formation for the synthesis of **1** are still under investigation.

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Supplementary Material Available: ^1H NMR, IR, $[\alpha]_D$, mp, and elemental analytical or high-resolution mass spectral data for key intermediates and synthetic **2**, ^1H NMR (360 MHz) and HPLC analysis data of dipeptide B, and ^1H NMR (360 MHz) data of synthetic tetrahydroechinocandin D and natural tetrahydroechinocandin D (18 pages). Ordering information is given on any current masthead page.

Dramatic Differences in Intramolecular Reactivities of Singlet Arylcarbenes and Benzyl Cations

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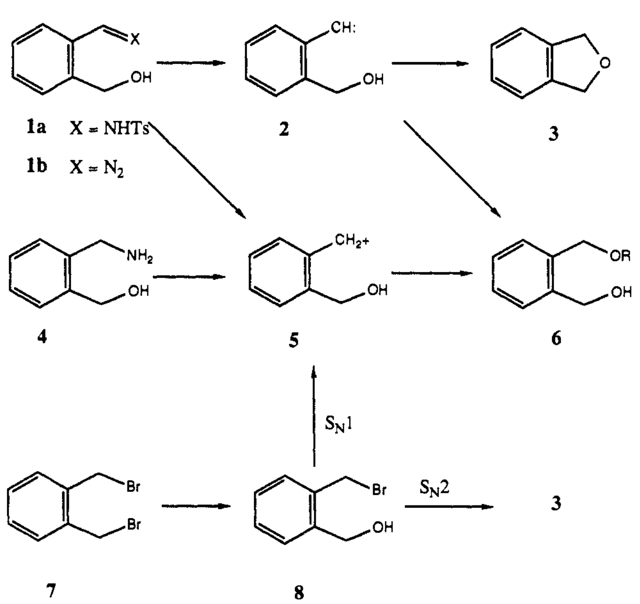
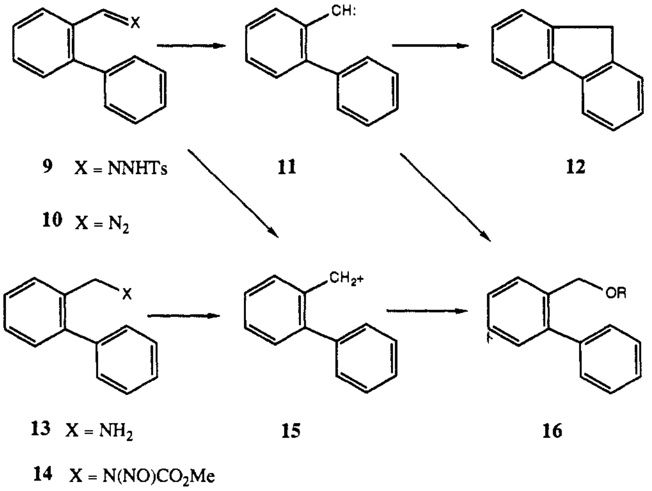
Many reactions of singlet carbenes are closely analogous to those of carbocations,[1,2] since the reactivities of both species are dictated by an electrophilic vacant 2p orbital. Nevertheless, we report here experimental evidence that arylcarbenes react readily with nucleophilic groups on ortho substituents, whereas simple benzyl cations do not, in spite of similar intermolecular reactivities of carbenes and cations. This difference can be rationalized in terms of the rotational barriers of the two systems, which we have determined by ab initio molecular orbital calculations.



Photolysis of the sodium salt of tosylhydrazone **1a** proceeds via diazo compound **1b**[3] and gives a strongly solvent-dependent ratio of intramolecular and intermolecular O–H insertion products. The ratio of **3**/**6** is 71:29, 51:49, 38:62, 10:90, and 2:98 in *tert*-butyl alcohol, ethanol, methanol, water, and trifluoroethanol, respectively, using 0.2 M sodium alkoxide in alcohol as the base. Although it might be expected that increasing solvent nucleophilicity should lead to more of the intermolecular trapping product **6**, the opposite is found experimentally. As solvent nucleophilicity decreases, the amount of **6** increases. This parallels the increase in solvent acidity, which should increase the rate of formation of the cation, **5**, from carbene **2**.[4] This trend indicates that the benzyl cation **5** does not undergo intramolecular nucleophilic substitution whereas the carbene **2** gives rise to both **3** and **6**. In fact, nitrous acid deamination of 2-(aminomethyl)benzyl alcohol (**4**) affords **6**-OH exclusively. The hydrolysis of α,α'-dibromo-*o*-xylene (**7**), which proceeds via bromo alcohol **8**, yields large quantities of **3** under S_N2 conditions. For example, **3** and **6** are formed in 74:26 ratio in 9:1 NaOH/dioxane. Essentially only **6** is formed when polar solvents (e.g., 7:93 **3**/**6** in 1:1 H_2O/dioxane) and electrophilic catalysis are employed (e.g., 3:97 **3**/**6** in 1:1 H_2O/dioxane with 1 equiv of $AgBF_4$).

Carbene **11** gives fluorene (**12**) by intramolecular insertion.[5] In the presence of alcohols, intermolecular O–H insertion competes with the formation of **12**. Thus, **12** and **16** are formed in ratios of 67:33, 57:43, 54:46, and 14:86 in *tert*-butyl alchol, ethanol, methanol, and trifluoroethanol, respectively. Nitrous acid deamination of **13** and deacylation of **14** did not produce fluorene; the benzyl cation **15** does react intermolecularly with arenes, for example, in benzene–methanol mixtures.



The rate constants for the reaction of aromatic carbenes with alcohols are known to be on the order of 10^9–10^{10} M^{-1} s^{-1}.[6] The rate constant for the reaction of *p*-methylphenethyl cation in water is also estimated to be 10^{10} M^{-1} s^{-1}, while stabilized cations react more slowly.[7] Reaction rates in ethanol are known to be of the same order of magnitude.[8] These data suggest that the difference in selectivity observed in our systems does not arise from a higher reactivity of the cation than the carbene with alcoholic solvents. Instead, the difference in reactivity must arise from the difference in ability of carbenes and cations to achieve a reactive conformation.

Rotation about the bond connecting the sp^2 carbon of the carbene or cation to the ring must occur in order for intramolecular insertions to take place. We postulate that arylcarbenes have considerably lower barriers to rotation about this bond than do

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Table I. Rotational Barriers of Cations and Carbenes

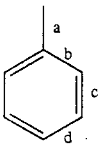
compound	$C_6H_5CH_2^+$	C_6H_5CH	$C_3H_5^+$	C_3H_4
split valence	45.4	11.2	34.3[a]	9.2[c]
higher level			37.7[b]	8.4[d]

[a] HF/3-21G//3-21G.[14] [b] MP2/6-31G**//HF/6-31G*.[15] [c] HF/4-31G.[16] [d] SDQCI//SCF(DZP).[17]

the analogous benzyl cations. Although a similar 90° rotation about an aryl-carbon bond is required in the cyclization of both benzyl and diphenylmethyl 1,5-diradicals[9] the latter cyclize much more easily than the former since rotation about the aryl-carbon bond is facile in the diphenylmethyl system but not for the benzyl radicals. Similarly, earlier reports[10,11] indicate that triphenylmethyl carbocations do undergo intramolecular cyclizations to give the corresponding phthalans. In such systems, steric crowding of the ground state leads to much lower rotational barriers than in the simple benzyl cations included in our study.

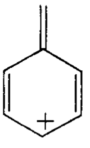
To verify that the divergent intramolecular reactivities of arylcarbenes and benzyl cations arise from the higher rotational barriers in the latter, we have performed ab initio molecular orbital calculations[12] on both the benzyl cation and singlet phenylcarbene, with complete geometry optimizations of planar minima and perpendicular rotation transition states in each case, using the 3-21G basis set.[13]

The rotational barriers from our calculations, together with those reported[14-17] for the allyl cation and vinylcarbene, are shown in Table I. The most relevant features of the geometries of the aromatic species are shown in structure **17**. The rotational barrier calculated for the cation is about 4 times that for the carbene. Our confidence in these values arises from previous studies of the allyl cation and singlet vinylcarbene, which give a similar trend using either split valence basis sets (3-21G or 4-31G)[14,16] or much larger basis sets and inclusion of correlation energy corrections.[15,17,18-23]



17

Planar cation:	a=1.356, b=1.434, c=1.361, d=1.400
Perpendicular cation:	a=1.450, b=1.393, c=1.382, d=1.384
Planar carbene:	a=1.462, b=1.400 (1.398) c=1.378 (1.381), d=1.389 (1.385)
Perpendicular carbene:	a=1.478, b=1.392, c=1.382, d=1.384



18

The origin of this large difference in barriers is revealed by a comparison of the optimized geometries (see structure **17**). In the planar benzyl cation, the exocyclic C–C bond length is 1.357 Å. In the perpendicular form this bond length is 1.450 Å. These bond lengths are very similar to the ones found in polyenes[24] for localized double (1.35 Å) and single (1.48 Å) bonds, respectively. This is indicative of the large extent of conjugation present in the planar form, which is lost upon rotation. The analogous bond length in singlet phenylcarbene is only slightly increased in going from the planar to the perpendicular conformation, from 1.462 to 1.478 Å. The calculated charges also indicate that there exists significant delocalization in the planar cation and little or none in the carbene. Indeed, the planar cation is best represented by structure **18**, while the remaining species are better represented as aromatic compounds.

The exocyclic double bond character in **18** is thus larger than one would expect if the five resonance structures of the cation gave equal contributions. The loss of aromaticity in three resonance structures is compensated by delocalization of the charge on the secondary carbon atoms of the ring, which formally bear a positive charge more favorably than the exocyclic methylene carbon. In the planar carbene, resonance donation from the phenyl group to the vacant p orbital of the carbene occurs only with unfavorable charge separation. Consequently, the exocyclic bond largely retains single-bond character, so that the rotational barrier is low enough to allow the molecule to achieve a nonplanar conformation without difficulty.

Furhter examples of this difference in behavior between arylcarbenes and aryl cations will be reported in due course.

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Unexpected Dissociative Kinetics for CO Exchange in the 17-Electron Complexes Carbonylbis(η^5-pentadienyl)vanadium(II), Carbonyl(η^5-cyclopentadienyl)(η^5-pentadienyl)vanadium(II), and Carbonyl(η^5-cyclopentadienyl)(η^5-2,4-dimethylpentadienyl)vanadium(II)

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Several kinetic studies of 17-electron metal carbonyls such as $V(CO)_6$,[1] $Mn(CO)_5$,[2] $Re(CO)_5$,[3] and $Fe(CO)_3(PR_3)_2^+$[4] have

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