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REACTIONS OF SULFOXONIUM ALLYLIDES WITH NITRILE OXIDES AND RING TRANSFORMATIONS OF THEIR REACTION PRODUCTS

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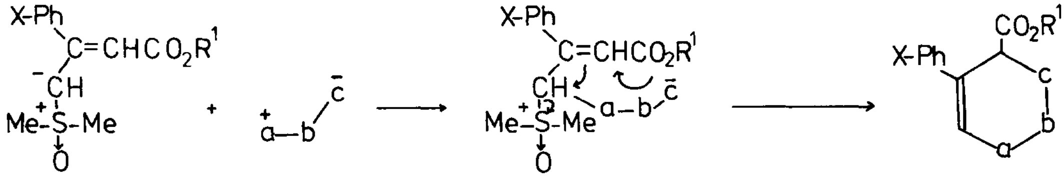
Summary: Reactions of allylides (1) with nitrile oxides (2) afforded furanylglyoxylate oxime (3) and 6H-1,2-oxazine (4). Ring transformations of 3 and 4 gave 4 and pyrrolinone (6), respectively.

The great potential of 1,3-dipolar compounds offers, via [3+2]cycloaddition, valuable entries to heterocyclic systems.1) In this communication we wish to report on reactions of stable sulfoxonium allylides (1) with nitrile oxides (2) and novel ring transformations of resulting reaction products.

It was previously reported that 1 possesed a significant necleophilicity, and that treatment of 1 with triethylamine led to 1,3-butadiene derivatives by [2.3] sigmatropic rearrangement.2) On the basis of these results, reactions of 1 with 1,3-dipolar reagents may provide a new route to synthetic methods for heterocyclic compounds via [3+3]cycloaddition reaction.3)



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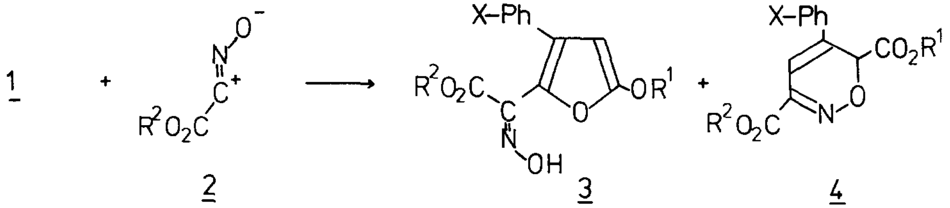
Reactions of 1 with 24) in the presence of excess triethylamine in THF at room temperature for 30 min afforded furanylglyoxylate oxime (3) as a main product and 6H-1,2-oxazine (4), resulting from [3+3]cycloaddition, as a minor one.5)



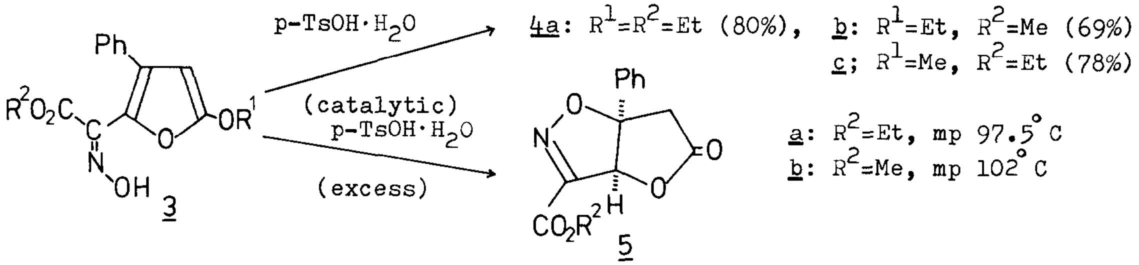
2 3 4

Yields of 3 and 4 are summarized in Table 1.

Table 1 Reaction Products from Allylide (1)[6] and Nitrile Oxide (2)

No.	R^1	X	R^2	Product	Yield(%)	mp of Products (°C)
				3	4	
a	Et	H	Et	68	9	3a; 146-148, 4a; 66-67
b	Et	H	Me	50	8	3b; 110-111, 4b; 80-81
c	Me	H	Et	41	6	3c; 119-121, 4c; 104.5-105.5
d	Et	p-Me	Et	35	-	3d; 85-87

When the oxime 3 was refluxed with a catalytic amount of p-toluenesulfonic acid monohydrate (p-TsOH·H_2O) in benzene for 5 min, ring transformation occurred to give the same oxazine 4 in good yield as obtained by [3+3]cycloaddition of 1. On the other hand, treatment of 3 with excess the acid in chloroform at room temperature for 30 min furnished bicyclic lactone (5).



4a: $R^1=R^2=Et$ (80%), b: $R^1=Et$, $R^2=Me$ (69%)
c; $R^1=Me$, $R^2=Et$ (78%)

a: $R^2=Et$, mp 97.5° C
b: $R^2=Me$, mp 102° C

Another ring transformation involving 1,2-migration of the ethoxycarbonyl group was found in the reaction of the oxazine 4 with triethylamine, i.e., 4 was refluxed with the amine in benzene for 2 hr afforded pyrrolinone (6).[7] Yields of 6 are summarized in Table 2.

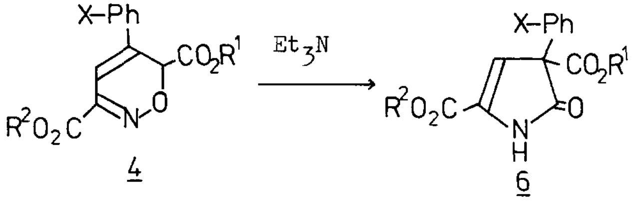
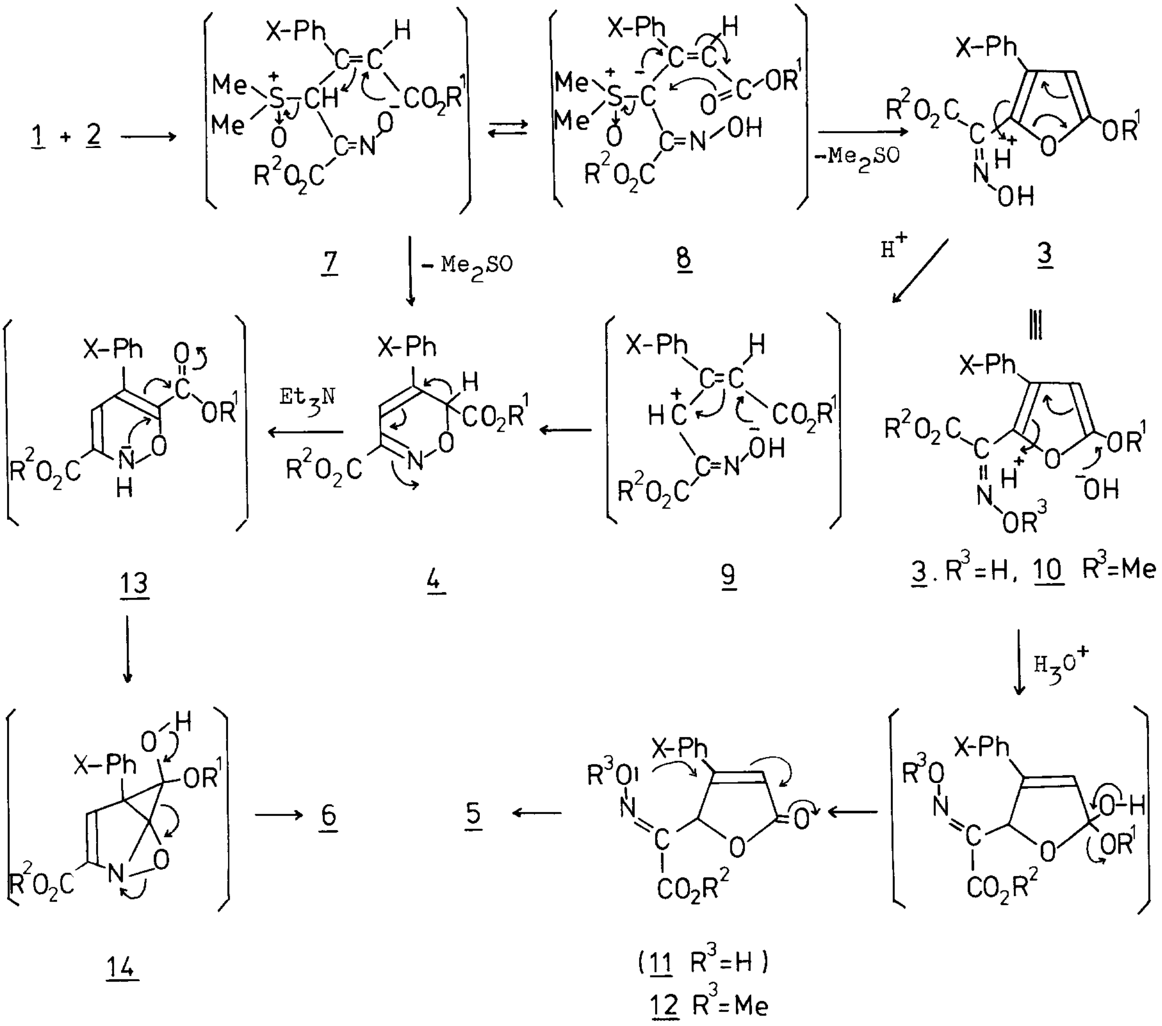


Table 2 4-Pyrrolin-2-ones (6)

No.	R^1	X	R^2	mp (°C)	Yields (%)
a	Et	H	Et	106 - 107	90
b	Et	H	Me	142 - 143.5	60
c	Me	H	Et	132 - 133.5	92
d	Et	p-Me	Et	99.5 - 100.5	70

The course of the reactions forming two heterocyclic compounds (3 and 4) would be depicted as the following: the initial adduct (7) from the allylide 1 and the nitrile oxide 2 is a common key intermediate. Conversion of 7 into oxime allylide (8) by prototropy followed by cyclization from the carbonyl group of the ester moiety gives 3. Only a few reports were found in cyclization involving the carbonyl group of the ester moiety.[8)] The cyclization from 8 to 3 may be favored in Baldwin's intramolecular cyclization rule.[9)] On the other hand, direct cyclization of 7 from the oximate anion to the double bond with elimination of DMSO leads to 4.



The ring transformation of 3 to 4 using acid catalyst may proceed through allylic cation (9) as an intermediate generated by protonation of the furan ring. In the presence of excess p-TsOH·H_2O, hydration occurs at the furan ring of 3 to afford α,β-unsaturated lactone (11), which undergoes intramolecular Michael addition of the hydroxy group of the oxime group to the double bond to give the bicyclic lactone 5. Methoxime 10a (R^1=R^2=Et, X=H; mp 66-67°C) obtained by methylation of 3a with diazomethane resulted only in the formation of α,β-unsaturated lactone methoxime (12a; mp 111.5-113°C) under the same conditions as for 3a, which also supports the presence of 11 as the intermediate.

Another ring transformation of 4 to the pyrrolinone 6 with a shift of the alkoxycarbonyl group may be explained by assuming cyclopropyl hemiketal (14) which is formed from 13 given by isomerization of 4. Ring cleavage of 14 leads to 6. For the migration of alkoxycarbonyl groups, cyclic hemiketals are proposed as intermediates by Grovenstein.[10]

References and Notes

1) R. Huisgen, Angew. Chem. Internat. Edit., 2, 565 (1963).

2) J. Ide and Y. Kishida, This letters, 1966, 1787; Idem, Chem. Pharm. Bull., 16, 784 (1968); Idem. Ibid., 16, 793 (1968).

3) For recent cycloaddition reactions using a three carbon unit as one component. See Y. Hayakawa, K. Yokoyama and R. Noyori, J. Am. Chem. Soc., 100, 1791 (1978) and references cited therein; Idem. Ibid., 100, 1799 (1978); J. P. Marino and L.C. Katterman, J. Chem. Soc., Chem. Commun., 1979, 946.

4) G.S. Skinner, J. Am. Chem. Soc., 46, 731 (1924).

5) All new compounds described herein gave satisfactory elemental analysis, and their IR, NMR (^{1}H and ^{13}C) and mass spectra are consistent with assigned structures.

6) Allylides 1c and 1d were prepared from dimethylsulfoxonium methylide and corresponding phenylpropiolates using the method reported previously.[2]

7) Structures of the furanyl oxime 3a, the 1,2-oxazine 4c and the pyrrolinone 6d were fully confirmed by X-ray analysis using the direct method for solution.

8) T. Takeda, M. Ueda and T. Mukaiyama, Chem. Lett., 1977, 245.

9) J.E. Baldwin, J. Chem. Soc. Chem. Commun., 1976, 734.

10) E. Grovenstein, Angew. Chem. Internat. Edit., 17, 313 (1978).

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