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A NOVEL ALDEHYDE SYNTHESIS BASED ON ANHYDRO-BASES OF THE s-TRIAZOLE SERIES

Gábor Doleschall

Research Group for Alkaloid Chemistry of the Hungarian Academy of Sciences

1111 Budapest, Gellért tér 4, Hungary

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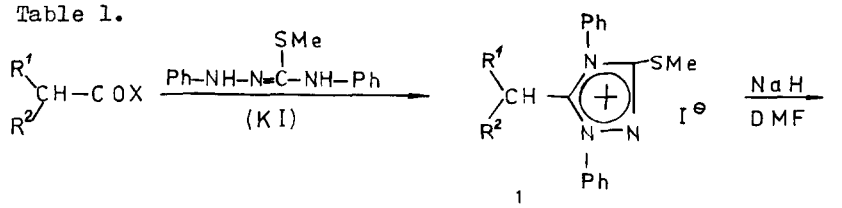
Stable anhydro-bases of the s-triazole series have been known since some time.[1,2] Based on the ability of the anhydro-bases 2 /which are easily accessible from the s-triazolium salts 1[3]/ to undergo ready C-alkylation, a novel method of synthesis of aldehydes 5 starting with carboxylic acids or acid chlorides and alkyl halides has been devised. The results are summarized in Table 1.



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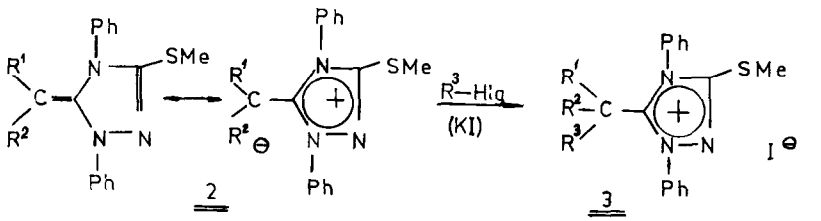

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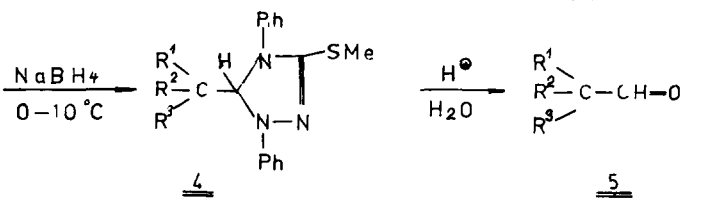

4 5

The anhydro-bases 2 were obtained by allowing to react the triazolium iodides 1[3] with NaH in DMF at 0°C and then at r.t. 2 /$R^1 = R^2$ = Ph/ is an isolable stable compound /71 %, based on diphenylacetic acid; m.p. 204 °C/. The other anhydro-bases were not isolated. After the excess NaH had been

filtered off, alkyl halides were added to their DMF solutions; the alkylations took place under evolution of heat and, after additions of aqueous KI, the compounds 3 separated. The latter were in general reduced without purification with aqueous $NaBH_4$, and the resulting compounds 4 were cleaved with acid to yield the aldehydes 5 as described earlier.[3] The anhydro-base, obtained from 1 /R^1 = Cl-C_2H_4, R^2 = H; m.p. > 320 °C, d; yield: 65 %/ suffers intramolecular C-alkylation in the course of its preparation to furnish cyclopropanecarbaldehyde as the final product.

The products were identified by comparison with authentic samples and the new intermediates of types 3 and 4 were characterized by microanalyses, IR and NMR spectra. The present procedure is a useful simple alternative to the method of Meyers.[4]

Table 1

					3		4		5
R^1	R^2	X	R^3	Hlg	m.p.	yield[a]	m.p.	yield[a]	yield[a,b]
H	H	Cl	Me	I	218-20	60	90-91	53	47
H	H	Cl	Et	I	238-40	54	65-66	-	31
H	H	Cl	$MeOOCCH_2$	Cl	232-34	55	-	-	29[c]
Me	H	OH	Me	I	243-45	40	-	-	34
Me	Me	OH	Me	I	268-70	43	82-83	34	32
Cl-C_2H_4	H	Cl	-	-	252-54[d]	49	80-81	48[e]	30

a/ The yields are throughout based on the amount of the compounds R^1R^2CH-COX introduced.

b/ Isolated free aldehyde. c/ 2,4-Dinitrophenylhydrazone

d/ 5-Cyclopropyl-3-methylthio-1,4-diphenyl-s-triazolium iodide

e/ 5-Cyclopropyl-3-methylthio-1,4-diphenyl-Δ^3-s-triazoline

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