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Addition Reaction of 3-Substituted-4-methyl-5-(2-hydroxy)ethylthiazolium Salt with Diaryl Carbodiimide[1]

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Reactions of 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide (I) and 3-benzyl-4-methyl-5-(2-hydroxyethyl)thiazolium bromide (I′) with diaryl carbodiimides afforded corresponding (1: 1) adduct (III, III′) and (1: 2) cycloadduct (IV, IV′). Product distribution in these reactions was largely effect by a substituent of carbodiimide and of thiazolium nitrogen. For *para* substituent in carbodiimide in the reaction with (I), the product ratio IV/III was increased in the order $Me<H<NO_2$, which suggested that the formation of zwitterion (VI) by deprotonation of (1: 1) adduct is the rate determining step for the cycloaddition reaction. *ortho* substituent in carbodiimide markedly increased the formation of cycloadduct in the reaction both with I and with I′, while thiazolium N-benzyl group in I′ decreased the cycloadduct formation as compared to $N-CH_3$ group.

In connection with work related to the nucleophilic reactivity of thiazolium C-2 position of thiamine, we have previously reported that thiamine and related thiazolium ylides reacted with heterocumulenes such as isocyanate and isothiocyanate to give cycloadduct with an unique spiro heterocyclic system,[3a–c] while the reaction with aryl isothiocyanate bearing electron attracting substituent favored the formation of zwitterionic adduct.[4] In continuation of the study on the reaction of heterocumulene with thiazolium ylide, we have now investigated the addition reactions of diaryl carbodiimides with 3-substituted-4-methyl-5-(2-hydroxyethyl)thiazolium salts.

Reaction of 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide (I) with an equimolar amount of di-*p*-tolyl carbodiimide (IIa) in the presence of an excess amount of triethylamine (NEt_3) in N,N-dimethylformamide (DMF) for 4 hr at 40° yielded an (1: 1) adduct (IIIa; 57%) and a (1: 2) cycloadduct (IVa; 10%). Under the same condition, di-*o*-tolyl-, diphenyl-, di-*p*-nitrophenyl- and di-*o*-nitrophenyl carbodiimides (IIb—e) were allowed to react with I. Reactions of 3-benzyl-4-methyl-5-(2-hydroxyethyl)thiazolium bromide (I′) with these diaryl carbodiimides were also carried out. The results are summerized in Table I. The structures of the both adducts were confirmed by elemental analysis and comparison of their characteristic nuclear magnetic resonance (NMR) data to those of IIIa and IVa respectively (Table II, III). IIIa was analyzed as $C_{22}H_{26}ON_3SI$, and it showed infrared (IR) bands due to OH (3370 cm^{-1}), NH (3200 cm^{-1}) and C=N (1632 cm^{-1}), and an ultraviolet (UV) maximum at λ_{max}^{EtOH} 281.5 mμ (log ε=4.23). NMR spectrum of IIIa exhibited signals due to $N-CH_3$ (τ 6.13^s), thiazolium C_4-CH_3 (τ 7.58^s) and $-CH_2CH_2O-$ (τ 6.35^t, τ 7.00^t) besides the signals corresponding to two tolyl groups (τ 2.0—3.7^m, τ 7.68^s, τ 7.77^s). $NaBH_4$ reduction of IIIa in cold MeOH afforded a dihydro derivative, $C_{22}H_{27}ON_3S$ (V) as a mixture consisting of two stereoisomers in the ratio of 4: 1. NMR spectrum of V showed, in addition to a multiplet due to $-CHCH_2-$

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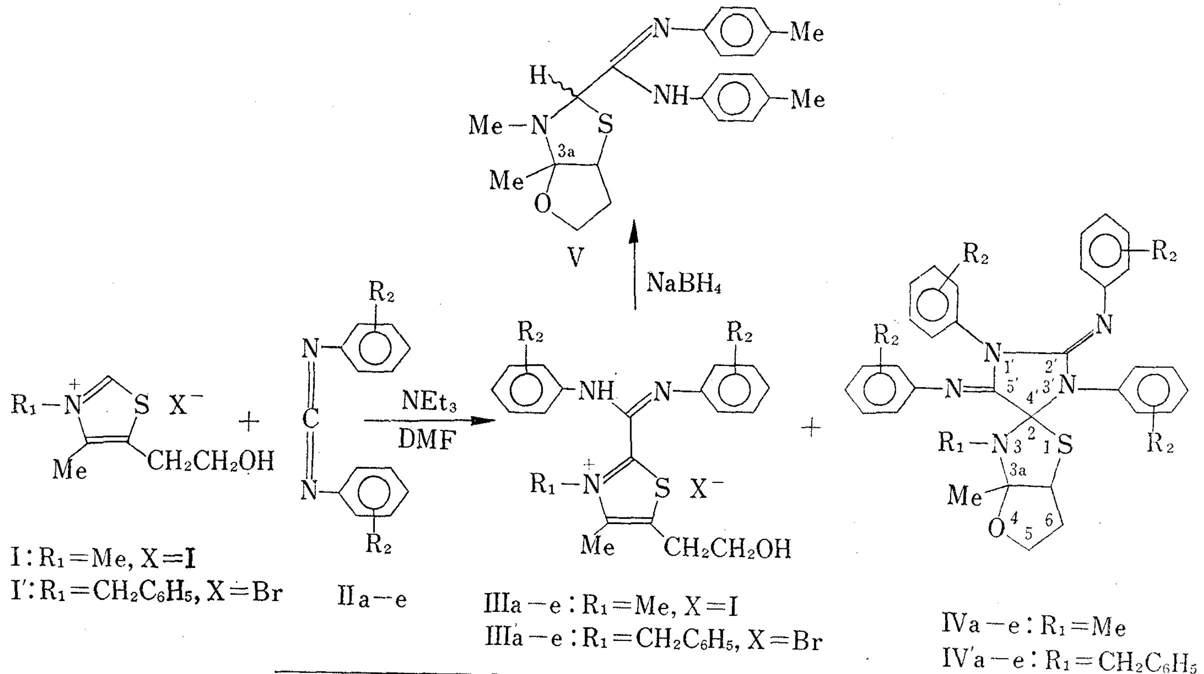
[1] A part of this work was reported preliminarily in *Tetrahedron Letters*, **1968**, 4027. This paper constitutes the part LXXXII of Studies on Pyrimidine Derivatives and Related Compounds. Part LXXXI: A. Takamizawa, S. Matsumoto, and S. Sakai, *Chem. Pharm. Bull.* (Tokyo), **22**, 293 (1974).

[2] Location: *Fukushima-ku, Osaka, 553 Japan.*

[3] *a*) A. Takamizawa, K. Hirai, S. Matsumoto, and T. Ishiba, *Chem. Pharm. Bull.* (Tokyo), **16**, 2130 (1968); *b*) A. Takamizawa, K. Hirai, S. Matsumoto, S. Sakai, and Y. Nakagawa, *ibid.*, **17**, 910 (1969); *c*) A. Takamizawa, K. Hirai, S. Matsumoto, and T. Ishiba, *ibid.*, **17**, 462 (1969).

[4] A. Takamizawa, S. Matsumoto, and S. Sakai, *Chem. Pharm. Bull.* (Tokyo), **22**, 293 (1974).



I: R_1=Me, X=I
I′: R_1=$CH_2C_6H_5$, X=Br

IIa–e

IIIa–e: R_1=Me, X=I
III′a–e: R_1=$CH_2C_6H_5$, X=Br

IVa–e: R_1=Me
IV′a–e: R_1=$CH_2C_6H_5$

	a	b	c	d	e
R_2	*p*-Me	H	*p*-NO_2	*o*-Me	*o*-NO_2

Chart 1

CH_2O- grouping in the region τ 6.08—8.30, signals corresponding to a methine proton at τ 5.33 and τ 5.37, an N-CH_3 at τ 7.66 and τ 7.63 and a C-CH_3 at τ 8.53 and τ 8.70 pairing in the ratio of 4: 1 respectively indicating that V is a mixture of two isomers which have 3,3a-dimethylperhydrofuro[2,3-*d*]thiazole ring system[4)] bearing a substituent at 2-position with different configuration. These evidences cited so far showed that the structure of IIIa could be assigned as 2-(N,N′-di-*p*-tolyl)amidino-3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide. On the other hand, IVa was analyzed as $C_{37}H_{39}ON_5S$, and it showed no IR band corresponding to OH or NH, while it showed NMR signals due to four tolyl groups (τ 2.9—3.85^m and τ 7.78^s, 7.81^s, 7.86^s, 7.96^s), a N-CH_3 (τ 7.31^s), a C-CH_3 (τ 9.00^{broad}) and -$CHCH_2CH_2O$- system (τ 6.50—8.70 m), being in quite parallel with those of the (1: 2) cycloadduct obtained from I and di-*p*-tolyl isothiocyanate.[4)] Thus, the structure of IVa could be assigned as spiro {3,3a-dimethylperhydrofuro[2,3-*d*]thiazole-2,4′-(2′,5′-di-*p*-tolylimino-1′,3′-di-*p*-tolylimidazolidine)}.

TABLE I. Product Distribution of the Reaction of 3-Substituted-4-methyl-5-(2-hydroxyethyl)-thiazolium Salts with Diaryl Carbodiimides

	R_2	R_1=Me			R_1=$CH_2C_6H_5$		
		III (%)	IV (%)	IV/III	III′ (%)	IV′ (%)	IV′/III′
a	*p*-Me	57	10	0.2	43	0	0
b	H	25	70	2.8	47	0	0
c	*p*-NO_2	2.5	22	8.8	17	2	0.1
d	*o*-Me	36	34	0.9	22	30	1.4
e	*o*-NO_2	0	52	>52	17	10	0.6

Yields were calculated for diaryl carbodiimides.

From the Table I, one can see the following points: a) The ratio of cycloadduct (IV)/(1: 1) adduct (III) is markedly effected by the substituent R_2 in carbodiimide, and it increases in the order Me<H<NO_2 for both *para* and *ortho* positions; b) N-Benzyl group in thiazolium ring considerably inhibits the formation of the (1: 2) cycloadduct as compared to N-methyl group; c) *ortho* substituent in diaryl carbodiimide relatively favors the formation of (1: 2) cycloadduct (VI′). It is notable that the (1: 1) adduct was obtained as a protonated form instead of the zwitterionic form in the presence of excess NEt_3, although the zwitterionic adduct has been isolated in the case of the reaction of certain phosphorus ylide with diaryl carbodiimide.[5] This indicates that the negative pole of the zwitterion (VI) has a particularly high basicity and is readily protonated by NEt_3-hydrogen halide which is present in the reaction mixture. It is surprising that the substituent effect observed for the reaction of I with diaryl carbodiimide appears to be contradictory to the previously reported result obtained in the reactions of aryl isothiocyanates with I, where an electron donating substituent in aryl group favored the formation of cycloadduct.[4] The present results, however, can be understood by considering that deprotonation of III to generate the zwitterion VI is the rate determining step for the formation of (1: 2) cycloadduct (IV). It is also surprising that the formation of sterically crowded (1: 2) cycloadduct (IV) is favored by the presence of *ortho* substituent in diaryl carbodiimide. The *o*-substituted N-aryl groups in IV can possibly have the conformations minimizing their steric repulsions, which is suggested by NMR evidence (*vide infra*). The increased formation of the cycloadduct is explainable if one supposes that the coplanarity of the π-systems of thiazolium ring and the negative pole of VI is inhibited by the bulkiness of *ortho* substituted aryl groups as shown by VII, and the negative charge is more localized than that of the *para* isomer, hence its 1,3-dipolar reactivity may thus be increased. Inhibition of cycloaddition in the case of I′ will be simply attributed to the steric hindrance due to N-benzyl group.

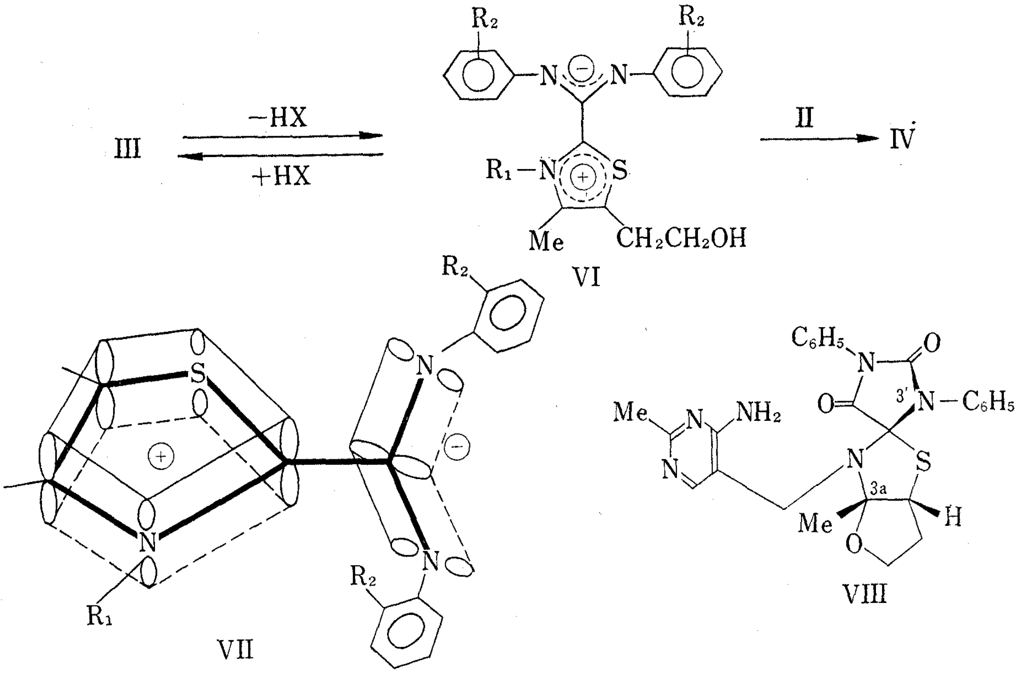


Chart 2

As to the stereo structure of the cycloadduct, two isomers can theoretically exist with regard to the configuration at spiro carbon by supposing that the perhydrofuro[2,3-*d*]thiazole ring system is *cis* fused. The direction of hydrofuran ring formation must be controlled only by steric factor. NMR spectra of the adducts of I with di-*p*-tolyl, diphenyl- and di-*p*-nitro-

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[5] F. Ramirez, J.F. Pilot, N.B. Desai, C.P. Smith, B. Hausen, and N. McKelvie, *J. Amer. Chem. Soc.*, **89**, 6273 (1967).

Table II. NMR Data of the (1: 1) Adducts (III, III′) (in τ value)

	IIIa	IIIb	IIIc	IIId	III′a	III′b	III′c	III′d	III′e
N-CH_3	6.13	6.12	5.95a)	6.05	—	—	—	—	—
N-CH_2-	—	—	—	—	4.38	4.28a)	4.23a)	4.22	3.53
C_4-CH_3	7.58	7.60	7.52a)	7.53	7.68	7.72a)	7.70a)	7.57	7.75

a) Determined in d_6-DMSO solution. All other spectra were determined in $CDCl_3$ solution.

Table III. NMR Data of the (1: 2) Cycloadducts (IV, IV′) (in τ value)

	IVa	IVb	IVc	IVd	IVe	IV′c	IV′d	IV′e
C_{3a}-CH_3	9.02	9.00	9.23a)	8.62(3) 8.45(2)	8.70(3) 8.86(2)	8.68(3) 8.75(1)	8.40(4) 8.59(3)	8.65(3) 8.40(2)
N-CH_3	7.31	7.33	7.23a)	7.01(3) 7.03(2)	6.92(3) 7.03(2)	—	—	—

a) Determined in d_6-DMSO solution. All other spectra were determined in $CDCl_3$ solution.

phenyl carbodiimides (IVa—c) showed a single peak corresponding to N-CH_3 and C_{3a}-CH_3 signals respectively indicating that they are stereochemically pure. The chemical shift of C_{3a}-CH_3 in these adducts is comparable to that of a previously reported compound (VIII)[3c)] having a same ring system in which the C_{3a}-CH_3 and 3′-N-phenyl group are situated in *cis* position. Thus the present adducts probably have the same stereochemistry as the model compound. On the other hand, as shown in Table III, the cycloadduct of I with *ortho* substituted diaryl carbodiimides (IVd, e) exhibits their N-CH_3 and C_{3a}-CH_3 signals at markedly lower field as compared to those of the *para* isomers, and the signals were accompanied by an isomer peak in the ratio of *ca.* 3: 2 respectively. In the case of the cycloadducts of I′ with both *para* and *ortho* substituted diaryl carbodiimides (IV′c—e), the C_{3a}-CH_3 signal is also accompanied by an isomer peak and it was observed in relatively down field. The down field NMR shift of C_{3a}-CH_3 in these adducts suggests that both *ortho* substituent in carbodiimide and thiazolium-N-benzyl group have a considerable effect on the conformation of N-aryl groups of the spiro imidazolidine ring in the (1: 2) cycloadduct, which results in a change of their anisotropic effect upon the C_{3a}-CH_3 protons. Contamination of a stereoisomer in these adducts is possibly correlated with this conformational alteration which will lead to the less selectivity in the stereochemical direction of hydrofuran ring formation.

Experimental

All melting points were determined in capillaries and uncorrected. Column chromatographies were carried out using SiO_2 (Davision, grade 950) or Al_2O_3 (Woelm, neutral, grade 1). Diaryl carbodiimides were prepared from corresponding aryl isocyanate by reacting a catalytic amount of 3-methyl-1-phenyl-3-phospholene-1-oxide according to the reported procedure.[6)] NMR spectra were taken on a Varian Associate A-60 spectrometer in $CDCl_3$ or d_6-DMSO solution with tetramethylsilane (TMS) as an internal standard. UV spectra were taken on a Hitachi EPS-3 spectrophotometer in 99% EtOH, and IR spectra were taken in nujol mull on a Japan Spectroscopic Company IR-S spectrophotometer using NaCl prisms.

General Procedure for the Reaction of 3-Substituted-4-methyl-5-(2-hydroxyethyl)thiazolium Salt with Diaryl Carbodiimide——0.01 mole of 3-substituted-4-methyl-5-(2-hydroxyethyl)thiazolium salts was dissolved in 30 ml of DMF, then 1.5 g of NEt_3 was added while cooling in an ice bath. After stirring for 30 min at room temperature, 0.01 mole of diaryl carbodiimide was added, and the mixture was stirred for 4 hr at 40°. DMF was removed by evaporation *in vacuo*, and the resulting residue was extracted with $CHCl_3$. The $CHCl_3$ extract was washed with water, dried over abs. Na_2SO_4 and concentrated to give a mixture of products which were separated by column chromatography. Occasionally, the products could be separated only by fractional crystallizations.

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6) T.W. Campbell, J.J. Monagle, and V.S. Foldi, *J. Amer. Chem. Soc.*, **84**, 3673 (1962).

Reactions of 3,4-Dimethyl-5-(2-hydroxyethyl)thiazolium Iodide (I) with Diaryl Carbodiimides——Di-*p*-tolyl Carbodiimide (IIa): 2.85 g of I and 2.22 g of IIa were allowed to react to afford 2.9 g (57%) of the (1: 1) adduct (IIIa) which was crystallized by addition of acetone to the concentrated mixture of the products. IIIa was recrystallized from acetone to give yellow prisms, mp 194—196°. *Anal.* Calcd. for $C_{22}H_{26}ON_3SI$: C, 52.06; H, 5.17; N, 8.28; S, 6.00; I, 24.93. Found: C, 52.14; H, 5.14; N, 8.13; S, 6.00; I, 25.16. IR ν_{max} cm^{-1}: 3370, 3200, 1632. UV λ_{max} mμ (log ε): 281.5 (4.23). NMR ($CDCl_3$, τ): -0.35^{broad} (1H, NH), 2.0—3.7^{m} (8H, 2×Ar), 6.13^{s} (3H, N–CH_3), 6.35^{t} and 7.00^{t} (each 2H, –CH_2CH_2O–), 7.58^{s} (3H, C_4–CH_3), 7.68^{s} and 7.77^{s} (each 3H, 2×Ar–CH_3). The mother liquor of IIIa was concentrated, and the residue was chromatographed with SiO_2–AcOEt system. The AcOEt eluate afforded 0.3 g (10%) of (1: 2) cycloadduct (IVa) which was recrystallized from MeOH to give colorless prisms, mp 134—136°. *Anal.* Calcd. for $C_{37}H_{39}ON_5S$: C, 73.84; H, 6.53; N, 11.63; S, 5.32. Found: C, 73.92; H, 6.48; N, 11.49; S, 5.27. NMR ($CDCl_3$, τ): 2.90—3.85^{m} (16H, 4×Ar), 6.50—8.70^{m} (5H, –$CHCH_2CH_2O$–), 7.31^{s} (3H, N–CH_3), 7.78^{s}, 7.81^{s}, 7.86^{s} and 7.96^{s} (each 3H, 4×Ar–CH_3), 9.00^{s} (3H, C_{3a}–CH_3).

Diphenyl Carbodiimide (IIb): 2.85 g of I and 1.94 g of IIb were allowed to react to afford a mixture from which 1.6 g of (1: 2) cycloadduct (IVb) was crystallized by addition of MeOH. The MeOH mother liquor was concentrated, and the residue was chromatographed with SiO_2–acetone system. The first acetone eluate further afforded 0.31 g of IVb (total 1.91 g, 70%), and the second eluate afforded 1.2 g (25%) of (1: 1) adduct (IIIb). IIIb was recrystallized from AcOEt to give yellow prisms, mp 170—173°. *Anal.* Calcd. for $C_{20}H_{22}ON_3SI$: C, 50.20; H, 4.63; N, 8.78; S, 6.70; I, 26.58. Found: C, 50.36; H, 4.62; N, 8.59; S, 6.24; I, 26.56. IVb was recrystallized from acetone to give colorless prisms, mp 201—202°. *Anal.* Calcd. for $C_{33}H_{31}ON_5S$: C, 72.65; H, 5.72; N, 12.84; S, 5.88. Found: C, 72.80; H, 5.50; N, 12.82; S, 5.69.

Di-*p*-nitrophenyl Carbodiimide (IIc): 2.85 g of I and 2.84 g of IIc were allowed to react to afford a gummy mixture which was dissolved in acetone. From the acetone solution, 140 mg (2.5%) of (1: 1) adduct (IIIc) was precipitated. The acetone mother liquor was concentrated, and the resulting residue was chromatographed with Al_2O_3–$CHCl_3$ system. The $CHCl_3$ eluate afforded 800 mg (22%) of (1: 2) cycloadduct (IVc). IIIc was recrystallized from MeOH–acetone to give orange prisms, mp 227—228° (decomp.). *Anal.* Calcd. for $C_{20}H_{20}O_5N_5SI$: C, 42.19; H, 3.54; N, 12.30; S, 5.63; I, 22.29. Found: C, 41.98; H, 3.60; N, 12.84; S, 5.45; I, 22.31. IVc was recrystallized from $CHCl_3$–acetone to give pale yellow prisms, mp 215—216° (decomp.). *Anal.* Calcd. for $C_{33}H_{27}O_9N_9S$: C, 54.62; H, 3.75; N, 17.37; S, 4.42. Found: C, 54.70; H, 3.77; N, 17.37; S, 4.66.

Di-*o*-tolyl Carbodiimide (IId): 2.85 g of I and 2.22 g of IId were allowed to react to afford a mixture of the products which were separated by column chromatography with SiO_2– acetone system. The first acetone eluate afforded 1.02 g (34%) of (1: 2) adduct (IVd) as a pale yellow amorphous powder. *Anal.* Calcd. for $C_{37}H_{39}ON_5S$: C, 73.81; H, 6.53; N, 11.63; S, 5.32. Found: C, 73.86; H, 6.54; N, 11.39; S, 4.84. The second acetone eluate afforded 1.8 g (36%) of (1: 1) adduct (IIId) as a yellow amorphous powder. *Anal.* Calcd. for $C_{22}H_{26}ON_3SI$: C, 52.06; H, 5.17; N, 8.28; S, 6.00; I, 24.93. Found: C, 51.73; H, 5.59; N, 8.33; S, 5.85; I, 25.25.

Di-*o*-nitrophenyl Carbodiimide (IIe): 2.85 g of I and 2.84 g of IIe were allowed to react to afford an oily mixture which was chromatographed with SiO_2–acetone system. The acetone eluate gave crude (1: 2) cycloadduct (IVe) which was rechromatographed with Al_2O_3–benzene system to give 1.9 g (52%) of an essentially pure IVe as an orange amorphous powder. *Anal.* Calcd. for $C_{33}H_{27}O_9N_9S$: C, 54.62; H, 3.75; N, 17.37; S, 4.42. Found: C, 54.09; H, 3.62; N, 17.59; S, 4.30. In the first column chromatography by SiO_2–acetone, (1: 1) adduct IIIe could not be eluted, and elution with MeOH–acetone (1: 10) mixture gave a mixture consisting of more than three compounds in which IIIe could not be detected.

Reactions of 3-Benzyl-4-methyl-5-(2-hydroxyethyl)thiazolium Bromide (I′) with Diaryl Carbodiimides——Di-*p*-tolyl Carbodiimide (IIa): 3.14 g of I′ and 2.22 g of IIa were allowed to react to give a mixture which was chromatographed with SiO_2–acetone system. The first acetone eluate gave an oily mixture, and the second acetone eluate gave 2.31 g (43%) of (1: 1) adduct (III′a) which was recrystallized from acetone to give yellow prisms, mp 193—194°. *Anal.* Calcd. for $C_{28}H_{29}ON_3SBr$: C, 62.80; H, 5.46; N, 7.85; S, 6.00; Br, 14.94. Found: C, 62.96; H, 5.67; N, 8.03; S, 6.34; Br, 14.89. UV λ_{max}mμ (log ε): 283 (4.25). IR ν_{max} cm^{-1}: 3340, 3170, 1638. NMR ($CDCl_3$, τ): -0.33^{broad} (1H, NH), 4.38^{s} (2H, $PhCH_2$), 6.10^{t} and 6.98^{t} (each 2H, –CH_2CH_2O–), 7.68^{s} (3H, C_4–CH_3), 7.73^{s} and 7.80^{s} (each 3H, 2×Ar–CH_3). The oily mixture obtained from the first acetone eluate was rechromatographed with Al_2O_3–AcOEt system to afford a small amount (45 mg) of 2-(N,N′-di-*p*-tolyl)amidino-3,4-dimethyl-5-(2-hydroxyethyl)thiazole, mp 152—153°. *Anal.* Calcd. for $C_{22}H_{27}ON_3S$: C, 69.02; H, 6.34; N, 11.50; S, 8.77. Found: C, 68.90; H, 6.40; N, 11.28; S, 8.85. NMR ($CDCl_3$, τ): 2.97^{broad} (8H, 2×Ar), 6.48^{t} and 7.20^{t} (each 2H, –CH_2CH_2O–), 7.67^{s} (3H, C_4–CH_3), 7.73^{s} (6H, 2×Ar–CH_3). IR ν_{max} cm^{-1}: 3360 (OH, NH), 1630 (C=N). UV λ_{max} mμ: 243, 298; $\lambda_{max}^{HCl-EtOH}$ mμ: 331.

Diphenyl Carbodiimide (IIb): 3.14 g of I′ and 1.94 g of IIb were allowed to react to give 1.9 g of (1: 1) adduct (III′b) which was crystallized by addition of MeOH to the concentrated mixture of the products. The MeOH mother liquor was concentrated and the resulting residue was chromatographed with SiO_2–acetone system. The first acetone eluate gave an oily mixture from which no identifiable product was isolated after repeated chromatographies with Al_2O_3–AcOEt system. The second acetone eluate of the first chromatography further afforded 0.5 g of IIIb′ (total, 2.4 g, 47%). III′b was recrystallized from EtOH to give yellow prisms, mp 190—191°. *Anal.* Calcd. for $C_{26}H_{26}ON_3SBr$: C, 61.41; H, 5.16; N, 8.26; S, 6.31; Br, 15.72. Found: C, 61.44; H, 5.20; N, 8.21; S, 6.55; Br, 15.71.

Di-*p*-nitrophenyl Carbodiimide (IIc): 3.14 g of I′ and 2.84 of IIc were allowed to react to give products as a gummy mixture which was chromatographed with SiO_2–acetone system. The first acetone eluate afforded an oily mixture, and the second fraction afforded 1.02 g (17%) of (1:1) adduct (III′c) which was recrystallized from acetone to give orange prisms, mp 160—161° (decomp.). *Anal.* Calcd. for $C_{26}H_{24}O_5N_5SBr$: C, 52.18; H, 4.04; N, 11.70; S, 5.36; Br, 13.35. Found: C, 52.04; H, 4.32; N, 11.89; S, 4.95; Br, 13.62. The oily mixture obtained from the first fraction was rechromatographed with Al_2O_3–$CHCl_3$ system to give 80 mg (2%) of (1:2) cycloadduct (IV′c) as a pale yellow powder. *Anal.* Calcd. for $C_{39}H_{31}O_9N_9S$: C, 58.42; H, 3.90; N, 15.72; S, 4.00. Found: C, 58.04; H, 3.59; N, 15.32; S, 4.17.

Di-*o*-tolyl Carbodiimide (IId): 3.14 g of I′ and 2.22 g of IId were allowed to react to give a mixture from which 1.16 g (22%) of (1:1) adduct (III′d) was precipitated by the addition of acetone. The acetone mother liquor was concentrated to give an oily residue which was chromatographed with Al_2O_3–benzene to give 1.0 g (30%) of (1:2) cycloadduct (IV′d). III′d was recrystallized from acetone to give yellow prisms, mp 181—182°. *Anal.* Calcd. for $C_{28}H_{29}ON_3SBr$: C, 62.80; H, 5.46; N, 7.85; S, 6.00; Br, 14.94. Found: C, 62.74; H, 5.75; N, 7.68; S, 5.92; Br, 15.13. IV′d was obtained as a pale yellow amorphous powder. *Anal.* Calcd. for $C_{43}H_{43}ON_5S$: C, 77.79; H, 6.53; N, 8.44; S, 4.83. Found: C, 77.88; H, 6.12; N, 8.90; S, 4.50.

Di-*o*-nitrophenyl Carbodiimide (IIe): 3.14 g of I′ and 2.84 g of IIe were allowed to react to give an oily mixture which was chromatographed with SiO_2–acetone system. The first acetone eluate afforded an orange powder, and the second acetone eluate afforded 1.02 g (17%) of (1:1) adduct (III′e) as a brown amorphous powder. *Anal.* Calcd. for $C_{26}H_{24}O_5N_5SBr$: C, 52.18; H, 4.04; N, 11.70; S, 5.36; Br, 13.35. Found: C, 51.72; H, 4.30; N, 12.25; S, 5.02; Br, 13.88. The orange powder obtained from the first acetone eluate was rechromatographed with Al_2O_3–$CHCl_3$ system to give 400 mg (10%) of (1:2) cycloadduct (IV′e) as pale yellow amorphous powder. *Anal.* Calcd. for $C_{39}H_{31}O_9N_9S$: C, 58.42; H, 3.90; N, 15.72. Found: C, 58.01; H, 4.42; N, 15.96.