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Facile formation of benzene from a novel cyclohexane derivative

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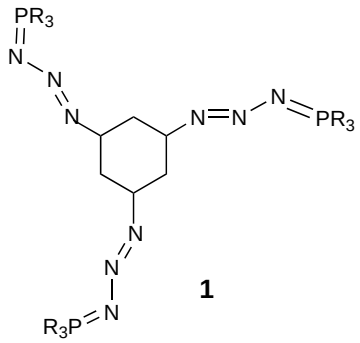
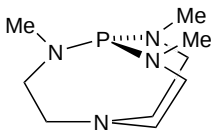
Abstract—Upon acidification, benzene forms at room temperature from the novel 1,3,5-*cis*-trisubstituted cyclohexane wherein the substituents are the azido phosphine cage moieties $N_3P(MeNCH_2CH_2)_3N$. The dominant reaction in the decomposition of this unusually thermally stable intermediate in the presence of HA is the formation of nitrogen and the salt $[H_2N{=}P(MeNCH_2CH_2)_3N]A$ in addition to benzene. Evidence for a transannulated cage intermediate is presented. © 2001 Published by Elsevier Science Ltd.

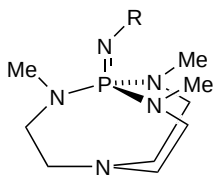
The aromatization of cyclohexane derivatives at room temperature is to our knowledge unknown in the literature. Such a transformation has been reported for cyclohexanedione dioximes upon treatment with polyphosphoric acid at 95–105°C[1] and in the oxidative aromatization of substituted cyclohexanes with $Pd(OAc)_2$ and $Na_2Cr_2O_7$ in CF_3CO_2H at 90°C.[2] Temperatures well above this range are required for aromatizations of cyclohexanes over bismuth phosphate,[3] stannic oxide,[3] a platinum complex,[4] and zeolitic[5] catalysts. Here we report that **1** undergoes a novel reaction with $PhCO_2H$ to form benzene (in 56% yield) within 1 h. Although a prohibitively expensive synthesis of benzene, this transformation represents the first example of



1

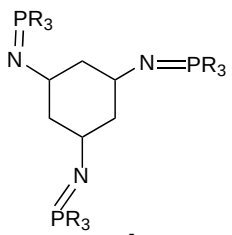


= PR_3 = **2**

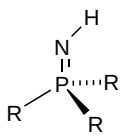


3

R
Me
Ph
CH_2Ph
Polymer



4



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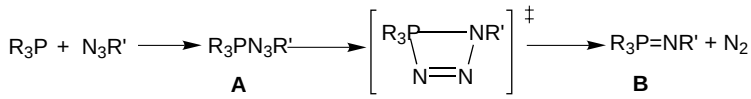
the aromatization of a cyclohexane derivative under very mild conditions.

The reaction of 3 equiv. of **2** with *cis*-1,3,5-triazidocyclohexane[6] in MeCN at 0°C in MeCN gave the triazido derivative **1** as an isolable thermally stable Staudinger intermediate, rather than the expected iminophosphine **4**. Compound **1** is very stable to thermolytic decomposition to the corresponding tris-iminophosphine derivative **4** even at 100°C/0.5 Torr for 10 h or in refluxing toluene for 24 h.

The Staudinger reaction is a two-step process involving the initial electrophilic addition of an alkyl or aryl azide to a P^{III} center followed by N_2 elimination from the intermediate phosphazide **A** to give the iminophosphine **B** in reaction 1.[7] Steric hindrance at the P^{III} center does not interfere with the electrophilic addition step, but it does suppress decomposition, since steric requirements in the four-membered ring transition state are much more rigorous than those in the addition transition state.[7] Donor character on the part of the P^{III} substituents stabilizes phosphazides,[7] and this factor apparently also operates in **1** to give it thermal stability. The unusual resistance of **1** to thermolysis may be enhanced by the rigidity of the cage structure, which by virtue of the planar geometry around the MeN nitrogens, maintains a methyl group in close proximity to the phosphorus–azido linkage.

stable 1:1 adducts in solution,[8] while strong acids cleave such compounds to the corresponding amine and phosphine oxide.[9] There is, however, a report describing the reaction of triphenylmethyl azido triphenylphosphine with acetic acid that gives N_2, $Ph_3CO_2CH_3$ and $Ph_3P{=}NH$.[10] In this reaction Ph_3C^+ was postulated to be an intermediate, as we believe is similarly the case in our reaction (**D** in Scheme 1). However, in this scheme carbocation formation facilitates proton abstraction by the product base **5** to form a C=C bond.

NMR studies showed that **1** does not undergo decomposition in the presence of acid at −30°C at an observable rate, although it does protonate. Thus, addition of $PhCO_2H$ to a solution of **1** in CD_3CN led to an initial dramatic upfield shift of the ^{31}P NMR resonance of the reaction mixture from 37.2 ppm to an asymptotically reached value of −11.0 ppm after 22.4 equiv. of $PhCO_2H$ had been added. This upfield shift strongly suggests that protonation in a rapidly established equilibrium is accompanied by the formation of species containing five-coordinated phosphorus arising from transannulation in the cage moieties. That such transannulation plays a role in the excellent leaving group properties exhibited by the cage moieties in **1** is strongly supported by the behavior in the presence of acids of its acyclic analogue **4** ($R = NMe_2$) which reacts about ten times slower and is also more susceptible to nitrogen evolution thermolytically when treated with acids at room temperature.



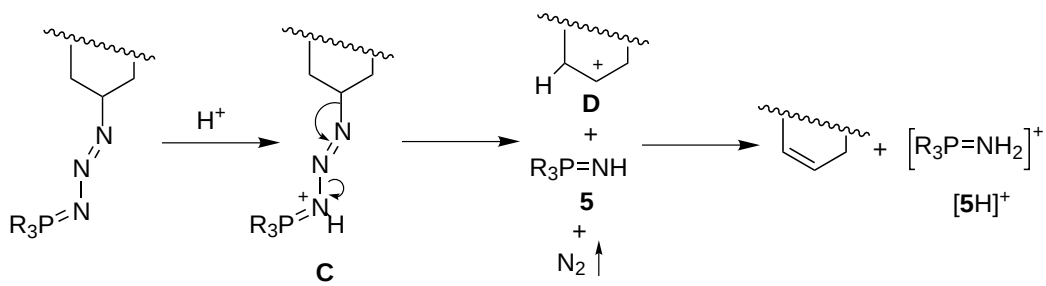
(1)

When **1** was treated with acids such as $PhCO_2H$, CH_3CO_2H, or CF_3CO_2H in CH_3CN at room temperature, an exothermic reaction accompanied by the rapid formation of N_2 (confirmed by GC–MS) and benzene (confirmed by ^1H NMR and GC mass spectroscopies) took place. In the case of $PhCO_2H$, benzene was formed in 56% yield (using toluene as a reference in the GC–MS experiment) within 1 h. Upon evaporation of the reaction mixture to dryness, crude [**5**H]$PhCO_2$ was isolated. Upon deprotonation of this salt with KO^{t}Bu in THF, the iminophosphine **5** was obtained.

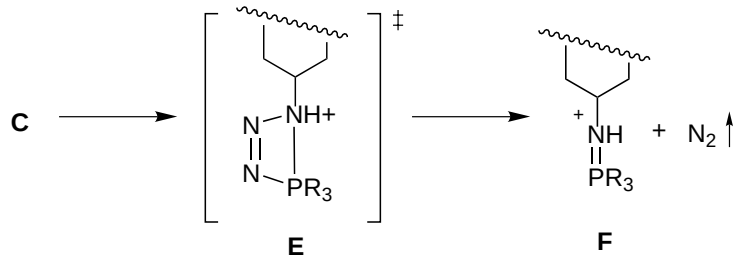
In contrast to our observation with **1**, weak acids have been reported to combine with azido phosphines to give

To better understand the mechanism of benzene formation in our reaction, we followed it over time by ESI mass spectroscopy. During the reaction of **1** with $PhCO_2H$, two intermediates [**6**H]$^+$ ($m/z = 597$) and [**7**H]$^+$ ($m/z = 338$) were detected, which disappeared upon reaction completion, while the product [**5**H]$^+$ ($m/z = 232$) increased over time. Two additional species [**8**H]$^+$ ($m/z = 541$) and [**9**H]$^+$ ($m/z = 310$) were observed as minor products.

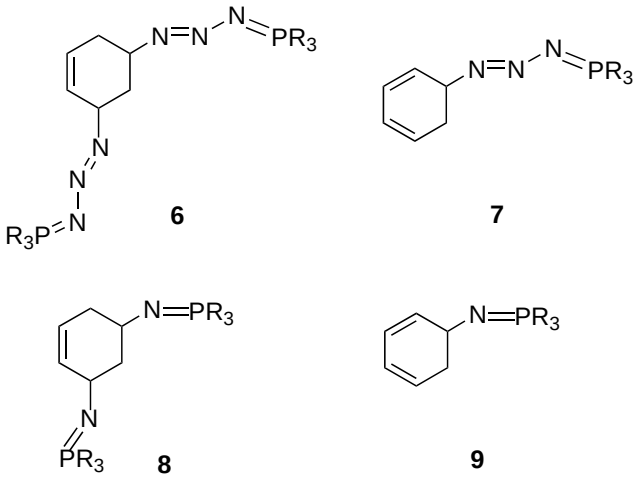
These observations are consistent with the reaction pathway shown in Scheme 1. The reaction begins with protonation of the exocyclic P–N nitrogen atom, which activates N_2 elimination to give **5** and a carbocation.



Scheme 1.



Scheme 2.



Then **5** serves as a base that quickly extracts a proton from the β carbon in the cyclohexane moiety to generate a new C=C bond. To gain further support for this mechanism, the proposed intermediate **6** was synthesized.[11] As expected, treatment of **6** with $PhCO_2H$ gave the same products as were observed with **1**.

The formation of impurities $[\mathbf{8}H]^+$ and $[\mathbf{9}H]^+$ in the reaction of **1** with $PhCO_2H$ may result from the competitive side reaction shown in Scheme 2. After protonation, a four-membered ring transition state **E** could form by rearrangement, followed by evolution of N_2 to give the protonated iminophosphine **F**.

Acknowledgements

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11. The formation of 3,5-*cis*-diazidocyclohexa-1-ene was observed in the present work as a minor product by ^1H NMR spectroscopy during the synthesis of 1,3,5-*cis*-triazidocyclohexane. This mixture, when subjected to silica gel column chromatography, gave 3,5-*cis*-diazidocyclohexa-1-ene in 10% yield. This product was combined with **2** in a 1:2 molar ratio in MeCN at 0°C, and then the reaction mixture was stirred at ambient temperature for 3 h. After evaporating the solvent and washing the residue with ether, compound **6** was obtained as a white solid in 85% yield.