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DECARBONYLATION REACTION OF SOME 5(4H)-THIAZOLONES: FORMATION OF CYCLOBUTENE DERIVATIVES

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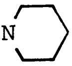
Thermal decarbonylation reactions of some 5(4H)-thiazolones were studied. In the case of 4,4-di(n-alkyl)-substituted 5(4H)-thiazolones, the novel formation of cyclobutene derivatives was found and attributed to the high reactivity of enamine intermediates.

In a previous paper, we described convenient syntheses of some 2-dialkylamino-4,4-disubstituted 5(4H)-thiazolones.1) Since these compounds have relatively weak CO-S linkage, we expected that they would decompose thermally or photochemically by expelling carbon monoxide to give N-alkylidene thioureas, which are equilibrated to enamines when 4-substituents are primary or secondary alkyl groups. Then they would afford new enamine reaction because of their high reactivity.2-4)

Here we examined the thermal decomposition of the above thiazolones in an inert solvent and obtained some novel results.

4,4-Diphenylthiazolone derivatives (Ia) and (Ib), when boiled in xylene for 4 hr., gave N-diphenylmethylidenethiourea derivatives (IIa), mp. 159-160^{o}(dec.), and (IIb), mp. 141-143^{o}(dec.), respectively, both in 80 % yields. The structures were supported by their uv spectra [λ_{max}^{EtOH}nm.(log ε) IIa, 259(4.43); IIb, 260 (4.57)] and their ir absorptions due to C=N linkage (νC=N IIa, 1630; IIb, 1620 cm^{-1}). The structure IIa was further confirmed by hydrolysis to benzophenone and morpholium isothiocyanate.

Next we studied the thermal decomposition of 2-piperidino-4,4-dimethyl-5(4H)-thiazolone (III) in tetralin at 150-170°C. In a period of six hours, about 80 % of calculated amounts of carbon monoxide was collected. Chromatographic separation of the reaction mixture (silicic acid/ EtOH(1 %)-$CHCl_3$) gave piperidinium isothiocyanate (57 %) and a new compound (IV), mp. 222-223° (31 %), $C_{12}H_{20}N_2S$ (Mol. Wt. determination, 224 found by isothermal distillation; ν_{Max}^{KBr} cm^{-1} 3180, 1565).

The presence of a -NH-CS-N  group in IV was deduced from its spectral data and the following reactions; IV gave, with boiling ethanol (p-TsOH), an ethyl thiourethane (V), mp. 154-156° (44 %), and gave, with methyl iodide in ethanol, an S-methyl thiuronium iodide (VI), mp. 191-193° (82 %), which was converted with dil. NaOH to a Schiff's base (VII), bp. 100°(1 mm Hg)(72 %). Examination of the nmr spectra of the compounds IV-VII revealed that the C_6H_9 residue remained unaltered during the reactions. The nmr spectrum of IV showed, besides the signals based on piperidine protons, the signals due to two equivalent methyl groups (δ 1.33 ppm. s), two equivalent protons of methylene function (δ 2.33 ppm. s) and an olefinic proton (δ 5.69 ppm. d, J = 1.4 Hz.), which coupled with a NH proton (δ 6.92 ppm. b)(deuterium exchange and decoupling experiments).

When we subtract two CH_3, one CH_2 and one CH from C_6H_9 residue, only C_2 remains as quaternary carbons. These considerations lead to four possible structures, IVa, IVb, IVc and IVd, for the compound (IV). As the vicinal coupling between methylene protons and olefinic one was not observed, the structures IVb and IVd were omitted. Likewise IVc was eliminated because the coupling constant between olefinic proton and NH one was smaller than the expected for the vicinal positions.[5,6] The structure IVa was only consistent with the chemical and physical behavior of IV.

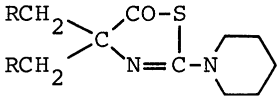
A similar experiment with 2-piperidino-4,4-diethyl-5(4H)-thiazolone (VIII) gave an analogous product (IX), mp. 178-180° (7.4 %), $C_{16}H_{28}N_2S$ [nmr spectrum, δ ppm.($CDCl_3$); 0.82(3H,t), 0.87(3H,t), 1.00(3H,d, J = 7 Hz.), 1.3-1.9(10H,m), 2.10(3H,s), 2.33(1H,q, J = 7 Hz.), 3.22(4H,b), 7.10(1H,b)].

The reaction sequence of the cyclobutene formation will be formulated as scheme 1 from the following considerations. As observed in the case of I, decarbonylation of III or VIII should produce X, which will partially isomerize to an enamine XI. Immediately after the formation of XI, it will attack on X to

(I) (II)

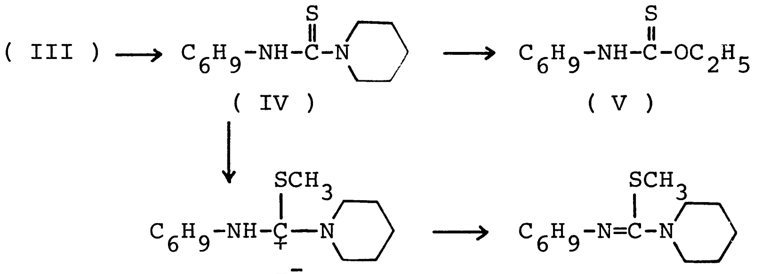
a, X = CH_2

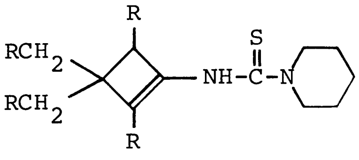
b, X = O



(III) R = H

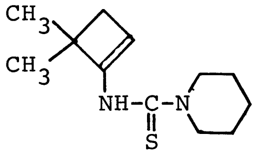
(VIII) R = CH_3



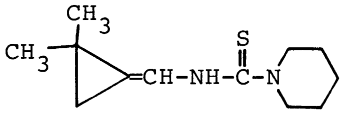


(IVa) R = H

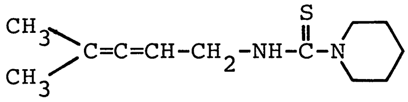
(IX) R = CH_3



(IVb)

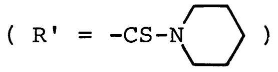


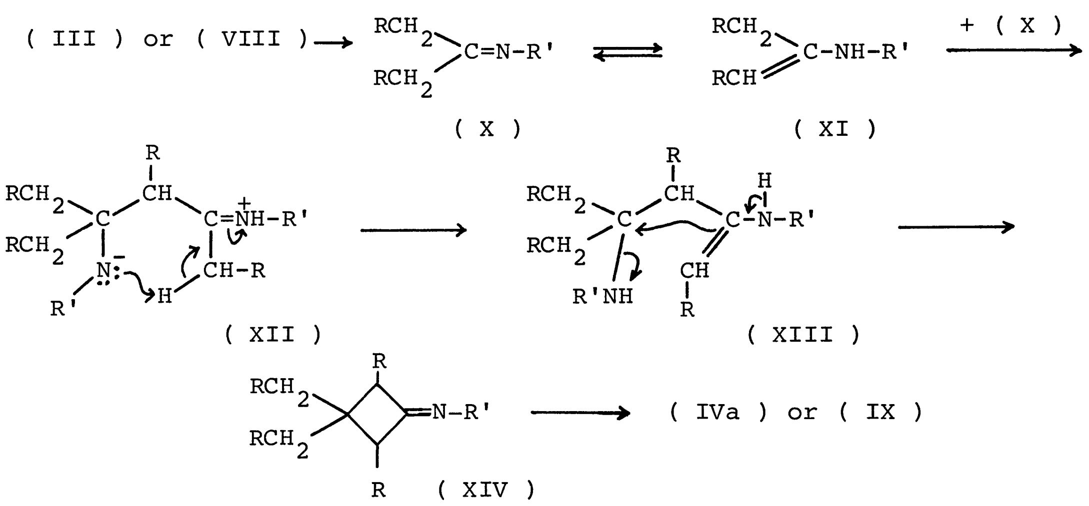
(IVc)



(IVd)

Scheme 1





give a dimer XII;3) subsequent prototropy and ring closure (XII → XIII → XIV) will give a cyclobutane derivative. The final step of the scheme is an isomerization of exo double bond to an endo position.7)

There is no precedent for thermal dimerization of enamine to cyclobutane derivative, although cyclobutane formation from enamines with conjugated ketones or esters has often been observed.8)

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