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A NOVEL ALDEHYDE SYNTHESIS BASED ON A "NUCLEOPHILIC CARBENE" OF THE *s*-TRIAZOLE SERIES, AND A NEW METHOD FOR THE DEGRADATION OF α-HYDROXYACIDS.

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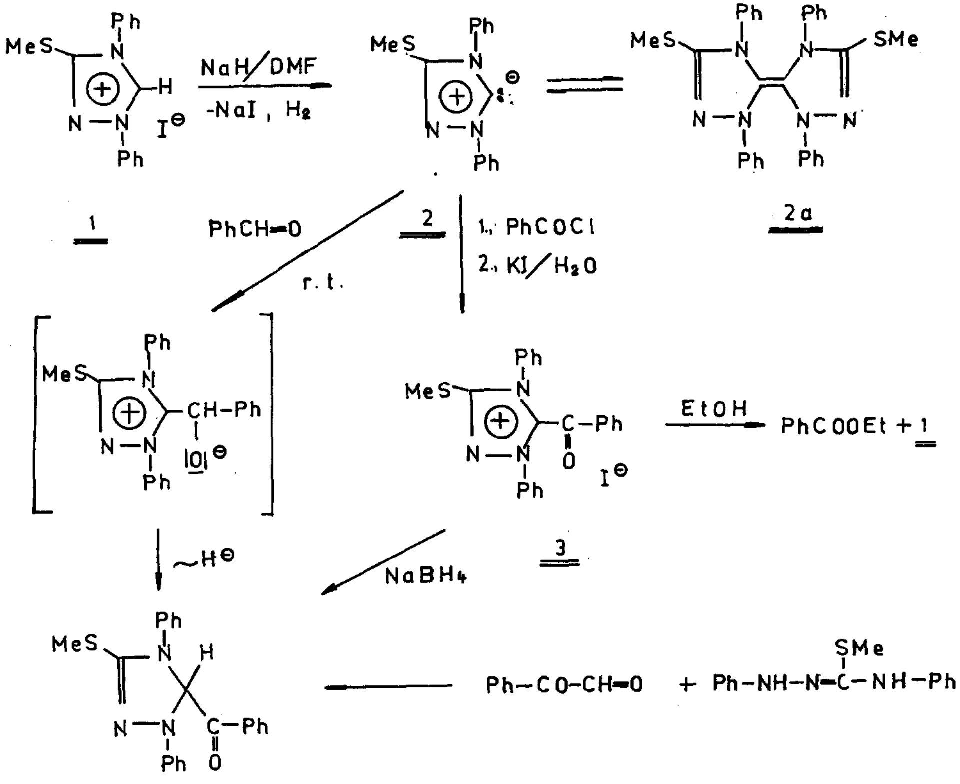
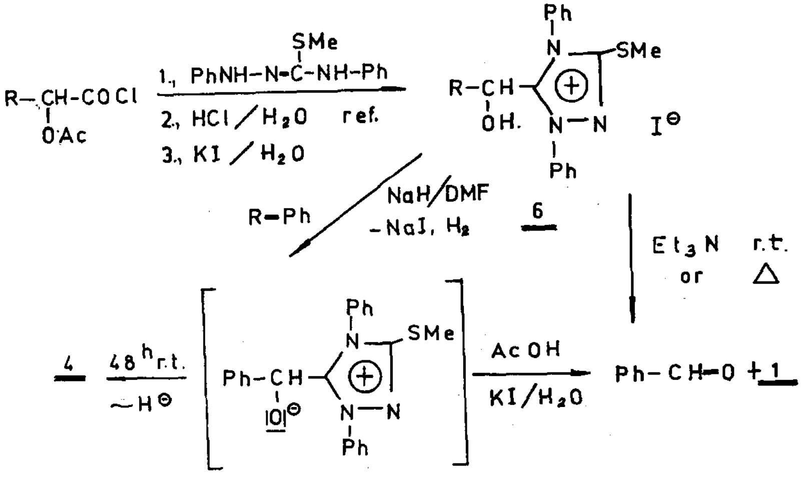
As has been shown mainly by Wanzlick et al.,[1-5] "nucleophilic carbenes" are readily formed from a variety of heterocyclic cations. 3-Methylthio-1,4-diphenyl-*s*-triazolium iodide (**1**)[6,7] - obtained in 71 % yield, m.p. 244-5°, according to a new method by treating 1,4-diphenylthiosemicarbazide succesively with methyl iodide and triethyl orthoformate in DMF -, when treated with excess NaH/DMF at 0°, furnished a similar "nucleophilic carbene" (**2**). The presence of **2** (or of its dimer **2a**) in the DMF solution (from which the NaI formed has been filtered off) is proven (Scheme 1) by the typical carbene reaction (cf. Ref. 2) with benzaldehyde to yield **4**, as well as by the reaction with 1 mole of benzoyl chloride at 0° and subsequent treatment with KI aqu. to yield **3**[8] (70 %, mp.: 212-4°, ν C=O 1675 cm^{-1}); the latter was reduced with $NaBH_4$ to yield **4** (39 %, based on the amount of benzoyl chloride, mp.: 149-50°) which was identical with an authentic sample obtained by allowing to react 3-methyl-1,4-diphenylisothiosemicarbazide and phenylglyoxal (98 % yield). When refluxed with EtOH, **3** furnished 72 % of ethyl benzoate and 67 % of **1**.

When DMF solutions of **2** were treated with primary halides and aqu. KI, 3-alkyl-5-methylthio-1,4-diphenyltriazolium iodides (**5**) were obtained (see Table 1). The latter were reduced and hydrolysed by known methods[9,10] to the corresponding aldehydes.

The above procedure is an alternative to the Corey aldehyde synthesis,[11] which does not require the use of an inert gas atmosphere, and in the final step of which the aldehyde is liberated by simple acid treatment.

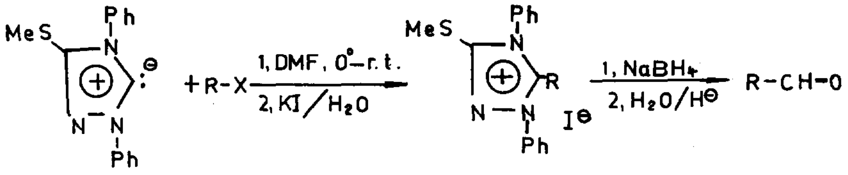


Scheme 1



Scheme 2

Table 1



2 5

R-X	5		R-CHO
	%[a/]	mp.	%[a/]
MeI	76	254-56[9]	45[12]
EtI	66	218-20[10]	52
n-BuI	76	221-23	79[b/]
$ClCH_2CH_2COOMe$	43	232-234[10]	30[c/]
$PhCH_2Cl$	72	183-84	44[c/]
$BrCH_2CH_2CH_2Cl$	42[d/]	252-54[d/]	26[e/]

a/ Based on the amount of the alkyl halide

b/ Without isolation of the intermediates

c/ Isolated in form of the 2,4-dinitrophenylhydrazone

d/ 5, R = cyclopropyl, formed by deprotonation of the initially formed cation 5 (R = $Cl-C_3H_6-$) by excess 2 to the corresponding anhydrobase[10], and subsequent intramolecular alkylation

e/ R = cyclopropyl.

In addition, a novel mild method was discovered for the degradation of α-hydroxyacids to the corresponding aldehydes containing one carbon atom less (Scheme 2). The triazolium iodides 6 (R = Me and Ph; m.p's. 192-3 and 163-5°,[14] yields, based on the corresponding α-acetoxyacyl chlorides, 68 and 43 %, respectively) were obtained according to a known method[9] and proved to be stable under acidic conditions. They are, however, decomposed even by a catalytic amount of Et_3N to 1 (89 %) and the aldehydes[12] in 73 (R = Me) and 57 % (R = Ph) yield, respectively.

6 (R = Ph) is decomposed also by simple heating at 170° to 1 (95 %)

and PhCHO[12] (75 %); the *O*-acetyl derivate of the latter (mp.: 224-5°; 53 % yield, based on α-acetoxyphenylacetyl chloride), when treated with Et_3N in anhydrous MeOH at r.t., furnishes the same products in 65 and 89 %[12] yield, respectively.

When treated with NaH in anhydrous DMF for 48 hrs at r.t., **6** (R = Ph) furnished 35 % of **4**. When the reaction mixture was acidified with AcOH immediately after the evolution of H_2 had ceased, and subsequently treated with KI aqu., **1** and benzaldehyde[12] were obtained in 76 and 80 % yield, respectively, proving thereby that the addition of **2** to benzaldehyde is a reversible process.

The known intermediates and products were identified by comparison with authentic samples, and the new products were characterized by microanalyses, IR and NMR spectra.

References and Notes

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12./ Isolated in form its condensations product[13] with 6-(2-aminophenyl)-3-methylthio-1,2,4-triazin-5(2*H*)-one.

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14./ When rapidly heated.