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Addition Reactions of Heterocumulenes. II.[1] 1,4-Cycloaddition Reactions of Diphenylketene with Azadienes[2]

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Reaction of diphenylketene (I) with azadienes (II—IX), having –C=N–C=N– multiple bond system between carbon-nitrogen double bond in heterocycles and their side-chain carbon–nitrogen double bond, gave the 1,4-cycloadducts (XI—XVIII), respectively. Hydrogenolysis of the 1,4-cycloadducts (XIb, XIIb, and XVIb), with lithium aluminum hydride in tetrahydrofuran gave the 1-propanol derivatives (XIX, XXI, and XXII), respectively.

On the other hand, reaction of I with 3-(*p*-anisylideneamino)-5-phenylisoxazole (Xb) and 2-benzylideneaminopyridine (XXIV) respectively afforded 1-[3-(5-phenylisoxazolyl)]-3,3-diphenyl-4-(*p*-anisyl)-2-azetidinone (XXIII) and 1-(2-pyridyl)-3,3,4-triphenyl-2-azetidinone (XXV).

During a last few years, cycloaddition reactions of ketenes with various reagents have been extensively investigated.[4] Cycloadditions of ketenes have been reported on various carbon-nitrogen double bonds to give exclusively β-lactam or 1:2-molar adducts.[5] On the other hand, the reaction of ketenes with –C=C–C=N– multiple bond system to give the corres-

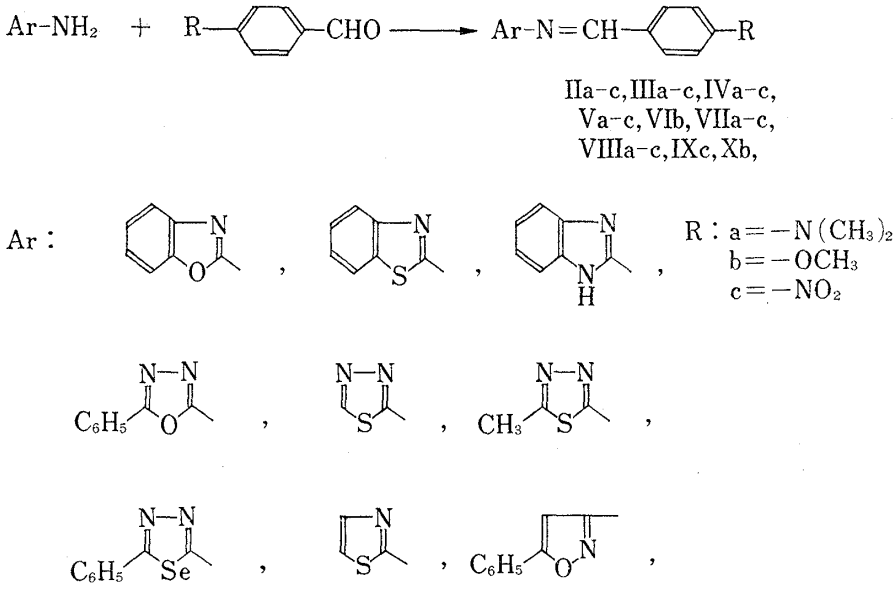

Chart 1

1) Part I: M. Sakamoto, K. Miyazawa, Y. Ishihara, and Y. Tomimatsu, *Chem. Pharm. Bull.* (Tokyo), **22**, 1419 (1974).
2) This work was presented at the 95th Annual Meeting of Pharmaceutical Society of Japan, Nishinomiya, April 1975. A part of this work was reported in the preliminary communication. M. Sakamoto, K. Miyazawa, K. Yamamoto, and Y. Tomimatsu, *Chem. Pharm. Bull.* (Tokyo), **22**, 2201 (1974).
3) Location: 35–23, *Nozawa 1-chome, Setagaya-ku, Tokyo, 154, Japan.*
4) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, London, 1967, p. 38; M. Kobayashi, *Kagaku To Kogyo* (Tokyo), **25**, 177 (1972).
5) R.D. Kimbrough, Jr., *J. Org. Chem.*, **29**, 1242 (1964); R.N. Pratt, G.A. Taylor, and S.A. Proctor, *J. Chem. Soc.* (*C*), **1967**, 1569.

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TABLE I. Ar-N=CH-C$_6$H$_4$-R

Compd. No.	Ar	R	mp (°C)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
IIa		$N(CH_3)_2$	215—220	$C_{16}H_{15}ON_3$	72.43	5.70	15.84	72.18	5.74	15.71
IIb		OCH_3	125—128	$C_{15}H_{12}O_2N_2$	71.41	4.80	11.11	71.41	4.86	11.23
IIc		NO_2	288—289	$C_{14}H_9O_3N_3$	62.92	3.39	15.73	62.70	3.31	15.69
IIIa		$N(CH_3)_2$	185—186	$C_{16}H_{15}N_3S$	68.30	5.36	14.93	68.36	5.51	15.12
IIIb		OCH_3	91— 92	$C_{15}H_{12}ON_2S$	67.15	4.51	10.44	67.01	4.49	10.41
IIIc		NO_2	254—256	$C_{14}H_9O_2N_3S$	59.35	3.20	14.83	59.45	3.22	14.95
IVa		$N(CH_3)_2$	248—250	$C_{16}H_{16}N_4$	72.70	6.10	21.20	72.68	6.09	21.42
IVb		OCH_3	230—231	$C_{15}H_{13}ON_3$	71.69	5.21	16.72	71.46	5.20	16.68
IVc		NO_2	265—267 (decomp.)	$C_{14}H_{10}O_2N_4$	63.15	3.79	21.04	63.21	3.88	21.18
Va		$N(CH_3)_2$	183—185.5	$C_{17}H_{16}ON_4$	69.84	5.52	19.17	69.90	5.56	19.59
Vb		OCH_3	154—155[a]	$C_{16}H_{13}O_2N_3$	68.80	4.69	15.05	68.94	4.48	15.45
Vc		NO_2	236—238	$C_{15}H_{10}O_3N_4$	61.22	3.43	19.04	61.16	3.38	19.22
VIb		OCH_3	142—143	$C_{10}H_9ON_3S$	54.78	4.13	19.16	54.90	4.12	19.24
VIIa		$N(CH_3)_2$	150	$C_{12}H_{14}N_4S$	58.51	5.72	22.74	58.44	5.70	22.86
VIIb		OCH_3	140—141	$C_{11}H_{11}ON_3S$	56.65	4.75	18.02	56.65	4.76	18.23
VIIc		NO_2	214—215	$C_{10}H_8O_2N_4S$	48.39	3.25	22.58	48.33	3.36	22.67
VIIIa		$N(CH_3)_2$	213—214	$C_{17}H_{16}N_4Se$	57.47	4.53	15.76	56.85	4.33	15.52
VIIIb		OCH_3	194.5—195	$C_{16}H_{13}ON_3Se$	56.15	3.82	12.27	56.26	3.72	12.52
VIIIc		NO_2	284—286[b]	$C_{15}H_{10}O_2N_4Se$	50.43	2.81	15.68	50.42	2.82	16.03
IXc		NO_2	186—187	$C_{10}H_7O_2N_3S$	51.51	3.03	18.02	51.98	3.20	18.31
Xb		OCH_3	149—150	$C_{17}H_{14}O_2N_2$	73.36	5.07	10.07	73.57	5.03	10.37

a) mp 200°: N.C. Misra and K.K. Patnaik, *J. Indian Chem. Soc.*, **48**, 309 (1971)
b) mp 260—261°: E. Bulka, D. Ehlers, and H. Storm, *J. Prakt. Chem.*, **315**, 164 (1973)

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ponding β-lactam[1,6] and or 1,4-cycloadduct[7] has been reported, but their reactions with –C=N–C=N– multiple bond system have received little attention.

In the present paper, we wish to report on the formation of 1,4-cycloadducts by the reaction of diphenylketene (I) with –C=N–C=N– multiple bond system having two potential sites of attack.

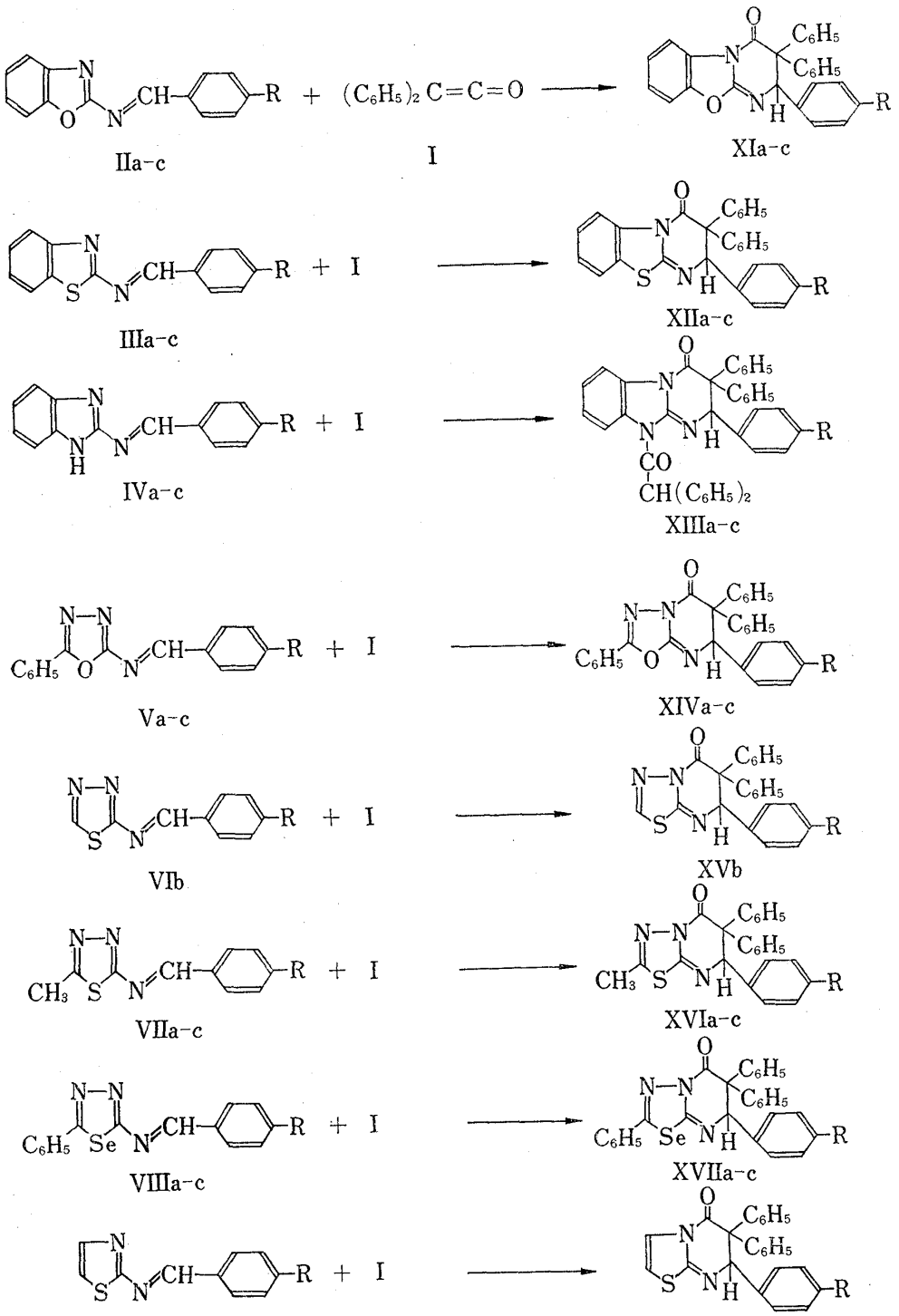

Chart 2

6) M. Sakamoto and Y. Tomimatsu, *Yakugaku Zasshi*, **90**, 1386 (1970).
7) T. Kato and T. Chiba, *Yakugaku Zasshi*, **89**, 1464 (1969); R. Gompper, *Angew. Chem.*, **81**, 348 (1969); S. Mohan, B. Kumar, and J.S. Sandhu, *Chem. Ind.* (London), **1971**, 671.

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According to the scheme in Chart 1, first we synthesized new azadienes, having –C=N–C=N– multiple bond system. Here, one of the carbon-nitrogen bond is a part of the aromatic system. The physical constants of azadienes are shown in Table I.

Refluxing of solution of 2-(*p*-anisylideneamino)benzoxazole (IIb) and I in dry xylene for 10 hr gave a crystalline compound, XIb, mp 144—145°, in 74% yield. The elemental analysis and molecular weight (M^+ 446) of XIb were consistent with those of the expected 1:1 adduct of IIb and I. The 1,4-cycloadduct of I as a dienophile to IIb and 1,2-cycloadduct of I to the carbon-nitrogen double bond in IIb, are possible for the structure of XIb. The infrared (IR) spectrum of XIb showed the presence of a carbonyl in six-membered ring lactam (1727 cm^{-1})[8] and imine (1606 cm^{-1}) groups, and its nuclear magnetic resonance (NMR) spectrum (ppm in $CDCl_3$) exhibited signals at δ 3.72 (3H, singlet, $-OCH_3$), 5.48 (1H, singlet, =N–CH–), and 6.44—7.84 (18H, multiplet, aromatic protons). These observations suggest that the 1:1 adduct is the 1,4-cycloadduct (XIb).

In order to obtain further evidence for its structure, hydrogenolysis of XIb with lithium aluminum hydride in tetrahydrofuran was attempted. As expected, the alcohol (XIX) was obtained and its structure was determined as 3-(2-benzoxazolylamino)-3-(*p*-anisyl)-2,2-diphenyl-1-propanol from spectroscopic data and elemental analysis. That is, NMR spectrum (ppm in d_6-DMSO) of XIX indicated signals at δ 3.72 (3H, singlet, $-OCH_3$), 4.41 (2H, singlet, $-CH_2-OH$), 5.74 (1H, broad, –OH), 5.92 (1H, doublet, J=8.0 Hz, –NH–CH–), and 8.02 (1H, doublet, J=8.0 Hz, –NH–CH–). The signals at δ 5.74 and 8.02 disappeared on addition of D_2O. Furtheremore, its ultraviolet (UV) absorption spectrum is very similar to that of 2-(*p*-

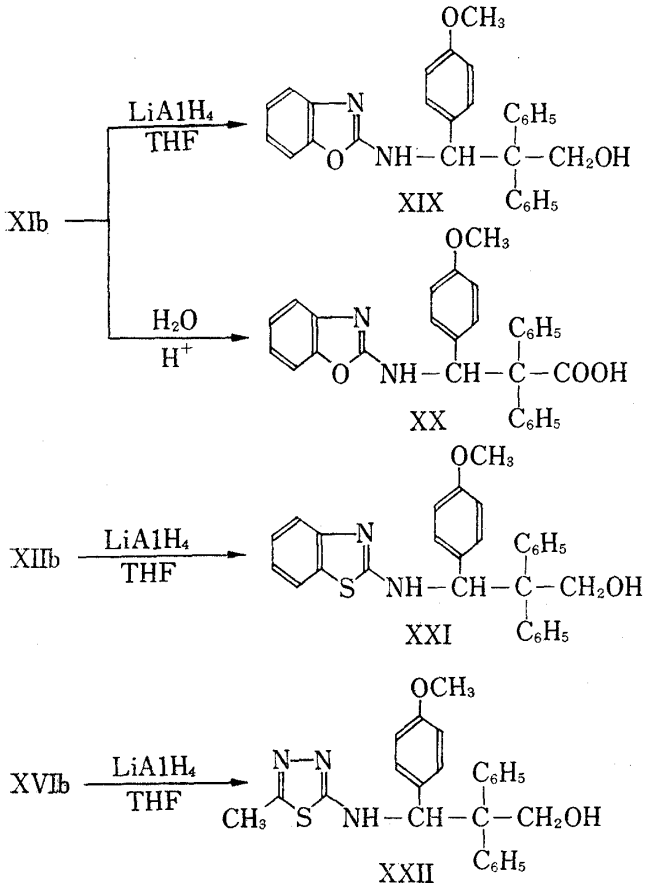


Chart 3

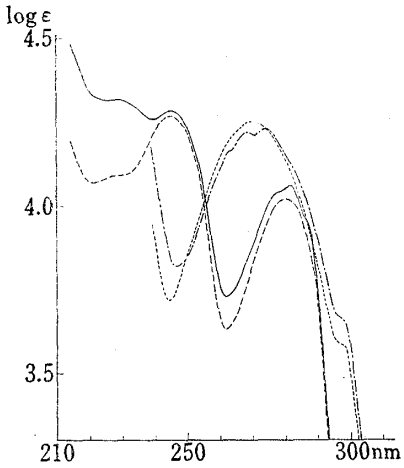
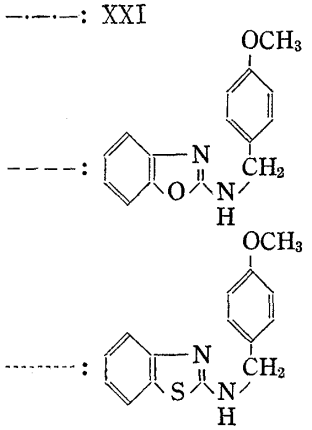


Fig. 1

———: XIX
—·—·—: XXI



8) Y. Shiokawa and S. Ohoki, *Chem. Pharm. Bull.* (Tokyo), **21**, 981 (1973).

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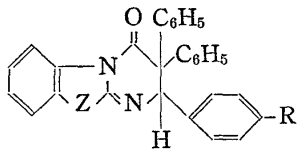
TABLE II.



Compd. No.	Z	R	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N	IR(KBr) cm^{-1} C=O	C=N	NMR δ (in $CDCl_3$) $C_{(2)}$–H	UV λ_{max}^{EtOH} nm (log ε)
XIa	O	$N(CH_3)_2$	50	218—219	$C_{30}H_{25}O_2N_3$	78.41 (78.17)	5.48 (5.40)	9.15 (9.22)	1727	1616	5.41(s)	263 (4.33)
XIb	O	OCH_3	74	144—145	$C_{29}H_{22}O_3N_2 \cdot \frac{1}{2}EtOH$	76.74 (76.89)	5.36 (5.30)	5.96 (5.95)	1727	1606	5.48(s)	275.5 (3.94)
XIc	O	NO_2	86	227—229	$C_{28}H_{19}O_4N_3$	72.87 (72.79)	4.15 (4.21)	9.11 (9.06)	1738	1625	5.68(s)	275 (4.19)
XIIa	S	$N(CH_3)_2$	91	206—208	$C_{30}H_{25}ON_3S$	75.76 (75.97)	5.29 (5.20)	8.83 (9.11)	1718	1643	5.39(s)	240, 261, 292.5(sh) (4.44, 4.33, 3.98)
XIIb	S	OCH_3	87	153—155	$C_{29}H_{22}O_2N_2S$	75.30 (75.55)	4.78 (4.95)	6.05 (6.12)	1714	1648	5.45(s)	278, 285, 310(sh) (3.84, 3.84, 3.29)
XIIc	S	NO_2	70	221—222.5	$C_{28}H_{19}O_3N_3S$	70.42 (70.23)	4.00 (4.10)	9.00 (8.84)	1713	1647	5.66(s)	240, 277(sh) (4.40, 4.10)
XIIIa	N–CO–$CH(C_6H_5)_2$	$N(CH_3)_2$	84	237—239	$C_{44}H_{36}O_2N_4$	80.95 (80.81)	5.56 (5.66)	8.58 (8.66)	1733 1678	1614		254, 297 (4.37, 3.98)
XIIIb	N–CO–$CH(C_6H_5)_2$	OCH_3	81	223—224	$C_{43}H_{33}O_3N_3$	80.73 (80.51)	5.19 (5.32)	6.56 (6.47)	1733 1681	1614		251(sh), 286.5, 297.5 (4.35, 4.00, 4.00)
XIIIc	N–CO–$CH(C_6H_5)_2$	NO_2	75	217—218	$C_{42}H_{30}O_4N_4 \cdot EtOH$	75.41 (75.69)	5.18 (5.01)	8.00 (8.37)	1737 1691	1618		253, 287.5, 297(sh)

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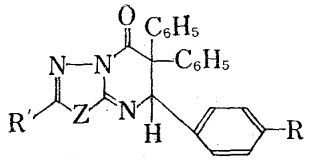
TABLE III.



Compd. No.	Z	R	R′	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N	IR(KBr) cm^{-1} C=O	C=N	NMR δ (in $CDCl_3$) $C_{(7)}$–H	UV λ_{max}^{EtOH} nm (log ε)
XIVa	O	$N(CH_3)_2$	C_6H_5	33	182—183	$C_{31}H_{26}O_2N_4$	76.52 (76.72)	5.39 (5.31)	11.52 (11.73)	1727	1614	5.47(s)	244, 262 (4.34, 4.37)
XIVb	O	OCH_3	C_6H_5	58	195—196.5	$C_{30}H_{23}O_3N_3$	76.09 (75.98)	4.90 (4.65)	8.87 (8.99)	1728	1617	5.49(s)	261, 291.5, 304(sh) (4.22, 4.08, 4.03)
XIVc	O	NO_2	C_6H_5	36	237—238.5	$C_{29}H_{20}O_4N_4$	71.30 (71.30)	4.13 (3.98)	11.47 (11.53)	1729	1620	5.67(s)	241, 284 (4.31, 4.32)
XVb	S	OCH_3	H	87	204	$C_{24}H_{19}O_2N_3S$	69.71 (69.60)	4.62 (4.70)	10.16 (10.02)	1727	1638	5.47(s)	253.5 (3.90)
XVIa	S	$N(CH_3)_2$	CH_3	63	209—210	$C_{26}H_{24}ON_4S$	70.88 (70.67)	5.48 (5.49)	12.71 (12.72)	1721	1642	5.37(s)	261 (4.28)
XVIb	S	OCH_3	CH_3	67	212—214	$C_{25}H_{21}O_2N_3S$	70.23 (70.20)	4.94) (5.09)	(9.82 (9.72)	1722	1641	5.43(s)	253 (3.96)
XVIc	S	NO_2	CH_3	79	213—214	$C_{24}H_{18}O_3N_4S$	65.15 (65.13)	4.10 (4.08)	12.66 (12.97)	1726	1642	5.60(s)	263 (4.11)
XVIIa	Se	$N(CH_3)_2$	C_6H_5	43	212—213	$C_{31}H_{26}ON_4Se$	67.75 (67.77)	4.76 (4.78)	10.19 (10.32)	1724	1633	5.46(s)	260.5, 297(sh) (4.55, 4.16)
XVIIb	Se	OCH_3	C_6H_5	54	218—220	$C_{30}H_{23}O_2N_3Se$	67.16 (66.91)	4.31 (4.31)	7.83 (7.83)	1731	1643	5.42(s)	261.5, 294(sh), 321 (4.37, 3.93, 3.81)
XVIIc	Se	NO_2	C_6H_5	78	252—254	$C_{29}H_{20}O_3N_4Se\cdot C_6H_6$	66.77 (67.06)	4.15 (4.02)	8.89 (8.99)	1725	1626	5.66(s)	262 (4.43)

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methoxybenzylamino)benzoxazole regarded as a model compound of alcohol (Fig. 1). Hydrolysis of XIb in the presence of sulfuric acid gave the corresponding acid (XX) and its structure was determined as 3-(2-benzoxazolylamino)-3-(*p*-anisyl)-2,2-diphenylpropionic acid from spectroscopic data and elemental analysis. Therefore, it was decided that the adduct (XIb) was 2-(*p*-anisyl)-2,3-dihydro-4-oxo-3,3-diphenyl-4H-pyrimido[2,1-*b*]benzoxazole.

The pathway of the formation of XIb would be explained as nucleophilic attack of endocyclic nitrogen atom on a carbon-carbon double bond in the ketene, followed by nucleophilic attack on the substituted carbon atom of imine group by carbanion.

Similar reactions of azadienes (II—VIII) with I gave the corresponding 1,4-cycloadducts (XI—XVII), respectively. The yield, elemental analyses and physical properties are summarized in Table II and III.

Furtheremore, reaction of 2-(*p*-nitrobenzylideneamino)thiazole (IXc) with I gave 2-(*p*-nitrophenyl)-2,3-dihydro-4-oxo-3,3-diphenyl-4H-pyrimido[2,1-*b*]thiazole (XVIIIc) in good yield. The IR spectrum of XVIIIc showed the presence of a carbonyl in six-membered ring lactam (1721 cm^{-1})[8] and imine (1643 cm^{-1}) groups, and its NMR spectrum (ppm in $CDCl_3$) exhibited signal at δ 5.54 (1H, singlet, =N–CH–).

The characteristic found in NMR data is the chemical shift of methine proton (–C=N–CH–) of the heterocycles; that is, as shown in Table II and III, the methine proton appears at near 5.4 ppm as a singlet. The IR spectra of these products showed carbonyl and imino groups absorptions at near 1725 and 1620 cm^{-1}.

Hydrogenolysis of XIIb with lithium aluminum hydride in tetrahydrofuran gave the corresponding alcohol (XXI) and its structure was determined as 3-(2-benzothiazolylamino)-3-(*p*-anisyl)-2,2-diphenyl-1-propanol from spectroscopic data and elemental analysis. That is, ultraviolet (UV) spectrum of XXI is very similar to that of 2-(*p*-methoxybenzylamino)benzothiazole regarded as a model compound of XXI (Fig. 1). Furthermore, its structure was confirmed by comparing the NMR spectrum of XXI with that of XIX. In the same manner XVIb gave 3-[2-(5-methyl-1,3,4-thiadiazolylamino)]-3-(*p*-anisyl)-2,2-diphenyl-1-propanol (XXII). On the basis of spectroscopic data mentioned above, the adducts of diphenylketene with II—IX were assigned as the corresponding 1,4-cycloadducts (XI—XVIII).

On the other hand, the reaction of 3-(*p*-anisylideneamino)-5-phenylisoxazole (Xb) with I in refluxing dry xylene gave the 1:1 adduct (XXIII). From the characteristic carbonyl stretching[1,9] at 1766 cm^{-1}, the structure of XXIII was established to be 1,2-cycloadduct, 1-[3-(5-phenylisoxazolyl)]-3,3-diphenyl-4-(*p*-anisyl)-2-azetidinone (XXIII).

Similarly, reaction of 2-benzylideneaminopyridine (XXIV)[10] with I gave 1-(2-pyridyl)-3,3,4-triphenyl-2-azetidinone (XXV).

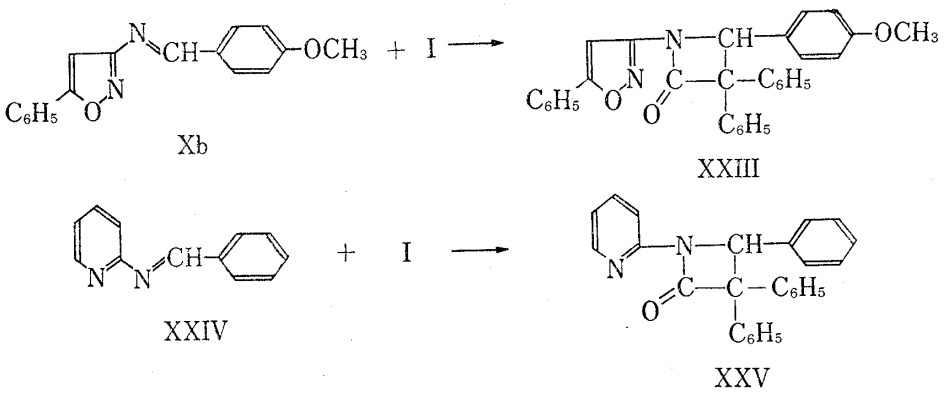

Chart 4

9) H. Bestian, H. Biener, K. Clauss, and H. Heyn, *Ann. Chem.*, **718**, 94 (1968); C.W. Bird, *J. Chem. Soc.*, **1965**, 3016; R. Huisgen, B.A. Davis, and M. Morikawa, *Angew. Chem. Intern. Ed. Engl.*, **7**, 826 (1968).
10) A. Kirpal and E. Reiter, *Chem. Ber.*, **60**, 664 (1927).

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Experimental

All melting points were measured in a Yanagimoto micro melting points apparatus and are uncorrected. NMR spectra were measured with Japan Electron Optics Co., Model PS-100 (100 MHz) spectrometer with tetramethylsilane as an internal reference. Abbreviation used s=singlet, d=doublet, t=triplet, m=multiplet, b=broad. Mass spectra were taken on a Japan Electron Optics Co., JMS-OISG-2 spectrometer. IR absorption spectra were measured on a Nihon Bunko Jasco DS-701G spectrometer. UV absorption spectra were obtained with a Hitachi Model 124 spectrometer.

Reaction of 2-Aminobenzoxazole with *p*-Anisaldehyde——General Procedure: A mixture of 3.1 g of 2-aminobenzoxazole, one molar equivalent of *p*-anisaldehyde and a trace of *p*-toluenesulfonic acid in 150 ml of toluene was refluxed under water separator for 10 hr, and the reaction mixture was condensed *in vacuo* to give a crystalline substance. Recrystallization from acetone gave 2-(*p*-anisylideneamino)benzoxazole (IIb) as yellow needles, mp 125—128°. Yield 1.9 g (33%).

The other compound (II—X) were made by similar procedure and these data were summarized in Table I.

Reaction of Diphenylketene with 2-(*p*-Anisylideneamino)benzoxazole (IIb)——General Procedure: A mixture of 1.9 g of IIb and one molar equivalent of diphenylketene in 20 ml of dry xylene was refluxed for 10 hr, and the reaction mixture was condensed *in vacuo*, and the residue was washed with ether. Recrystallization from EtOH gave 2-(*p*-anisyl)-2,3-dihydro-4-oxo-3,3-diphenyl-4H-pyrimido[2,1-*b*]benzoxazole (XIb), mp 144—145°. Yield 2.5 g (74%). Mass Spectrum *m/e*: 446 (M^+).

The other compounds (XI, XII, XIV—XVIII) were made by similar procedure and these data were summarized in Table II and III.

Reaction of Diphenylketene with 2-(*p*-Dimethylaminobenzylideneamino)benzimidazole (IVa)——As above, IVa (0.3 g) was treated with two molar equivalent of diphenylketene in 20 ml of dry xylene to give 3-(*p*-dimethylaminophenyl)-2,3-dihydro-1-oxo-2,2-diphenyl-5-diphenylacetylbenzimidazo[2,1-*b*]pyrimidine (XIIIa) as colorless needles, mp 237—239°. Yield 0.62 g (84%). Mass Spectrum *m/e*: 652 (M^+).

The other compounds (XIIIb—c) were made by similar procedure and these data were summarized in Table II.

Reaction of Diphenylketene with 2-(*p*-Nitrobenzylideneamino)thiazole (IXc)——As above, IXc (0.5 g) was treated with one molar equivalent of diphenylketene in 15 ml of dry xylene to give 2-(*p*-nitrophenyl)-2,3-dihydro-4-oxo-3,3-diphenyl-4H-pyrimido[2,1-*b*]thiazole (XVIIIc) as colorless prisms, mp 188—189°. Yield 0.57 g (59%). Mass Spectrum *m/e*: 427 (M^+). *Anal.* Calcd. for $C_{24}H_{17}O_3N_3S$: C, 67.44; H, 4.02; N, 9.83. Found: C, 67.60; H, 3.92; N, 10.11. IR ν_{max}^{KBr} cm^{-1}: 1722 (C=O), 1643 (C=N). NMR (in $CDCl_3$) δ: 5.54 (1H, s, –C=N–CH–).

Hydrolysis of XIb with H_2SO_4——To a suspension of XIb (0.5 g) in EtOH (40 ml) was added 2 ml of 95% H_2SO_4 and the mixture was heated under reflux for 4 hr. The reaction mixture was condensed to dryness *in vacuo*. To a residue was added 30 ml of H_2O and crystals were separated by suction, washed with H_2O and dried. Purification by recrystallization from EtOH gave 3-(2-benzoxazolylamino)-3-(*p*-anisyl)-2,2-diphenylpropionic acid (XX) as colorless needles, mp 228—230°. Yield 0.4 g. Mass Spectrum *m/e*: 464 (M^+). *Anal.* Calcd. for $C_{29}H_{24}O_4N_4 \cdot H_2O$: C, 72.18; H, 5.43; N, 5.81. Found: C, 72.46; H, 5.62; N, 5.48. UV λ_{max}^{EtOH} nm (log ε): 274 (3.66). IR ν_{max}^{KBr} cm^{-1}: 3380 (NH), 1685 (C=O). NMR (in d_6-DMSO) δ: 3.76 (3H, s, $-OCH_3$), 5.27 (1H, d, J=4.0 Hz, –NH–CH–), 6.42—7.55 (18H, m, aromatic protons), 8.64 (1H, d, J=4.0 Hz, –NH–CH–), 9.92 (1H, s, –COOH).

Hydrogenolysis of XIb with $LiAlH_4$——To a suspension of $LiAlH_4$ (0.15 g) in THF (10 ml) was added a solution of XIb (0.6 g) in THF (15 ml) dropwise with stirring at room temperature over a period of 25 min. Stirring was continued with refluxing on a water bath for 6 hr. After cooling, the excess reagents was decomposed with H_2O (20 ml) and the residue separated was filtered off, and filtrate was concentrated to 20 ml under reduced pressure. The resulting aqueous layer was alkalified with 10% NaOH solution and extracted with AcOEt. The extract was washed with an aqueous solution of NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The oily residue was washed with ether, and the resulting precipitates were collected by filtration and recrystallized from EtOH to give 3-(2-benzoxazolylamino)-3-(*p*-anisyl)-2,2-diphenyl-1-propanol (XIX) as colorless crystals, mp 135—137°. Yield 0.3 g. Mass Spectrum *m/e*: 450 (M^+). *Anal.* Calcd. for $C_{29}H_{26}O_3N_2 \cdot H_2O$: C, 74.34; H, 6.02; N, 5.98. Found: C, 74.74; H, 6.03; N, 6.27. UV λ_{max}^{EtOH} nm (log ε): 228.5 (4.32), 246 (4.28), 282 (4.06). IR ν_{max}^{KBr} cm^{-1}: 3410, 1640, 1580, 1243, 742, 698. NMR (in d_6-DMSO) δ: 3.72 (3H, s, $-OCH_3$), 4.41 (2H, b, $-CH_2OH$), 5.74 (1H, b, –OH), 5.92 (1H, d, J=8.0 Hz, –NH–CH–), 6.61—7.30 (18H, m, aromatic protons), 8.02 (1H, d, J=8.0 Hz, –NH–CH–).

Hydrogenolysis of 2-(*p*-Anisyl)-2,3-dihydro-4-oxo-3,3-diphenyl-4H-pyrimido[2,1-*b*]benzothiazole (XIIb) with $LiAlH_4$——XIIb (0.6 g) was treated with the same method as the preparation of XIX. Recrystallization from EtOH gave 3-(2-benzothiazolylamino)-3-(*p*-anisyl)-2,2-diphenyl-1-propanol (XXI) as colorless prisms, mp 145—146°. Yield 0.27 g. Mass Spectrum *m/e*: 467 (M^++1), 466 (M^+). *Anal.* Calcd. for $C_{29}H_{26}O_2N_2S \cdot C_2H_5OH$: C, 72.63; H, 6.29; N, 5.47. Found: C, 72.55; H, 6.45; N, 5.44. UV λ_{max}^{EtOH} nm (log ε): 268.5 (4.22), 273.5 (4.23), 298 (sh.) (3.66). IR ν_{max}^{KBr} cm^{-1}: 3360, 1540, 1247, 754, 698.NMR (in d_6-DMSO) δ:

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3.67 (3H, s, $-OCH_3$), 4.23 (2H, b, $-CH_2OH$), 5.43 (1H, b, -OH), 5.98 (1H, d, $J=8.0$ Hz, $-NH-\underset{|}{C}H-$), 6.58—7.63 (18H, m, aromatic protons), 8.09 (1H, d, $J=8.0$ Hz, $-N\underline{H}-\underset{|}{C}H-$).

Hydrogenolysis of 7-(*p*-Anisyl)-6,7-dihydro-2-methyl-5-oxo-6,6-diphenyl-7*H*-1,3,4-thiadiazolo[3,2-*a*]-pyrimidine (XIVb) with $LiAlH_4$——XIVb (0.5 g) was treated with the same method as the preparation of XIX. Recrystallization from EtOH gave 3-[2-(5-methyl-1,3,4-thiadiazolylamino)]-3-(*p*-anisyl)-2,2-diphenyl-1-propanol (XXII) as colorless crystals, mp 197—198°. Yield 0.16 g. Mass Spectrum *m/e*: 431 (M^+). *Anal.* Calcd. for $C_{25}H_{25}O_2N_3S$: C, 69.59; H, 5.84; N, 9.74. Found: C, 69.15; H, 5.84; N, 9.45. IR ν_{max}^{KBr} cm^{-1} 3265, 1608, 1530, 1509, 1243, 694. NMR (in d_6-DMSO) δ: 2.43 (3H, s, $=\underset{|}{C}-CH_3$), 3.73 (3H, s, $-OCH_3$), 4.20 (2H, b, $-C\underline{H}_2-OH$), 5.31 (1H, b, -OH), 5.85 (1H, d, $J=8.0$ Hz, $-NH-\underset{|}{C}\underline{H}-$), 6.58—7.35 (14H, m, aromatic protons), 7.62 (1H, d, $J=8.0$ Hz, $-N\underline{H}-\underset{|}{C}H-$).

Reduction of 2-(*p*-Anisylideneamino)benzoxazole (IIb) with $LiAlH_4$——By a similar treatment as described in the hydrogenolysis of XIb, colorless product was obtained from IIb. Recrystallization from EtOH gave 2-(*p*-methoxybenzylamino)benzoxazole as colorless needles, mp 147—148°. Mass Spectrum *m/e*: 254 (M^+). *Anal.* Calcd. for $C_{15}H_{14}O_2N_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 71.20; H, 5.60; N, 11.17. UV λ_{max}^{EtOH} nm (log ε): 245 (4.27), 281.5 (4.02). IR ν_{max}^{KBr} cm^{-1}: 3160 (NH). NMR (in $CDCl_3$) δ: 3.85 (3H, s, $-OCH_3$), 4.64 (2H, s, $-NH-C\underline{H}_2-$), 5.91 (1H, b, $-N\underline{H}-CH_2-$).

Reduction of 2-(*p*-Anisylideneamino)benzothiazole (IIIb) with $LiAlH_4$——By a similar treatment as described in the hydrogenolysis of XIb, colorless product was obtained from IIIb. Recrystallization from EtOH gave 2-(*p*-methoxybenzylamino)benzothiazole as colorless needles, mp 170—171°. Mass Spectrum *m/e*: 270 (M^+). *Anal.* Calcd. for $C_{15}H_{14}ON_2S$: C, 66.65; H, 5.22; N, 10.37. Found: C, 66.41; H, 5.16; N, 10.43. UV λ_{max}^{EtOH} nm (log ε): 270 (4.25), 298 (sh.) (3.58). IR ν_{max}^{KBr} cm^{-1}: 3190 (NH). NMR (in d_6-DMSO) δ: 3.81 (3H, s, $-OCH_3$), 4.60 (2H, d, $J=5.5$ Hz, $-NH-C\underline{H}_2-$), 8.37 (1H, t, $J=5.5$ Hz, $-N\underline{H}-CH_2-$).

Reaction of Diphenylketene with 3-(*p*-Anisylideneamino)-5-phenylisoxazole (Xb)——A mixture of 0.31 g of Xb and one molar equivalent of diphenylketene in 10 ml of dry xylene was refluxed for 10 hr, and the reaction mixture was condensed *in vacuo*, and the residue was washed with ether. Recrystallization from MeOH gave 1-[3-(5-phenylisoxazolyl)]-3,3-diphenyl-4-(*p*-anisyl)-2-azetidinone (XXIII) as colorless prisms, mp 171—173°. Yield 0.22 g (42%). Mass Spectrum *m/e*: 472 (M^+). *Anal.* Calcd. for $C_{31}H_{24}O_3N_2$: C, 78.79; H, 5.12; N 5.93. Found: C, 78.81; H, 5.25; N, 5.95. IR ν_{max}^{KBr} cm^{-1}: 1766 (C=O). NMR (in $CDCl_3$) δ: 3.67 (3H, s, $-OCH_3$), 5.92 (1H, s, $-\underset{|}{N}-\underset{|}{C}H-$), 6.62—7.76 (15H, m, aromatic protons).

Reaction of Diphenylketene with 2-Benzylideneaminopyridine (XXIV)——XXIV (0.9 g) was treated with the same method as the preparation of XXIII. Recrystallization from EtOH gave 1-(2-pyridyl)-3,3,4-triphenyl-2-azetidinone (XXV) as colorless needles, mp 152—153°. Yield 1.23 g (66%). Mass Spectrum *m/e*: 376 (M^+). *Anal.* Calcd. for $C_{26}H_{20}ON_2$: C, 82.95; H, 5.36; N, 7.44. Found: C, 82.90; H, 5.38; N, 7.53. IR ν_{max}^{KBr} cm^{-1}: 1742 (C=O). NMR (in $CDCl_3$) δ: 6.13 (1H, s, $-\underset{|}{N}-\underset{|}{C}H-$), 6.91—8.09 (19H, m, aromatic protons).

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