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THE BF_3 CATALYZED DECOMPOSITION OF DIAZOCARBONYL COMPOUNDS IN NITRILES: SYNTHESIS OF OXAZOLES

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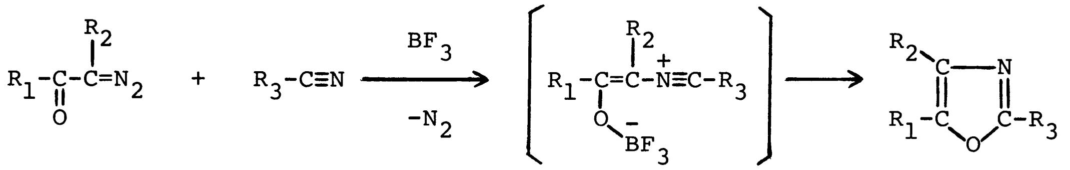
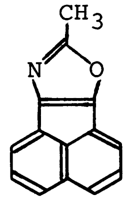
The BF_3 catalyzed decomposition of diazocarbonyl compounds in nitriles afforded the corresponding oxazoles in high yield. This method is applicable to diazocarbonyl compounds such as m- and p-substituted diazoacetophenones, ethyl diazoacetate, azibenzil, dibenzoyldiazomethane, dimethyl diazomalonate, 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,$^{1)}$ photochemical$^{2)}$ and transition metal$^{1)}$ catalyzed decomposition of diazocarbonyl compounds. The yields of oxazoles were not so high even though the copper$^{1a, 1b)}$ and π-allylic palladium$^{3)}$ catalysts were used. Nozaki and his co-workers improved the yield up to 66% using WCl_6 as a catalyst.$^{4)}$ Recently Doyle and his co-workers reported that the $AlCl_3$ 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-phenyloxazole (4a) 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.



(1) (2) (3) (4)



(5)

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

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

	R_1	R_2	R_3	Reaction Temp (°C)	Yield of 4 (%)	NMR (δ)	
						CH_3(=R_3)	H (=R_2)
a	C_6H_5	H	CH_3	5	94	2.48	7.15
b	C_6H_5	H	C_2H_5	5	99	-	7.13
c	C_6H_5	H	CH_2Ph	5	77	-	7.20
d	C_6H_5	H	C_6H_5	5	92	-	?
e	p-$CH_3OC_6H_4$	H	CH_3	5	95	2.50	7.08
f	p-$CH_3C_6H_4$	H	CH_3	5	96	2.45	7.08
g	m-$CH_3C_6H_4$	H	CH_3	5	93	2.45	7.13
h	p-ClC_6H_4	H	CH_3	5	83	2.47	7.15
i	m-ClC_6H_4	H	CH_3	5	91	2.48	7.18
j	p-BrC_6H_4	H	CH_3	5	88	2.52	7.47
k	p-$NO_2C_6H_4$	H	CH_3	5	84	2.42	7.45
l	C_2H_5O	H	CH_3	20	62	2.02	5.95
m	C_6H_5	C_6H_5	CH_3	5	68	2.55	-
n	C_6H_5	C_6H_5CO	CH_3	80	79	2.50	-
o	CH_3O	CH_3OOC	CH_3	80	32	2.35	-

When the reaction of diazoacetophenone was carried out in an acetonitrile solution containing a trace amount of water, oxazole (4a) was accompanied by phenacyl alcohol and N-phenacylacetamide which may be derived from the reaction of H_2O with a reaction intermediate (3a: R_1=Ph, R_2=H, R_3=CH_3). This implys that the stepwise addition mechanism via the ylide type intermediate (3) seems to be favorable in this reaction rather than the direct 1,3-dipolar cycloaddition of carbonylcarbene to nitriles.

The $AlCl_3$ 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 $AlCl_3$.

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