b	25.0	TFE	2.10×10^{-2}	16.8	−9.9
	12.7		5.81×10^{-3}		
	4.0		2.28×10^{-3}		
1b	56.4	HOAc	3.55×10^{-4}		
	41.2		6.46×10^{-5}		
	25.0		8.00×10^{-6}	23.0	−4.8
1b	25.0	HFIP	0.235		
	25.0	HCO_2H	2.02×10^{-2}		
	25.0	80% EtOH	2.52×10^{-4}		
	25.0	100% EtOH	3.00×10^{-5}		
1c	121.0	TFA	1.06×10^{-4}		
	105.9		3.98×10^{-5}		
	91.4		1.12×10^{-5}		
	25.0[b]		1.53×10^{-8}	20.9	−24.1
1d	115.0	TFA	7.66×10^{-4}		
	100.9		2.73×10^{-4}		
	80.5		4.18×10^{-5}		
	25.0[b]		9.69×10^{-8}	22.4	−15.6

[a] Duplicate runs at each temperature, ±5%. [b] Extrapolated from data at other temperatures. [c] TFA is CF_3CO_2H, TFE is 97% CF_3CH_2OH, HFIP is 97% $(CF_3)_2CHOH$.



a, R = CF_3; X = H
b, R = CF_3; X = MeO
c, R = CF_3; X = F
d, R = CN; X = H
e, R = CH_3; X = H
f, R = H; X = H

The rate of **1f**[1a] relative to **1a** is 54 at 25 °C in CF_3CO_2H. Corresponding $k(H)/k(CF_3)$ ratios for **1b** are 2.4–5.2 (six different solvents) and for **1d** the ratio is 1.1. These ratios are extraordinarily small: values for substrates with only one destabilizing group range from 2×10^3 to 10^7 for CF_3[1] and 10^2 to 10^6 for CN.[2]

Three of the possible causes for the unexpectedly high reactivity of **1a–d** include strong electron donation by the group R, ground-state strain, and charge delocalization onto the aryl group. As to the first of these, π-electron donation by CN is well documented,[2] but for CF_3 theoretical studies[7] suggest this effect will be considerably less important.

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