CHEMISTRY LETTERS, pp. 1827 - 1830, 1984.

N-(TRIMETHYLSILYLMETHYL)CARBODIIMIDES AND -KETENIMINE AS PRECURSORS OF IMINO- AND ALKYLIDENE-2-AZAALLYL ANIONS

Otohiko TSUGE,* Shuji KANEMASA, and Koyo MATSUDA
Research Institute of Industrial Science, and Department
of Molecular Science and Technology, Interdisciplinary
Graduate School of Engineering Sciences, Kyushu University,
Kasugakoen, Kasuga 816

The fluoride-induced desilylation of N-(trimethylsilylmethyl)-carbodiimides and -ketenimine generates imino- and alkylidene-2-azaallyl anions which cycloadd to a variety of aldehydes giving regioisomeric 1,3-oxazolidines as cycloadducts.

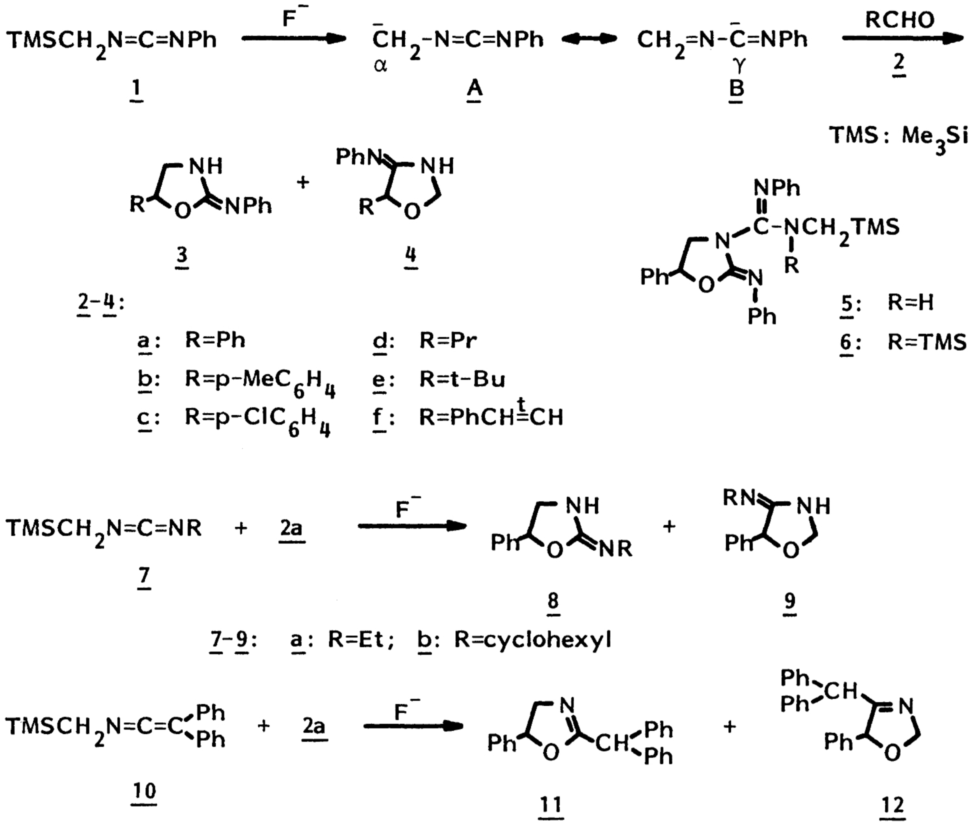
As the central sp carbon of heterocumulenes is highly electrophilic,[1)] the generation of carbanion at the α-position of heterocumulenes may lead to the formation of synthetically important synthons that are expected to undergo an anionic polar cycloaddition reaction to electron-deficient unsaturated bonds. However, such carbanion generation by deprotonation is quite limited because of the high reactivity of heterocumulene moiety toward bases.[1)] Only the heterocumulenes carrying at least one anion-stabilizing substituent at the α-position have been successfully deprotonated.[2,3)]

An elegant preparation of isothiocyanato carbanions was recently demonstrated by the desilylation of some silylated methyl isothiocyanates.[4)] Although this process looked promising, the lack of availability of silylated heterocumulenes has restricted its wide applications to other systems. However, this barrier will be soon removed since we have quite recently found a convenient route to a variety of trimethylsilylmethyl-substituted heterocumulenes.[5)]

The present communication describes the first example of the fluoride-induced desilylation of N-(trimethylsilylmethyl)carbodiimides and -ketenimine leading to the generation of imino- and alkylidene-2-azaallyl anions. These anions cycloadd to aldehydes as ambident ions giving regioisomeric 1,3-oxazolidines.

The reaction of 1-phenyl-3-(trimethylsilylmethyl)carbodiimide <u>1</u>[5)] with two equivalents of benzaldehyde <u>2a</u> in the presence of tetrabutylammonium fluoride (TBAF, 10 mol%) in dry hexamethylphosphoric triamide (HMPA) at room temperature for 1 h and the work-up with water gave two isomeric adducts <u>3a</u> (38%) and <u>4a</u> (34%) which were separated from each other and purified through a chromatography over silica gel (Scheme 1 and Table 1). On the basis of the spectral data[6)] as well as the elemental analyses,[7)] their structures were assigned 5-phenyl-2-phenylimino-<u>3a</u> and 5-phenyl-4-phenylimino-1,3-oxazolidine <u>4a</u>. The exocyclic carbon-nitrogen double bonds of both 3a and 4a were confirmed on the ground of the ^{1}H-NMR spectra that showed no signal for the ortho two hydrogens of anilino moiety.[8)]

The product 3a (designated as α-mono-adduct) corresponds to the cycloadduct that has been formed through the nucleophilic attack of the α-carbon of anion A and 4a (designated as γ-mono-adduct) the γ-carbon of B. In a sence of organic synthesis, the formation of γ-adduct 4a is particularly noteworthy because the natural polarity of carbodiimide as a heterocumulene has been reversed. Though only one example is known for the reversal of polarity of this kind,[2c)] it is a particular case where the α-carbon is sterically too hindered to be attacked by an electrophile. As our result offers an interesting regioselection of 2-azaallyl anion that carries no substituent at the α-carbon, the same reaction was investigated under various conditions and the results are summarized in Table 1.



Scheme 1.

In the presence of a catalytic amount (10 mol%) of TBAF,[9)] the reaction of 1 with 2a was so rapid as to be completed in a few minutes at room temperature in HMPA, and even at -10 °C it proceeded at a moderate rate (entries 2 and 3). Tetrahydrofuran (THF) as a solvent is favored for the formation of γ-mono-adduct 4a, but the total yield was poor (entries 7 and 8). When the reaction was carried out under rather mild conditions, the third product 5 was obtained (entries 2, 3, and

5). The structure of 5 was assigned as the 1:1 adduct of 1 onto the ring nitrogen of α-mono-adduct 3a on the basis of the spectral data[10] as well as by the comparison with the authentic samples.[11]

From the fact that 5 was only isolated at the early stage of the reaction (entries 2, 3, 4, and 5), this reaction must involve an intermediate that provides 5 on the hydrolytic work-up. The reaction pathway can be figured out as follows: The competitive reaction of A and B with 2a forms each silylated derivatives of 3a and 4a. As soon as it is formed, silylated 3a smoothly reacts with another molecule of 1 to give 6. Fluoride-induced desilylation of 6 causes the retro addition into 3a and 1 which repeats the reaction. So far it is not clear how the formation of 6 is concerned with the regioselectivity of this reaction.

Table 1. Reactions of N-Silylmethyl Cumulenes with Aldehydes in the Presence of Fluorides

Entry	Reagents				Reaction conditions			Products (isolated yields/%)			
	Cumulene	Aldehyde	Fluoride	Molar ratio C-A-F[a]	Solvent	Temp °C	Time h	Total	α-Mono	γ-Mono	Bis
1	1	2a	TBAF	1-2-0.1	HMPA	rt	1	72	3a (38)	4a (34)	-
2	1	2a	TBAF	1-5-0.1	HMPA	-10	1	88	3a (21)	4a (32)	5 (35)
3	1	2a	TBAF	1-5-0.1	HMPA	rt	1/12	84	3a (22)	4a (32)	5 (30)
4	1	2a	TBAF	1-5-0.1	HMPA	rt	1	86	3a (44)	4a (42)	-
5	1	2a	TBAF	1-5-0.03	HMPA	rt	45	88	3a (14)	4a (34)	5 (40)
6	1	2a	TBAF	1-5-1	HMPA	rt	1/6	70	3a (28)	4a (42)	-
7	1	2a	TBAF	1-5-0.1	THF	rt	1	58	3a (6)	4a (52)	-
8	1	2a	TBAF	1-5-0.1	THF	70	1	60	3a (11)	4a (49)	-
9	1	2a	CsF	1-5-0.1	HMPA	80	5	41	3a (13)	4a (28)	-
10	1	2b	TBAF	1-5-0.1	HMPA	rt	1	91	3b (48)	4b (43)	-
11	1	2c	TBAF	1-5-0.1	HMPA	80	1	60	3c (16)	4c (44)	-
12	1	2d	TBAF	1-5-0.1	HMPA	rt	1	83	3d (22)	4d (61)	-
13	1	2e	TBAF	1-5-0.1	HMPA	rt	1	75	3e (35)	4e (40)	-
14	1	2f	TBAF	1-5-0.1	HMPA	rt	1	38	-	4f (28)	b)
15	7a	2a	TBAF	1-5-0.1	HMPA	rt	1	69	8a (35)	9a (34)	-
16	7b	2a	TBAF	1-5-0.1	HMPA	80	1	50	8b (21)	9b (29)	-
17	10	2a	TBAF	1-5-0.1	HMPA	rt	1	91	11 (45)	12 (46)	-

a) Molar ratios among the cumulenes (C), aldehydes (A), and fluorides (F). b) The bis-adduct of type 5 was given in 10% yield.

Similar reactions were performed between 1 and aromatic 2b-2c, aliphatic aldehydes 2d-2e, α,β-unsaturated aldehyde 2f and between several N-alkyl-substituted carbodiimides 7a-7b[5] and 2a (Scheme 1 and Table 1). N-(Trimethylsilylmethyl)diphenylketenimine 10[5] also readily reacted with 2a, under similar conditions, to give two isomeric α-mono- 11 and γ-mono-adduct 12 in comparable yields.

References

1) As comprehensive reviews on heterocumulenes: H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York-London (1967); S. Patai, "The Chemistry of Cyanates and Their Thio Derivatives," John Willey and Sons, Chichester-New York-Brisbane-Tronto (1977); S. Patai, "The Chemistry of Ketenes, Allenes and Related Compounds," John Willey and Sons, Chichester-New York-Brisbane-Tronto (1980).

2) Several examples have been reported for the deprotonation of alkyl isothiocyanates: a) D. Hoppe, Angew. Chem., 84, 956 (1972); b) D. Hoppe and R. Hollman, Chem. Ber., 109, 3047 (1976); c) I. Hoppe, D. Hoppe, and U. Schöllkopf, Tetrahedron Lett., 1976, 609.

3) A. M. van Leusen, H. J. Jeuring, J. Wildeman, and S. P. J. M. van Nispen, J. Org. Chem., 46, 2069 (1981).

4) T. Hirao, A. Yamada, Y. Oshiro, and T. Agawa, Angew. Chem., Int. Ed. Engl., 20, 126 (1981); T. Hirao, A. Yamada, K. Hayashi, Y. Oshiro, and T. Agawa, Bull. Chem. Soc. Jpn., 55, 1163 (1982).

5) O. Tsuge, S. Kanemasa, and K. Matsuda, J. Org. Chem., 49 (1984) in press.

6) 3a: Colorless prisms from benzene-hexane; mp 126-127 °C; IR (KBr) 3230 (NH) and 1660 cm^{-1} (C=N); ^{1}H-NMR ($CDCl_3$) δ3.73 (1H, dd, J=11.5 and 7.8 Hz, one of 4-CH_2), 4.20 (1H, dd, J=11.5 and 9.3 Hz, the other of 4-CH_2), 5.48 (1H, dd, J=9.3 and 7.8 Hz, 5-H), 6.43 (1H, br. s, NH), and 6.90-7.40 ppm (10H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ58.18 (t, 4-C), 80.79 (d, 5-C), 119.30 (d), 122.24 (d), 125.76 (d), 128.40 (d), 128.69 (d), 128.81 (d), 139.85 (s), 140.84 (s), and 157.22 ppm (s, 2-C); MS m/z 238 (M^{+}).

   4a: Colorless prisms from benzene-hexane; mp 123-124 °C; IR (KBr) 3350 (NH) and 1650 cm^{-1} (C=N); ^{1}H-NMR ($CDCl_3$) δ5.35 (1H, dd, J=3.8 and 3.0 Hz, 5-H), 5.54 (1H, dd, J=7.9 and 3.0 Hz, one of 2-CH_2), 5.72 (1H, dd, J=7.9 and 3.8 Hz, the other of 2-CH_2), 5.76 (1H, br. s, NH), and 6.90-7.50 ppm (10H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ83.49 (d, 5-C), 93.94 (t, 2-C), 118.42 (d), 122.76 (d), 125.23 (d), 127.52 (d), 128.87 (d), 129.05 (d), 129.87 (d), 137.62 (s), 139. 61 (s), and 158.11 ppm (s, 4-C); MS m/z 238 (M^{+}).

7) All the new compounds reported in the present communication gave the satisfactory elemental analyses.

8) In general, the ortho hydrogens of N-alkyl- or N,N-dialkylanilines appear fairly upfield of those of N-alkylideneanilines (N. F. Chamberlain, "The Practice of NMR Spectroscopy," Plenum Press, New York-London (1974), Chap. 4, pp. 75-91.

9) In the absence of fluoride ion, 1 did not react with 2a in HMPA at 80 °C for 12 h, both 1 and 2a being quantitatively recovered.

10) 5: Colorless prisms from hexane; mp 119-120 °C; IR (KBr) 3180 (NH), 1680 (C=N), 1250, and 850 cm^{-1} (Me_3Si); ^{1}H-NMR ($CDCl_3$) δ0.03 (9H, s, Me_3Si), 2.34 (2H, d, J=4.8 Hz, CH_2), 3.89 (1H, dd, J=10.8 and 7.8 Hz, one of 4-CH_2), 4.40 (1H, dd, J=10.8 and 8.4 Hz, the other of 4-CH_2), 5.27 (1H, dd, J=8.4 and 7.8 Hz, 5-H), 6.80-7.40 (15H, m, ArH), and 8.99 ppm (1H, t, J=4.8 Hz, NH); MS m/z 442 (M^{+}).

11) The compound 5 was obtained in 78% yield in the reaction of 1 with 3a in THF at room temperature for 2 h. The ^{1}H-NMR spectrum shows that the compound 5 carries an NH group adjacent to CH_2 moiety and no anilino substituent. On the other hand, 1 added to the exo nitrogen of 4a giving an isomer of 5. Its structure was confirmed on the basis of the spectral data (IR (neat) 3280 (NH), 1250, and 850 cm^{-1} (Me_3Si); ^{1}H-NMR ($CDCl_3$) δ-0.05 (9H, s, Me_3Si), 2.28 (2H, d, J=4.8 Hz, CH_2), 5.50-5.80 (3H, m, 2-CH_2 and 5-H), 6.45 (2H, br. d, the ortho hydrogens of anilino moiety), 6.80-7.30 (13H, m, ArH), and 8.96 ppm (1H, t, J=4.8 Hz, NH); MS m/z 442 (M^{+}).).

(Received July 30, 1984)