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Nitrile Ylide Dimerization: Investigation of the Carbene Reactivity of Nitrile Ylides

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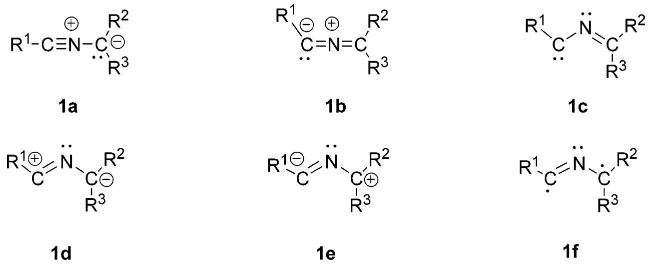
A series of novel hexaaryl diazatrienes **5** ("nitrile ylide dimers") were synthesized directly from the corresponding diaryl ketimines **12** and dichlorotoluenes **13** in a facile one-pot synthesis. The carbene character of the nitrile ylides was investigated by varying the substituents on the aromatic ring adjacent to the carbene center. The isolation of the corresponding carbene dimers as stable crystalline materials with absorption maxima (λ_{max}) from 363 to 422 nm was shown to be promoted by the absence of strongly electron-withdrawing substituents. The crystal structures indicate that the *E*-isomers were isolated when phenyl, 3-methylphenyl, and 3-chlorophenyl substituents are present at the carbene carbon; the *Z*-isomer was isolated when the more sterically hindered 2,4,6-trimethylphenyl substituent (Mes) is present. The ^{1}H NMR spectra of the *E*-isomers demonstrate the nonequivalence of the aromatic rings, in which two of the aromatic rings of the imine moiety are pseudoaxial and the remaining aromatic rings are pseudoequatorial. The reactions proceed via the intermediate nitrile ylides **1** generated by the base-promoted 1,1-elimination of HCl from the intermediate chloroimine **14**. The nitrile ylide was also generated by 1,3-elimination of HCl from the imidoyl chloride **18**, confirming common pathways via the nitrile ylide as the dimer products obtained from these different routes were identical. The strongly electron-withdrawing 4-nitrophenyl substituent promotes the linear carbanion character of the 1,3-dipole and no dimer is formed.

Introduction

Nitrile ylides **1** are 1,3-dipolar species that were first predicted and prepared by Rolf Huisgen in the 1960s when he was investigating and studying 1,3-dipoles and their cycloaddition reactions.[1,2] They are classified as "nitrile ylides" due to the presence of the −C≡N− moiety at the cationic center and are described by a C−N−C framework containing six electrons in n and π orbitals, and three ligands linked with the carbon atoms. The nitrile ylides can be described by using six electronic arrangements with either a bent or linear framework (Scheme 1), illustrating two possible octet forms **1a** and **1b**, one carbene-like sextet structure **1c**, two zwitterionic sextet forms **1d** and **1e**, and a diradical structure **1f**.

In 1961, Huisgen generated the first nitrile ylide (Scheme 2), via the base-promoted 1,3-elimination of hydrogen chloride from the imidoyl chloride *N*-(4-nitrobenzyl)benzoic acid imidoyl chloride **2**, using triethylamine at 0−20 °C;[1a] triethylammonium chloride was separated and a deep purple solution of the nitrile ylide benzonitrile-4-nitrobenzylide **3** resulted. The nitrile ylide **3** was not isolated from the reaction mixture but could be trapped with dipolarophiles, e.g. in the presence of acrylonitrile two diastereoisomeric Δ^1-pyrrolines **4** were obtained.

SCHEME 1. Electronic Arrangements of Nitrile Ylide



We have previously reported[3] the formation of kinetically stable trifluoromethyl-substituted nitrile ylides in acetonitrile and aqueous dioxane solutions using this method. Highly colored solutions typified by long-wavelength absorbances were observed when the nitrile ylides contained a 4-nitrophenyl substituent. Trapping reactions using dipolarophiles such as acrylonitrile and methyl acrylate confirmed the presence of these 1,3-dipoles.

Nitrile ylides may also be generated by a number of methods including thermolysis of Δ^3-oxazolinones[4] and

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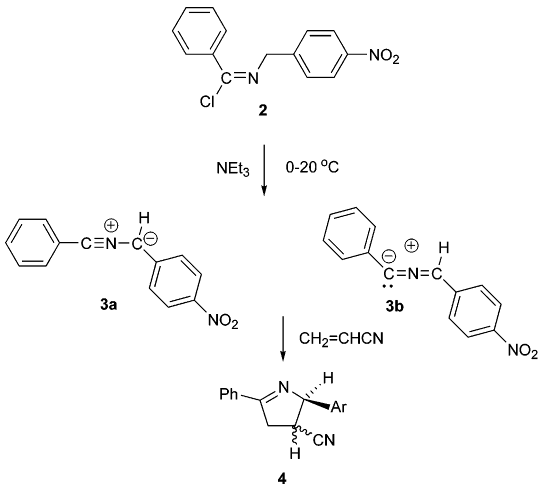
(1) (a) Huisgen, R.; Stangl, H.; Sturm, H. J.; Wagenhofer, H. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 50. (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. (c) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633. (d) Huisgen, R.; Grashey, R.; Sauer, J. In *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience: New York, 1964; pp 806−878. (e) Huisgen, R. *J. Org. Chem.* **1968**, *33*, 2291. (f) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403.

(2) Nitrile ylide review: Hansen, H. J.; Heimgartner, H. *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; p 177.

(3) Hegarty, A. F.; Eustace, S. J.; Tynan, N. M.; Pham-Tran, N. N.; Nguyen, M. T. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1239.

10.1021/jo049748g CCC: $27.50

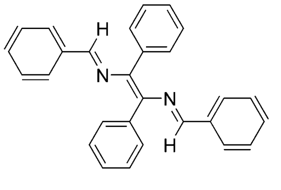
SCHEME 2. Huisgen's Generation of Nitrile Ylide



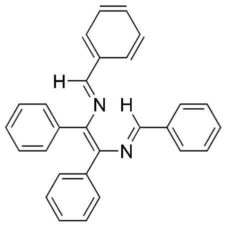
oxazaphospholes,[5] the reactions of carbenes with nitriles[6] and isonitriles with triphenylborane,[7] and the photolysis of 2*H*-azirines.[8] Recently it was reported that the photolysis of 3-pyridylcarbene and 3-pyridylnitrene results in ring opening to nitrile ylides.[9] Presently, the most efficient and convenient pathways for the generation of nitrile ylides are the photolysis of 2*H*-azirines together with Huisgen's method employing imidoyl chlorides.

Huisgen originally suggested that the bent form of a nitrile ylide would be less stable than the linear form, since allyl resonance would be at a maximum with the linear arrangement.[1c] However, ab initio LCAO-MO-SCF and MINDO calculations carried out by Houk and Caramella show that the parent nitrile ylide is bent with an HCN angle of 114−116°.[10] The stabilization over the optimized linear form was calculated to be 11.1 kcal/mol (4-31G).

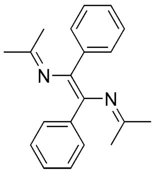
There are limited reports on the behavior of these nitrile ylides as imine-stabilized carbenes. The carbene-like reactivity of nitrile ylides is supported by their observed dimerization in the absence of trapping reagents to form diazahexatrienes **5**. Padwa was the first to isolate such structures **5a** and **5b**, from the photolysis of 2*H*-azirines;[8e−g,11] Heimgartner and Schmid have reported on the dimerization of nitrile ylides produced photochemically from 2*H*-azirines,[12] and similarly, Taniguchi[13] isolated an aryl-substituted diazahexatriene **5c**, which was also formed via the azirine.



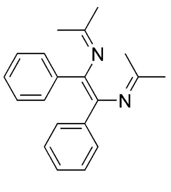
5a(E)



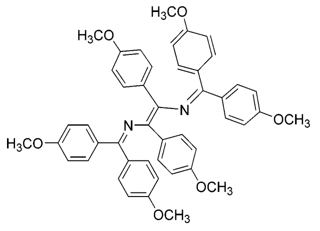
5a(Z)



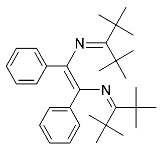
5b(E)



5b(Z)



5c



5e

The diazahexatriene **5d** is postulated as an intermediate in the formation of dimer **7** from the thermolysis or photolysis of 4,5-dihydro-1,3,$2\lambda^5$-dioxaphosphole **6** with the cycloelimination of phosphoric acid ester (Scheme 3).[14] There is one further example of such a diazahexatriene **5e**, which was probably also generated via the ylide, although these results were not explained.[15]

We wish to report a study on the factors which promote (or suppress) the "carbene-like" character of the 1,3-dipoles. These imine nitrogen stabilized structures **1c** are

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(4) Steglich, W.; Gruber, P.; Ulrich, H. H.; Kneidl, F. *Chem. Ber.* **1971**, *104*, 3816.

(5) (a) Burger, K.; Fehn, J.; Moll, E. *Chem. Ber.* **1971**, *104*, 1826. (b) Burger, K.; Fehn, J. *Chem. Ber.* **1972**, *105*, 3814. (c) Wentrup, C.; Fischer, S.; Berstermann, H.-M.; Kuzaj, M.; Lüerssen, H.; Burger K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 85.

(6) (a) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Thomas, M. *J. Org. Chem.* **1985**, *50*, 4415. (b) Padwa, A.; Gasdaska, J. R.; Thomas, M.; Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 6739. (c) Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 2101.

(7) (a) Hesse, G.; Witte, H.; Bittner, G. *Liebigs Ann. Chem.* **1965**, *687*, 9. (b) Bittner, G.; Witte, H.; Hesse, G. *Liebigs Ann. Chem.* **1968**, *713*, 1.

(8) (a) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I., Jr. *Pure Appl. Chem.* **1973**, *33*, 269. (b) Padwa, A. *Acc. Chem. Res.* **1976**, *9*, 371. (c) Padwa, A.; Smolanoff, J. *J. Am. Chem. Soc.* **1971**, *93*, 548. (d) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1945. (e) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 1954. (f) Padwa, A.; Wetmore, S. I., Jr. *J. Org. Chem.* **1973**, *38*, 1333. (g) Padwa, A.; Wetmore, S. I., Jr. *J. Org. Chem.* **1974**, *39*, 1396. (h) Padwa, A.; Wetmore, S. I., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2414. (i) Gilgen, P.; Heimgartner, H.; Schmid, H. *Heterocycles* **1977**, *6*, 143. (j) Gakis, N.; Märky, M.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 748. (k) Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 745. (l) Claus, P.; Doppler, T.; Gakis, N.; Gerorgarakis, M.; Giezendanner, H.; Gilgen, P.; Heimgartner, H.; Jackson, B.; Märky, M.; Narasimhan, N. S.; Rosenkranz, H. J.; Wunderli, A.; Hansen, H. J.; Schmid, H. *Pure Appl. Chem.* **1973**, *33*, 339.

(9) (a) Bednarek, P.; Wentrup, C. *J. Am. Chem. Soc.* **2003**, *125*, 9083. (b) Maltsev, A.; Bally, T.; Tsao, M.-L.; Platz, M. S.; Kuhn, A.; Vosswinkel, M.; Wentrup, C. *J. Am. Chem. Soc.* **2004**, *126*, 237.

(10) (a) Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397. (b) Caramella, P.; Gandour, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N. *J. Am. Chem. Soc.***,** **1977**, 99, 385.

(11) (a) Padwa, A.; Clough, S.; Dharan, M.; Smolanoff, J.; Wetmore, S. I. *J. Am. Chem. Soc.* **1972**, *94*, 1395. (b) Padwa, A.; Wetmore, S. I. *J. Chem. Soc., Chem. Commun.* **1972**, 1116. See also the following for a review of carbenes in heterocyclic chemistry: Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 231−361.

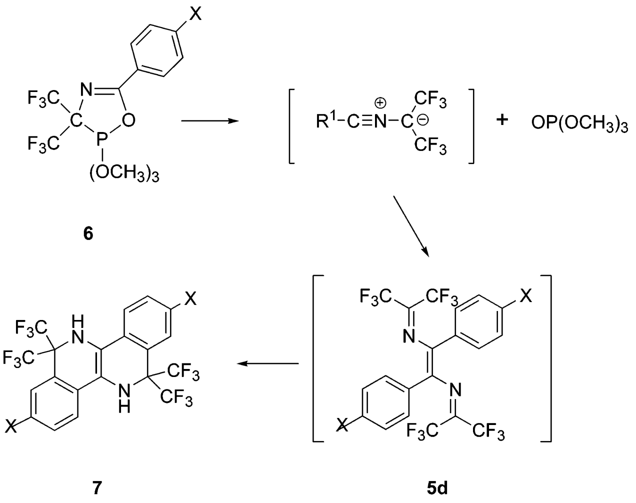
(12) (a) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1977**, *58*, 2662. (b) Gakis, N.; Märky, M.; Hansen, H.-J.; H.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 748. (c) See also: George, M. V.; Mitra, A.; Sukumuran, K. B. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 973.

(13) (a) Kitamura T.; Kobayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1979**, *18*, 1619. (b) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1984**, *49*, 4755.

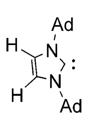
(14) Burger, K.; Einhellig, K.; Süss, G.; Gieren, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 156.

(15) Weidner, R.; Würthwein, E. U. *Chem. Ber.* **1989**, *122*, 1095.

SCHEME 3. Thermolysis or Photolysis of 4,5-Dihydro-1,3,2λ^5-dioxaphosphole



related to the Arduengo bisamino-stabilized carbenes **8**,[16] and the recently reported aminoarylcarbenes **9**,[17] where substituents can be varied on an aromatic ring directly attached to the carbene center.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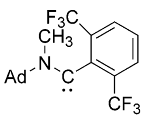
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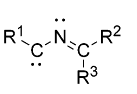
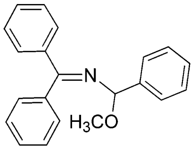

1c

The intermediates **1** were formed by the 1,1-elimination of HCl upon condensation of diaryl ketimines **12** with a variety of α,α-dichlorotoluenes **13** (Scheme 4) and in certain cases by the 1,3-elimination from the corresponding imidoyl halides.

Results and Discussion

1,1-Elimination. Under suitable alkylation conditions, diaryl ketimines undergo reaction to form *N*-substituted imines; benzophenone imine **12i** reacts with α-chlorobenzylmethyl ether and dichlorodiphenylmethane to form the *N*-substituted imines, *N*-(diphenylmethylene)-α-methoxybenzylamine (**10**)[15] and diphenylketiminodiphenylmethyl chloride (**11**),[18] respectively. However, when the condensation is carried out with benzophenone imine **12i** and α,α-dichlorotoluene **13** under a wide variety of experimental conditions, we have found that the expected chloride product **14** could not be isolated (Scheme 4). No reaction occurred when triethylamine in benzene was employed as the base, or on changing the solvent from benzene to the more polar acetonitrile.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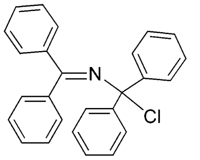
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SCHEME 4. Formation of Nitrile Ylide Dimers

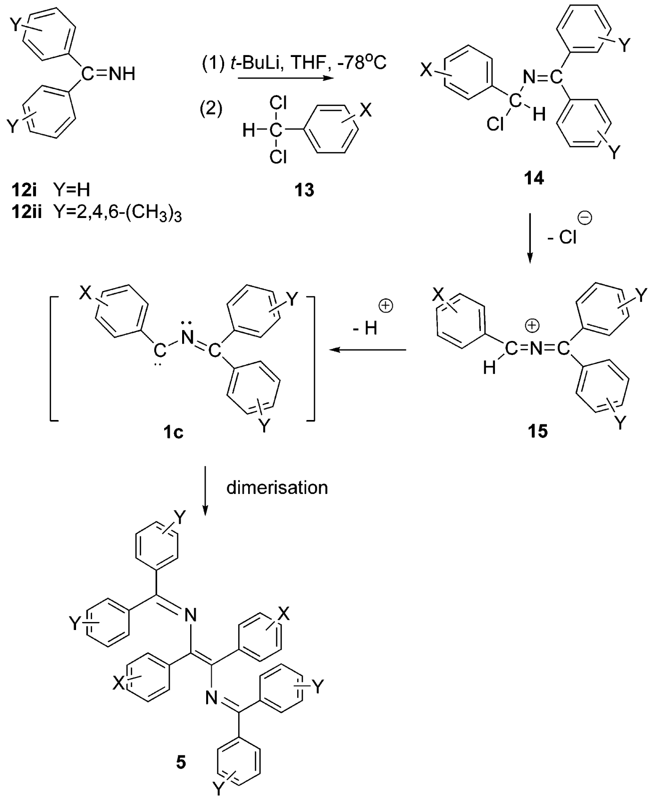

TABLE 1. Yields (%) of Dimers 5

5	X	Y	yield
f	H	H	27
g	2-CH_3	H	11
h	3-CH_3	H	25
i	4-CH_3	H	13
j	4-OCH_3	H	11
k	3-Cl	H	4
l	2,4,6-$(CH_3)_3$	H	2.4
m	2,4,6-$(CH_3)_3$	2,4,6-$(CH_3)_3$	6
n	H	4-CH_3	6
o	4-CH_3	4-CH_3	7

Elemental analysis, in conjunction with mass spectrometry, indicated loss of a second mole of HCl followed by dimerization had occurred. The structure and stereochemistry of this dimer, which was isolated only as the *E*-isomer **5f**, was determined by X-ray crystallography (see Figure S1 in the Supporting Information).

This reaction was successfully repeated for a number of substituted analogues **5f**−**o** (Table 1) with either electron-donating substituents (3-methyl [σ_m −0.06], 4-methyl [σ_p −0.14], 4-methoxy [σ_p −0.27]) or the electron-withdrawing 3-chlorophenyl (σ_m 0.37) substituent present at the C1 carbon atom of the nitrile ylide.

In contrast, however, no dimerization was observed when the strongly electron-withdrawing 4-NO_2-phenyl substituent (σ_p 0.78) was present. In this case the alkene (*E*)-α,α′-dichloro-4,4′-dinitrostilbene **16** was isolated from the reaction mixture. A reaction pathway (Scheme 5)

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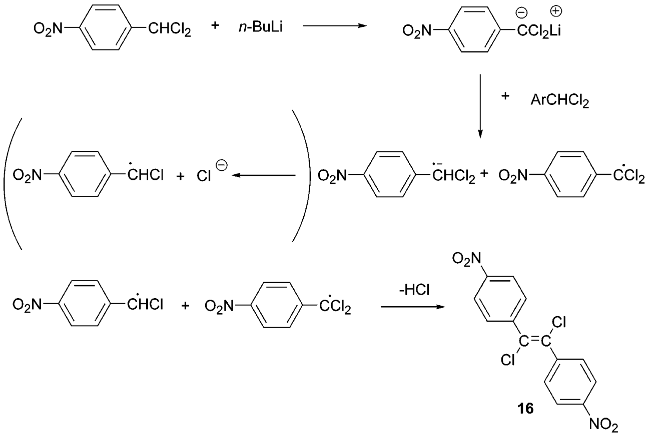
[16] Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913.

[17] (a) Solé, S.; Pradel, C.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2001**, *292*, 1901. (b) Cattoën, X.; Solé, S.; Pradel, C.; Gornitzka, H.; Miqueu, K.; Bourissou, D.; Bertrand, G. *J. Org. Chem.* **2003**, *68*, 911.

[18] (a) Samuel, B.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1968**, 1081. (b) Samuel, B.; Wade, K. *J. Chem. Soc. (A)* **1969**, 1742.

SCHEME 5. Reaction Pathway Formation of 16



observed by Chan[19] accounts for the formation of **16**, indicating that the reaction of base with the aryl halide forms radicals, which subsequently dimerize followed by elimination of HCl to give **16**.

In an attempt to optimize the yield of dimer, the base (its nature and the number of equivalents), the time of reaction, and the temperature were varied. It is concluded from these reactions that the main difficulty encountered in the reaction sequence was the removal of the imine hydrogen (benzophenone imine **12i** has a reported pK_a of 31).[20]

Initially the base *n*-butyllithium was used but the yield of the dimer **5f** was low (33.4%) as determined from HPLC product analysis. Other bases that were examined include LDA, *tert*-butyllithium, and a 1:1 mixture of *n*-butyllithium and potassium *tert*-butoxide, referred to as a "superbase".[21] Also investigated were the effects of temperature variation and the addition of a second equivalent of base when the α,α-dichlorotoluene **13** was added at −78 °C. It was concluded that using 1 equiv of *tert*-butyllithium affords the maximum formation of dimer although product analysis showed that some unreacted starting material remained in the reaction mixture under these conditions.

TABLE 2. Product Distribution(%) of Imidoyl Chloride 18 Formation

compd	imidoyl chloride	von Braun
18a	88	12
18b	95	5

1,3-Elimination. The generation of nitrile ylides by the 1,3-elimination of hydrogen chloride from imidoyl chlorides was also examined. The imidoyl chlorides **18** were prepared by reacting phosphorus pentachloride (PCl_5) and the corresponding amide **17** in dry benzene. Once synthesized, the imidoyl chlorides were stored under nitrogen at 0 °C as they are highly susceptible to hydrolysis. They were used in all cases either immediately or within 1−2 days.

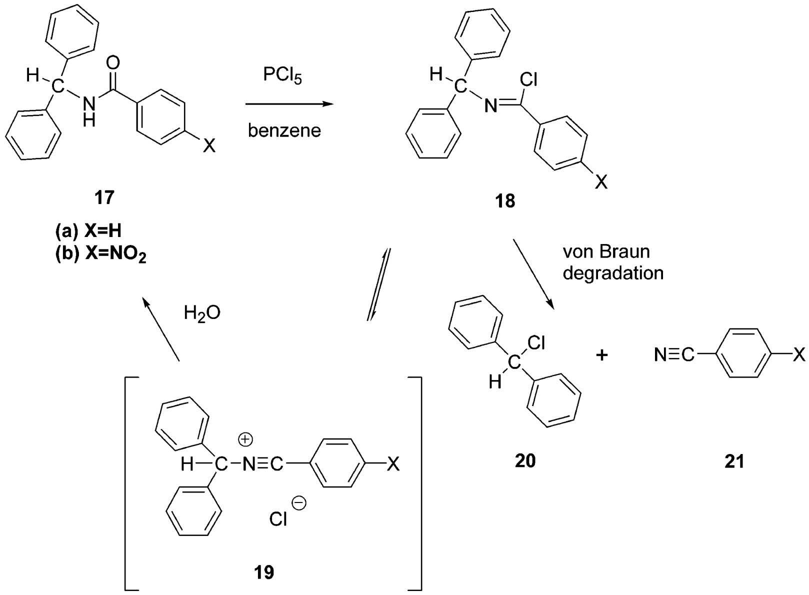
A competing pathway, known as von Braun degradation,[22] proved problematic during their synthesis. This reaction resulted in the formation of the chloride **20** and the nitrile **21** (which were observed spectroscopically), via the nitrilium ion **19** (Scheme 6).

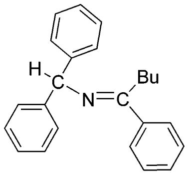
It was found that the extent of von Braun degradation is minimized by avoiding heat when removing the reaction solvent during the workup of the imidoyl chlorides. After solvent removal, the product is placed on a vacuum pump immediately to remove any traces of $POCl_3$, which is an ionizing solvent, thus helping to promote von Braun degradation. The optimized product distribution during the formation of the imidoyl chlorides **18** is shown in Table 2.

Huisgen's method to generate nitrile ylides from imidoyl chlorides using the base triethylamine proved unsuccessful in the 1,3-elimination pathway. The *N*-butyl-substituted imine **22** was formed when *n*-butyllithium was employed as base.

However, the more sterically hindered and less nucleophilic base LDA successfully generated the nitrile ylide from the corresponding imidoyl chloride and in the absence of a dipolarophile the hexaaryl diazatrienes **5** ("nitrile ylide dimers") were again formed.

SCHEME 6. Von Braun Degradation of Imidoyl Chlorides





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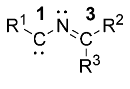
The addition of LDA to the imidoyl chloride *N*-benzhydryl-4-nitrobenzimidoyl chloride **18b** resulted in the initial formation of a purple solution. As indicated above, a purple color is characteristic of nitrile ylides containing a 4-nitrophenyl substituent. The reaction mixture turned a dark orange/brown color after being warmed to ambient temperature and stirred overnight. Unlike the case with *N*-benzhydrylbenzimidoyl chloride **18a** (where a phenyl substituent is present at the carbene carbon of the nitrile ylide), no evidence for the 4-nitrophenyl dimer in the mass spectrum of the crude product was present.

Carbene Character of Nitrile Ylide. The hexaaryltrienes **5** were isolated as the *E*-isomers in the cases of **5f**, **5h**, and **5k** when a phenyl, 3-methylphenyl, and 3-chlorophenyl substituent are present respectively adjacent to the carbene center.

However, in the case of **5l** (Figure S25 in the Supporting Information) the sterically hindered Mes substituent adopts the *Z*-configuration. The Schekal program was used to display the crystal structures allowing rotation of the molecule, but it was not possible to rotate 180° about the double bond in **5l** illustrating that the *E*-isomer is destabilized by the presence of the Mes substituents.

Recrystallization of the products by using the mixed solvent system chloroform/acetonitrile afforded the dimers as highly colored compounds with absorption maxima (λ_{max}) from 363 to 422 nm. The dimers do not appear to be stable on silica; further decomposition of the dimers appeared on thin-layer chromatography (TLC) after separation. Previous reports by Padwa[8b] on the behavior of similar structures indicate that during separation via column chromatography protonation followed by hydrolysis occurs resulting in the decomposition of the phenyl dimer **5f** to produce benzophenone **23** and 2-amino-1,2-diphenylethanone **24** as shown in Scheme 7.

Padwa[23] has reported on the role of substituents in controlling *intramolecular* cycloaddition reactions of nitrile ylides. He has demonstrated that electron-donating substituents, e.g., CH_3 on carbon C3 of the nitrile ylide, favor the carbene character resulting in 1,1-cycloadditions where the nitrile ylide has a bent geometry, whereas electron-withdrawing substituents at this position, e.g., CF_3 and C_6H_5-4-NO_2, and a H substituent promote 1,3-dipolar cycloadditions with linear geometry of the nitrile ylide.



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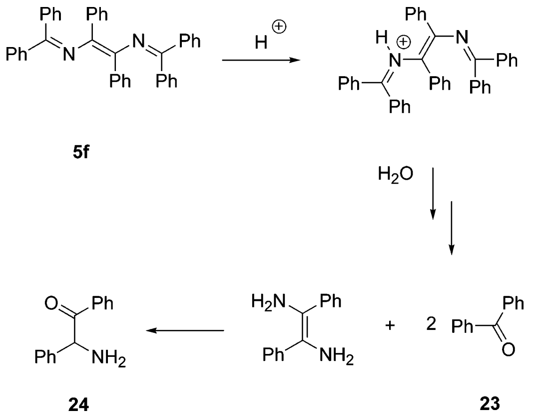
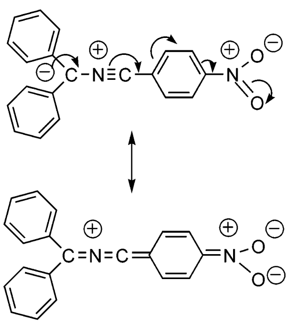
SCHEME 7. Hydrolysis of Diazatrienes



SCHEME 8. Delocalization by Nitro Group on Nitrile Ylide



From our results on *intermolecular* reactions of nitrile ylides, it appears that the primary control of carbene behavior of the nitrile ylides is through electronic effects at C1. The use of strongly electron-withdrawing substituents diminishes the carbene-like reactivity of the nitrile ylides and promotes its linear and carbanion character resulting in a lower yield of isolated dimer. This is also evident in comparing the yields of isolated phenyl dimer **5f** and 3-chloro dimer **5k**. The steric effects offered by the electron-donating 2-methylphenyl and Mes substituents result in lower yields of their isolated dimers, presumably due to steric shielding of the reactive site at the carbene center C1, which reduces the yield of dimer.

The presence of the strongly electron-withdrawing 4-nitrophenyl substituent on the nitrile ylide (generated via 1,3-elimination of HCl from the *N*-benzhydryl-4-nitrobenzimidoyl chloride **18b** or via the 1,1-elimination pathway) suppresses the formation of the resulting dimer product. The presence of the nitro group on the phenyl ring allows the negative charge formed to be delocalized throughout the molecule, resulting in the linear nitrile ylide as shown in Scheme 8.

Mechanism. Steenken[24] has shown that nitrile ylides generated on the photochemical ring opening of 2*H*-azirines **25** react rapidly in the presence of proton donors (such as alcohols) to form the aza-allenium cations **26** as intermediates ultimately yielding the alkoxyimines **27**. This occurs in preference to protonation on the other

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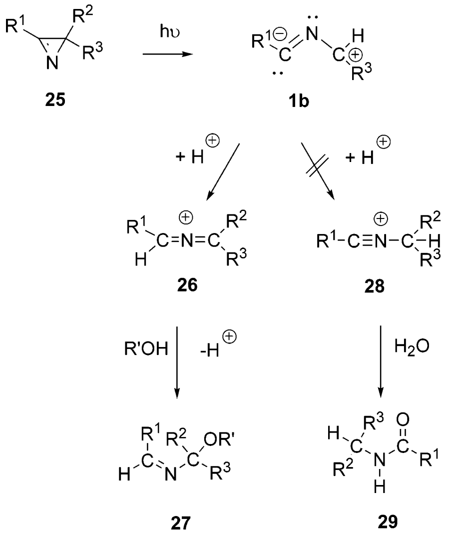
SCHEME 9. Protonation of Nitrile Ylides



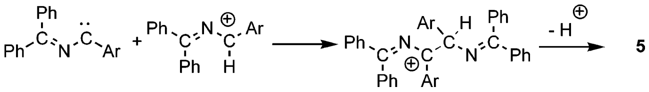
carbon (C3), which would give the nitrilium cation **28**, yielding the amides **29** upon reaction with water (Scheme 9).[25] However, an amide of type **29** is formed with an electronegatively substituted nitrile ylide [$(CF_3)_2$ at C3] and hence a linear carbanion nitrile ylide.[5c]

Condensation of diaryl ketimines **12** with a variety of α,α-dichlorotoluenes **13** most likely proceeds via the chloroimine **14,** which then ionizes to the aza-allenium ion **15** followed by loss of a proton in the presence of a strong base. Evidence to support this mechanism (Scheme 4) comes from the isolation of the intermediate imine in cases when ionization to the cation is unfavorable due to the lack of a suitable leaving group (for example, in compounds **10** and **11**).

The dimerization of singlet carbenes normally involves the attack of the occupied in-plane σ lone pair of one carbene center on the out-of-plane vacant p_π orbital of a second carbene.[26] Alder[27] has observed ^{13}C NMR and X-ray evidence for the interaction between stable diaminocarbenes and imidazol-2-ylidene with lithium, sodium, and potassium species in toluene and THF solutions. The question of alkali metal coordination is important with regard to the generation of carbenes by deprotonation, using bases with alkali metal counterions (e.g. *n*-BuLi, NaH, LDA) as the carbene may be complexed with a metal or held in a solvent cage with a salt. Recently Bertrand has reported a new synthetic route to form stable metal-free diaminocarbenes and transient monoaminocarbenes.[28]

It must be stated that when formal carbene dimers are isolated, a mechanism of nucleophilic attack of one carbene upon its conjugate acid followed by proton elimination may also explain their formation (Scheme 10), as suggested by Chen and Jordan.[29] However, the basic conditions used in the present study make this unlikely.

SCHEME 10. Carbene Dimer Formation



Structure of Dimers and NMR Spectra. The crystal structures of the hexaaryl diazatrienes **5h** and **5k** isolated as the *E*-dimer do not deviate or illustrate unusual properties relative to the unsubstituted phenyl dimer **5f**. The *Z*-isomer **5l** is not equiplanar about the C═C, with an angle of 5° between both planes. There is a distance of 2.66 Å between H*21* of the Mes substituent and C*8* of the adjacent Mes substituent.

The NMR spectra of these dimeric structures were assigned by using ($^1H-^1H$) COSY and ($^1H-^1H$) NOESY. The ^1H spectra of the dimers clearly illustrate the consistency of the doublets corresponding to the ortho protons in the aromatic rings of the imine moiety, which occur at 6.6−6.7 ppm for the pseudoequatorial rings, and at 7.5−7.6 ppm for the pseudoaxial rings.

Two of the aromatic rings of the imine moiety are pseudoaxial whereas the remaining aromatic rings are pseudoequatorial. This nonequivalence in each of the aromatic rings may be explained in terms of slow interconversion of the imine functionalities, which generally occurs via nitrogen inversion. There is no evidence for π-stacking of the equatorial aromatic rings from their crystal structures.

Conclusion

A series of novel hexaaryl diazatrienes **5** ("nitrile ylide dimers") were formed via the nitrile ylide **1** generated by the base-promoted 1,1-elimination of HCl from the intermediate chloroimine **14**. These dimers were isolated as stable crystalline materials in both the *E* and *Z* configurations depending on the substituents present on the aromatic ring adjacent to the carbene center. A second route, using 1,3-elimination of HCl from the imidoyl chloride **18**, was also successfully used to synthesize the dimer product **5**, confirming that the two pathways proceed via the same nitrile ylide intermediate. It was found that the 1,1-elimination of HCl from the intermediate chloroimines **14** was generally a less problematic and more facile route to the nitrile ylides than the 1,3-elimination of HCl from the corresponding imidoyl chlorides **18**.

It is concluded that the reaction most likely proceeds via the chloroimine **14**, which then ionizes to the aza-allenium ion **15** followed by loss of a proton.

The behavior of nitrile ylides is controlled by the substituent groups present, with the bent carbene form **1c** favored with electron-donating substituents or a 3-chlorophenyl substituent; however, the strong electron-withdrawing substituents (i.e., 4-NO_2-C_6H_4) suppress the carbene-like reactivity of the nitrile ylides.

Experimental Section

Dimer Synthesis: 1,1,3,4,6,6-Hexakisphenyl-2,5-diaza-1,3,5-hexatriene (5f). A solution of **11i** (0.5 mL, 3.0 mmol) in dry THF (5 cm^3) was cooled to −78 °C. Dropwise addition

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of *tert*-butyllithium (1.7 M, 1.76 mL, 8.56 mmol) resulted in a bright red solution, which was stirred for 1 h at −78 °C and 30 min at ambient temperature. The addition of α,α-dichlorotoluene (0.38 mL, 3.0 mmol) in dry THF (3 mL) was subsequently carried out at −78 °C. The cooling bath was removed and the red solution was left to stir overnight at ambient temperature. The following day, the solvent was removed and the residue dissolved in toluene before filtration to remove insoluble inorganic materials. The solvent was removed in vacuo to give **5f** (0.22 g 27%) as an orange/red material, which was recrystallized from chloroform/acetonitrile. Mp 213-214 °C. UV (CH_3CN, nm) 249 (ϵ 35 022), 411 nm (ϵ 5830). IR (KBr, cm^{-1}) 1615 (C═N), 1595 (C═C, aromatic). ^1H NMR (500 MHz, $CDCl_3$) δ 6.64 (4H, d, $J = 7.44$ Hz, *H10, H14*), 6.98−7.06 (6H, m, *H5*−*H7*), 7.11−7.15 (8H, m, *H4, H8, H11, H13*), 7.23 (2H, m, *H12*), 7.29 (4H, m, *H17, H19*), 7.36 (2H, m, *H18*), 7.58 (4H, d, $J = 7.52$ Hz, *H16, H20*). ^{13}C NMR (126 MHz, $CDCl_3$) δ 126.0, 127.3, 127.4, 127.5, 128.0, 128.1, 128.2, 128.4, 129.1, 129.2, 130.2, 132.9, 137.9, 139.7, 139.8, 168.7. Anal. Calcd for $C_{40}H_{30}N_2$: C, 89.30; H, 5.62; N, 5.21. Found: C, 88.90; H, 5.70; N, 5.15. MS 538 (M^+, 19%), 269 ($M^+/2$, 23%), 165 (100%).

Synthesis of Imines. The imines were prepared by a procedure reported by Pickard and Tolbert.[30] The process involves a Grignard reaction with an aryl nitrile and subsequent decomposition of the complex with anhydrous methanol.

2,4,6,2′,4′,6′-Hexamethylbenzophenoneimine (12ii). Bromomesitylene **30** (5.0 g, 0.025mol) was added dropwise to magnesium turnings (0.75 g, 0.3mol) in 20 mL of dry THF under an atmosphere of nitrogen. A crystal of iodine was necessary to initiate the Grignard reaction. The reaction was refluxed for 2 h. Then the THF was distilled from the reaction mixture and a solution of 2,4,6-trimethylbenzonitrile **32** (2.78 g, 0.019mol) in dry toluene (30 mL) was added slowly. The reaction mixture was refluxed for 12 h. After cooling, dry methanol (15 mL) was added slowly, the gummy mixture was filtered ,and the filtered solid was washed ether. The solvent was removed in vacuo and recrystallization of the brown solid was carried out with absolute alcohol to give **12ii** (2.61 g, 52%) as pale brown crystals. Mp 128−130 °C (lit.[31] mp 130 °C). IR (KBr, cm^{-1}) 3253 (N−H), 2961 (ν_{as} CH_3), 2916 (ν_s CH_3), 1608 (C═N), 1598 (C═C, aromatic). ^1H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 12H), 2.27 (s, 6H), 6.84 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 21.2, 129.9, 136.3, 138.4, 178.6. Anal. Calcd for $C_{19}H_{23}N$: C, 85.99; H, 8.74; N, 5.28. Found: C, 85.79; H, 8.75; N, 5.53. MS 265 (M^+, 1%), 250 (M^+ − NH, 100%), 235 (22%), 219 (3%), 144 (12%), 118 (12%).

Synthesis of α,α-Dichlorotoluenes. The α,α-dichlorotoluenes were used immediately due to their high reactivity, which also made microanalyses difficult to obtain.

1-Dichloromethyl-2-methylbenzene (13g). A solution of *o*-tolualdehyde (4.00 mL, 0.035 mol) in dry toluene (30 mL) was added dropwise via cannula to a suspension of PCl_5 (7.20 g, 0.035 mol) in dry toluene (40 mL). The reaction was maintained under an atmosphere of nitrogen and stirred overnight at ambient temperature.

The pale pink solution was poured onto ice, the organic layer was washed with bicarbonate solution, dried over $MgSO_4$, and filtered, and solvent was removed in vacuo to give a clear oil. Vacuum distillation was carried out to purify the product **13g** (4.85 g, 80%). Bp 54 °C (0.2 mbar Hg) [lit. bp[32] 225 °C]. IR (liq film, cm^{-1}) 1604 (C═C, aromatic), 727 (C−Cl). ^1H NMR (300 MHz, $CDCl_3$) δ 2.43 (3H, s), 6.91 (1H, s), 7.12−7.77 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0, 69.9, 127.0, 127.2, 130.1, 131.0, 134.4, 138.4.

***N*-Benzhydrylbenzamide (17a).** A solution of freshly distilled triethylamine (8.08 mL, 0.058 mol) and aminodiphenylmethane (10.0 mL, 0.058 mol) in dry CH_2Cl_2 (50 mL) was added dropwise over 30 min to a vigorously stirred solution (large magnetic bob) of benzoyl chloride (6.73 mL, 0.058 mol) in dry CH_2Cl_2 (50 mL). Upon complete addition, the reaction mixture was refluxed for 3 h. After cooling, deionized water was added and the organic layer was washed with deionized water, 1 M HCl, followed by sat. NaCl solution. The organic layers were dried over $MgSO_4$ and filtered and solvent removed in vacuo to give a pale yellow crystalline solid. Recrystallization with absolute alcohol yielded **17a** (14.88 g, 89.3%) as white crystals. Mp 169−172 °C (lit. mp[33] 174 °C). UV (CH_3CN, nm) 221 nm (ϵ 16 475). IR (KBr, cm^{-1}) 3310 (N−H), 3054 (ν_{as} CH), 3028 (ν_s CH), 1638 (C═O), 1601 (C═C, aromatic). ^1H NMR (300 MHz, $CDCl_3$) δ 6.45 (d, 1H, $J = 7.615$ Hz), 6.75 (d br, 1H, $J = 7.029$ Hz), 7.25−7.53 (m, 13H), 7.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.3, 127.3, 127.8, 127.8, 128.9, 129.0, 131.9, 134.6, 141.8, 167.8. Anal. Calcd for $C_{20}H_{17}NO$: C, 83.95; H, 5.96; N, 4.87. Found: C, 83.59; H, 5.95; N, 4.91. MS 287 (M^+, 46%), 210 (8%), 182 (23%), 165 (21%), 105 (100%).

***N*-Benzhydrylbenzimidoyl Chloride (18a).** A solution of PCl_5 (1.07 g, 5.14 mmol) in dry benzene (45 mL) was added via cannula to a suspension of **17a** (1.44 g, 5.01 mmol) in dry benzene (50 mL) at 0 °C. The reaction was left to stir overnight at ambient temperature. The following day, the benzene was removed in vacuo and traces of $POCl_3$ were removed immediately, using the vacuum pump to yield **18a** (1.51 g). IR (liq film, cm^{-1}) 2967 (ν_{as} CH), 2928 (ν_s CH), 1660 (C═N), 1601 (C═C, aromatic), 672 (C−Cl). ^1H NMR (300 MHz, $CDCl_3$) δ 6.25 (s, 1H), 7.21−7.51 (13H, m), 8.11 (2H, dd, $J = 8.347$ Hz, $J = 1.464$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 71.3, 127.5, 127.9, 128.0, 128.3, 128.5, 128.6, 128.8, 129.5, 131.7, 136.2, 140.9, 142.96.

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Supporting Information Available: General experimental information, characterization data for **5g**−**o**, **13h**−**m**, **16**, **17b**, and **18b**, supplementary IR data for **5f** and **13g**, synthesis of **5f** by the 1,3-elimination pathway, synthesis of **12i** and **30**−**32**, ^1H NMR for **5f**−**o**, **17a**, and **17b**, ^{13}C NMR for **5f**−**k**,**m**−**o**, COSY NMR for **5f**−**k**, NOESY NMR for **5g**−**k**, X-ray crystal structures for **5f**,**h**,**k**,**l**, and X-ray crystal structure data for **5f**,**h**,**k**,**l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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