THE BF₃ CATALYZED DECOMPOSITION OF DIAZOCARBONYL COMPOUNDS IN NITRILES: SYNTHESIS OF OXAZOLES

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The BF₃ catalyzed decomposition of diazocarbonyl compounds in nitriles afforded the corresponding oxazoles in high yield. This method is applicable to diazocarbonyl compounds such as m- and p-substituted diazoacetophenones, ethyl diazoacetate, azibenzil, dibenzoyl-diazomethane, dimethyl diazomalonate, and 7-diazo-8-acenaphthenone.

The 1,3-dipolar cycloaddition of carbonylcarbenes to carbon-nitrogen triple bonds of nitrile group has been recognized to give oxazoles in the thermal,¹⁾ photochemical²⁾ and transition metal¹⁾ catalyzed decomposition of diazocarbonyl compounds. The yields of oxazoles were not so high even though the copper^{1a, 1b)} and π -allylic palladium³⁾ catalysts were used. Nozaki and his co-workers improved the yield up to 66% using WCl₆ as a catalyst.⁴⁾ Recently Doyle and his co-workers reported that the AlCl₃ catalyzed reaction of α -unsubstituted diazoketones and nitriles gives oxazoles in high yield.⁵⁾ Their report prompted us to publish our results on the title reaction.

When diazoacetophenone (3 mmol) was decomposed by adding a solution of BF_3^- etherate (3 mmol) in an excess of acetonitrile (20 ml) at 5°C, vigorous evolution of nitrogen was observed and color of the reaction mixture turned pale red. column chromatography of the reaction mixture (silica gel-benzene) yielded 2-methyl-5-phenyl-oxazole (<u>4a</u>) in 94% yield after usual work up. Other nitriles such as propionitrile, phenylacetonitrile, and benzonitrile also gave the corresponding oxazoles in good yields. This method is applicable to other m- and p-substituted diazoacetophenones, ethyl diazoacetate, azibenzil, dibenzoyldiazomethane, and dimethyl diazomalonate.



Furthermore, 7-diazo-8-acenaphthenone gave a condensed oxazole (5) in a yield of 54% besides two other unidentified products.

-	R	R ₂	R3	Reaction	Yield of	NMR (δ)	
	1	L	5	Temp (°C)	<u>4</u> (%)	$CH_{3}(=R_{3})$	H (=R ₂)
a	с ₆ н ₅	Н	CH3	5	94	2.48	7.15
b	с ₆ н ₅	Н	с ₂ н ₅	5	99	-	7.13
с	с ₆ н ₅	н	CH2Ph	5	77	-	7.20
d	C ₆ H ₅	Н	с ₆ н ₅	5	92	-	?
е	p-CH3 ^{OC6H4}	н	CH ₃	5	95	2.50	7.08
f	p-CH3C6H4	н	CH3	5	96	2.45	7.08
g	m-CH ₃ C ₆ H ₄	Н	сн ₃	5	93	2.45	7.13
h	p-ClC ₆ H ₄	Н	сн ₃	5	83	2.47	7.15
i	m-ClC ₆ H ₄	Н	сн _з	5	91	2.48	7.18
j	p-BrC ₆ H4	н	сн ₃	5	88	2.52	7.47
k	p-NO2C6H4	Н	CH ₃	5	84	2.42	7.45
l	с ₂ н ₅ о	Н	CH ₃	20	62	2.02	5.95
m	с ₆ н ₅	^С 6 ^Н 5	CH ₃	5	68	2.55	-
n	^С 6 ^Н 5	с ₆ н ₅ со	CH ₃	80	79	2.50	-
0	сн ₃ о	сн ₃ оос	CH ₃	80	32	2.35	-

Table 1. Yields and NMR Data of Oxazoles (4)

When the reaction of diazoacetophenone was carried out in an acetonitrile solution containing a trace amount of water, oxazole (<u>4a</u>) was accompanied by phenacyl alcohol and N-phenacylacetamide which may be derived from the reaction of H_2O with a reaction intermediate (<u>3a</u>: R_1 =Ph, R_2 =H, R_3 =CH₃). This implys that the stepwise addition mechanism via the ylide type intermediate (<u>3</u>) seems to be favorable in this reaction rather than the direct 1,3-dipolar cycloaddition of carbonylcarbene to nitriles.

The AlCl₃ catalyzed reaction is reported to be affected by the reaction condition and to yield chlorinated products.^{4,5)} Therefore, BF_3 -etherate is recommendable as the more convenient catalyst than AlCl₂.

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