On the Reaction of *N*-Arylnitrilium Salts with Acetylenes: Synthesis of Substituted Quinolines

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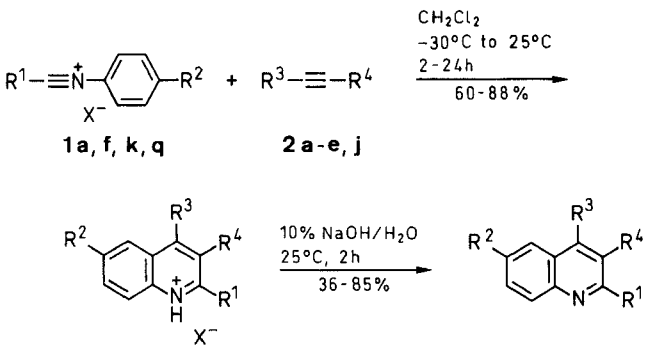
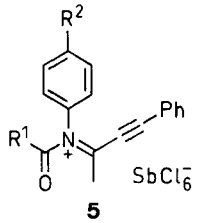
Quinolinium salts **3** are obtained from the reaction of *N*-arylnitrilium salts **1** with acetylenes **2**. With aqueous base the salts **3** are transformed into the corresponding quinolines **4**.

In the preceeding communication reactions of *N-alkyl*nitrilium salts with acetylenes have been described.[1] Quite different reactions leading to quinolinium salts **3** are observed between *N-aryl*nitrilium salts **1** and acetylenes **2**. The transformation of *N*-phenylimidoyl chlorides with phenylacetylene in the presence of tin(IV) chloride to give 4-phenylquinolinium salts has been reported by Schmidt[2] who pointed out that this polar $[4^+ + 2]$ cyclization[3] should be mechanistically related to Meerwein's quinazoline synthesis.[4]

In this note we would like to point out that the reaction of *N*-arylnitrilium salts with acetylenes is not restricted to phenylacetylene. Using the nitrilium hexachloroantimonates **1a,f,k,q** and the acetylenes **2a–e, j** we prepared the quinolinium hexachloroantimonates **3a–i, k–q**, from which the quinolines **4** can be obtained with aqueous sodium hydroxide (Table). Instead of the hexachloroantimonates **1** the tetrachloroaluminates can be used as well.





1–4	R^1	R^2	R^3	R^4	1–4	R^1	R^2	R^3	R^4
a	Me	H	Ph	H	**j**	Ph	H	Bu	H
b	Me	H	Ph	Ph	**k**	4-ClC_6H_4	Cl	Ph	H
c	Me	H	Et	Et	**l**	4-ClC_6H_4	Cl	Ph	Ph
d	Me	H	MeS	MeS	**m**	4-ClC_6H_4	Cl	Et	Et
e	Me	H	Ph	Ac	**n**	4-ClC_6H_4	Cl	Bu	H
f	Ph	H	Ph	H	**o**	4-ClC_6H_4	Cl	MeS	MeS
g	Ph	H	Ph	Ph	**p**	4-ClC_6H_4	Cl	Ph	Ac
h	Ph	H	MeS	MeS	**q**	Me	MeO	Ph	H
i	Ph	H	Ph	Ac					

X = $SbCl_6^-$ or $AlCl_4^-$

Scheme

The reactions are exothermic and are carried out at room temperature or below. In one case, **3j**, the formation of an intermediate of unknown constitution is observed. NMR data of this intermediate are reported in the experimental section.

Noteworthy is the clean reaction of the acetylated acetylene **2e** with nitrilium salts **1**. Recently, we reported on the reaction of ketones with nitrilium salts to give *N*-acyliminium salts.[5,6] The question arose, whether **2e** would react with nitrilium salts as a ketone to afford the *N*-acyliminium salts **5** or as an acetylene to furnish quinolinium salts **3**. Exclusively, quinolinium salts **3** are formed.

Under the conditions described mono- and disubstituted alkyl- and arylacetylenes react equally well. However, no reactions are observed between acetylene and the nitrilium salts **1 f,k**. While the monoacylated acetylene **2e** still reacts with nitrilium salts **1**, no reaction is observed between the electron deficient diethyl acetylenedicarboxylate and, for instance, **1f**. The reaction of **1k** with 3,3-dimethyl-1-butyne led to a tarry mixture of compounds. In conclusion, *N*-arylnitrilium salts **1** seem to react only with acetylenes, which are more nucleophilic than acetylene itself. Furthermore, steric hindrance may prevent ring closure to **3**.

N-Arylnitrilium salts **1** with R^1 = aryl are conveniently prepared by abstraction of chloride from the corresponding imidoyl chlorides with Lewis acids,[7,8] while salts **1** with R^1 = alkyl are best obtained by Beckmann rearrangement of the corresponding oxime.[9] Furthermore, *N*-arylnitrilium salts can be prepared by treating aryldiazonium salts with nitriles in the presence of Lewis acids.[10–12] In those cases, where the nitrilium salts are readily accessible, their reaction with acetylenes can be recommended as a convenient route to quinolines complementing other quinoline syntheses.[13–17]

The structures of the quinolines **3, 4** can be deduced from the spectra, the elemental analyses, and by comparison with authentic quinolines **4** (Table). In all cases studied so far the acetylenes add completely regioselectively to the nitrilium salts. Since it is known that phenylacetylene reacts with nitrilium ions in the way that the most stable carbenium ion is formed,[2] the same should also be true for the reactions of the acetylenes **2e,n**.

All solvents were dried by standard methods. All experiments were carried out with exclusion of moisture. The melting points are uncorrected. The nitrilium salts **1a,f** (X = $SbCl_6$),[9] **1k,q**

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(X = $SbCl_6$),[23] and **1f** (X = $AlCl_4$)[24] as well as acetylene **2e**[25] were prepared according to known procedures. However, for the preparation of **1f** (X = $AlCl_4$) CH_2Cl_2 instead of nitrobenzene was used as solvent.

Quinolinium Salts 3; General Procedure:
A solution of acetylene **2** (11 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a cold (−30 °C) suspension of *N*-arylnitrilium salt **1** (10 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at −30 °C for 1 h. Then, the temperature was raised to 25 °C and the mixture stirred at this temperature for the time specified in the Table. Et_2O (100 mL) was added. The precipitate was filtered off and washed with Et_2O. The product **3**, which was in most cases analytically pure, could be crystallized at −20 °C from: MeCN (10 mL)/Et_2O (60 mL) **(3a)**; CH_2Cl_2 (20 mL)/Et_2O (20 mL) **(3b,d)**; CH_2Cl_2 (20 mL)/Et_2O (100 mL) **(3c)**; CH_2Cl_2 (40 mL)/MeCN (5 mL)/Et_2O (100 mL) **(3f)**; CH_2Cl_2 (50 mL)/Et_2O (50 mL) **(3g)**; CH_2Cl_2 (12 mL)/Et_2O (40 mL) **(3h)**; CH_2Cl_2 (30 mL)/Et_2O (90 mL) **(3l,m,p)**; CH_2Cl_2 (25 mL)/Et_2O (60 mL) **(3n,q)**; CH_2Cl_2 (15 mL)/Et_2O (50 mL) **(3o)**.

Quinolines 4; General Procedure:
To a suspension (or solution) of salt **3** (10 mmol) in CH_2Cl_2 (50 mL) aq NaOH (10%, 50 mL) was added. The mixture was stirred for 2 h. The organic layer was separated and washed with H_2O. Usual workup afforded the pure base **4**, which could be crystallized at −20 °C from: CH_2Cl_2 (5 mL)/pentane (30 mL) **(4a,k)**; CH_2Cl_2 (50 mL)/pentane (5 mL) **(4b)**; CH_2Cl_2 (5 mL)/pentane (20 mL) **(4g,h,n)**; $CHCl_3$ **(4i)**; CH_2Cl_2 (10 mL)/pentane (40 mL) **(4l,m,o,p)**. The yields given in the Table were calculated relative to the nitrilium salt used.

2,4-Diphenylquinoline (4f):
The tetrachloroaluminate was prepared from **1f** (X = $AlCl_4$) (3.49 g, 10 mmol) and **2a** (1.12 g, 11 mmol) according to the general procedure. The mixture was stirred at 25 °C for 4 h and then hydrolyzed without prior isolation of the salt. Crystallization at −20 °C from CH_2Cl_2 (5 mL//pentane (20 mL) gave pale-brown cubes (2.11 g, 75%).

Table. Selected NMR and IR Data, Melting Points and Experimental Data of the New Compounds

Product	Molecular Formula[a] Appearance	^1H NMR[b] δ, J (Hz)	^{13}C NMR[b] δ	IR[c] ν (cm^{-1})	Yield (%)	mp (°C)	Time[d] (h)
3a	$C_{16}H_{14}Cl_6NSb$ (554.8) green powder	3.01 (CH_3)	21.2 (CH_3), 120.8, 124.8, 126.5, 128.4, 130.1, 130.6, 130.7, 131.6, 135.7, 135.9, 138.9 (aryl, C3), 157.7, 159.8 (C2, 4)	1605, 1636[g]	79[e]	194–197[f]	4
3b	$C_{22}H_{18}Cl_6NSb$ (630.8) yellow-green needles	2.70 (CH_3), 13.53 (NH)	21.6 (CH_3), 120.4, 128.4, 129.0, 129.1, 129.5, 129.9, 130.2, 130.8, 130.9, 135.0, 135.1, 135.6, 136.8, 137.7 (aryl, C3), 157.9, 158.4 (C2, 4)	1578, 1632[g]	81[e]	203–206[f]	6
3c	$C_{14}H_{18}Cl_6NSb$ (534.8) green powder	1.28 (t, J = 7.5), 1.35 (t, J = 7.6), 2.94 (CH_3), 2.99 (q, J = 7.5), 3.35 (q, J = 7.6, CH_2), 13.11 (NH)	14.1, 15.4, 20.2, 22.6, 23.4 (CH_3, CH_2), 120.8, 126.5, 127.5, 130.3, 134.5, 136.6, 136.8 (aryl), 157.4, 161.4 (C2, 4)	1590, 1636[g]	61[h]	180–183[f]	8
3d	$C_{12}H_{14}Cl_6NS_2Sb$ (570.8) green cubes	2.48, 2.86, 3.09 (CH_3), 13.39 (NH)	18.9, 21.8, 22.0 (CH_3), 121.0, 128.4, 128.8, 130.5, 134.7, 135.9, 136.7 (aryl, C3), 159.6, 168.3 (C2, 4)	1563, 1601, 1625[g]	74[e]	158–161[f]	8
3e	$C_{18}H_{16}Cl_6NOSb$ (596.8) colorless powder	2.01, 2.90 (CH_3), 13.55 (NH)	20.3, 31.9 (CH_3), 120.7, 127.6, 129.0, 130.3, 130.6, 131.4, 131.9, 133.5, 136.5, 138.3 (aryl, C3), 155.0, 155.9 (C2, 4), 201.6 (C=O)	1578, 1632,[i] 1710[g]	81[e]	199–201[f]	24
3f	$C_{21}H_{16}Cl_6NSb$ (616.8) green crystalline powder	13.25 (NH)	121.4, 122.7, 127.2, 128.5, 130.0, 130.1, 130.6, 130.7, 130.9, 131.4, 131.6, 134.4, 136.0, 136.1, 139.5 (aryl), 154.8, 160.9 (C2, 4)	1605, 1628[g]	88[e]	250–252[f]	16
3g	$C_{27}H_{20}Cl_6NSb$ (692.9) yellow needles	13.45 (NH)	120.9, 128.7, 128.8, 128.9, 129.0, 129.3, 129.8, 130.2, 130.9, 131.2, 131.9, 132.2, 132.3, 135.0, 135.2, 136.0, 136.1, 138.1 (aryl), 156.2, 159.9 (C2, 4)	1601, 1612,[i] 1628[e]	84[h]	267–270[f]	8
3h	$C_{17}H_{16}Cl_6NS_2Sb$ (632.9) green needles	2.21, 2.93 (CH_3), 12.96 (NH)[j]	19.3, 21.9 (CH_3), 121.6, 128.3, 129.5, 129.7, 130.8, 131.1, 132.5, 132.9, 134.6, 136.3, 136.9 (aryl), 157.5, 169.4 (C2, 4)[j]	1555, 1615,[i] 1621[h]	86[h]	158–160[f]	2
3i	$C_{23}H_{18}Cl_6NOSb$ (658.9) colorless powder	1.92 (CH_3), 13.54 (NH)[j]	32.6 (CH_3), 121.2, 128.6, 129.1, 129.9, 130.2, 130.3, 130.7, 131.0, 131.4, 131.8, 133.5, 133.6, 137.0, 137.2, 138.8 (aryl), 153.5, 157.5 (C2, 4), 200.4 (C=O)[j]	1574, 1605, 1625,[i] 1698, 1720[e, g]	60[e]	262–263[f]	10
3j	$C_{19}H_{20}Cl_6NSb$ (596.8)[k]	1.01 (t, J = 7.4, CH_3), 1.55 (m), 1.84 (m), 3.38 (m) (CH_2), 13.62 (NH)	14.1, 23.4, 33.1, 33.8 (CH_3, CH_2), 122.0, 122.2, 126.4, 126.6, 127.7, 130.2, 130.7, 131.5, 134.2, 135.9, 138.9 (aryl), 154.5, 164.5 (C2, 4)				
3k	$C_{21}H_{14}Cl_8NSb$ (685.7) green crystalline powder		123.6, 123.9, 127.5, 128.4, 130.1, 130.4, 130.7, 131.2, 132.0, 132.1, 135.7, 136.9, 137.2, 138.4, 141.0 (aryl), 154.2, 160.4 (C2, 4)[j]	1601, 1628[g, i]	82[e]	273–276[f]	4

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Table. (continued)

Product	Molecular Formula[a] Appearance	^{1}H NMR[b] δ, J (Hz)	^{13}C NMR[b] δ	IR[c] ν (cm^{-1})	Yield (%)	mp (°C)	Time[d] (h)
3l	$C_{27}H_{18}Cl_8NSb$ (761.8) yellow-green needles	13.81 (NH)	123.1, 127.8, 129.0, 129.3, 129.4, 129.7, 130.0, 130.2, 130.3, 130.8, 131.9, 132.8, 134.5, 134.6, 136.7, 136.8, 137.2, 137.3, 138.5 (aryl), 155.4, 159.1 (C2, 4)	1571, 1601[g]	87[h]	147–150[f]	16
3m	$C_{19}H_{18}Cl_8NSb$ (665.7) pale-green crystalline powder	1.10 (t, J = 7.5), 1.42 (t, J = 7.6, CH_3), 2.91 (q, J = 7.5), 3.42 (q, J = 7.6, CH_2), 13.29 (NH)	15.0, 15.5 (CH_3), 23.2, 23.9 (CH_2), 123.2, 125.4, 129.1, 130.0, 130.7, 131.7, 135.5, 135.6, 136.6, 137.6, 138.2 (aryl), 155.5, 162.9 (C2, 4)	1490, 1594[g]	65[e]	213–215[f]	2
3n	$C_{19}H_{18}Cl_8NSb$ (665.7) pale-yellow crystalline powder	1.01 (t, J = 7.3, CH_3), 1.55 (m), 1.84 (m), 3.36 (m) (CH_2), 13.30 (NH)	14.1, 23.4, 32.9, 33.8 (CH_3, CH_2), 123.1, 123.6, 125.6, 128.7, 129.9, 130.9, 131.7, 136.4, 136.5, 137.3, 140.4 (aryl), 153.7, 164.0 (C2, 4)	1601, 1628[g]	68[h]	180–183[f]	4
3o	$C_{17}H_{14}Cl_8NS_2Sb$ (701.8) green powder	2.20, 2.92 (CH_3), 13.30 (NH)	19.2, 21.7 (CH_3), 123.7, 127.0, 130.0, 130.5, 130.8, 132.7, 135.5, 135.9, 136.7, 137.1, 139.0 (aryl), 156.5, 168.1 (C2, 4)	1551, 1598[g]	72[e]	165–170[f]	6
3p	$C_{23}H_{16}Cl_8NOSb$ (727.7) green needles	1.92 (CH_3), 13.60 (NH)[j]	32.6 (CH_3), 123.3, 127.8, 129.4, 129.6, 130.2, 130.3, 130.7, 131.9, 132.4, 132.9, 137.4, 137.7, 137.8, 137.9, 140.0 (aryl), 152.7, 156.6 (C2, 4), 200.4 (C=O)[j]	1574, 1598, 1629,[i] 1717[g]	75[e]	237–239[f]	10
3q	$C_{17}H_{16}Cl_6NOSb$ (584.8) dark-green crystalline powder	2.93, 3.85 (CH_3)	20.7, 56.8 (CH_3), 106.5, 122.4, 125.1, 127.8, 128.4, 130.3, (2C?), 131.6, 134.7, 136.3 (aryl), 154.6, 158.1, 160.9 (C2, 4, 6)	1621[g]	66[h]	177–178[f]	4
4a	$C_{16}H_{13}N$ (219.3) brownish crystalline powder	2.76 (CH_3)[l]	25.3 (CH_3), 122.2, 125.0, 125.6, 125.7, 128.3, 128.5, 129.0, 129.3, 129.5, 138.1, 148.4, 148.5, 158.4 (aryl)[l]	1493, 1598[m]	85[h]	92–94 (98–99[18])	
4b	$C_{22}H_{17}N$ (295.4) beige leaflets	2.55 (CH_3)[l]	25.4 (CH_3), 125.8, 126.2, 126.5, 126.7, 127.1, 127.6, 127.8, 128.6, 129.0, 129.9, 130.0, 134.0, 136.7, 138.6, 146.4, 147.1, 157.7 (aryl)[l]	1490, 1567, 1601[m]	71[h]	171–173[19]	
4f	$C_{21}H_{15}N$ (281.4) pale-brown cubes		119.3, 125.6, 125.7, 126.3, 127.5, 128.3, 128.5, 128.8, 129.3, 129.4, 129.5, 130.1, 138.3, 139.6, 148.8, 149.1, 156.8 (aryl)[l]	1493, 1500,[i] 1510,[i] 1590[m]	75[h, n]	105–106 (114[20])	
4g	$C_{27}H_{19}N$ (357.5) colorless needles		126.3, 126.5, 126.6, 127.2, 127.3, 127.5, 127.6, 127.7, 129.3, 129.7, 129.9, 130.2, 131.3, 132.9, 136.9, 138.3, 141.1, 147.3, 147.6, 158.9 (aryl)[l]	1520, 1598, 1648, 1660[i, m]	80[h, n]	198–200 (198–199[21])	
4h	$C_{17}H_{15}NS_2$ (297.5) pale-brown powder	2.10, 2.59 (CH_3)[l]	19.8, 20.1 (CH_3), 126.1, 127.2, 127.9, 128.3, 128.7, 129.0, 129.7, 130.0, 134.9, 141.3, 146.6, 150.5, 161.4 (aryl)[l]	1439, 1474, 1528[m]	82[h, n]	70–71	
4i	$C_{23}H_{17}NO$ (323.4) pale-brown powder	1.86 (CH_3)	33.1 (CH_3), 126.6, 127.3, 128.2, 129.3, 129.4, 129.6, 129.8, 130.0, 130.5, 130.7, 131.3, 135.9, 136.4, 141.4, 146.1, 148.5, 156.0 (aryl), 205.2 (C=O)[j]	1524, 1551, 1601, 1698[m]	60[h]	119–120	
4j	$C_{19}H_{19}N$ (261.4) pale-brown oil	0.93 (t, J = 7.3, CH_3), 1.42 (m), 1.71 (m), 3.00 (m) (CH_2)[l]	13.9, 22.8, 32.2 (CH_3), 118.4, 123.2, 125.7, 126.4, 127.4, 128.6, 128.9, 130.3, 139.7, 148.3, 149.0, 156.7 (aryl)[l]	1598[m]	38[o]	–	
4k	$C_{21}H_{13}Cl_2N$ (350.2) pale-brown needles		119.5, 124.5, 126.5, 128.7, 128.8, 128.9, 129.1, 129.4, 130.6, 131.7, 132.4, 135.8, 137.5, 137.6, 147.2, 148.7, 155.7 (aryl)[l]	1551, 1574, 1601, 1651, 1667[m]	76[h]	189–190[f] (159–160[22])	
4l	$C_{19}H_{17}Cl_2N$ (330.2) pale-pink needles	0.99 (t, J = 7.3, CH_3), 1.47 (m), 1.74 (m), 2.99 (m) (CH_2)[l]	13.9 (CH_3), 22.8, 32.0, 32.1 (CH_2), 118.7, 122.5, 127.3, 128.7, 128.9, 130.1, 131.9, 132.0, 135.6, 137.8, 146.8, 148.7, 155.7 (aryl)[l]	1493, 1594[m]	82[h]	210–212[f]	

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Table. (continued)

Product	Molecular Formula[a] Appearance	^{1}H NMR[b] δ, J (Hz)	^{13}C NMR[b] δ	IR[c] ν (cm^{-1})	Yield (%)	mp (°C)	Time[d] (h)
4m	$C_{27}H_{17}Cl_2N$ (426.3) brown powder		125.4, 126.8, 127.5, 127.6, 127.7, 127.9, 128.0, 130.1, 130.5, 131.1, 131.2, 131.3, 132.7, 133.6, 134.0, 136.1, 137.7, 139.2, 145.7, 147.2, 157.9 (aryl)[l]	1474, 1493, 1520, 1559, 1582, 1601[m]	49[h]	115–116	
4n	$C_{19}H_{17}Cl_2N$ (330.2) pale-brown powder	1.05 (t, J = 7.5), 1.36 (t, J = 7.7, CH_3), 2.77 (q, J = 7.5), 3.12 (q, J = 7.7, CH_2)[l]	15.1, 15.3 (CH_3), 21.4, 22.6 (CH_2), 122.4, 127.2, 128.3, 129.2, 129.8, 131.7, 132.1, 133.2, 133.9, 139.9, 144.4, 146.7, 160.0 (aryl)[l]	1490, 1532, 1555, 1582, 1605[m]	74[e, n]	92–93	
4o	$C_{17}H_{13}Cl_2NS_2$ (366.3) pale-brown powder	2.13, 2.59 (CH_3)[l]	19.8, 20.1 (CH_3), 125.2, 128.3, 129.7, 130.6, 130.9, 131.7, 133.7, 134.8, 136.1, 139.2, 145.0, 149.9, 160.3, 174.9 (aryl)[l]	1466, 1493, 1520, 1601[m]	59[h]	120–122	
4p	$C_{23}H_{15}Cl_2NO$ (392.3) pale-brown needles	1.91 (CH_3)[l]	–[p]	1474, 1540, 1601, 1694[m]	36[h]	198–200	

[a] Satisfactory microanalyses obtained: C ±0.71, H ±0.15, N ±0.45%.
[b] At 250 MHz at 295 K in CD_3CN with TMS as internal standard; Bruker AC-250 and WM-250 spectrometers.
[c] Mattson Polaris FTIR Spectrometer.
[d] Time for stirring the mixture at 25°C.
[e] Yield before recrystallization.
[f] With decomposition.
[g] In CH_2Cl_2.
[h] Yield after recrystallization.
[i] Shoulder.
[j] At 333 K.
[k] The compound was not isolated.
[l] In $CDCl_3$.
[m] In CCl_4.
[n] Compounds **4f,g,h,n** were prepared from nitrilium tetrachloroaluminates as described for **4f** in the experimental section. However, the mixtures for the preparations of **4h,n** were stirred at 25°C for 18 h.
[o] After chromatography. See experimental section.
[p] Low solubility.

4-Butyl-2-phenylquinoline (4j):
The salt **3j** was prepared from **1f** (5.15 g, 10 mmol) and **2n** (0.91 g, 11 mmol) according to the general procedure (time 10 h). With Et_2O (100 mL) an approximately equimolecular mixture of two compounds was precipitated, one of which could be assigned to **3j** by comparison with the spectra of the other compounds **3**. The ^{1}H NMR spectrum (CD_3CN) of the other component, **6**, shows a signal for NH (δ = 12.05), a broadened singlet corresponding to one H at δ = 6.28 and signals for a butyl group shifted to higher field as compared to the corresponding resonances of **3j**. In the ^{13}C NMR (CD_3CN) for **6** 3 resonances for butyl and 13 signals between δ = 117 and 180 were observed, *inter alia* a line at δ = 117.1 and 2 resonances at δ = 176.2 and 179.8 (the resonances for C2,4 of **3j** appeared at δ = 154.5 and 164.7). On standing the signals of **6** gradually disappeared, while the signals for **3j** increased. If the original mixture of components was hydrolyzed with NaOH (general procedure) an approximately equimolecular mixture of **4j** (Table) and a base **7** of unknown structure was obtained as a dark brown oil. On standing in solution in CD_3CN the signals of **7** disappeared within a few h, while the signals of **4j** increased. In the ^{1}H NMR spectrum ($CDCl_3$) compound **7** shows a br s (corresponding to one H) at δ = 5.95. Chromatography of the mixture of **4j** and **7** on silica gel [eluent: CH_2Cl_2/EtOAc (20:1)] afforded pure **4j** as a pale brown oil (0.99 g, 38%).

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(1) Abu-El-Halawa, R.; Jochims, J.C. *Synthesis* **1992**, 871.
(2) Schmidt, R.R. *Angew. Chem.* **1964**, *76*, 991; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 804.
(3) Schmidt, R.R. *Angew. Chem.* **1973**, *85*, 235; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 212.
(4) Meerwein, H.; Laasch, P.; Mersch, R.; Nentwig, J. *Chem. Ber.* **1956**, *89*, 224.
(5) Jochims, J.C.; Glocker, M.; Hofmann, J.; Fischer, H. *Tetrahedron* **1991**, *47*, 205.
(6) Jochims, J.C.; Abu-El-Halawa, R.; Glocker, M.O.; Zsolnai, L.; Huttner, G. *Synthesis* **1990**, 763.
(7) Grundmann, C. In *Houben-Weyl*, Falbe, J., Ed.; Thieme: Stuttgart, 1985; Vol. E5, p. 1572, and references therein.
(8) Lykkeberg, J.; Klitgaard, N.A. *Acta Chem. Scand.* **1970**, *24*, 2268.
(9) Jochims, J.C.; Hehl, S.; Herzberger, S. *Synthesis* **1990**, 1128.
(10) Meerwein, H.; Laasch, P.; Mersch, R.; Spille, J. *Chem. Ber.* **1956**, *89*, 209.
(11) Schmidt, R.R.; Schneider, W.; Karg, W.; Burkert, U. *Chem. Ber.* **1972**, *105*, 1634.
(12) Petterson, R.C.; Bennett, J.T.; Lankin, D.C.; Lin, G.W.; Mykytka, J.P.; Troendle, T.G. *J. Org. Chem.* **1974**, *39*, 1841.
(13) Jones, G. *The Chemistry of Heterocyclic Compounds*, Vol. 32, part 1, 2, 3.
Weissberger, A.; Taylor, E.C. Ed.; Wiley: New York, 1977, 1982, 1990.
(14) Kametani, T.; Kasai, H. *Stud. Nat. Prod. Chem.* **1989**, *3*, 389.
(15) Grundon, M.F. *Alkaloids* **1988**, *32*, 341.
(16) Sakamoto, T.; Kondo, Y.; Yamanaka, H. *Heterocycles* **1988**, *27*, 2225.
(17) Cheng, C.C.; Yan, S.J. *Org. React.* **1982**, *22*, 37.
(18) Beyer, C. *J. Prakt. Chem.* **1880**, [2] 33, 393.
Beyer, C. *Ibid*, **1880**, [2] 33, 420.
(19) Glinka, J. *Pol. J. Chem.* **1978**, *52*, 1039.
(20) Borsche, W.; Sinn, F. *Liebigs Ann. Chem.* **1939**, *538*, 283.
(21) Fehnel, E.A. *J. Org. Chem.* **1966**, *31*, 2899.
(22) Toi, Y.; Isagawa, K.; Fushizaki, Y. *Nippon Kagaku Zasshi* **1968**, *89*, 1096; *Chem. Abstr.* **1969**, *70*, 87508.
(23) Al-Talib, M.; Jochims, J.C.; Hamed, A.; Wang, Q.; Ismail, A.E. *Synthesis*, **1992**, 697.
(24) Hall, D.; Ummat, P.K. *J. Chem. Soc. (A)* **1967**, 1612.
(25) Tohda, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1977**, 777.

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