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REACTIONS OF ENAMINES WITH THIOACYLKETENE THIOACETALS. THIOPHILIC REACTION OF ENAMINES[1)]

Fumio ISHII, Renji OKAZAKI, and Naoki INAMOTO
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

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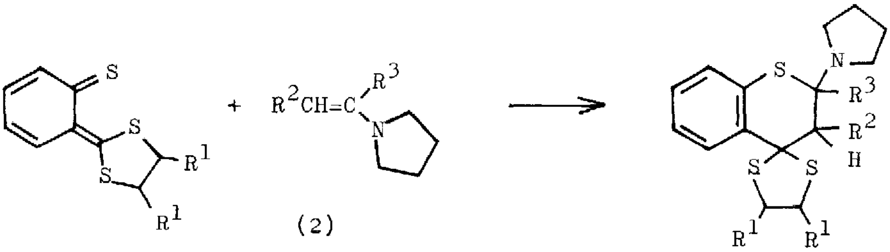
Reactions of conjugated ketene thioacetals have been the subject of increasing interest in the last few years.[2)] We have recently disclosed that o-thioquinonemethide (1)[3)] and thioacylketene thioacetals (4)[4)] undergo 1,4-cycloaddition reactions with electron deficient olefins and acetylenes. We now report these conjugated thiones can also react with electron rich olefins, enamines, thus demonstrating the ambident nature of thioacylketene thioacetal functionality and the thiophilicity of enamines.

o-Thioquinonemethide (1)[3)] reacted with excess enamine (2) in refluxing acetonitrile (1-2 hr) to give 1:1 adduct (3).[5)] The orientation of the cycloaddition was established for (3c) by Raney-nickel desulfurization affording 2-methyl-1-phenyl-3-pyrrolidinopropane.



(1)

$R^1R^1=(CH_2)_4$

(2)

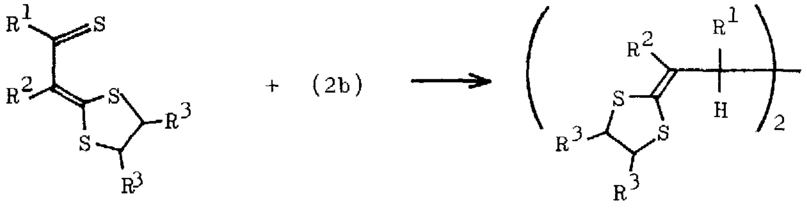
(3a-c)

a: $R^2R^3=(CH_2)_3$; 77%

b: $R^2R^3=(CH_2)_4$; 47%

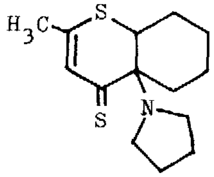
c: $R^2=CH_3$, $R^3=H$; 62%

The reaction of thiobenzoylketene thioacetals (4a-c)[6,7] with enamine (2b) (acetonitrile, reflux, 10-20 hr) afforded 2,3-diphenylbutane derivative (5),[5,8] and the reaction of (4d) (R^1=CH_3, R^2=R^3=H)[7] with (2b) (acetonitrile, reflux, 2 hr) gave conjugated thione (6) (10%).[5]

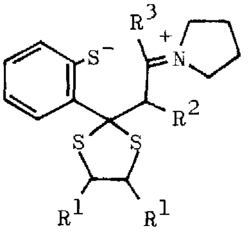


(4) (5)

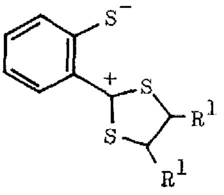
a: R^1=C_6H_5, R^2=C_6H_5, R^3R^3=$(CH_2)_4$; 48%
b: R^1=C_6H_5, R^2=H, R^3R^3=$(CH_2)_4$; 24%
c: R^1=C_6H_5, R^2=CH_3, R^3=H; 2%



(6)



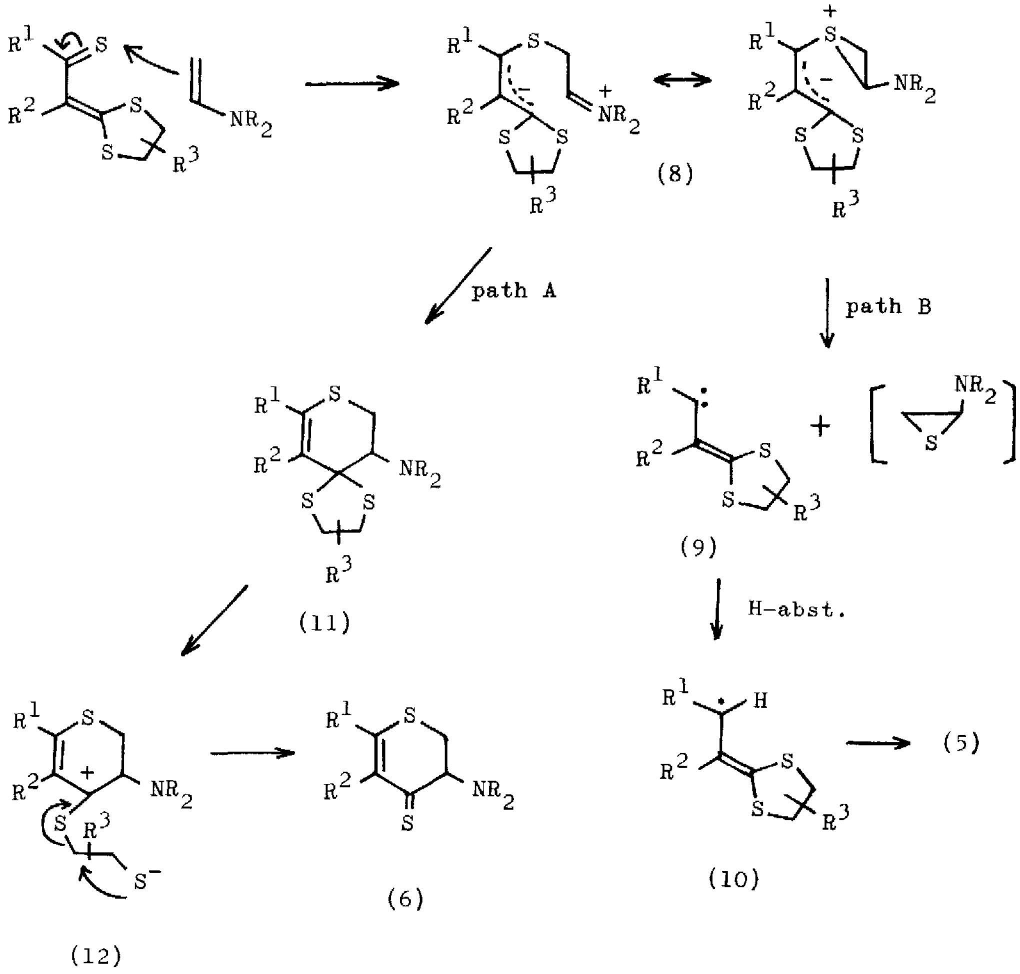
(7)



(13)

The adduct (3) is presumably formed by nucleophilic attack of an enamine to the carbon of the ketene thioacetal group to give a zwitter ionic intermediate (7) followed by cyclization,[9] while the formation of (5) and (6) is most likely explained in terms of initial attack of an enamine to thiocarbonyl sulfur as depicted in the following scheme although further studies must be awaited to establish the detailed mechanism. The zwitter ionic intermediate (8) would undergo cyclization to (11) (path A) or fragmentation to carbene (9) (path B). This carbene is a vinylog of a dithiacarbene and path B is reminiscent of formation of a dithiacarbene from trithiocarbonate by desulfurization with an organolithium compound.[10] The formation of (5) results from hydrogen abstraction (probably from excess enamine) of (9) followed by dimerization of

(10). The triplet ground state and hydrogen abstraction of a vinylcarbene have recently been demonstrated.[11] Heterolytic cleavage of (11) to (12) might be assited by such factors as stability of the carbonium ion formed, participation of α-nitrogen, and high polarity of the solvent. The present findings are the first demonstration that an enamine can react with thiocarbonyl sulfur[12] like an organometalloid, where such thiophilic reactions have been intensively studied in recent years.[13] The difference in reactivity between (1) and (4) might result from the greater contribution of an ionic canonical structure (13) in the former, which would not only render the thioacetal carbon more susceptible to nucleophilic attack by an enamine but also reduce the thionic nature of (1).



References and Footnotes

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