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ON THE [1,4] SIGMATROPIC REARRANGEMENT OF AMMONIUM BENZYLIDES

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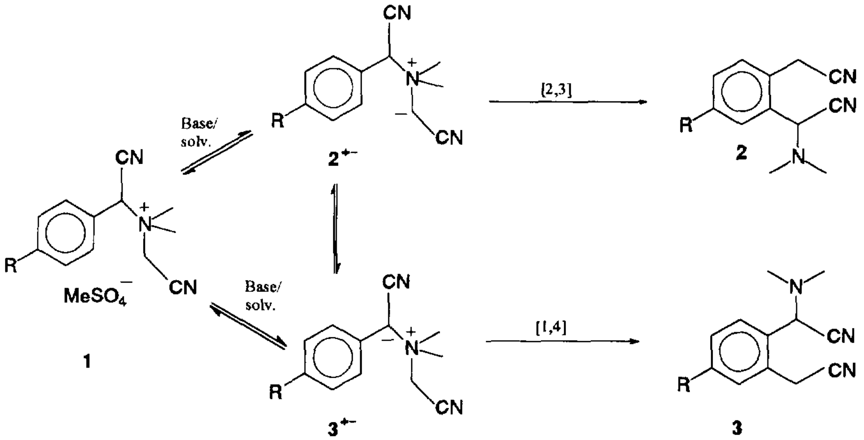
Abstract: ^{13}C NMR investigations revealed that salt **1a** enriched in ^{13}C at one of cyano groups, when treated with a base, generated ylides **2a**$^{+-}$ and **3a**$^{+-}$ which entered [2,3] and [1,4] sigmatropic rearrangements, respectively.

Ammonium benzylides typically enter [2,3] (Sommelet-Hauser) rearrangement which is a well-established synthetic tool for ortho functionalization of aromatic compounds.[1] Isomeric [1,4] ("reverse" Sommelet-Hauser) rearrangement of benzylides has not been realized until recently.[2] Previously, it has been shown that ylides generated from benzyltrimethylammonium iodide by means of sodium amide in liquid ammonia reacted exclusively via the [2,3] mode rather than the [1,4] mode.[3]

We have shown[2] that the salts **1**, when treated with a weak base, under mild conditions, afforded products **2** or mixtures of **2** and **3**, the structures of which were proved by chemical means. The products **3** resulted from ylides **3**$^{+-}$ via a new [1,4] sigmatropic rearrangement (Scheme 1).

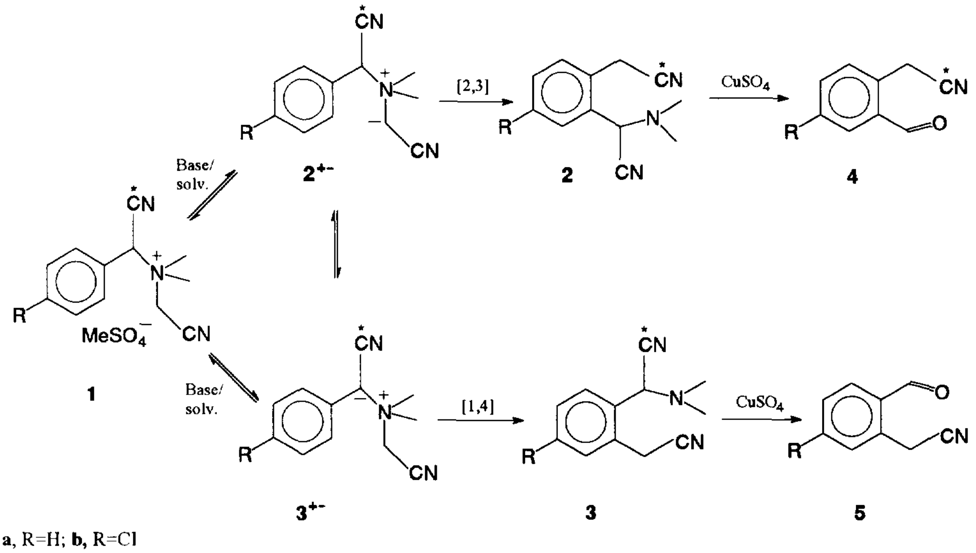


a, R=H; **b**, R=Cl
Base/solv.=25%aq. NaOH/PhH; solid K_2CO_3/DMF; 25%aq. NH_3/CH_2Cl_2

Scheme 1

If in the salt **1**, R=H, the products **2** and **3** are, of course, the same and the mode of rearrangement cannot be deduced by chemical means. Now, to solve this problem we have used ^{13}C NMR spectroscopy.

Thus, the salt **1a**, one of cyano groups of which was enriched with a definite quantity of ^{13}C (up to 10%),[4] was treated with different base-solvent systems, and the products were analyzed by ^{13}C NMR spectra, or cleaved by means of cupric sulphate in aq. ethanol, and then analyzed. Results of the rearrangements of the salt **1b**[4] were also included for comparative purposes (Scheme 2, Table).



Scheme 2

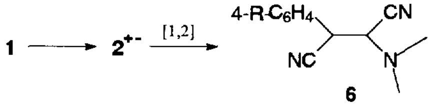
Table. Rearrangements of Salts **1a,b**

Entry	Salt	Base	Solvent	Temp. (°C)	Method of analysis[a,b]	Yield (%)	Products [2,3]	Products [1,4]
1	**1a**	solid K_2CO_3	DMF	-30	A B	80	**2a**, 87 **2a**, 83	**3a**, 13 **3a**, 17
2		solid K_2CO_3	DMSO	20	A B	80	**2a**, 45 **2a**, 43	**3a**, 55 **3a**, 57
3		25% aq. NH_3	CH_2Cl_2	-30	A, B C	83 77	**2a**, 100 **4a**, 100	**3a**, 0 **5a**, 0
4	**1b**	solid K_2CO_3	DMF	-25 to -30	-	90	**2b**, 54[c]	**3b**, 46[c]
5		solid K_2CO_3	DMSO	20	D	77	**2b**, 33	**3b**, 67
6		25% aq. NH_3	CH_2Cl_2	-30	D	72	**2b**, 100	**3b**, 0

[a] Ref. 5. [b] Methods A and B gave similar results. Estimated error is $\leq \pm 5\%$. [c] Ref. 2.

Thus, the salt **1a**, unsubstituted in the phenyl ring, entered not only the well-known [2,3] rearrangement, but also a new [1,4] one. The para chlorine atom which stabilizes the negative charge in ylide **3b**$^{+-}$(as compared to **3a**$^{+-}$) favours the formation of the [1,4] product **3b**.

Under suitably selected conditions, benzylides generated from the salts **1** entered still another rearrangement. Thus, both **1a** and **1b**, when stirred with solid $NaHCO_3$ in DMF (-30°C, 1.5 h), afforded with good yields the products of [1,2] (Stevens) rearrangement, **6a** and **6b**, derived from ylides **2a**$^{+-}$ and **2b**$^{+-}$, respectively[6] (Scheme 3). Some amounts (ca. 10%) of Stevens products were also formed if reactions of **1a,b** were carried out with solid K_2CO_3 in DMF at 0°C.[2] It is evident that the kind of base-solvent system decisively affected the ratio of [2,3] / [1,4] / [1,2] products formed. Particularly significant is an effect of $NaHCO_3$, unlike K_2CO_3, which in DMF caused [1,2] shift.



a, R = H, 50%, mixture of diastereoisomers I + II (4 : 3)
b, R = Cl, 85%, one diastereoisomer

Scheme 3

Due to the presence of the aryl group, the benzylidene hydrogen in **1** is more acidic than the methylene one, and the formation of **3**$^{+-}$ should be kinetically preferred. Yet, the products of [1,4] rearrangement of **3**$^{+-}$ are only observed under some conditions. Thus the stability of the ylide does not govern the direction of rearrangement, a conclusion which has already been drawn from studies of other ylides.[1a] Unequivocal [2,3] shift in aq. NH_3 may indicate that the fairly acidic water acts as a proton transfer agent to favour **2**$^{+-} \rightleftharpoons$ **3**$^{+-}$ equilibration. Our data and the literature show that subtle base and solvent effects, not fully understood at present, govern the rearrangements of benzylides.

So far, the [1,4] rearrangement is restricted to benzylides of specific structure **3**$^{+-}$. We are currently looking for other benzylammonium salts which would generate ylides prone to [1,4] rearrangement.

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References and Notes

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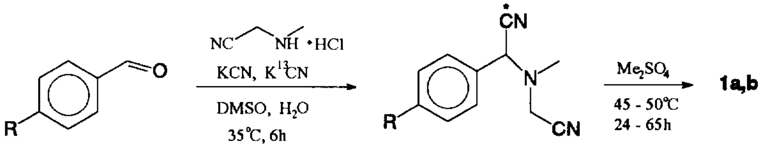
2. (a) Jończyk, A.; Lipiak, D.; Sienkiewicz, K. *Synlett* **1991**, 493-496. (b) Jończyk, A.; Lipiak, D. *J. Org. Chem.* **1991**, *56*, 6933-6937.

3. Jones, F.H.; Hauser, C.R. *J. Org. Chem.* **1961**, *26*, 2979-2980.
4. The salts **1** were prepared by the Strecker reaction of the corresponding aldehydes followed by quaternization with methyl sulphate:



a, R = H	30%	87%
b, R = Cl	40%	85%

^{13}C NMR (DMSO-d_6, 50 MHz): **1a**, δ=111.08 (CN), 112.81 (*CN); **1b**, δ=111.12 (CN), 112.55 (*CN).

5. A - comparison of integral intensities of ^{13}C NMR signals (CDCl$_3$, 50 MHz) of cyano and quaternary aryl (as internal intensity standard) carbons in the samples of rearranged products **2a** and **3a** of natural population and population enriched in ^{13}C isotopomers; δ_C=113.74 ($CH\underline{C}N$), 117.25 ($CH_2\underline{C}N$), 130.94 (CAr).

   B - comparison of integral intensities of ^{13}C satellites of signals of benzyl (δ_C=20.52, $J_{C\text{-}CN}$=58.16 Hz) and benzylidene (δ_C=61.06, $J_{C\text{-}CN}$=52.47 Hz) carbons to entire integral intensity of signals of these carbons in the mixture of **2a** and **3a** of population enriched in ^{13}C isotopomers.

   C - comparison of integral intensities of ^{13}C NMR signals of cyano (δ_C=117.18) and quaternary aryl (δ_C=132.66) carbons in the samples of aldehydes **4a/5a** of natural population and population enriched in ^{13}C isotopomers, and/or comparison of integral intensities of ^{13}C satellites of signals of benzyl carbon (δ_C=21.62, $J_{C\text{-}CN}$=58.37 Hz) to entire integral intensity of signals of this carbon in the sample of **4a/5a** of population enriched in ^{13}C isotopomers.

   D - integration of ^{1}H NMR signals (CDCl$_3$, 200 MHz) of CH$_3$, CH$_2$ and CH in **2b** and **3b**.
6. Given structures of Stevens products **6a** and **6b** are based on ^{13}C NMR spectra (CDCl$_3$, 50 MHz):

   6a I(II): δ=40.29 (40.19)(CH); 41.87 (42.37)(CH$_3$N); 63.73 (63.20)(CHN); 112.94 (113.19)[$CH(\underline{C}N)N$]; 117.10 (117.48)($CH\underline{C}N$); 127.81, 128.35, 129.32, 129.36, 129.39, 129.41, 129.48, 129.63 (CHAr); 130.53 (131.36)(CAr).

   6b: δ=39.75 (CH); 42.04 (CH$_3$); 63.59 (CH-N); 112.73 (CN); 116.63 (CN); 129.80, 129.88 (CHAr); 128.86, 136.12 (CAr).

   Previously, isomeric ylides **3a**$^{+-}$ and **3b**$^{+-}$ were suggested as precursors of the [1,2] rearrangement products.[2]

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