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Cycloaddition of Diphenylcyclopropenone with Carboximidate, Carboximidamide, and Carboximidothioate

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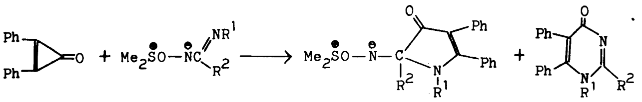
Synopsis. The reaction of diphenylcyclopropenone with $R^1N=C(R^2)X$ (**2**) (R^1, R^2=alkyl, aryl, X=MeO, EtO, MeS, or Me_2N) gave 2-pyrrolin-4-one (**3**) in good yield. The less reactive carboximidothioate (**2**, R^1=4-MeC_6H_4, R^2=Ph, X=MeS) yielded isomeric 3-pyrrolin-2-one together with **3**.

In a previous paper[1)] we have reported the reaction of *N*-imidoyl sulfoximide with diphenylcyclopropenone to yield the sulfoximide substituted with pyrrolinone ring together with pyrimidinone *via* [2+3] and [3+3]cycloaddition reactions:



Eicher and his coworkers have reported that ketimine reacts with diphenylcyclopropenone **1** to yield 2-pyrrolin-4-one derivative by [2+3]cycloaddition reaction.[2)] However, no work has been undertaken on the *N,N,N'*-trisubstituted carboximidamide, carbiximidate, and carboximidothioate (**2**). In this paper we report the reactivities of these compounds with diphenylcyclopropenone.

An equimolar mixture of **1** and **2** in benzene (reaction at 80 °C) or xylene (over 100 °C) was heated at suitable temperature. The reaction was followed by TLC. The products isolated by column chromatography were 2-pyrrolin-4-one (**3**), but in the case of **2j**, **3j**, and 3-pyrrolin-2-one (**4j**) were obtained. The yields of **3** and **4** and their physical properties are summarized in Table 1.

The structures of the products were elucidated on the basis of their elemental analyses, ^1H-NMR and mass spectroscopic studies as well as chemical transformations. Mass spectra of **3c**, **3g**, and **3j** showed peaks corresponding to the groups PhC=C(Ph)-NR^1 together with the parent peaks. Although **4j** showed a peak corresponding to PhC=C(Ph)-CPh, no such peak was observed for **3j**.

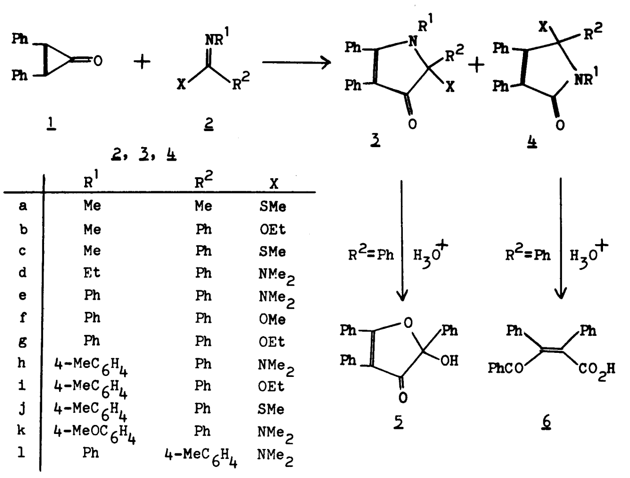
Some products were subjected to drastic hydrolysis. On treating with hot mixture of aqueous acetic and sulfuric acids, **3b**, **3e**, **3g**, **3i**, and **3j** gave the known triphenylfuranone (**5**)[2c)] in moderate yields, while the isomer **4j** yielded the acid **6**.[3)]

It has been reported that *N*-methyl and *N*-phenylketimines react completely with **1** in boiling 1,2-dimethoxyethane (at about 83 °C) within 20 min and 2—5 h respectively.[2c)] Table 1 indicates that the reactivity of **2** decreased in orders on R^1: alkyl>aryl, X: NMe_2> OMe, and OEt>SMe. Although the reactivities of **2** were lower than those of ketimines, the electron-releasing effects of substituents on R^1 and X would account for the reactivities of **2**. Nucleophilic attack of the imino nitrogen on the cyclopropenone **1** gave **3** or **4** depending on the attacking site. The major products were 2-pyrrolin-4-ones (**3**) whereas the less reactive **2j** showed lower selectivity under more drastic conditions giving a mixture of **3j** and **4j**. In conclusion, the reaction of **1** with

TABLE 1. YIELDS AND PHYSICAL PROPERTIES OF **3** AND **4**

Reactant	Reaction conditions		Product	Yield	Mp	(Recryst	^1H-NMR (δ in $CDCl_3$)[b)]	M^+	Found (Calcd) (%)		
	Temp/°C	Time/h		%	θ_m/°C	solvent)[a)]			C	H	N
2a	110	2	**3a**	90	105—106	(E-P)	1.65 (3H, s, MeC-N), 2.00 (3H, s, MeS) 3.05 (3H, s, MeN)	309	73.79 (73.75)	6.27 (6.19)	4.44 (4.53)
2b	80	3	**3b**	73	157—158	(E-P)	1.36 (3H, t, *J*=7 Hz, $\underline{Me}CH_2$), 2.76 (3H, s, MeN), 3.65 (2H, q, CH_2)	369	81.51 (81.27)	6.18 (6.27)	3.83 (3.79)
2c	110	4	**3c**	88	96	(E-P)	2.09 (3H, s, MeS), 2.97 (3H, s, MeN)	371	77.24 (77.57)	5.81 (5.70)	3.91 (3.77)
2d	110	2	**3d**	85	142	(C-P)	0.55 (3H, t, *J*=7 Hz, $\underline{Me}CH_2$), 2.56 (6H, s, Me_2N), 3.30 (2H, dq, *J*=5 and 7 Hz, CH_2)	382	81.69 (81.64)	6.77 (6.85)	7.41 (7.32)
2e	110	16	**3e**	71	177—179	(C-P)	2.64 (6H, s, Me_2N)	430	83.47 (83.69)	6.11 (6.09)	6.49 (6.51)
2f	130	8	**3f**	61	165—168	(E-P)	3.65 (3H, s, MeO)	417	83.42 (83.43)	5.39 (5.55)	3.04 (3.35)
2g	130	8	**3g**	87	190—191	(E-P)	1.28 (3H, t, *J*=7 Hz, Me), 3.86 (2H. q. CH_2)	431	83.61 (83.50)	5.92 (5.84)	3.16 (3.25)
2h	110	10	**3h**	82	208—210	(C-P)	2.12 (3H, s, $\underline{Me}C_6H_4$), 2.52 (6H, s, Me_2N)	444	83.83 (83.75)	6.35 (6.35)	6.43 (6.30)
2i	130	8	**3i**	83	178—180	(E-P)	1.27 (3H, t, *J*=7 Hz, $\underline{Me}CH_2$) 2.16 (3H, s, $\underline{Me}C_6H_4$), 3.86 (2H, q, CH_2)	445	83.21 (83.57)	6.28 (6.11)	3.04 (3.15)
2j	140	18	**3j**	48	97—99	(P)	2.27 (3H, s, $\underline{Me}C_6H_4$), 2.34 (3H, s, MeS)	400[c)]	80.77 (80.50)	5.64 (5.63)	2.99 (3.13)
			4j	33	104—106	(P)	1.98 (3H, s, MeS), 2.28 (3H, s, $\underline{Me}C_6H_4$)	400[c)]	80.39 (80.50)	5.45 (5.63)	3.61 (3.13)
2k	110	10	**3k**	73	163	(C-P)	2.58 (6H, s, Me_2N), 3.68 (3H, s, MeO)	460	80.62 (80.81)	6.24 (6.12)	6.11 (6.08)
2l	110	10	**3l**	80	98—100	(C-P)	2.14 (3H, s, $\underline{Me}C_6H_4$), 2.46 (6H, s, Me_2N)	444	83.72 (83.75)	6.29 (6.35)	6.54 (6.30)

a) C: $CHCl_3$, E: EtOH, P: petroleum ether. b) Aryl ring protons were observed at δ 6.4—8.1 as multiplets. c) M^+ −SMe.



2, 3, 4

	R^1	R^2	X
a	Me	Me	SMe
b	Me	Ph	OEt
c	Me	Ph	SMe
d	Et	Ph	NMe_2
e	Ph	Ph	NMe_2
f	Ph	Ph	OMe
g	Ph	Ph	OEt
h	$4\text{-}MeC_6H_4$	Ph	NMe_2
i	$4\text{-}MeC_6H_4$	Ph	OEt
j	$4\text{-}MeC_6H_4$	Ph	SMe
k	$4\text{-}MeOC_6H_4$	Ph	NMe_2
l	Ph	$4\text{-}MeC_6H_4$	NMe_2

2 has proven to be a useful method for the preparation of 2-pyrrolin-4-ones (**3**).

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 Carboximide, Carboximidate, and Carboximidothioate. The compounds **2** were prepared by the usual methods.[4] Carboximidamides **2d**, **e**, **h**, **k**, and **2l** were obtained from the corresponding imidoyl chlorides and excess dimethylamine in benzene. Carboximidates **2b**, **f**, **g**, and **2i** were prepared from the imidoylchlorides and sodium alkoxide in alcohol. Carboximidothioates **2a**, **c**, and **2j** were obtained by the reaction of the corresponding thioamides with methyl iodide followed by treatment with aqueous sodium hydroxide. The purity of the products was confirmed by ^{1}H-NMR. New compounds were as follows: **2h** (85%): oil; ^{1}H-NMR ($CDCl_3$) δ=2.04 (3H, s, Me), 2.83 (6H, s, Me_2N), and 6.2—7.6 (9H, m, Arom); *m/e* 238 (M^+). **2l** (93%): oil; ^{1}H-NMR ($CDCl_3$) δ=2.17 (3H, s, Me), 2.89 (6H, s, Me_2N), and 6.4—7.4 (9H, m, Arom); *m/e* 238 (M^+).

The Reaction of 1 with 2. A solution of **1** (1.5 mmol) and **2** (2 mmol) was refluxed in a minimum amount of benzene or xylene (3—5 cm^3). The reaction was checked by TLC (aluminum oxide, petroleum ether : ethyl acetate, 1 : 1, v/v) until **1** reacted completely. After cooling, the mixture was chromatographed over silica gel (petroleum ether : ethyl acetate, 4 : 1, v/v). The products were crystallized from appropriate solvents.

Hydrolyses of 3 and 4. In a boiling mixture of acetic acid and sulfuric acid in water (50 : 1 : 25, v/v, 5 cm^3) pyrrolinone (50 mg) was hydrolyzed for 2 d. The resulting mixture was poured into water and extracted with chloroform. The extract was dried over sodium sulfate and evaporated under reduced pressure. **3b**, **e**, **g**, **i**, and **3j** gave triphenyl-3-(2*H*)-furanone **5**: mp 191—192 °C (lit, mp 192—193 °C).[2c] In contrast **4j** yielded the acid **6**: mp 172—174 °C (lit, mp 172 °C).[3]

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