ro-1-butene concentration decreases more rapidly as the pressure in the system increases.

This result indicates that any collisional processes does not enhance the dissociation but mainly deactivate the excited molecules. Collision may occur during and after the pulse. During the pulse, the excited molecules above activation energy may proceed to three paths; further absorption of photons (pumping process), unimolecular decomposition and collisional deactivation. As the pressure increases, collisional deactivation can compete with the pumping process and unimolecular decomposition. Collisional effect will lead to decrease the average energy of molecules and so reduce the dissociation yield in general. After the pulse the excited molecules undergo either unimolecular decomposition or collisional deactivation. The collisional deactivation effectively occures in molecules with the long lifetime, and so the decrease of the dissociation yield of low energy dissociation channel will be more significant. The experimental result show that collisional deactivation by bath gas is more significant for low energy channel (HBr elimination) as expected.

Conclusion

(1) 1-Bromo-4-chlorobutane has two closely located dissociation channels: HCl and HBr elimination. The former has 55.2 kcal/mol activation energy and the latter has 50.9 kcal/mol activation energy.
(2) With focused geometry and 0.3J laser energy the experimentally observed product ratios and the RRKM calculation lead us to conclude that the BCB molecule has been excited to ca. 80 kcal/mol, well above the dissociation limit.
(3) The pressure dependence of product yields lead us to conclude that the collisional deactivation by the inert gas decreases the yield of low energy dissociation channel more significantly.

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Reactivity of the Biheterocyclic Betaine with the *para*-Substituted Phenacyl Bromides for the Ring Transformation Reaction

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7-Dithiocarboxy-3-phenyl-5,6-dihydro imidazo[2,1-b]thiazolium-betaine (2) was prepared by treatment of 3-phenyl-5,6-dihydro imidazo[2,1-b] thiazole (1) with carbon disulfide in acetone at room temperature. On the reaction of 2 with *para*-substituted phenacyl bromides (4) having the electron withdrawing property by virtue of (+) resonance (R)<(−) inductive (I) or (−) resonance (R), (−) inductive (I) effect, ring transformation product *p*-substituted-2-[2-[7-(*p*-substituted benzoyl)-5-thioxo-2,3-dihydro-1H-imidazo[1,2-c] thiazol-1-yl]-2-phenylvinylthio] acetophenone (6) was obtained; however, when R is electron donating grops with (+) resonance (R)>(−) inductive (I) effect the quarternary ammonium salt 7-(*p*-substituted phenyl) carbonyl methyl-3-phenyl-5,6-dihydro imidazo [2,1-b] thiazolium bromide (8) is formed. The reaction of 2 with unsubstituted-phenacyl bromide (R = H), on the other hand, gives 6a and 8a to the similar ratio, respectively.

Introduction

N-bridged thiazolo compounds, 3-substituted-5,6-dihydro imidazo [2,1-b] thiazoles[1-3] and 3-substituted-6,7-dihydro-5H-thiazolo[3,2-a] pyrimidines[2,3,8] have been synthesized by condensing cyclic thioureas with α-halo ketones. Their thiazolium salts were well known for pharmacological property such as hypoglycaemic, growth promotant and acaricidal activity.[4-7]

3-substituted-5,6-dihydro imidazo[2,1-b]thiazoles react with electrophiles such as aryl isothiocyanate, aryl isocyanate, alkyl isothiocyanate, alkyl isocyanate and carbon disulfide in acetone at room temperature to yield the corresponding betaines.[9,10] The ring transformation reaction by treatment of 8-phenyl(thiocarbamoyl)-3-phenyl-6,7-dihydro-5H-thiazolo[3,2-a] pyrimidinium-betaine with alkylating agents was reported in the earlier publications.[11,12]

We report here on the reactivity of 7-dithiocarboxy-3-phenyl-5,6-dihydro imidazo[2,1-b] thiazolium-betaine(**2**) with a series of *para*-substituted phenacyl bromides (**4**) and the preparation of new biheterocyclic compounds via ring transformation. The betaine (**2**) is easily obtained from the reac-

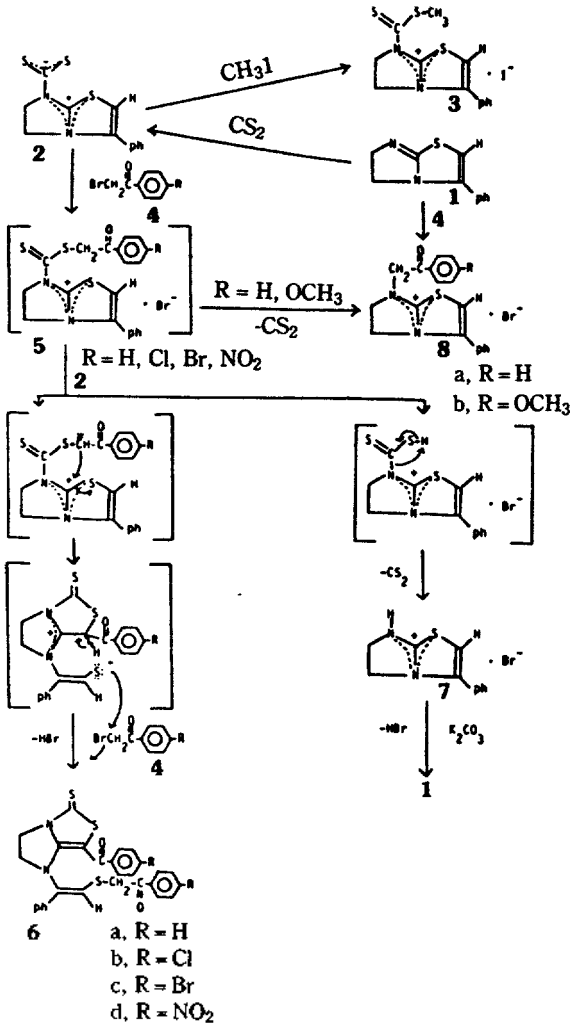
tion of 3-phenyl-5,6-dihydro imidazo [2,1-b] thiazole (**1**) with carbon disulfide in acetone at room temperature.

Results and Discussion

The solution of carbon disulfide in acetone is added to 3-phenyl-5,6-dihydroimidazo[2,1-b] thiazole (**1**) in acetone to give 7-dithiocarboxy-3-phenyl-5,6-dihydro imidazo [2,1-b] thiazolium-betaine (**2**) having the N-ylid structure at room temperature.

The reaction of the betaine (**2**) with methyl iodide, which undergoes the S-alkylation reaction, leads to the 7-[(methylthio) thiocarbonyl[-3-phenyl-5, 6-dihydro imidazo[2, 1-b]thiazolium iodide (**3**).

On the reaction with the *para*-substituted phenacyl bromides (**4**), however, is quite different from the previous. In case that the substituent R is chloro, bromo, or nitro group, having the electron withdrawing property by virtue of (+) resonance (R) < (-) inductive (I) or (-) resonance (R), (-) inductive (I) effect, the ring transformation product *p*-substituted-2-[2-[7-(*p*-substituted benzoyl)-5-thioxo-2,3-dihydro-1H-imidazo[1,2-c]thiazol-1-yl]-2-phenylvinyl thio]acetophenone (**6**) is obtained. But when R is methoxy group having (+) resonance (R) > (-) inductive (I) effect to donate electron, 7-(*p*-substituted phenyl)carbonylmethyl-3-phenyl-5,6-dihydro imidazo[2,1-b[thiazolium bromide (**8**) is formed via the unstable intermediate (**5**). The reaction of **2** with unsubstituted phenacyl bromide(R = H), on the other hand, gives **6a** and **8a** to the similar ratio, respectively. The existence of **7** and **8a** in mixture was identified by the ^{1}H-NMR spectrum of the salt formed during the reaction. Here the formation of HBr salt (**7**) means that of product (**6a**). This phenomenon appears remarkably in case that R is nitro, and methoxy group than R is hydro, chloro, and bromo group. The scheme 1 shows the results obtained above.

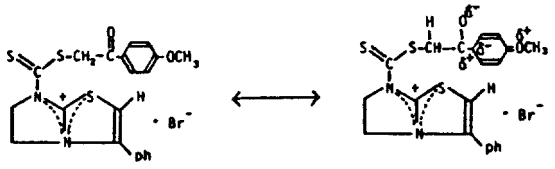


6 a, R = H
b, R = Cl
c, R = Br
d, R = NO_2

Scheme 1

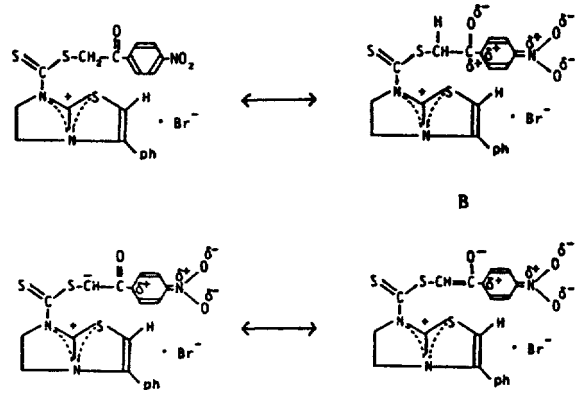
It is expected that the electron withdrawing groups (Cl, Br, NO_2) to activate the acidity of methylene group via aromatic ring lead to the ring transformation reaction but the electron donating groups(OCH_3) to deactivate give the ordinary alkylation reaction.

When the *para* substituent is methoxy group, the following structures can be drawn in intermediate (A).



A

In case that *para* group is nitro, bromo or chloro group withdrawing electron due to the inductive effect mainly, the intermediate(B) having two adjacent positive charges is formed.[13] This unstable salt is stabilized to (C,D) by neutralization of the charge on the carbonyl carbon with elimination of α-hydrogen. This may become driving force to the ring transformation reaction.



B C D

The ring transformation products(**6**) so prepared were separated by column chromatography(Kieselgel n-hexane/ethyl acetate 2.5:1).

Experimental

Melting points were determined on a Thomas-Hoover melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 267 spectrophotometer using potassium bromide pellets. Only selected adsorptions are reported. ^{1}H-NMR spectra were obtained on Bruker AM-200-SY nmr spectrometer. Chemical shift values from TMS were reported on the scale. Kieselgel 60 (70-230

mesh ASTM, MERCK) was used for column chromatography.

General Procedure for the Preparation of Ring Transformation Compounds. *p*-Chloro-2-[2-[7-(*p*-chloro benzoyl)-5-thioxo-2,3-dihydro-1H-imidazo[1,2-c] thiazol-1-yl]-2-phenylvinylthio] acetophenone (**6b**). A solution of the equimolar amount of *p*-chloro phenacyl bromide in acetone was added to a solution of 7-dithiocarboxy-3-phenyl-5,6-dihydro imidazo [2,1-b] thiazolium-betaine(**2**)[9,10] (3.59mmol, 1.0g) in acetone and a reaction mixture was refluxed. In a few hours the HBr salt (m.p. > 250 °C) (**7**) was precipitated, and the reaction mixture was further reacted for 8hrs. Then the white salt (**7**) was filtered, and the filtrate was concentrated, chromatographed on silica-gel (n-hexane/ethyl acetate 2.5:1). The separated product was recrystallized from chloroform-ethanol; yield 0.26g(12.4%), m.p. 134-136 °C as the bright yellow solids; IR(KBr) 1700(s C=O), 1630(vs ArC=C)cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ 4.12-4.27(m, 4H, NCH_2, CH_2N), 4.47(s, 2H, SCH_2), 6.32(s, 1H, =CH), 7.16-8.01(m, 13H, ArH); *Anal.* Calcd. for $C_{28}H_{20}N_2O_2S_3Cl_2$: C, 57.62; H, 3.46; N, 4.80. Found: C, 57.2; H, 3.42; N, 4.7.

2-[2-[7-Benzoyl-5-thioxo-2,3-dihydro-1H-imidazo[1,2-c] thiazol-1-yl]-2-phenylvinylthio] acetophenone(**6a**); yield 0.21g(11.4%), m.p. 191-192 °C; IR(KBr) 1680(s C=O), 1580(vs ArC=C)cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 4.11-4.40(m, 4H, NCH_2, CH_2N), 4.45(s, 2H, SCH_2), 6.27(s, 1H, =CH), 7.12-8.03(m, 15H, ArH); *Anal.* Calcd. for $C_{28}H_{22}N_2O_2S_3$: C, 65.34; H, 4,32; N, 5.44. Found: C, 64.5; H, 4.25; N, 5.2.

p-Bromo-2-[2-[7-(*p*-bromo benzoyl)-5-thioxo-2,3-dihydro-1H-imidazo[1,2-c]thiazol-1-yl]-2-phenylvinylthio] acetophenone(**6c**): yield 0.16g(6.64%), m.p. 199-202 °C; IR(KBr) 1685(s C=O), 1585(vs ArC=C)cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ 4.20-4.26(m, 4H, NCH_2, CH_2N), 4.47(s, 2H, SCH_2), 6.31(s, 1H, =CH), 7.12-7.93(m, 13H, ArH); *Anal.* Calcd. for $C_{28}H_{20}N_2O_2S_3Br_2$: C, 50.01; H, 3.00; N, 4.17. Found: C, 49.4; H, 2.96; N, 3.5.

p-Nitro-2-[2-[7-(*p*-nitro benzoyl)-5-thioxo-2,3-dihydro-1H-imidazo[1, 2c]thiazol-1-yl]-2-phenylvinylthio]acetophenone(**6d**): yield 0.53g(24.4%), m.p. 157-159°C; IR(KBr) 1690(s C=O), 1580(vs ArC=C)cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ4.17-4.27(m, 4H, NCH_2, CH_2N), 4.62(s, 2H, SCH_2), 6.36(s, 1H, =CH), 7.10-8.36(m, 13H, ArH); *Anal.* Calcd. for $C_{28}H_{20}N_4O_6S_3$: C, 55.61; H, 3.34; N, 9.27. Found: C, 55.3; H, 3.42; N, 9.00.

General Procedure for the Preparation of Quarternary Ammonium Salts. 7-(*p*-Methoxy phenyl)carbonylmethyl-3-phenyl-5,6-dihydro imidazo[2,1-b] thiazolium bromide(**8b**). The reaction mixture of *p*-methoxy phenacyl bromide and (**2**) (3.59mmol, 1.0g) in acetone afforded the quarternary ammonium salt (**8b**) after stirring for several hours under reflux. It was additionally refluxed for 5hr, the resulting solution was concentrated, filtered, washed with cold acetone and dried to give the pale yellow solids; yield 0.68g(37.4%), m.p. 201-203 °C(dec.); IR(KBr) 1670(s C=O), 1610(vs ArC=C)cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 3.87(s, 3H, OCH_3), 4.35-4.67(m, 4H, NCH_2, CH_2N), 5.40(s, 2H, CH_2CO), 7.11(s, 1H, =CH), 7.13-8.02(m, 9H, ArH); *Anal.* Calcd. for $C_{21}H_{19}N_2O_2S_3Br$: C, 55.69; H, 4.45; N, 6.50. Found: C, 55.0; H, 4.40; N, 6.57.

7-Phenylcarbonylmethyl-3-phenyl-5,6-dihydro imidazo [2,1-b]thiazolium bromide(**8a**): yield 0.28g(16.4%), m.p. 222-224 °C(dec.); IR(KBr) 1695(s C=O), 1590(vs ArC=C)cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 4.50-4.74(m, 4H, NCH_2, CH_2N), 5.48(s, 2H, CH_2CO), 7.15(s, 1H, =CH), 7.52-8.06(m, 10H, ArH).

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