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FREE RADICAL ADDITION OF 3-CHLORO-4,4-DIMETHYL-2-OXAZOLIDINONE TO ALLYLSTANNANE AND ALLYLSILANE

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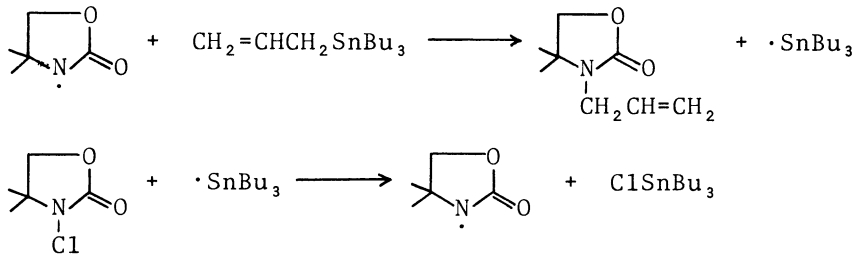
Free radical reaction of 3-chloro-4,4-dimethyl-2-oxazolidinone (NCDMO) to allylstannane and allylsilane were found to give 3-allyl-4,4-dimethyl-2-oxazolidinone. The formation of the product was interpreted in terms of addition of the acylamino radical. NCDMO does not react with ordinary olefin, perhaps owing to inhibiting behavior of enamine which may be derived from the adduct of NCDMO to olefin.

There have been scarcely known the examples of addition of acylamino radicals generated from N-halogeno compounds under thermal conditions to olefinic compounds.[1] Sakai, Koga and Anselme[2] showed addition of succinimidyl radical from N-bromosuccinimide (NBS) to a peculiar substrate, in which steric and electronic factors tend to favor the addition process over the so called Goldfinger mechanism.[3]

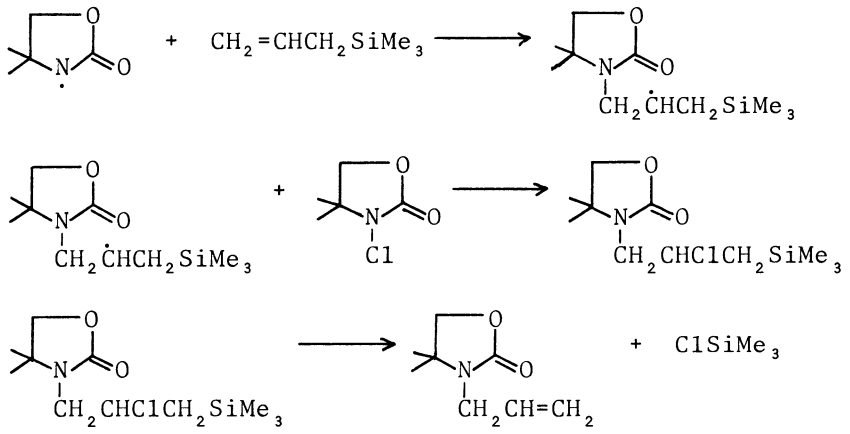
Recently, Kaminski and Bodor[4] reported that 3-halo-4,4-dimethyl-2-oxazolidinone is much more stable than N-halosuccinimide toward protic reagents, e.g., hydrogen halides. We are interested in surveying potential abilities of such compounds to undergo the reaction involving amino radicals. Here, we wish to communicate that 3-chloro-4,4-dimethyl-2-oxazolidinone (NCDMO) can react with allylstannanes and allylsilanes under thermal conditions involving the acylamino radical.

The reactions were carried out by heating degassed equimolar mixtures of NCDMO and the substrates including small amounts of addenda in sealed tubes. Products were analyzed by GLC and their structures were determined by spectroscopic analysis. The results obtained are summarized in TABLE.

As TABLE shows, the yields of 3-allyl-4,4-dimethyl-2-oxazolidinone were raised by the presence of radical generators and lowered by the presence of p-quinone, a radical scavenger. These findings indicate that the allylated product is formed by a chain process involving the acylamino radical. In the reaction with allyltin compounds, the process may be represented by the following equations, since allyltin compounds undergo S_H' type reaction with free radicals, releasing organotin radical.[5,6]



On the other hand, β-silylalkyl radical does not loose silyl radical easily.[7] Then, the reaction with allylsilane is thought to proceed by addition of NCDMO followed by elimination of chlorosilanes.[8,9]



Since this mechanistic consideration suggests that NCDMO should be able to add to ordinary olefin, we have examined the reactions with octene-1, cyclohexene, allylbenzene, vinyl phenyl ether and allyl bromide. However, no addition products, but most of NCDMO, remaining unchanged, were detected in the reaction mixtures. This means some inhibitors, probably, enamines which may be derived from dehydrochlorination of the adducts, were formed in early stages of the reactions.

Indeed, as TABLE shows, it was found that the presence of enamine retarded the reaction of NCDMO with allylsilane.

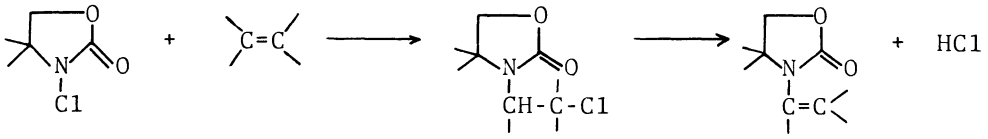


TABLE. Reaction of NCDMO with Allylic Compounds

Allylic Compounds	Temp. °C	Time hr.	Added Materials		Product Yields (%) $=NCH_2CH=CH_2$ [b]	amine [c]
$CH_2=CHCH_2SnBu_3$	80	5	AIBN	5 %	25 %	33 %
	80	15	BPO	5	13	42
	80	5	—		3	50
	80	5	AIBN	5	6.6	46
			p-quinone	10		
$CH_2=CHCH_2SiMe_3$	80	5	AIBN	5	14	56
	80	15	BPO	5	21	35
	80	5	—		0	43
	80	5	AIBN	5	1	48
			p-quinone	10		
	80	5	AIBN	5	3.6	50
			$MeCH=CHNEt_2$	10		
					$=NCHMeCH=CH_2$ [d]	$=NH$ [c]
$CH_3CH=CHCH_2SnBu_3$ [a]	80	15	BPO	5	9	52
$CH_3CH=CHCH_2SiMe_3$ [a]	80	15	BPO	5	6	50

a) E, Z mixtures
b) 3-allyl-4,4-dimethyl-2-oxazolidinone
c) 4,4-dimethyl-2-oxazolidinone
d) 3-α-methylallyl-4,4-dimethyl-2-oxazolidinone

REFERENCES

1) S. F. Nelsen, "Free Radicals" vol. II, edited by J. K. Kochi, p. 534, John Wiley & Sons (1973).
2) K. Sakai, N. Koga, and J. P. Anselme, Tetrahedron Lett., 1970, 4543.
3) J. Adam, P. A. Gosselain, and P. Goldfinger, Nature, 171, 704 (1953).
4) J. Kaminski and N. Bodor, Tetrahedron, 32, 1097 (1976).
5) M. Kosugi, K. Kurino, K. Takayama, and T. Migita, J. Organometal. Chem., 56, C11 (1973).
6) J. Grignon, C. Servens, and M. Pereyre, ibid., 96, 225 (1975) .
7) T. Migita, M. Kosugi, K. Takayama, and Y. Nakagawa, Tetrahedron, 29, 51 (1973) .
8) Y. Nagai, M. Kosugi, K. Takeuchi, and T. Migita, ibid., 26, 2791 (1970) and refs. cited.
9) H. Sakurai, A. Hosomi, and M. Kumada, J. Org. Chem., 34, 1764 (1969).

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