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A NOVEL SELECTIVE METHOD FOR THE TRANSFORMATION OF CARBOXILIC ACIDS INTO ALDEHYDES

Gábor Doleschall

Research Group of Alkaloid Chemistry of the Hungarian Academy of Sciences

1111 Budapest, HUNGARY

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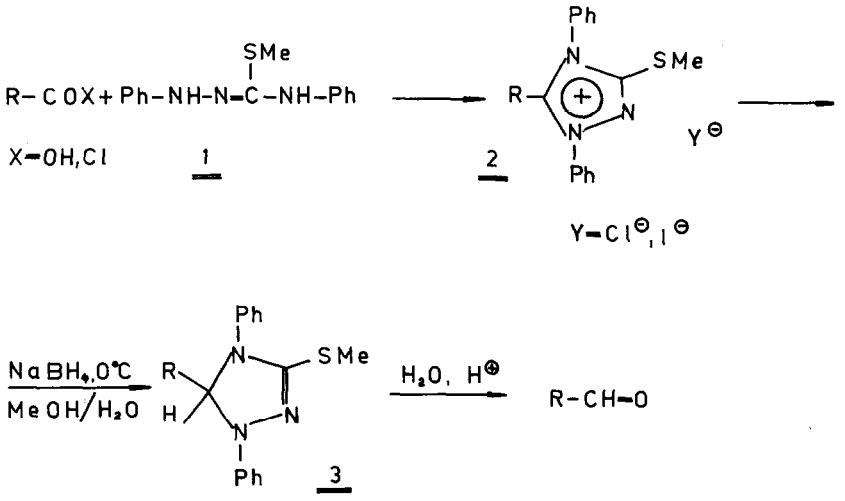
I wish to describe a very simple, efficient and selective method for the transformation of acyl chlorides into aldehydes.

When equimolar mixtures of the easily accessible 3-methyl-1,4-diphenyl-isothiosemicarbazide /1/ [1] and carboxylic acid chlorides, or of carboxylic acids, 1 and $POCl_3$ were refluxed in anhydrous dioxane and anhydrous pyridine, respectively, the corresponding 3-methylthio-1,4-diphenyl-5-R-s-triazolium /2/ chlorides or, after treating the resulting product with aqueous KI, iodides were obtained in practically quantitative yields. Methanolic solutions of these salts were reduced with equimolar amounts of aqueous $NaBH_4$ solutions at 0°C to yield the 3-methylthio-1,4--diphenyl-5-R-4,5-dihydro-s-triazoles /3/ which were decomposed by warm aqueous sulfuric acid or by cold aqueous formaldehyde - hydrochloric acid mixtures to give the desired aldehydes. The products, as well as the known intermediates were identified by comparison with authentic samples. Most of the intermediates 2 and 3 were new and were characterized by microanalyses, IR and NMR spectra. The intermediates could be used in the subsequent steps without further purification or even isolation.

The selectivity of the method is demonstrated by examples 3-5 of the Table, as well as by the observation that 2 /R=Ph/ was reduced to 3 /R=Ph/ even in the presence of a tenfold molar excess of butanal in 82 % yield.



R	2 chloride		3		R-CHO yield[a]
	mp.	yield	mp.	yield[a]	
Me	240-2°C [b]	94 %	77°C	91 %	>55 %
Ph	320°C /dec/	95 %	108-110°C[c]	92 %	90 %
p-MeOOC-C_6H_4-	220°C /dec/[d]	95 %	111-2°C	73 %	66 %
EtOOC-/CH_2/$_5$-		-		-	46 %
Ph-CH=CH-	240°C /dec/[d]	95 %	-		83 %
1/2 p-C_6H_4< [e]	320°C /dec/[d]	89 %	182-3°C	63 %	55 %

a./ Based on the amount of the acyl chloride or carboxylic acid introduced

b./ Lit. m.p.: 240-2°C [2]

c./ Lit. m.p.: 103-4°C [1]

d./ M.p. and yield of the triazolium iodide

e./ Starting compound: terephthalic acid, product: terephthalic aldehyde

References

1./ M. Busch and H. Holzmann: Ber. 34, 366 /1901/

2./ K.T. Potts, S.K. Boy and D.P. Jones: J. org. Chem. 32 2245 /1967/