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

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Abstract: ¹³C NMR investigations revealed that salt 1a enriched in ¹³C 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 shown² 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] signatropic rearrangement (Scheme 1).



a, R=H; b, R=Cl Base/solv.=25%aq. NaOH/PhH; solid K2CO3/DMF; 25%aq. NH3/CH2Cl2

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 ¹³C 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 1b⁴ were also included for comparative purposes (Scheme 2, Table).



Scheme 2

Entry	Salt	Base	Solvent	Temp.	Method of	Yield	Products	
				(°C)	analysis ^{a,b}	(%)	[2,3]	[1,4]
1	1a	solid K ₂ CO ₃	DMF	-30	A B	80	2a , 87 2a , 83	3a , 13 3a , 17
2		solid K ₂ CO ₃	DMSO	20	A B	80	2a, 45 2a, 43	3a , 55 3a , 57
3		25% aq. NH_3	CH ₂ Cl ₂	-30	A, B C	83 77	2a , 100 4a , 100	3a, 0 5a, 0
4	1b	solid K ₂ CO ₃	DMF	-25 to -30	-	90	2b , 54°	3b , 46°
5		solid K ₂ CO ₃	DMSO	20	D	77	2b , 33	3b , 67
6		25% aq. NH3	CH_2Cl_2	-30	D	72	2b, 100	3b, 0

Table. Rearrangements of Salts 1a,b

*Ref. 5. ^bMethods A and B gave similar results. Estimated error is ≤±5%. ^cRef. 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 NaHCO₃ 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 $2b^{+-}$, respectively⁶ (Scheme 3). Some amounts (ca. 10%) of Stevens products were also formed if reactions of 1a,b were carried out with solid K₂CO₃ 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 NaHCO₃, unlike K₂CO₃, which in DMF caused [1,2] shift.



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. NH₃ 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

- 1. (a) Pine, S.H. Org. Reactions, 1970, 18, 403-464. (b) Machida Y.; Shirai, N.; Sato, Y. Synthesis 1991, 117-122 and references cited therein.
- (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:



¹³C NMR (DMSO-d₆, 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 ¹³C NMR signals (CDCl₃, 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 ¹³C isotopomers; δ_c=113.74 (CH<u>C</u>N), 117.25 (CH₂CN), 130.94 (CAr).
 - B comparison of integral intensities of 13 C satellites of signals of benzyl (δ_c =20.52, J_{C-CN} =58.16 Hz) and benzylidene (δ_c =61.06, J_{C-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 ¹³C 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 ¹³C isotopomers, and/or comparison of integral intensities of ¹³C satellites of signals of benzyl carbon (δ_c =21.62, J_{C-CN} =58.37 Hz) to entire integral intensity of signals of this carbon in the sample of **4a/5a** of population enriched in ¹³C isotopomers.
 - D integration of ¹H NMR signals (CDCl₃, 200 MHz) of CH₃, CH₂ and CH in **2b** and **3b**.
- 6. Given structures of Stevens products 6a and 6b are based on ¹³C NMR spectra (CDCl₃, 50 MHz):
 6a I(II): δ=40.29 (40.19)(CH); 41.87 (42.37)(CH₃N); 63.73 (63.20)(CHN); 112.94 (113.19)[CH(<u>C</u>N)N]; 117.10 (117.48)(CH<u>C</u>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 (CH₃); 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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