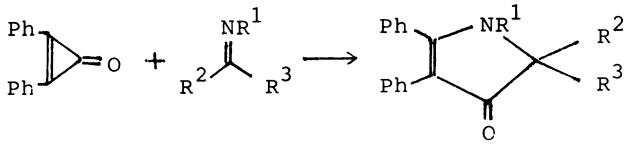
Preparation of 5-Substituted-2-pyrrolin-4-ones from *N*-(4-Oxo-2-pyrrolin-5-yl)sulfoximines

Hiroshi YOSHIDA,* Shoichi BANDO, Shosuke NAKAJIMA,
Tsuyoshi OGATA, and Kiyoshi MATSUMOTO†
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432
†*College of Liberal Arts and Sciences, Kyoto University, Kyoto 606*
(Received December 13, 1983)

Synopsis. In trifluoroacetic acid, immonium cations were generated from *S,S*-dimethylsulfoximines in which the pyrrolinone ring was substituted. Nucleophiles such as alcohols, thiocyanic acid, thiols, or acetylacetone reacted with the immonium salts to yield 5-substituted 2-pyrrolin-4-ones.

In previous papers[1,2] we have reported the reaction of diphenylcyclopropenone with compounds in which C=N groups such as imidate, amidine, imidothioate, or *N*-imidoyl sulfoximine were substituted, giving pyrrolinone derivative as the major product:



R^1,R^2=Alkyl, Aryl: R^3=RO, R_2N, RS, $Me_2\overset{\oplus}{S}(O)\overset{\ominus}{N}$

In the continuation of our studies on the chemical and physical properties of imines and ylides, we have been much interested in the chemical nature of the pyrrolinone-substituted sulfoximines (**1a—d**) which posess high thermostability.

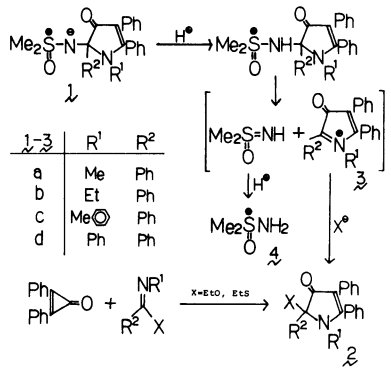
Table 1. The reaction of the pyrrolinone-substituted sulfoximines **1a—d** with nucleophiles

Reactants		Product	
Sulfoximide	XH		Yield/%
1a	EtOH	**2a**(X=EtO)	94
	HOH	**2a**(X=OH)	89
	t-BuSH	**2a**(X=*t*-BuS)	71
1b	EtOH	**2b**(X=EtO)	80
	Ac_2CH_2	**2b**(X=Ac_2CH)	85
1c	HSCN	**2c**(X=NCS)	84
	Ac_2CH_2	**2c**(X=Ac_2CH)	77
	MeOH	**2c**(X=MeO)	88
	EtOH	**2c**(X=EtO)	93
	i-PrOH	**2c**(X=*i*-PrO)	81
	HOH	**2c**(X=OH)	96
	PhSH	**2c**(X=PhS)	74
	4-ClC_6H_4SH	**2c**(X=4-ClC_6H_4S)	65
	EtSH	**2c**(X=EtS)	58
	t-BuSH	**2c**(X=*t*-BuS)	64
1d	EtOH	**2d**(X=EtO)	90

Table 2. Physical properties of pyrrolinones **2a—d**

2	Mp θ_m/°C	^{1}H-NMR (δ in $CDCl_3$)[a]	M+	Anal Found (Calcd) (%)		
				C	H	N
2a(X=OH)	151—152	2.83(3H, s, Me)	341	80.65 (80.92)	5.60 (5.61)	3.89 (4.10)
2a(X=*t*-BuS)	205—207	1.46(9H, s, *t*-Bu), 3.08(3H, s, MeN)	413	78.84 (78.41)	6.36 (6.58)	3.45 (3.39)
2b(X=Ac_2CH)	145—146	0.80(3H, t, J=7 Hz, $\underline{CH_3}CH_2$), 2.24(3H, s, Ac), 2.27(3H, s, Ac), 3.19(2H, dq, J=4 and 7 Hz, CH_2), 5.29(1H, s, CHCO)	437	79.12 (79.61)	6.26 (6.22)	3.24 (3.20)
2c(NCS)	174—176	2.16(3H, s, Me)	458	78.37 (78.58)	4.73 (4.84)	5.93 (6.11)
2c(Me_2NCSNH)	148—150	2.13(3H, s, $\underline{Me}C_6H_4$), 3.03(6H, s, Me_2N)	503	76.28 (76.31)	5.63 (5.80)	8.07 (8.34)
2c(Ac_2CH)	214—215	1.98(3H, s, Ac), 2.10(3H, s, Ac), 2.13(3H, s, $\underline{Me}C_6H_4$) 4.70(1H, s, CHCO)	499	81.87 (81.74)	5.73 (5.85)	2.86 (2.80)
2c(*i*-PrO)	185—188	1.15(3H, d, J=7 Hz, $\underline{Me}CH$), 1.42(3H, d, J=7 Hz, $\underline{Me}CH$), 2.13(3H, s, $\underline{Me}C_6H_4$), 3.9—4.5(1H, m, CHCO)	459	83.25 (83.63)	6.33 (6.36)	2.81 (3.05)
2c(OH)	202—206	2.14(3H, s, Me)	417	83.50 (83.43)	5.42 (5.55)	2.89 (3.35)
2c(PhS)	164	2.18(3H, s, Me)	509	82.14 (82.48)	5.16 (5.34)	2.93 (2.75)
2c(4-ClC_6H_4S)	185—190	2.16(3H, s, Me)	543	77.06 (77.26)	4.66 (4.82)	2.72 (2.57)
2c(*t*-BuS)	170—172	1.48(9H, s, *t*-Bu), 2.13(3H, s, Me)	489	81.16 (80.94)	6.48 (6.39)	2.77 (2.86)

a) Aryl ring protons were observed at δ 6.4—8.1.



Scheme 1.

Table 3. ^{1}H-NMR spectra of the terminal group R^1 of the parent sulfoximines **1a—c** and the corresponding cations **3a—c**

	δ in $CDCl_3$[a]
1a	2.80(s, MeN)
3a	3.07(bs, MeN)[b]
1b	0.61(t, CH_3), 3.34(dq, CH_2N)
3b	0.98(t, CH_3), 3.3—3.9(bm, CH_2N)[b]
1c	2.09(s, $\underline{Me}C_6H_4$)
3c	2.20(s, $\underline{Me}C_6H_4$)[b]

a) Phenyl ring protons appeared at δ 6.4—8.0 as multiplets. b) Trifluoroacetic acid (10% v/v) was added.

The sulfoximines **1a—d** were stable in ethanolic sodium hydroxide. In acidic ethanol (hydrochloric or trifluoroacetic acid). However, **1a—d** decomposed easily within one day to **2a—d** (X=EtO) in good yields. In trifluoroacetic acid **1a—d** gave dark brown solutions within 5 min. Treatment of these with nucleophiles such as alcohols, thiols, thiocyanic acid, or acetylacetone yielded 2-pyrrolin-4-one derivatives **2a—d** (X) as listed in Table 1, while, treatment of the acid solution of **1a** with primary or secondary amine gave no amino-substituted products, with only resinous mass being formed. The products **2a** (X=EtO), **2b** (X=EtO), **2c** (X=EtO, EtS), and **2d** (X=EtO) were identical to the compounds obtained from the reaction of diphenylcyclopropenone with the corresponding imidates or imidothioate. The structure of the other compounds listed in Table 1 was elucidated on the basis of their ^{1}H-NMR, MS, and elemental analyses (Table 2).

The structure of the product obtained by the reaction with thiocyanic acid was found to be not thiocyanate but isothiocyanate, since **2c** (X=NCS) reacted with dimethylamine to yield **2c** (X=Me_2NCSNH) in a good yield.

A plausible mechanism for the formation of **2a—d** was shown in Scheme 1. The initial step involves the protonation of the imino nitrogen of **1a—d** followed by the elimination of sulfoximine to give iminium cations **3a—d**. The eliminated sulfoximine yielded S-aminosulfoxonium salt in trifluoroacetic acid.[3] The formation of the cations has been supported as follows. The color of the solution of **1a—d** in $CDCl_3$ changed from yellow to dark brown immediately on addition of trifluoroacetic acid. ^{1}H-NMR spectra of the brown solutions showed the signals of the substituents of **3a—c** shifted to lower field compared with those of the parent sulfoximines **1a—c** (Table 3) together with aminodimethylsulfoxonium ion **4** (δ=3.49). The down field shift of the alkylsubstituents of carbonium ions has been well documented.[4] The cations **3a—d** in trifluoroacetic acid were stable at room temperature for a day when they were kept from the atmospheric moisture. Addition of a nucleophile to the solutions, the color of which turned yellow within a minute, gave 5-substituted pyrrolinones **2a—d(X)**; none of the starting **1a—d** was recovered.

Experimental

General. Melting points are uncorrected. ^{1}H-NMR spectra were recorded on a Hitachi-Perkin Elmer R-24 (60 MHz) spectrometer using TMS as an internal standard, and mass spectra on a Hitachi RMU-7M mass spectrometer.

Preparation of Pyrrolinone-substituted Sulfoximines 1a—d. Sulfoximines **1a—d** were prepared according to the previously reported method.[1]

The Reaction of the Sulfoximines 1a—d with Nucleophiles. In a stoppered flask, sulfoximine **1** (1 mmol) in trifluoroacetic acid (3 cm^3) was stirred for 5 min to give a dark brown solution. To the solution was added a nucleophile [alcohol, sodium thiocyanate, acetylacetone (3 mmol) or thiol (1 mmol)]. We stirred the mixture until the color of the solution changed to yellow. To the mixture, water (15 cm^3) was added and the product was extracted with chloroform. The extract was dried over sodium sulfate and evaporated under reduced pressure. The crude product was either recrystallized from an appropriate solvent or purified by chromatography over silica gel. The results are collected in Table 1 and physical properties of new compounds are shown in Table 2.

References

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3) The authors are indebted to the referees for the discussion.

4) a) G. Frankel and D. G. Farnum, "Carbonium Ions" vol I, ed by G. A. Olah and P. v. R. Schleyer, Interscience Publishers, New York (1968), p. 237; b) L. M. Jackmann and S. Sternhill, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford (1969), P. 249.