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THE SYNTHESIS AND THERMAL DECOMPOSITION OF THE SODIUM SALTS OF SOME N'-(p-TOSYL)HYDRAZIMIDOCARBOXYLATE ESTERS

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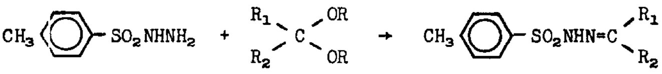
The thermal and photolytic decomposition of the salts of p-tosylhydrazones in aprotic solvents has become a frequently used method for the generation of carbenes (2). Recently there have been several reports in the literature (3) on the preparation of alkoxycarbenes using several methods including one postulating the intermediacy of diethoxycarbene from the thermal decomposition of the sodium salt of diethyl N'-(p-tosyl)-hydrazimidocarbonate (IIIf) (3d). In the course of our investigation of alkoxycarbenes we have discovered a convenient synthesis of N'-(p-tosyl)-hydrazimidocarboxylate esters (III) which are possible precursors to these carbenes and have examined the thermal decomposition of the sodium salts of three of these hydrazimidocarboxylate esters.

When p-toluenesulfonylhydrazine (I) is mixed with a slight excess of an orthocarboxylic ester at room temperature, stirred for 45 minutes, and filtered, the precipitate obtained is the hydrazimidocarboxylate ester III. The reaction was also successful with acetone dimethyl ketal giving IIIg (4).



I II III

a. R = CH_3, R_1 = OCH_3, R_2 = H
b. R = C_2H_5, R_1 = OC_2H_5, R_2 = H
c. R = C_2H_5, R_1 = OC_2H_5, R_2 = CH_3
d. R = C_2H_5, R_1 = OC_2H_5, R_2 = C_2H_5
e. R = CH_3, R_1 = OCH_3, R_2 = C_6H_5
f. R = C_2H_5, R_1 = R_2 = OC_2H_5
g. R = R_1 = R_2 = CH_3

Table 1 summarizes some of the physical properties of the hydrazimidocarboxylate esters III prepared by this method, which offers high yields and simplicity (5). The thermal decompositions of the sodium salts of IIIa, IIIc, and IIIe (prepared <u>in situ</u> with sodium hydride) have been studied.

Table 1

Compound[a]	m.p.[b]	% Yield	$\nu_{C=N}$[c]
IIIa	151.5-153°	93	6.02
b	118.5-119.5°	89	6.01
c	162 - 165°	85	6.07
d	151 - 152.5°	74	6.03
e	141 - 143.5°	86	6.05
f	86.5 - 87.5°[d]	87	5.96
g	157 - 158°[e]	87	6.08

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[a] All new compounds have given satisfactory analysis.

[b] Melting points were determined on a calibrated Kofler hot stage.

[c] Infrared spectra were determined using a Perkin-Elmer model 137 double beam recording spectrophotometer.

[d] Lit. (3d) reports m.p. 85-86°.

[e] Lit. (2a) reports m.p. 156°.

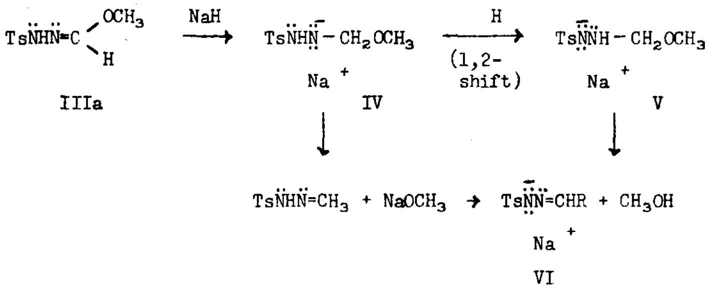
When IIIa was added to a suspension of sodium hydride in triglyme at 25°, decomposition occurred as evidenced by several color changes and liberation of a gas. This gas was collected and shown to contain hydrogen and nitrogen, and traces of carbon monoxide and methane. The solid products isolated from this room temperature decomposition were the sodium salt of IIIa (14%), sodium p-toluenesulfinate (84%), and methyl N'-methyl-N'-(p-tosyl) hydrazimidoformate (2%), m.p. 96-98°. The fraction which distilled from the reaction mixture below 60° (1 mm.) contained methanol (35.3%), and very small amounts of two as yet unidentified components neither of which is 1,2-dimethoxyethylene.

It was possible to isolate the sodium salt of IIIa by slowly adding IIIa to a stirred, well cooled suspension of sodium hydride in tetrahydrofuran. When a suspension of this salt was heated, decomposition, as evidenced by gas evolution, was not observed below 210°. The products of this decomposition have not been identified, other than p-toluenesulfinate (70%).

The sodium salt of IIIc required heating to 175° before decomposition occurred. The solid isolated from the reaction mixture contained sodium p-toluenesulfinate (95%), and IIIc (1.5%). A Dry Ice trap connected to the reaction flask contained diethyl ether (1.4%), ethyl vinyl ether (10.0%), acetaldehyde (1.1%), ethyl acetate (0.2%), acetal (24.3%), and ethanol (22.2%). The gas from the reaction contained nitrogen, ethylene, and carbon monoxide in the ratio 365:3:1.

Heating the sodium salt of IIIe at 120° in diglyme resulted in its decomposition to sodium p-toluenesulfinate (79%), methoxybenzalazine (66%), benzaldehyde (1.4%), benzaldehyde dimethyl acetal (2.1%), and methyl benzoate (3.6%). No methanol was observed. The gas collected from the reaction mixture contained nitrogen and methane in relative proportions of 65:1.

We do not believe that the room temperature reaction of IIIa with sodium hydride is proceeding via normal proton abstraction. A mechanistic route which appears to explain these results is initial addition of sodium hydride to IIIa to form IV followed by a 1,2-proton shift to give V. Methanol can now be eliminated leaving the sodium salt of formaldehyde p-tosylhydrazone (VI, R=H). An alternate possibility from IV to VI (R=H) is also given. The problem with this mechanism is that VI (R=H), or



products derived from it, are not observed.

However, certain of the products from the preparation and decomposition of the sodium salt of IIIc (acetaldehyde, diethyl ether and ethylene) appear to require the intermediacy of VI (R=CH_3). The formation of small amounts of benzaldehyde and benzaldehyde dimethyl acetal in the preparation and decomposition of the sodium salt of IIIe are also accommodated by this mechanism. This unexpected mode of reaction with sodium hydride might be anticipated to decrease in the order IIIa > IIIc > IIIe from steric and electronic considerations as is observed.

The major products from the second and third thermal decompositions (above) appear to require the corresponding diazo compounds and carbenes as intermediates. The formation of methoxybenzalazine is believed to be a function of the stability of both the diazo compound and α-methoxyphenylcarbene (6).

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4. The product of I with diethyl ketene acetal was IIIc, which we believe is formed by methylene protonation by I to give 1,1-diethoxyethyl carbonium ion followed by reaction with more I and elimination of alcohol. Diethyl cyclopropanone ketal failed to react with I.

5. In contrast to a report (3d) published while our work was in progress, we have observed only very slight decomposition of IIIf; after nine months storage the compound had a slight odor of diethyl carbonate and melts at 81-83.5 with very little change in the infrared spectrum. IIIc was found to be fairly unstable.

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