On the Reaction of 1-Aza-2-azoniaallene Salts with Acetylenes

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1-Aza-2-azoniaallene cations **3**, prepared in situ from geminal chloro(alkylazo) compounds **2**, react with acetylenes **4** to give either 1*H*-pyrazolium salts **6** or 4*H*-pyrazolium salts **7** or mixtures of both. 4*H*-Pyrazolium salts with a hydrogen atom attached to C(4) rearrange to the protonated 1*H*-pyrazoles **8**, from which the free bases **9** are obtained upon treatment with aqueous NaOH. According to AM1 calculations the cycloaddition of acetylenes to 1-aza-2-azoniaallene cations is a concerted process, which can be classified as a "1,3-dipolar cycloaddition with reverse electron demand". The cycloaddition forming the intermediates **5** is followed by an [1,2] alkyl shift to furnish the final products **6**–**8**. The direction of the [1,2] shift has been found to be governed by subtle steric effects.

1-Aza-2-azoniaallene ions **3** (Scheme 1) have been used for the preparation of indazoles[1]. Cations **3** derived from α,β-unsaturated ketones undergo an intramolecular addition to the olefinic double bond to form pyrazoles[2]. Mechanistically, this reaction may well be related to the oxidation of formazanes to tetrazolium salts[3] and to the oxidation of hydrazones of ketones $R^1-N=CR^2-C(R^3)=O$ affording triazolium salts[4]. A few reactions of cations **3** with heterocycles and azomethines have been studied[5–7]. *N*-Acylated 1-aza-2-azoniaallene ions (**3**, R^3 = acyl) cyclize to give 1,3,4-oxadiazoles[8–13]. Recently, related intramolecular cyclizations to triazoles and triazines have been reported for cations **3** with $R^3 = RC=NR'$[14].

In preceding papers we have described cycloadditions of cations **3** to nitriles[15] as well as to carbodiimides[16]. In this paper we report on a new synthesis of pyrazolium salts **6**–**8**, **10** by way of cycloaddition of heterocumulenes **3** to acetylenes **4** (Scheme 1).

The hydrazones **1** were oxidized with *tert*-butyl hypochlorite to afford the chloro(alkylazo) compounds **2**[17–20]. On treatment with Lewis acids like $AlCl_3$ or $SbCl_5$ at −60°C in dichloromethane compounds **2** formed the unstable orange salts **3**, which were intercepted with acetylenes to give the pyrazolium salts **6** or **7** via 3*H*-pyrazolium salts **5**. With unsymmetric acetylenes the cycloadditions occurred with complete regioselectivity.

Alkyl and aryl mono- and disubstituted acetylenes can be used. However, electron-deficient acetylenes, e.g. acetylenedicarboxylates, did not react with **3**. The use of antimony pentachloride as Lewis acid often led to tarry products. Apparently, the acetylenes were oxidatively destroyed by $SbCl_5$. No such decomposition was encountered with $AlCl_3$ as the Lewis acid. However, due to their extreme moisture sensitivity some of the tetrachloroaluminates could not be obtained analytically pure.

The scope of the reaction is limited by the fact that the primarily formed 3*H*-pyrazolium salts **5** rearrange to mixtures of 1*H*- and 4*H*-pyrazolium salts **6** and **7** (Table 1). Thus, from the acetone hydrazone **1a** and 3-hexyne (**4a**) only the 4*H*-pyrazolium salt **7a** was obtained (88%). However, the same acetylene reacted with 2-butanone hydrazone **1b** to give an equimolecular mixture of **6b** and **7b** (85%). This ratio remained unchanged when the mixture of **6b** and **7b** was subjected to the reaction conditions again or when the time for the reaction of **1b** with **4a** was extended to two days. Finally, from 3-methyl-2-butanone hydrazone **1c** and 3-hexyne the 1*H*-pyrazolium salt **6c** was formed exclusively (56%).

With monosubstituted acetylenes (R^4 = H) the intermediate 4*H*-pyrazolium salts **7** could not be obtained. Instead, 1*H*-pyrazolium salts **8** resulting from a [1,3]-prototropic rearrangement of **7** were isolated and characterized as the free bases **9** or as their picrates. Again, from the 3,3-dimethyl intermediates **5d**, **e** only the salts **8d**, **e** were formed, while with the 3-ethyl-3-methyl compound **5f** approximately equimolecular mixtures of **6f** and **8f** were obtained. Subtle steric effects seem to direct the direction of the alkyl migration. Thus, the tetramethylene salt **5g** rearranged to **8g** (isolated as **9g**) exclusively, while the pentamethylene derivative **5h** was converted into 1:1 mixtures of **6h** and **8h** (Table 1). Corresponding results were observed for the cycloaddition reactions with phenylacetylene (**4i**) etc.

The cycloaddition is not restricted to R^3 = 2,4,6-trichlorophenyl, which was used because the products readily crystallize and because 2,4,6-trichlorophenylhydrazine is

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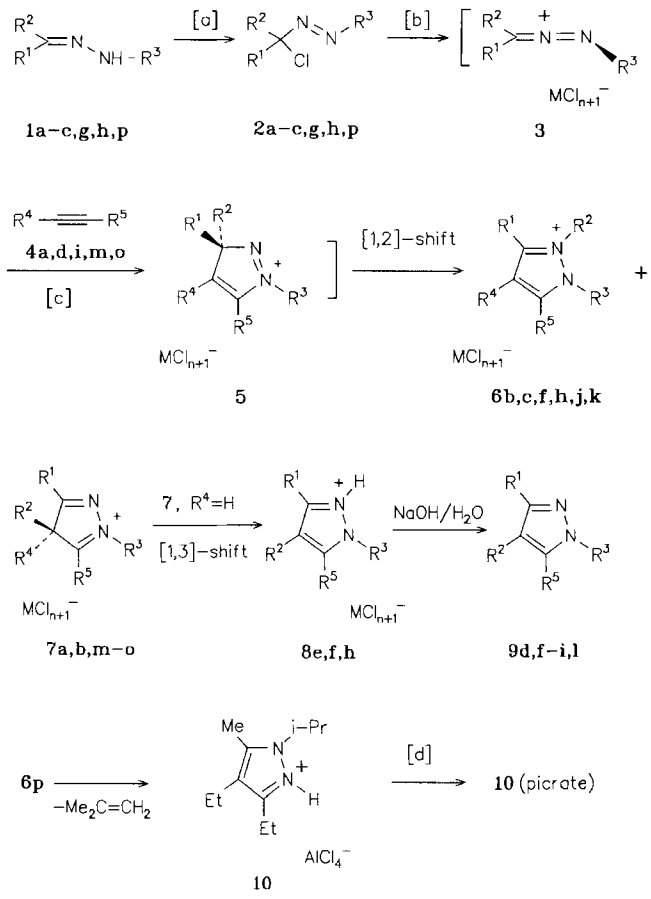
Scheme 1. [a] *t*BuOCl, $CHCl_3$, −50 to 0°C, 3 h, 88–99%. – [b] $SbCl_5$ or $AlCl_3$, CH_2Cl_2 or $ClCH_2CH_2Cl$, −60 to −30°C. – [c] 1 h −60°C, 1 h 0°C. – [d] $NaOH/H_2O$; picric acid in EtOH



1a–c,g,h,p 2a–c,g,h,p 3 4a,d,i,m,o 5 6b,c,f,h,j,k 7a,b,m–o 8e,f,h 9d,f–i,l 10

	R^1	R^2	R^3	R^4	R^5	MCl_{n+1}
a	Me	Me	2,4,6-$Cl_3C_6H_2$	Et	Et	$AlCl_4$
b	Me	Et	2,4,6-$Cl_3C_6H_2$	Et	Et	$AlCl_4$
c	Me	i-Pr	2,4,6-$Cl_3C_6H_2$	Et	Et	$AlCl_4$
d	Me	Me	2,4,6-$Cl_3C_6H_2$	H	Bu	$AlCl_4$
e	Me	Me	2,4,6-$Cl_3C_6H_2$	H	Bu	$SbCl_6$
f	Me	Et	2,4,6-$Cl_3C_6H_2$	H	Bu	$AlCl_4$
g	$(CH_2)_4$		2,4,6-$Cl_3C_6H_2$	H	Bu	$AlCl_4$
h	$(CH_2)_5$		2,4,6-$Cl_3C_6H_2$	H	Bu	$AlCl_4$
i	Me	Me	2,4,6-$Cl_3C_6H_2$	H	Ph	$AlCl_4$
j	Me	Et	2,4,6-$Cl_3C_6H_2$	H	Ph	$AlCl_4$
k	Me	i-Pr	2,4,6-$Cl_3C_6H_2$	H	Ph	$AlCl_4$
l	$(CH_2)_4$		2,4,6-$Cl_3C_6H_2$	H	Ph	$AlCl_4$
m	Me	Me	2,4,6-$Cl_3C_6H_2$	Me	Ph	$AlCl_4$
n	Me	Et	2,4,6-$Cl_3C_6H_2$	Me	Ph	$AlCl_4$
o	Me	Me	2,4,6-$Cl_3C_6H_2$	Pent	Ph	$AlCl_4$
p	Me	i-Pr	t-Bu	Et	Et	$AlCl_4$

Table 1. Rearrangements of compounds **5**: distribution of the products

5	products: yield [%]	thereof [%]: 6	7	8	9
a	88	0	100	–	–
b	85	50	50	–	–
c	56	100	0	–	–
d	95	0	–	–	100
e	100	0	–	100	–
f	100	45	–	55	–
g	100	0	–	–	100
h	91	50	–	50	–
i	71	0	–	–	100
j	63	100	–	0	–
k	52	100	–	0	–
l	86	0	–	–	100
m	82	0	100	–	–
n	91	0	100	–	–
o	83	0	100	–	–
p	100	100[a]	0	–	–

[a] Isolated as **10**.

commercially available. However, R^3 should be inert against chlorination by *tert*-butyl hypochlorite. For instance, a phenyl substituent R^3 is partially chlorinated during the transformation **1** → **2**[17–19]. *tert*-Butyl-substituted hydrazones eliminate isobutene during the reaction (cf. preparation of **10**), thus permitting the synthesis of pyrazoles unsubstituted on N(2).

The constitutions of compounds **6**–**10** were easily derived from the NMR spectra (Table 2). For instance, the ^{1}H-NMR spectrum (recorded in CD_3CN) of a mixture of **6h** and **8h** obtained from the cycloaddition of **3h** to 1-hexyne (**4d**) showed one multiplet for NCH_2 at δ = 4.09 together with five multiplets for the $C-CH_2$ groups (δ = 2.41 to 3.11) bound directly to the heterocyclic ring, indicating that only two products were formed, of which one contained an NCH_2 group. The ^{13}C-NMR resonances for C(4) of compounds **7** appear at higher field (**7a**: δ = 73.1 in CD_3CN, Table 2) than expected for atoms C(3) (δ > 90[21]) of isomers of **7**, which could have been formed from **5** by an 1,3-shift of R^2. Treatment of **8h** with aqueous NaOH yielded the free base **9h**, which was characterized as the picrate. Only a regioisomer **8** with the butyl substituent in the 5-position could give a base **9h**. The ^{13}C-NMR resonances of C(4) of pyrazolium salts always appear at higher field (**6h**: δ = 109.1, in CD_3CN) than the signals for C(3) and C(5) (**6h**: δ = 153.6, 156.5)[22]. From a gated decoupling experiment it was concluded that **6h** has a hydrogen atom attached to C(4).

Table 2. Selected NMR and IR data for the new compounds

No. IR[b]	^{1}H NMR (CD_3CN, 295 K) δ, J[Hz] [a]	^{13}C NMR (CD_3CN, 295 K) δ[a]
6b[c]	1.07 (t, J=7.6), 1.15-1.30 (6H), 2.54 (CH_3), 2.32-2.68 (4H), 4.08 (q, J=7.3) (CH_2), 7.89 (aryl)	11.0, 12.9, 14.4, 14,7, 16.7, 18.7, 44.2 (CH_3, CH_2), 123.7, 126.8, 131.5, 137.3, 141.3, 149.3. 151.6 (C=)
6c 1567	1.07 (t, J=7.6), 1.19 (t, J=7.6), 1.54 (d, J= 7.0, 6H), 2.63 (CH_3), 2.53 (q, J=7.6), 2.62 (q, J=7.6) (CH_2), 4.37 (sept, J=7.0, CH), 7.89 (aryl)	12.0, 12.9, 14.8, 16.6, 18.9, 21.2 (2C) (CH_3, CH_2), 55.6 (CH), 124.9, 127.0, 131.6, 137.6, 141.3, 149.0, 151.1 (C=)
6h 1563	0.87 (t, J=7.3, CH_3), 1.33 (m), 1.61 (m), 1.77 (m, 4H), 1.89 (m), 2.45 (t, J=7.7), 3.09 (m), 4.09 (m) (CH_2), 6.76 (CH), 7.88 (aryl)	13.8 (CH_3), 22.6, 25.4, 26.0, 27.2, 27.5, 29.7, 30.2, 50.8 (CH_2), 109.1, 126.2, 131.4, 137.5, 141.5, 153.6, 156.5 (C=)
6j 1567	1.28 (t, J=7.3), 2.69 (CH_3), 4.22 (q, J=7.3, CH_2), 7.08 (CH), 7.34-7.58 (phenyl), 7.79 (aryl)	13.0, 14.5 (CH_3), 44.7 (CH_2), 110.8 (^{2}J=189, CH), 125.7, 127.4, 129.3, 130.4, 131.5, 132.8, 137.5, 141.5, 151.7, 152.0 (C=)
6k 1567	1.61 (d, J=7.0, 6H), 2.79 (CH_3), 4.48 (sept, J=7.0), 7.08 (CH), 7.79 (aryl)	14.2, 21.2 (2C) (CH_3), 56.3 (CH), 112.5, 125.8, 127.6, 129.2, 130.3, 131.4, 132.7, 137.8, 141.4, 151.5, 151.8 (C=)
7a 1567, 1598	0.79 (t, J=7.6), 1.20[d], 1.70, 2.42 (CH_3), 2.41 (m), 3.05[d] (CH_2), 7.87 (q, J=2.1, aryl)	10.0, 10.5, 13.3, 21.0, 23.0, 30.2 (CH_3, CH_2), 73.1 (C), 130.7, 131.3, 131.4, 132.9, 133.3, 140.8 (aryl), 189.0, 200.9 (C3, C5)
7b 1567	0.80 (t, J=7.6, 6H), 1.20 (t, J=7.6), 2.42 (CH_3), 2.39 (m), 2.50 (m), 3.06 (q, J=7.6) (CH_2), 7.88 (aryl)	9.4, 10.3 (2C), 13.5 (CH_3), 23.6[d], 31.1 (2C) (CH_2), 79.0 (C), 131.1, 131.3, 132.9, 140.8 (aryl), 188.0, 200.9 (C=N)
7m 1567	1.84 (2C), 2.51 (CH_3), 7.64-7.87 (aryl)	13.3, 22.0 (2C), 67.4 (C), 123.3, 129.8, 131.3, 131.5, 131.9, 133.3, 137.7, 140.6 (aryl), 189.4, 190.3 (C3, C5)
7n 1567	0.79 (t, J=7.5), 1.93, 2.51 (CH_3), 2.39 (m, CH_2), 7.64-7.91 (aryl)	10.1, 13.4, 22.1, 31.6 (CH_3, CH_2), 73.2 (C), 188.7, 189.6 (C3, C5)
7o 1567	0.78 (m), 1.94, 2.50 (CH_3), 1.06-1.21 (m, 6H), 2.31 (m) (CH_2), 7.65-7.89 (aryl)	13.5, 14.0, 22.4, 22.5, 25.5, 31.8, 37.7 (CH_3, CH_2), 72.6 (C), 188.8, 189.5 (C3, C5)
8a 1474, 1567[h]	0.84 (t, J=7.2), 2.14, 2.45 (CH_3), 1.31 (m), 1.45 (m), 2.58 (m) (CH_2), 7.83 (aryl), 11.40 (NH)	7.9, 10.6, 13.8 (CH_3), 22.8, 24.5, 30.1 (CH_2), 117.8, 128.3, 130.9, 136.8, 140.7, 149.0, 151.7 (C=)
8h[i]	0.82 (t, J=7.2, CH_3), 1.20-2.00 (10H), 2.55 (t, J=8.0), 2.69 (m), 2.90 (m) (CH_2), 7.81 (aryl), 12.89 (NH)	13.8 (CH_3), 22.7, 24.8, 26.9, 27.6, 30.7, 31.8 (CH_2), 128.5, 130.8, 136.9 140.5, 150.4, 154.2
9d 1459[j], 1497, 1551, 1582[f]	0.82 (t, J=7.1), 2.00, 2.25 (CH_3), 1.26 (m), 1.32 (m), 2.37 (t, J= 7.8) (CH_2), 7.45 (aryl) [e]	8.3, 12.2, 13.7 (CH 22.2, 24.1, 30.5 (C 112.1, 128.4, 135.3 136.1, 141.8, 149.4 158.1 (C=) [e]
9f 1459, 1497, 1551, 1578[f]	0.81 (t, J=7.1), 1.14 (t, J=7.6), 2.27 (CH_3), 1.20-1.40 (m, 4H), 2.36 (m), 2.44 (q, J= 7.6) (CH_2), 7.45 (aryl) [e]	12.2, 13.7, 15.4, 1 22.4, 24.2, 31.0 (C CH_2), 118.9, 128.6, 135.0, 135.5, 136.4 141.8, 149.2 (C=) [e
9g 1443, 1497, 1555, 1578[f]	0.82 (t, J=7.1, CH_3), 1.26 (m), 1.39 (m), 1.82 (m, 4H), 2.36 (t, J=7.7), 2.53 (m), 2.72 (m) (CH_2), 7.45 (aryl) [e]	13.7 (CH_3), 20.7, 2 23.2, 23.4, 23.5, 2 30.0 (CH_2), 114.0, 128.4, 134.9, 135.3 136.1, 140.2, 151.0 (C=) [e]
9g[g] 1520, 1570[h]	0.86 (t, J=7.2, CH_3), 1.30 (m), 1.47 (m), 1.93 (m, 4H), 2.45 (t, J=7.9), 2.62 (m), 2.99, (m) (CH_2), 7.49, 8.86 (aryl), 13.73 (NH) [e]	13.6 (CH_3), 20.0, 2 22.0, 22.3, 22.4, 2 29.3 (CH_2), 116.6, 126.0, 129.2, 129.7 131.0, 136.0, 138.6 140.5, 145.4, 149.3 159.2 (C=) [e]
9h 1443, 1497, 1547, 1574[f]	0.81 (t, J= 7.1, CH_3), 1.26 (m, 4H), 1.68 (m, 4H), 1.83 (m), 2.35 (t, J=7.6), 2.50 (m), 2.79 (m) (CH_2), 7.45 (aryl) [e]	13.7 (CH_3), 22.1, 2 25.0, 28.0, 29.5, 2 31.0, 32.6 (CH_2), 1 128.4, 134.9, 135.3 136.3, 141.1, 155.9 (C=) [e]
9h[g] 1550, 1585, 1620[h]	0.75 (t, J=7.1, CH_3), 1.21 (m, 4H), 1.62 (m, 4H), 1.82 (m), 2.35 (m), 2.49 (m), 2.69 (m) (CH_2), 7.93, 8.64 (aryl), 9.65 (NH) [k]	13.4 (CH_3), 21.4, 2 24.2, 27.6, 28.9, 2 30.5, 31.9 (CH_2), 1 124.9, 125.1, 128.9 134.1, 135.2, 135.4 140.9, 141.8, 154.7 160.3 (C=) [k]
9i 1455[j], 1486, 1547, 1574[f]	2.05, 2.33 (CH_3), 7.19-7.29 (aryl) [e]	8.6, 12.2 (CH_3), 11 128.4, 128.8, 129.8 135.2, 135.3, 136.1 142.8, 150.3 (C=) [e
9l 1443, 1482, 1509, 1543[f,j]	1.76-1.96 (4H), 2.63 (m), 2.82 (m) (CH_2), 7.17-7.32 (phenyl), 7.34 (aryl) [e]	21.4, 23.2, 23.4, 2 (CH_2), 115.4, 128.1 128.2, 128.4, 128.5 129.9, 135.3, 135.5 136.1, 141.0, 151.8
10[g] 1560, 1620[h]	1.16 (t, J=7.6), 1.22 (t, J=7.6), 1.63 (d, J=6.9, 6H), 2.39 (CH_3), 2.49 (q, J=7.6), 2.72 (q, J=7.4) (CH_2), 4.75 (sept, J=6.9, CH), 8.92 (aryl), 13.30 (NH) [e]	9.6, 13.2, 15.0, 17 21.2 (2C) (CH_3, CH_2 52.9 (CH), 120.1, 1 129.6, 140.5, 141.3 148.4, 160.5 (C=) [e

[a] TMS as internal standard. – [b] In CH_2Cl_2; cm^{-1}. – [c] Spectra recorded from a 1:1 mixture of **6b** and **7b**. – [d] Very broad. – [e] In $CDCl_3$. – [f] In CCl_4. – [g] Picrate. – [h] KBr disk. – [i] Spectra recorded from a 1:1 mixture of **6h** and **8h**. – [j] Shoulder. – [k] In $[D_6]$DMSO.

Discussion of the Reaction Mechanism; AM1 Calculations

According to AM1 calculations[23,24] the C=N=N moiety of the cation **3a** is bent [C(1)–N(2)–N(3) = 159°] (Figure 1). The planes through C(15), C(19), C(1) and through N(2), N(3), C(4) are perpendicular with respect to each other [C(15)–C(1)–N(2)–N(3) = 90°, C(1)–N(2)–N(3)–C(4) = –177°]. The cation has a plane of symmetry [N(2)–N(3)–C(4)–C(5) = 5°].

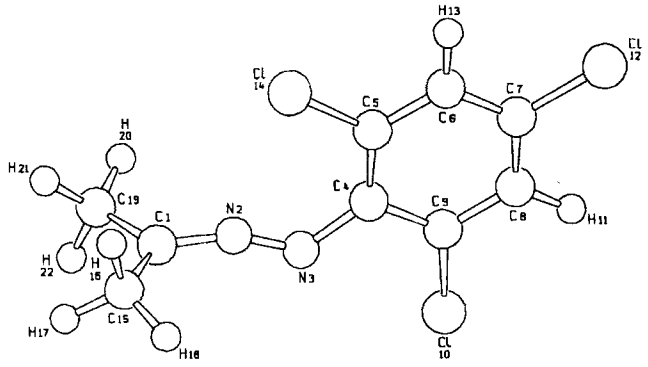


Figure 1. AM1-calculated geometry for the cation **3a**

The reaction of **3a** with 2-butyne furnishing **5q** was calculated to be exothermic by 92 kJmol^{-1} (Figure 2). Noteworthy, no intermediate could be located, in contrast to the reaction of **3a** with carbodiimides[16]. Thus, a stepwise addition eventually leading to the formation of an unstable vinyl cation is avoided. The concerted reaction of **3a** with 2-butyne proceeds asynchronously. In the transition structure the bond formation between C(4) and C(3) was calculated to be more advanced than that between C(5) and N(1) [distance C(4)–C(3) about 0.7 times the distance C(5)–N(1)]. An activation enthalpy of about 77 kJmol^{-1} for the cycloaddition and of 169 kJmol^{-1} for the reverse process was calculated. Experimentally, the cycloadditions of **3** to acetylenes **4** were found to be fast below 0°C.

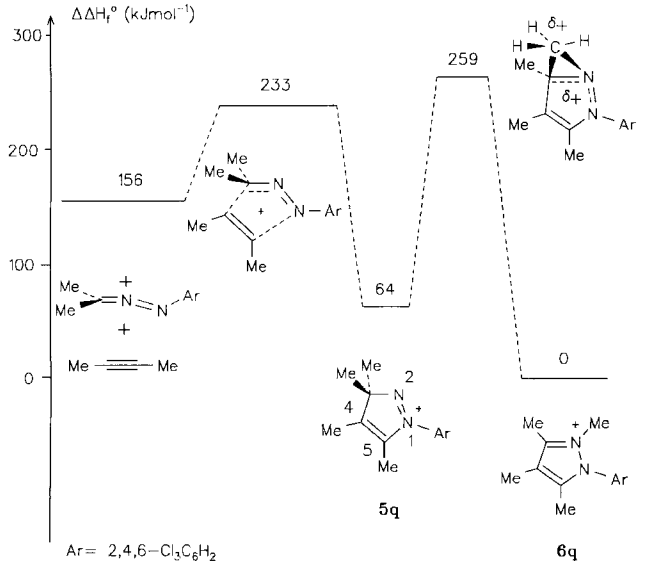


Figure 2. AM1-calculated heats of formation for the reaction of **3a** with 2-butyne, relative to ΔH_f^0 = 930 kJmol^{-1} for **6q**

A concerted cycloaddition of **3** to acetylenes is electronically related to a 1,3-dipolar cycloaddition[25] with the cumulene **3** acting as the "1,3-dipole" and the acetylene as the dipolarophile. The cation **3a** has 37 filled molecular orbitals (MO's). The filled MO no. 35 and the empty MO no. 39 are π-MO's located essentially on the C=N=N moiety. These two MO's have the correct symmetry to interact with LUMO or HOMO of the acetylene. The dominant interaction is that between HOMO of the acetylene and the empty orbital no. 39 of the cumulene (Figure 3). Lowering the HOMO energy of the acetylene should slow down the cycloaddition to the cumulene. Experimentally it was observed that electron-deficient acetylenes (e.g. $R^4 = R^5 = CO_2Me$) do not react with **3**.

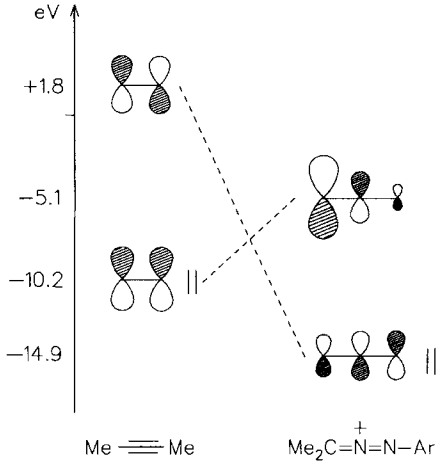


Figure 3. AM1 calculation for the interacting frontier orbitals of 2-butyne and **3a**

In compliance with the Diels-Alder reaction "with reverse electron demand"[26] the present situation may be classified as a "1,3-dipolar cycloaddition with reverse electron demand" ("Type III" according to Sustmann's classification[27]).

A similar regime has been described by Passmore et al.[28,29] for the cycloaddition of the dithionitronium ion SNS^+ to acetylenes and other dipolarophiles. Furthermore, certain cycloadditions of norbornadiene to sulfur nitrides can be classified as [1,3]-dipolar cycloadditions with reverse electron demand[30,31].

For unsymmetrically substituted acetylenes like **4d**, **i**, **m**, **o** the question of the regioselectivity of the cycloaddition arises. The regioselectivity is determined by orbital overlap of the termini with the largest orbital coefficients[32]. For instance, MO no. 39 of **3a** has a large coefficient on C(1) ($c_{\pi\text{-}p}$ = 0.75). For phenylacetylene the coefficient of the HOMO π orbital is larger on C(2) (0.41) than on C(1) (0.25) (AM1 calculation). This explains the regioselectivity observed for the reaction of phenylacetylene with **3a**, whereby only **5i** was formed.

Facile alkyl migrations similar to that observed for the rearrangements **5** → **6** or **5** → **7** have been reported to take place in the course of the cycloadditions of **3** to nitriles and carbodiimides[15,16]. [1,5]-Sigmatropic rearrangements of 3*H*-pyrazoles are referred to as van Alphen-Hüttel rearrangements[33–36]. These rearrangements usually require temperatures above 100°C or acid catalysis.

Recently, Gstach and Warkentin et al. described fast thermal rearrangements of 3*H*-pyrazoles[37–39]. A two-step

mechanism involving an intermediate carbenium ion and an aromatic pyrazole instead of a pericyclic [1,5]-sigmatropic shift was proposed[38,39]. Our observation[15,16] that the alkyl group forming the more stable carbenium ion migrates exclusively seems to support Warkentin's view. According to AM1 calculations for **5q** (Figure 2) the methyl group (C_m) migrates to N(2). In the transition structure the positively charged migrating CH_3 group is planar and is positioned above the N(2)–C(3) bond [(N(1)–N(2)–C(3)–C(m) = 98°] and is closer to C(3) than to N(2) [N(2)–C(3)–C(m) = 90°]. For a pericyclic [1,5]-sigmatropic rearrangement the direction of the migration should be governed by the HOMO π-p orbital coefficients of the aromatic pyrazole[32]. These orbital coefficients were calculated to be +0.29 on N(2) and −0.63 on C(4). Thus, there is no correlation between the HOMO orbital coefficients and the terminus of the migration.

We considered the possibility that the direction of the migration is determined in a way that the thermodynamically most stable product is formed. However, this hypothesis is not supported by the calculations. The calculated heats of formation for compounds **6q** and **7q** are almost equal (**6q**: ΔH_f^0 = 930, **7q**: 932 kJmol^{-1}).

While the cycloaddition of 2-butyne to **3a** was not studied experimentally, it has been mentioned above that methyl migration in **5a** occurs exclusively to C(4) giving **7a**, while the isopropyl group of the closely related cation **5c** migrates exclusively to N(2) producing **6c**. In the case of the ethyl compound **5b** an equimolecular mixture of **6b** and **7b** was obtained. This points to steric effects determining the course of the migration.

In contrast to the experiment, the AM1 calculations for the cation **5a** predicts methyl migration to N(2). We then found that the outcome of the calculations depends on minor changes of the bond lengths of the heterocycle. For the transition structure of the methyl migration to N(2) (**5a** → **6a**) a bond distance C(3)–C(4) of 147 pm was calculated. Reducing this bond length by just 1 pm changed the direction of the methyl migration. Now, the transition structure relaxed to give the C(4)-methylated cation **7a**. The crucial point seems to be the distance between the migrating carbon atom and the adjacent atoms in the transition structure. If in the transition structure the rearranging carbon atom is closer to N(2) than to C(4) migration occurs to N(2), otherwise to C(4). This critical distance is determined not only by the nature of the migrating group but also by the substituents of the heterocycle. The scenario resembles much more generalized 1,2-Wagner-Meerwein shifts[40,41] than pericyclic [1,5]-sigmatropic rearrangements: The rate of the migration of an alkyl group (R^2 in **5**) parallels a) the ability of the migrant to stabilize a positive charge and b) the electron deficiency of an adjacent atom [e.g. N(2) in **5**]. However, the migration does not necessarily end at the most electron-deficient neighbour. Rather, the distance in the transition state of the migrating centre to its neighbours [e.g. C(4) or N(2) in **5**] is decisive: migration occurs to the closest neighbour. The transition may best be described as a π complex of a migrating cation and a double bond (e.g. C=N or C=C in **5**), that is, migration occurs within the coordination sphere of the migrant-carrying remnant (e.g. the heterocycle). Only a migrant forming especially stable carbenium ions (Gstach's and Warkentin's examples[37–39]) can escape the coordination sphere to undergo intermolecular alkylation reactions.

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Experimental

Melting points: uncorrected. – IR: Mattson Polaris FT-IR spectrometer. – ^{1}H and ^{13}C NMR: Bruker WM 250 and AC 250 spectrometers (Table 2). – All experiments were carried out with exclusion of moisture in solvents dried by standard methods.

Formation of Pyrazolium Tetrachloroaluminates (**6–8, 10**) *from α-Chloro(alkylazo) Compounds* **2** *and Acetylenes* **4**. – *General Procedure:* A solution of **2** (10 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a cold (−60°C) suspension of $AlCl_3$ (1.33 g, 10 mmol) in CH_2Cl_2 (20 ml). After 5 min a solution of the acetylene **4** (12 mmol) in CH_2Cl_2 (20 ml) was added dropwise to the reaction mixture. After stirring at −60°C for 1 h and then at 0°C for 1 h, pentane (40 ml) or ether (100 ml) were added dropwise. A moisture-sensitive orange oil precipitated, which solidified at −20°C.

2,4,5-Triethyl-3-methyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**6b**) *and 4,4,5-Triethyl-3-methyl-1-(2,4,6-trichlorophenyl)-4H-pyrazolium Tetrachloroaluminate* (**7b**): From **2b**[15] (3.00 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4a** (0.99 g, 12 mmol). With ether an orange oil was precipitated, which crystallized at −20°C to afford fine yellow prisms (4.40 g, 85%). According to the ^{1}H-NMR spectra the product consisted of an approximately equimolecular mixture of **6b** and **7b**. Reprecipitation from CH_2Cl_2 (20 ml)/ether (120 ml) gave in one case pure **7b** (3.08 g) as a moisture-sensitive pale yellow powder; m.p. 108–113°C (dec.). The compound turned blue within one week. – $C_{16}H_{20}AlCl_7N_2$ (515.5): calcd. C 37.28, H 3.91, N 5.43; found C 37.06, H 4.23, N 5.58.

4,5-Diethyl-2-isopropyl-3-methyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**6c**): From **2c**[15] (3.14 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4a** (0.99 g, 12 mmol). After stirring for 1 h at 0°C, the reaction mixture was concentrated to a volume of 15 ml. Slow addition of ether (60 ml) afforded a yellow precipitate (2.97 g, 56%), which was reprecipitated at −20°C from CH_3CN (10 ml)/ether (40 ml) to give very moisture-sensitive colorless leaflets (2.51 g), for which correct combustion analytical data could not be obtained; m.p. 149–151°C. In the mother liquor of the first precipitation a compound **7c** could not be detected (^{1}H NMR). – $C_{17}H_{22}AlCl_7N_2$ (529.5): calcd. C 38.56, H 4.19, N 5.29; found C 37.82, H 4.55, N 5.18.

5-Butyl-2-ethyl-3-methyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**6f**), *5-Butyl-4-ethyl-3-methyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate* (**8f**), *and 5-Butyl-4-ethyl-3-methyl-1-(2,4,6-trichlorophenyl)pyrazole* (**9f**): From **2b** (3.00 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4d** (0.99 g, 12 mmol). Evaporation of the solvent afforded a semisolid orange residue (5.16 g, 100%), which according to the ^{1}H- and the ^{13}C-NMR spectra consisted of a mixture of the isomers **8f** and **6f** (ratio 1.2:1). The mixture was suspended in ether (50 ml). At 0°C a solution of NaOH (2.40 g, 60 mmol) in H_2O (30 ml) was added. After stirring for 5 min and workup (see **9d**), an orange oil (1.13 g, 42%)

was obtained. According to the NMR spectra this oil consisted of pure **9f**. – $C_{16}H_{19}Cl_3N_2$ (345.7): calcd. C 55.59, H 5.54, N 8.10; found C 55.66, H 5.67, N 8.00.

2-Butyl-1,4,5,6,7,8-hexahydro-1-(2,4,6-trichlorophenyl)-pyrazolo[1,5-a]azepinium Tetrachloroaluminate (**6h**), *3-Butyl-2,4,5,6,7,8-hexahydro-2-(2,4,6-trichlorophenyl)cycloheptapyrazolium Tetrachloroaluminate* (**8h**), *3-Butyl-2,4,5,6,7,8-hexahydro-2-(2,4,6-trichlorophenyl)cycloheptapyrazole* (**9h**), *and the Picrate of* **9h**: From **2h**[15] (3.26 g, 10 mmol), **4d** (0.99 g, 12 mmol), and $AlCl_3$ (1.33 g, 10 mmol). Evaporation of the solvent, dissolution of the residue in CH_2Cl_2 (10 ml) and slow addition of ether (60 ml) afforded a moisture-sensitive orange oil (4.94 g, 91%), which according to the ^{1}H-NMR spectrum consisted of an equimolecular mixture of **6h** and **8h**. The oil was dissolved in CH_2Cl_2 (10 ml), and ether (30 ml) was added to the solution. At −20°C a colorless powder (1.83 g, 32%) of **6h** crystallized; m.p. 85−88°C. – $C_{18}H_{22}AlCl_7N_2$ (541.5): calcd. C 39.92, H 4.09, N 5.17; found C 39.77, H 4.19, N 5.07.

Workup of the reaction mixture as described for **9d** furnished a viscous orange oil (**9h**, 2.90 g, 39%), which was characterized as the picrate; m.p. 126−128°C. – $C_{24}H_{24}Cl_3N_5O_7$ (600.8): calcd. C 47.97, H 4.03, N 11.66; found C 48.00, H 4.16, N 11.46.

2-Ethyl-3-methyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**6j**): From **2b** (3.00 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4i** (1.23 g, 12 mmol). Finally, the reaction mixture was stirred at 23°C for 1 h. Evaporation of the solvent, dissolution of the residue in CH_2Cl_2 (10 ml), and precipitation by slow addition of ether (60 ml) afforded a pale brown powder (3.36 g, 63%), which was reprecipitated from CH_2Cl_2 (10 ml)/ether (70 ml) to give a moisture-sensitive colorless powder (2.36 g); m.p. 139−141°C. – $C_{18}H_{16}AlCl_7N_2$ (535.5): calcd. C 40.37, H 3.01, N 5.23; found C 40.22, H 3.32, N 5.13.

2-Isopropyl-3-methyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**6k**): From **2c** (1.91 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4i** (1.23 g, 12 mmol). Yield: 2.84 g (52%) of a very moisture-sensitive colorless powder, which was dissolved in CH_2Cl_2 (50 ml). Filtration of the solution and addition of ether (100 ml) to the filtrate afforded a colorless powder; m.p. 205−207°C. – $C_{19}H_{18}AlCl_7N_2$ (549.5): calcd. C 41.53, H 3.30, N 5.10; found C 40.93, H 3.41, N 5.08.

4,5-Diethyl-3,4-dimethyl-1-(2,4,6-trichlorophenyl)-4H-pyrazolium Tetrachloroaluminate (**7a**): From **2a** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4a** (0.99 g, 12 mmol). With pentane (30 ml) an orange oil was precipitated, which crystallized at −20°C to give fine pale yellow needles (4.40 g, 88%). Reprecipitation from CH_2Cl_2 (20 ml)/ether (40 ml) gave a colorless crystalline powder, which turned dark with decomposition at −20°C within a few days; m.p. 115−120°C (dec). – $C_{15}H_{18}AlCl_7N_2$ (501.5): calcd. C 35.93, H 3.62, N 5.59; found C 35.49, H 3.69, N 5.51.

3,4,4-Trimethyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**7m**): From **2a** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4m**[42] (1.39 g, 12 mmol). After completion of the reaction the solvent was evaporated. The oily residue was dissolved in CH_2Cl_2 (20 ml). On slow addition of ether (100 ml) to the solution a yellow powder precipitated (4.40 g, 82%). Reprecipitation at −20°C from acetonitrile (40 ml)/ether (160 ml) afforded very moisture-sensitive colorless leaflets (3.43 g), for which correct combustion analytical data were not obtained; m.p. 181−184°C. – $C_{18}H_{16}AlCl_7N_2$ (535.5): calcd. C 40.37, H 3.01, N 5.23; found C 39.58, H 3.20, N 5.07.

4-Ethyl-3,4-dimethyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**7n**): From **2b** (3.00 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4m** (1.39 g, 12 mmol). Evaporation of the solvent and precipitation at −20°C from CH_2Cl_2 (20 ml)/ether (120 ml) gave a very moisture-sensitive yellow powder (5.00 g, 91%). Crystallization at −20°C from acetonitrile (20 ml)/ether (100 ml) afforded colorless leaflets (2.40 g); m.p. 172−175°C. – $C_{19}H_{18}AlCl_7N_2$ (549.5): calcd. C 41.53, H 3.30, N 5.10; found C 41.21, H 3.38, N 5.07.

3,4-Dimethyl-4-pentyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Tetrachloroaluminate (**7o**): From **2a** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4o** (2.07 g, 12 mmol, Aldrich). After completion of the reaction the solvent was evaporated. The dark oily residue was dissolved in CH_2Cl_2 (20 ml). At −20°C ether (60 ml) was added. A brown oil precipitated, which was dissolved in acetonitrile (40 ml). Filtration of the solution from a mucous impurity and evaporation of the solvent from the filtrate afforded a moisture-sensitive brown oil (4.88 g, 83%). – $C_{22}H_{24}AlCl_7N_2$ (591.6): calcd. C 44.67, H 4.09, N 4.74; found C 44.37, H 4.22, N 5.00.

5-Butyl-3,4-dimethyl-1-(2,4,6-trichlorophenyl)-1H-pyrazolium Hexachloroantimonate (**8e**): A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (−60°C) solution of **2a** (2.86 g, 10 mmol) in CH_2Cl_2 (20 ml). After 5 min a solution of **4d** (0.99 g, 12 mmol) in CH_2Cl_2 (20 ml) was added dropwise. After stirring at −60°C for 1 h and then at 0°C for 1 h, the solvent was evaporated. The oily residue was dissolved in CH_2Cl_2 (10 ml). On slow addition of pentane (60 ml) to the solution a red oil precipitated, which slowly solidified to give a brown powder (3.33 g, 100%). Reprecipitation from CH_2Cl_2 (20 ml)/pentane (60 ml) gave a brown powder (2.70 g, 81%); m.p. 123−125°C (dec.). – $C_{15}H_{18}Cl_9N_2Sb$ (667.2): calcd. C 27.01, H 2.72, N 4.20; found C 26.90, H 2.73, N 4.17.

5-Butyl-3,4-dimethyl-1-(2,4,6-trichlorophenyl)-1H-pyrazole (**9d**): From **2a** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4d** (0.99 g, 12 mmol). After stirring at −60°C for 1 h and at 23°C for 1 h, the reaction mixture was cooled to 0°C. A solution of NaOH (2.40 g, 60 mmol) in H_2O (30 ml) was added dropwise, and the mixture was stirred vigorously for 5 min. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 × 30 ml). The combined organic phases were washed with water and dried with Na_2SO_4. Evaporation of the solvent afforded a pale orange oil (3.16 g, 95%). – $C_{15}H_{17}Cl_3N_2$ (331.7): calcd. C 54.32, H 5.17, N 8.45; found C 53.90, H 5.19, N 8.50.

3-Butyl-4,5,6,7-tetrahydro-2-(2,4,6-trichlorophenyl)-2H-indazole (**9g**) *and its Picrate:* From **2g**[16] (3.12 g, 10 mmol), **4d** (0.99 g, 12 mmol), and $AlCl_3$ (1.33 g, 10 mmol) as described for **9d**. Yield: 3.56 g (100%) of an orange oil, which was purified by chromatography on silica gel (1.8 × 15 cm, eluent $CHCl_3$, last fraction) to give an orange oil (1.88 g, 53%). – $C_{17}H_{19}Cl_3N_2$ (357.7): calcd. C 57.08, H 5.35, N 7.83; found C 57.38, H 5.37, N 8.06.

Dissolution of **9g** (1.07 g, 3 mmol) in a saturated solution of picric acid in aqueous ethanol (10 ml) and keeping the mixture at −20°C afforded a pale green crystalline powder (1.45 g, 84%) of the picrate; m.p. 134−136°C. – $C_{23}H_{22}Cl_3N_5O_7$ (586.8): calcd. C 47.08, H 3.87, N 11.93; found C 47.05, H 3.76, N 12.04.

3,4-Dimethyl-5-phenyl-1-(2,4,6-trichlorophenyl)-1H-pyrazole (**9i**): From **2a** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4i** (1.23 g, 12 mmol). The solvent was evaporated, and the remaining red oil was dissolved in $CHCl_3$ (30 ml). A solution of NaOH (2.40 g, 60 mmol) in H_2O (30 ml) was added dropwise. Workup as described for **9d** afforded an orange oil, which was crystallized from ether (5 ml) to give an orange crystalline powder (2.48 g, 71%). Recrystallization from ethanol (15 ml) afforded a colorless powder (2.16 g);

m.p. 118–120°C. – $C_{17}H_{13}Cl_3N_2$ (351.7): calcd. C 58.06, H 3.73, N 7.97; found C 57.90, H 4.00, N 7.82.

4,5,6,7-Tetrahydro-3-phenyl-2-(2,4,6-trichlorophenyl)-2H-indazole (**9l**): From **2g** (3.12 g, 10 mmol), **4i** (1.23 g, 12 mmol), and $AlCl_3$ (1.33 g, 10 mmol) as described for **9i**. Yield: 3.26 g (86%) of a brown powder, which was crystallized from hot acetone (35 ml) to give fine brownish prisms (2.02 g); m.p. 146–148°C. – $C_{19}H_{15}Cl_3N_2$ (377.7): calcd. C 60.42, H 4.00, N 7.42; found C 60.51, H 4.14, N 7.25.

3,4-Diethyl-1-isopropyl-5-methyl-1H-pyrazolium Picrate (**10**): From **2p**[15] (1.91 g, 10 mmol) as described for **7a**, however with $ClCH_2CH_2Cl$ as solvent. The reaction mixture was boiled with reflux for 5 h. The solvent was removed under reduced pressure, and the brown oily residue was dissolved in CH_2Cl_2 (20 ml). Extraction of the solution at 0°C with aqueous NaOH [2.00 g, 50 mmol, in H_2O (20 ml)] and usual workup afforded a yellow oil (1.80 g, 100%), which was dissolved in a solution of picric acid (4.58 g, 20 mmol) in ethanol (35 ml). The mixture was concentrated to a volume of 10 ml. On addition of pentane (20 ml) an orange oil precipitated. The supernatant solvent was decanted. The oil crystallized on drying. Crystallization at –20°C from hot ethanol (15 ml) furnished a yellow crystalline powder (2.50 g, 61%); m.p. 104–106°C. – $C_{17}H_{23}N_5O_7$ (409.4): calcd. C 49.87, H 5.66, N 17.11; found C 49.56, H 5.58, N 16.83.

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