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AFTER VINYL- AND ARYL CATIONS, ALKYNYL CATIONS: MYTHOS OR REALITY?

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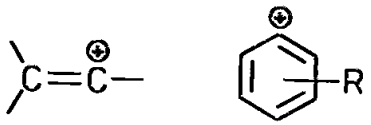
SUMMARY

Attempts to generate the hitherto unknown alkynyl cations by decomposition of several substituted alkynyl diazonium salts synthesized for the first time are discussed. It is concluded from the experimental results and ab initio calculations on thermal dediazoniation of ethynyldiazonium ions that such a reaction pathway is not suitable for the generation of ethynyl/alkynyl cations.

INTRODUCTION

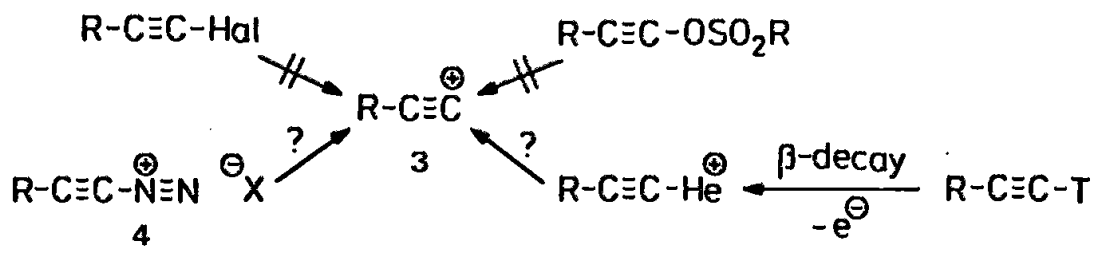
The existence of disubstituted cations, vinyl cations 1, has been fully integrated in mechanistic and preparative organic chemistry (ref. 1). Aryl cations 2 have also been generated not only by dediazoniation (ref. 2) but also through participation of triple bonds on vinyl cations (ref. 3). Recently formation of aryl cations by direct solvolytic reactions has been reported (ref. 4).



1 2

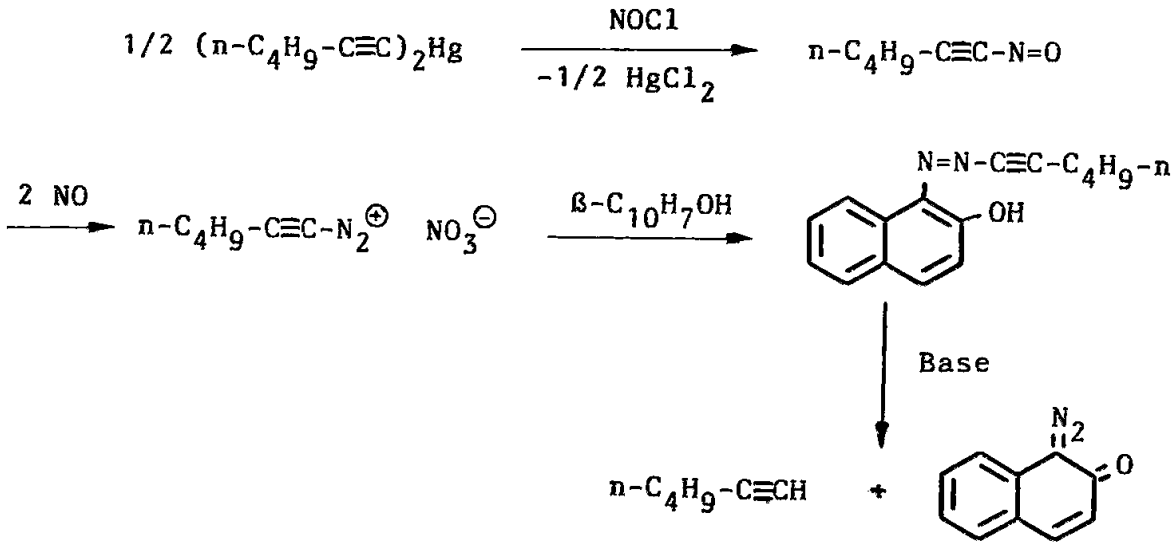
However, the monosubstituted alkynyl cations 3 have so far eluded its generation. Among the possible routes to generate alkynyl cations 3 given in Scheme 1, the obvious method of choice is via the alkynyldiazonium salts 4.

Scheme 1



Although alkenyldiazonium salts are known in the literature (ref. 5), only one isolated report on the formation of alkynyldiazonium ions is known (ref. 6). This has been carried out by the reaction of di-1-hexynyl mercury with nitrosyl chloride followed by diazotization of the 1-nitroso-1-hexine with nitric oxide (Scheme 2). The authors claim to have shown experimentally the intermediacy of the alkynyldiazonium ion by isolating the coupling product with ß-naphthol. We tried to repeat this sequence to the best of our ability, but in vain.

Scheme 2

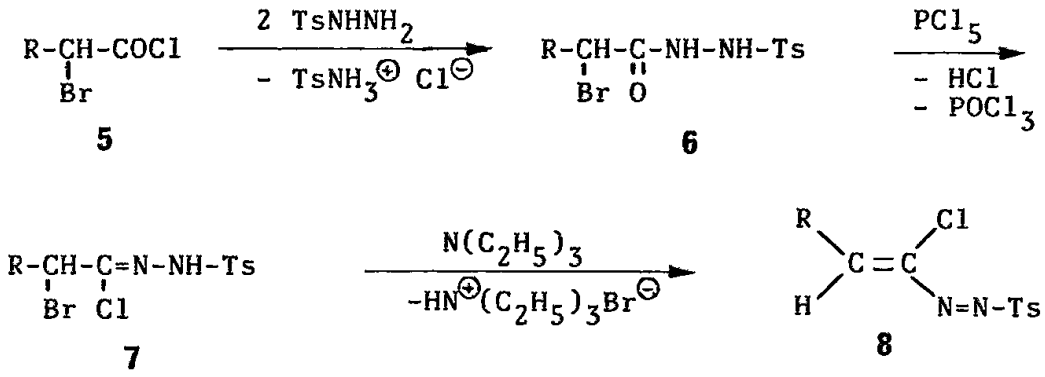


We report here on our attempts to prepare and identify various alkynyldiazonium salts and the possibility of their thermal decomposition to alkynyl cations. We have developed a method (ref. 7) to obtain alkynyldiazonium salts based on the synthesis of alkenyldiazonium salts (ref. 5).

Several 2-bromo-N-tosyl-acetohydrazonoylchlorides 7 were first prepared by the reaction of the p-tosylhydrazide 6 with phosphorous pentachloride. 6 can be easily obtained by treatment of α-bromoacid chlorides 5 with p-tosylhydrazine (Scheme 3).

The hydrazonoylchlorides 7 were converted to the (halogenalkenyl)-p-tosyldiazenes 8 with triethylamine. Some of the diazenes 8b,c,e,f,g [R = t-C_4H_9, C_6H_5, 4-Cl-C_6H_4, 4-$Si(CH_3)_3$-C_6H_4, 4-t-C_4H_9-C_6H_4] could be isolated and identified.

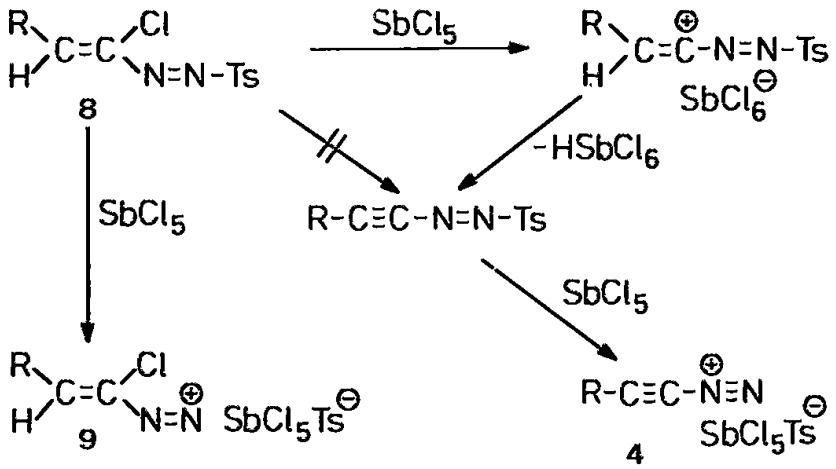
Scheme 3



	R		R
a	n-C_4H_9	e	4-Cl-C_6H_4
b	t-C_4H_9	f	4-$Si(CH_3)_3$-C_6H_4
c	C_6H_5	g	4-t-C_4H_9-C_6H_4
d	4-CH_3O-C_6H_4		

The removal of hydrogen chloride from 8 to give the alkynyldiazonium salts 4 was attempted using $SbCl_5$ (Scheme 4).

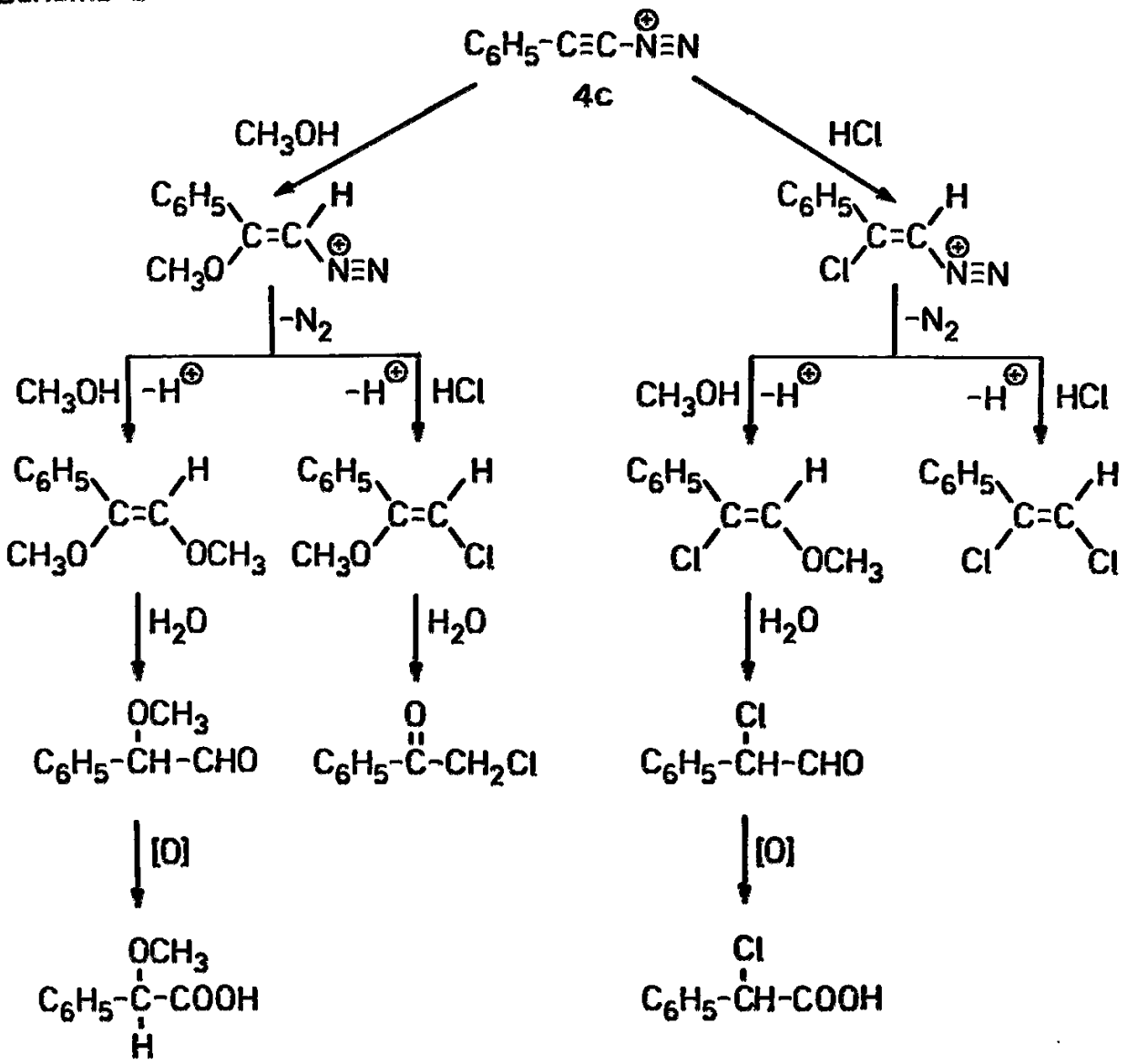
Scheme 4



The formation of alkynyldiazonium salts at low temperatures (-30°C) could be demonstrated with R = C_6H_5 and 4-Cl-C_6H_4 by IR spectroscopy. The CH_2Cl_2-solutions were colored olive green and red respectively and had IR absorptions in the region of 2150-2255 cm^{-1} for the acetylene triple bond.

The reaction of $SbCl_5$ with 8 is dependent on the temperature forming different diazonium salts. At -70°C, the alkenyldiazonium salts 9 are formed (Scheme 4). They are treated with nucleophiles such as methanol and water. The products obtained (Scheme 5) indicate the formation of the alkynyldiazonium salt in the case of 4c (R = C_6H_5) which is stable up to -20°C (ref. 8). 4c adds nucleophiles like methanol or water at the C≡C triple bond before releasing nitrogen (Scheme 5).

Scheme 5



According to the product analysis shown in Scheme 5, a decomposition of the alkynyldiazonium salts with an intermediate formation of an alkynyl cation does not occur at least using the reported conditions.

Our results on the alkynyldiazonium salts are supported by ab initio calculations on the ethynyldiazonium ion and the ethynyl cation, which are discussed below.

ab initio CALCULATIONS ON THE ETHYNYL CATION

The thermal dediazoniation [eqn. (1)] of the alkynyldiazonium ion, $HCCNN^+$, has been examined as a possible pathway for the generation of the alkynyl cation, HCC^+, using ab initio techniques.

$$H\text{-}C{\equiv}C\text{-}\overset{\oplus}{N}{\equiv}N \longrightarrow H\text{-}C{\equiv}C^{\oplus} + N_2 \qquad (1)$$

The diazonium cation was calculated in its $^1\Sigma^+$ ground state. Assuming that the dissociation reaction follows the Woodward-Hoffmann rules (ref. 9) and that the total spin multiplicity is maintained, the alkynyl cation has been calculated in its $^1\Sigma^+$ state. Earlier HF- (refs. 10-16), CI- (refs. 12,13) and perturbation calculations (refs. 14-16) of various states of HCC^+ showed that this cation can exist in several energetically close electronic states. An HF-SCF treatment can thus give only a rough estimate of the energies of the electronic states of HCC^+ and, hence, of the dissociation energy in question. The literature data indicate that correlation energy corrections according to second-order Møller-Plesset perturbation theory (ref. 17) should result in a sufficient accuracy for the present study (Table 1). The good agreement between the experimental (ref. 18) and the calculated (ref. 14) heats of formation of HCC^+ provides further evidence for the adequacy of this approach.

TABLE 1

Energies of the various states of ethynyl cation relative to its ground state $^3\pi$ in kcal mol^{-1}.

State	Configuration	SCF[a]	CI[a]	SCF[b]	MP2[c]	MP3[d]
$^1\Sigma^+$	$[core]\sigma^2\sigma^2\pi^4$	97.6	63.7	105.3	61.9	67.7
$^1\Delta$	$[core]\sigma^2\sigma^2\pi^2\sigma^2$	51.4	61.3	36.9	-	-
$^3\Sigma^-$	$[core]\sigma^2\sigma^2\pi^2\sigma^2$	22.8	35.3	7.6	6.6	2.4
$^1\pi$	$[core]\sigma^2\sigma^2\pi^3\sigma^1$	34.4	32.1	-	-	-

[a] Ref. 12.
[b] HF/6-31G*//HF/6-31G* from reference 14.
[c] MP2/6-31G*//MP2/6-31G* from reference 15.
[d] MP3/6-31G*//MP3/6-31G* from reference 15.

Structural optimizations of the molecules in eqn. 1 have been performed at the HF/6-31G* level as well as the MP2/6-31G* level. The CN-bond length has been found to be 1.32 Å at HF/6-31G* and 1.30 Å at MP2/6-31G*. Both values are close to the bond length of a CN-double bond (1.27 Å). At the HF/6-31G* level a dissociation energy of 148.1 kcal mol^{-1} has been obtained (Table 2). The application of second-order Møller-Plesset perturbation theory (MP2/6-31G*//HF/6-31G*) resulted in the higher dissociation energy of 165.4 kcal mol^{-1}.

TABLE 2

Total energies for the states $^1\Sigma^+$ of 4 and 3 and for N_2 in atomic units. The binding energies (BE) are given in kcal mol^{-1}.

Method	Total Energy 4. $^1\Sigma^+$	3. $^1\Sigma^+$	N_2	BE
HF/3-21G	-183.754916	-75.191164	-108.300958[a]	164.9
HF/6-31G*	-184.797724	-75.617755[b]	-108.943949	148.1
MP2//HF/6-31G*	-185.350244	-75.838390[b]	-109.249197	165.4
MP2/6-31G*	-185.364236	-75.842946[b]	-109.255278	166.9

[a]Ref. 20.
[b]Ref. 15.

Optimization at the MP2/6-31G* level has only little effect on the dissociation energy and a value of 166.9 kcal mol^{-1} has been obtained. Typical bond energies for CN-bonds are 147 kcal mol^{-1} (double) and 213 kcal mol^{-1} (triple). The calculated dissociation energy thus again indicates a rather strong CN-bond in the diazonium ion. The strong CN-bond is also confirmed by the contour map of the projected valence electron density function (ref. 19), (Figure 1).

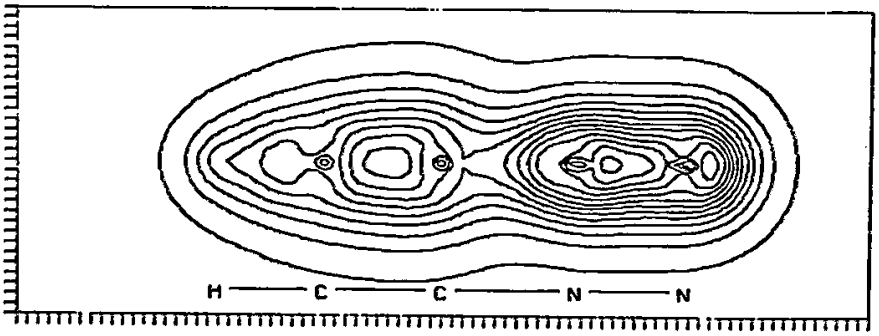


Fig. 1.

Structural, energetic and electronic arguments indicate that the CN-bond in the diazonium cation $HCCNN^+$ is rather strong with a bond order close to two. The significance of the calculated dissociation energy lies in its high magnitude. Higher-order Møller-Plesset calculations could be used to get a more accurate number, but the significant feature, the extremely high value of the dissociation energy, would presumably be taken over. Based on the presented data it is safe to conclude that the thermal dediazoniation of $HCCNN^+$ to form the alkynyl cation in its $^1\Sigma^+$ state is not a possible pathway for the generation of the alkynyl cation.

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