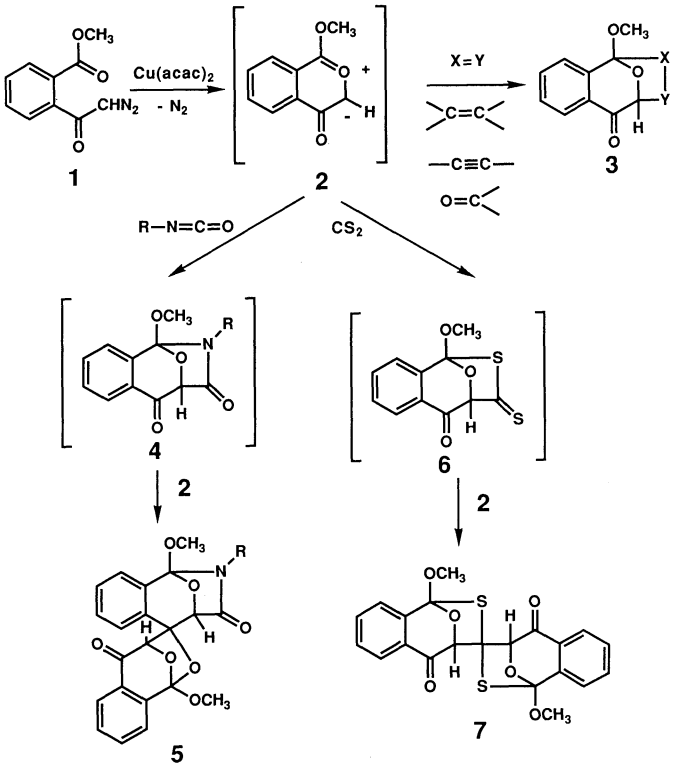
Formation and Reaction of Carbonyl Ylides. Reactions of 1-Methoxy-2-benzopyrylium-4-olate with Isothiocyanates

Toshikazu IBATA,* Hirofumi NAKANO, and Hatsue TAMURA
Institute of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560
(Received December 5, 1991)

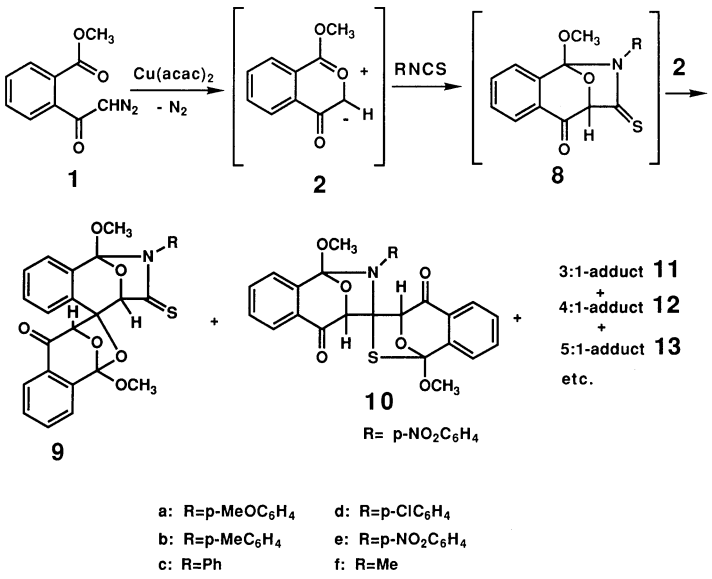
The 1,3-dipolar cycloaddition of 1-methoxy-2-benzopyrylium-4-olate (**2**) generated by $Cu(acac)_2$-catalyzed decomposition of methyl 2-diazoacetylbenzoate with various aryl isothiocyanates and methyl isothiocyanate gave 2 : 1-, 3 : 1-, 4 : 1-, and 5 : 1-adducts without affording 1 : 1-adduct. The first cycloaddition of **2** occurs on the C=N double bond of isothiocyanate. The cycloadditions of the following steps, such as second, third, fourth, and fifth cycloadditions, proceed on C=O group of the cycloadducts of each previous steps. The molecular structure of the 2 : 1-adduct of **2** with phenyl isothiocyanate was determined by means of X-ray crystallography. Colorless crystals of the adduct are monoclinic with the space group $P2_1/a$, and with the unit-cell dimensions of a=12.619 (4), b=16.432 (4), c=11.238 (2) Å, β=97.39 (1) °, and Z=4. The structure was calculated by direct methods (MULTAN 80) and refined by block-diagonal least-squares methods. All hydrogen atoms were revealed by a difference-Fourier synthesis, and further least-squares refinements gave the final R value of 0.046.

Recently, the reaction of carbene with carbonyl compounds has been studied extensively as one of the effective methods of the formation of carbonyl ylide.[1] We have studied the formation of 1-methoxy-2-benzopyrylium-4-olate (**2**), by the $Cu(acac)_2$-catalyzed decomposition of methyl 2-diazoacetylbenzoate (**1**),[2] and reported the 1,3-dipolar cycloaddition of **2** with various ethylenic,[3] acetylenic,[4] and carbonyl dipolarophiles,[5] to give adducts **3**. In the recent papers of this series we described the reaction of **2** with isocyanates to give 2 : 1-adducts **5** initiated by the 1,3-dipolar cycloaddition of **2** at C=N double bond of isocyanate.[6] The reaction with carbon disulfide has also been reported to give 2 : 1-adducts **7** through the double cycloadditions of **2** on two C=S double bonds of carbon disulfide together with 5-[(*o*-methoxycarbonyl)phenyl]-1,3-oxathiole-2-thione.[7] In these reactions, the site of the second attack of **2** on 1 : 1-adduct is different each other.

Isothiocyanate is a hetero cumulene compound having C=N and C=S double bonds which could be the active site for the 1,3-dipolar cycloaddition with **2**. Therefore, interesting results are expected for the reactivity and



Scheme 1.



Scheme 2.

regioselectivity of isothiocyanate in the reaction with **2** in comparison with the reactivity of isocyanates and carbon disulfide. In this paper we wish to report the reaction of benzopyrylium-4-olate **2** with isothiocyanates.

Results and Discussion

The $Cu(acac)_2$-catalyzed decomposition of methyl 2-diazoacetylbenzoate (**1**) in the presence of two molar equivalents of phenyl isothiocyanate in benzene solution at 80°C gave a mixture of 2 : 1-, 3 : 1-, and 4 : 1-adducts between the benzopyrylium-4-olate **2** and phenyl isothiocyanate. No 1 : 1-adduct **8c** (R=Ph) was isolated, despite the detailed investigation of the reaction mixture by column chromatography. This indicates that the produced 1 : 1-adduct has higher reactivity toward **2** than phenyl isothiocyanate used in excess as a dipolarophile.

The 2 : 1-adduct **9c** has two methoxyl signals at δ=4.14 and 3.78 and two methine signals at δ=5.43 and 5.35 in its ^{1}H NMR spectrum. There are many possible structures for 2 : 1-adduct **9**, because phenyl isothiocyanate has two reaction sites for cycloaddition to give four possible 1 : 1-adducts **8A–D**, and then each 1 : 1-adduct can give eight possible 2 : 1-adducts when it reacts with the second molecule of **2**.

For example, the 1 : 1-adduct **8A** has two sites for 1,3-dipolar cycloaddition, C=O and C=S double bonds, toward **2**. When **2** reacts with 1 : 1-adduct **8A** on its C=O group,[8] four 2 : 1-adducts **9A–D** are possible. Therefore, spectroscopic methods are useless for the structural determination of the 2 : 1-adduct. The X-ray crystallography solved this problem, and the 2 : 1-adduct **9c** was confirmed to have structure **9B** as is described below. The regiochemistry of the cycloaddition of **2** giving **9Bc** is consistent with that of **2** toward carbonyl compounds as described before.[5] The structure **9B**

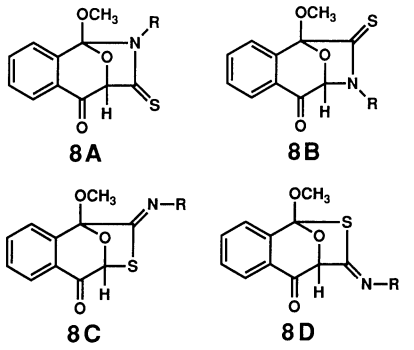


Fig. 1. Possible 1 : 1-adducts of **2** with isothiocyanate.

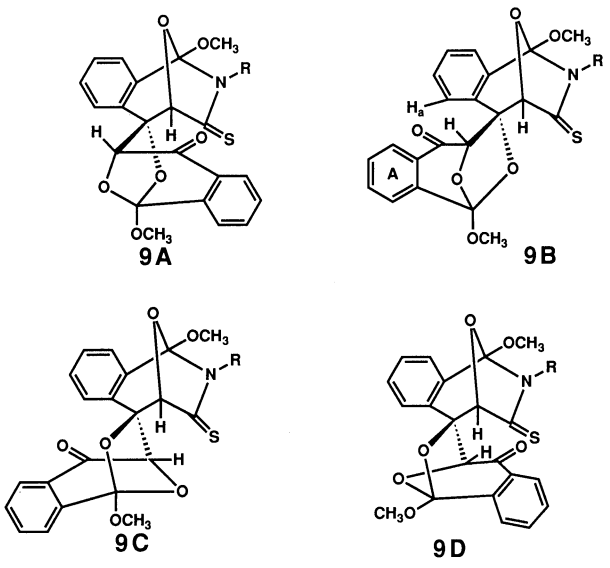


Fig. 2. Possible 2 : 1-adducts of **2** with isothiocyanate.

explains the high field shift of one aromatic proton **Ha** at δ=6.37—6.35 attributing to the magnetic anisotropy by ring current of adjacent benzene ring **A**.[9]

The 3 : 1-adduct **11c** between **2** and phenyl isothiocyanate has three methoxyl signals at δ=4.07, 3.74, and 3.42 together with three methine proton signals. When we assumed that the 3 : 1-adduct is derived by the cycloaddition of the third molecule of **2** on the 2 : 1-adduct **9Bc**, two structures are possible for the 3 : 1-adduct. One is the structure **11A** derived from the cycloaddition of **2** on C=O of the 2 : 1-adduct, the other is **11B** formed by the attack on C=S of the 2 : 1-adduct. The ^{13}C NMR signals attributable to thiocarbonyl carbon and carbonyl carbon at δ=195.55 and 190.68, respectively, support the structure **11A** as the 3 : 1-adduct **11c**. The high field signals of two aromatic protons at δ=6.11—6.08 and 5.97—5.95 also coincide with the structure **11A** having a similar steric relationship between benzopyrylium-4-olate moieties.

The 4 : 1-adduct **12c** has four methoxyl signals, four methine signals, and three high field aromatic proton signals in its ^{1}H NMR spectrum. This indicates that the 4 : 1-adduct has the structure **12c** which is formed by the cycloaddition of **2** on the carbonyl group of the 3 : 1-adduct **11Ac** in a similar approach. The typical C=S signal at δ=195.55 and C=O signal at δ=190.90 in the ^{13}C NMR spectrum of the 4 : 1-adduct also is consistent with the structure **12c**. No 5 : 1-adduct was isolated in the reaction of phenyl isothiocyanate.

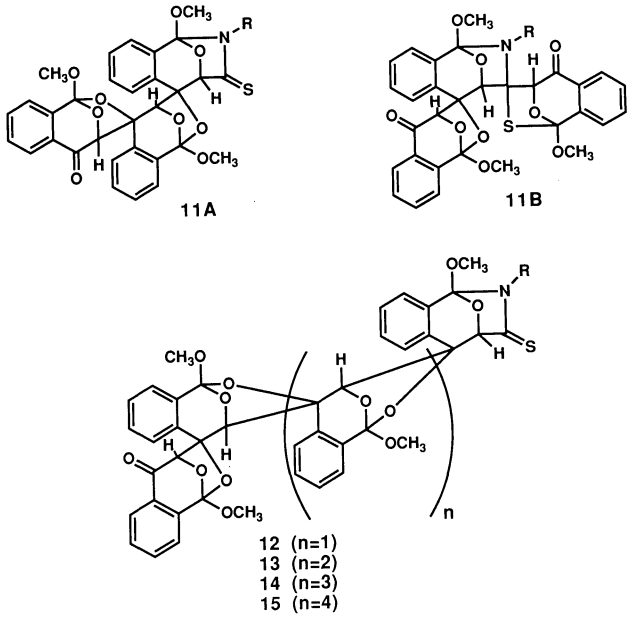


Fig. 3. Structure of 3 : 1-, 4 : 1-, 5 : 1-, 6 : 1-, and 7 : 1-adducts of **2** with isothiocyanate.

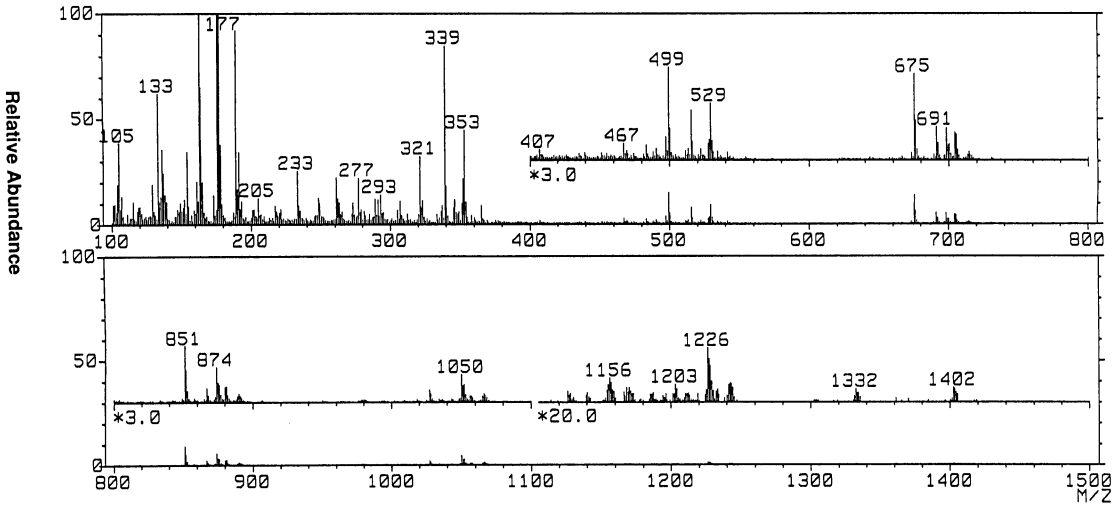
Other aryl isothiocyanates gave similar results as is shown in Table 1. Electron-withdrawing substituents such as *p*-NO_2 and *p*-Cl groups appreciably increased the yields of the 2 : 1-adducts. On the other hand, electron-donating *p*-MeO group decreased the yields of adducts accompanying the large amount (22%) of recovery of isothiocyanate used. This is attributed to the lower reactivity of *p*-methoxyphenyl isothiocyanate toward **2** than the carbonyl group of the 1 : 1-, 2 : 1-, and 3 : 1-adducts.

The 5 : 1-adducts **13** were isolated in the reactions of *p*-tolyl and *p*-chlorophenyl isothiocyanates and characterized by the spectroscopic data. Although isolation of adducts including more than five moieties of **2** was unsuccessful, formation of 6 : 1- and 7 : 1-adducts was confirmed by FAB MS measurement of the reaction mixture of $Rh_2(OAc)_4$-catalyzed decomposition of methyl 2-diazoacetylbenzoate in the presence of *p*-chlorophenyl isothiocyanate (Fig. 4). These adducts were assumed to have similar recurring structures **12d**—**15d**.

In the reaction of *p*-nitrophenyl isothiocyanate with **2**, two types of 2 : 1-adducts were isolated in 20.0 and 5.6% yields. Both adducts were confirmed to be 2 : 1-adducts on the basis of molecular ion peaks (*m*/*z* 532) of their mass spectra. Existence of two methoxyl and two methine proton signals in their ^{1}H NMR spectra also supports above conclusion. The ^{13}C NMR spectrum of the major adduct shows signals of the thiocarbonyl and a carbonyl carbon at δ=195.55 and 190.50, respectively, which are in similar positions with those of phenyl isothiocyanate 2 : 1-adduct **9Bc**. On the other hand, the minor adduct has two signals of carbonyl carbon at δ=189.58 and 189.33 without a signal attributable to thiocarbonyl carbon. These results indicate that the major 2 : 1-adduct has the **9Be** structure, and the minor adduct has the structure **10e** formed by the second attack of **2** on C=S double bond of the 1 : 1-adduct **8Ae**. Although stereochemistry of **10e** has not been determined yet, it was assumed that the compound has a similar structure with that of the 2 : 1-adduct **7**.[7b]

Table 1. Yields of 1,3-Dipolar Cycloadducts between Benzopyrylium-4-olate (**2**) and Isothiocyanates

Run	R	2:1-Adduct (**9B**)	3:1-Adduct (**11**)	4:1-Adduct (**12**)	5:1-Adduct (**13**)
a	*p*-$CH_3OC_6H_4$	—	3.0	4.9	—
b	*p*-$CH_3C_6H_4$	3.7	3.5	5.3	1.8
c	C_6H_5	3.2	4.1	6.4	—
d	*p*-ClC_6H_4	11.2	—	13.7	9.4
e	*p*-$NO_2C_6H_4$	20.0	12.7	—	—
f	CH_3	1.6	1.0	—	—



m/z	
875	4:1-adduct 12
1050	5:1-adduct 13
1226	6:1-adduct 14
1402	7:1-adduct 15

Fig. 4. FAB mass spectrum of the reaction mixture of **2** with *p*-chlorophenyl isothiocyanate.

Absence of a 2:1-adduct of **10e** type in the reaction mixture of other aryl isothiocyanates indicates that substitution of electron-withdrawing nitro group on phenyl isothiocyanate moiety increases the dipolarophilicity of C=S group of the 1:1-adduct **8Ae**.

Methyl isothiocyanate gave 2:1- and 3:1-adducts in quite low yields (Table 1, Run f) together with a mixture of unseparable polymeric products. This low reactivity of methyl isothiocyanate may be ascribed to the electron-donating effect of methyl group.

We would like to compare the reactivity of isothiocyanate with those of isocyanate and carbon disulfide. The reaction site of isothiocyanate toward **2** is the C=N double bond affording **8A** in the same manner as the reaction of isocyanate to give **4**. The 1:1-adduct **8A** has high reactivity toward **2**, and the second attack of **2** occurred preferentially on C=O double bond to afford the 2:1-adducts of type **9B**. This tendency is quite different from the high reactivity of C=S double bond of the intermediate **6** formed by the reaction between **2** and carbon disulfide.

X-Ray Crystal Structure Analysis of 9Bc. The crystal data of **9Bc** are listed in Table 2 along with the experimental details. The X-ray intensity data were measured on a Rigaku four-circle diffractometer with Ni-filtered Cu$K\alpha$ radiation. The number of nonzero reflections used in the structure determination were 2967. The space group $P2_1/a$ was confirmed by a statistical distribution of E values and a successful refinement of the structure. Using 340 reflections with $E>1.670$, the crystal structure was determined by direct methods with the MULTAN 80 program.[10] The E-map computed with the phase set of the highest combined figure of merit (3.00) revealed the position of all the non-hydrogen atoms. The isotropic refinement, followed by anisotropic refinement reduced R to 0.073. The hydrogen atoms were located on a difference map and their positional parameters were refined together with isotropic thermal parameters, while the other atoms were refined anisotropically by block-diagonal least-squares. The final R value was 0.046.

Table 2. Crystal Data and Experimental Details of the 2:1-Adduct **9Bc**

Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	12.619(4)
b/Å	16.432(4)
c/Å	11.238(2)
β/°	97.39(1)
V/Å^3	2311.0(9)
Z	4
D_m/Mg m^{-3}	1.439(3)
D_x/Mg m^{-3}	1.402
μ(Cu $K\alpha$)/cm^{-1}	16.010
Scan method	ω–2θ
Scan speed in ω/° min^{-1}	4
Scan width	$1.0°+0.15\tan\theta$
Back ground/s	2×4
$2\theta_{max}$/°	120
Number of reflections	2967 ($\|F_o\| \geqq 2\sigma(F_o)$)
R	0.046
Crystal size/mm	0.3×0.3×0.1

The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with the following weighting scheme: $w=1/(\sigma^2(F_o)+0.0271|F_o|+0.0086|F_o|^2)$. All the atomic scattering factors were taken from the "International Tables for X-Ray Crystallography." The computations were carried out

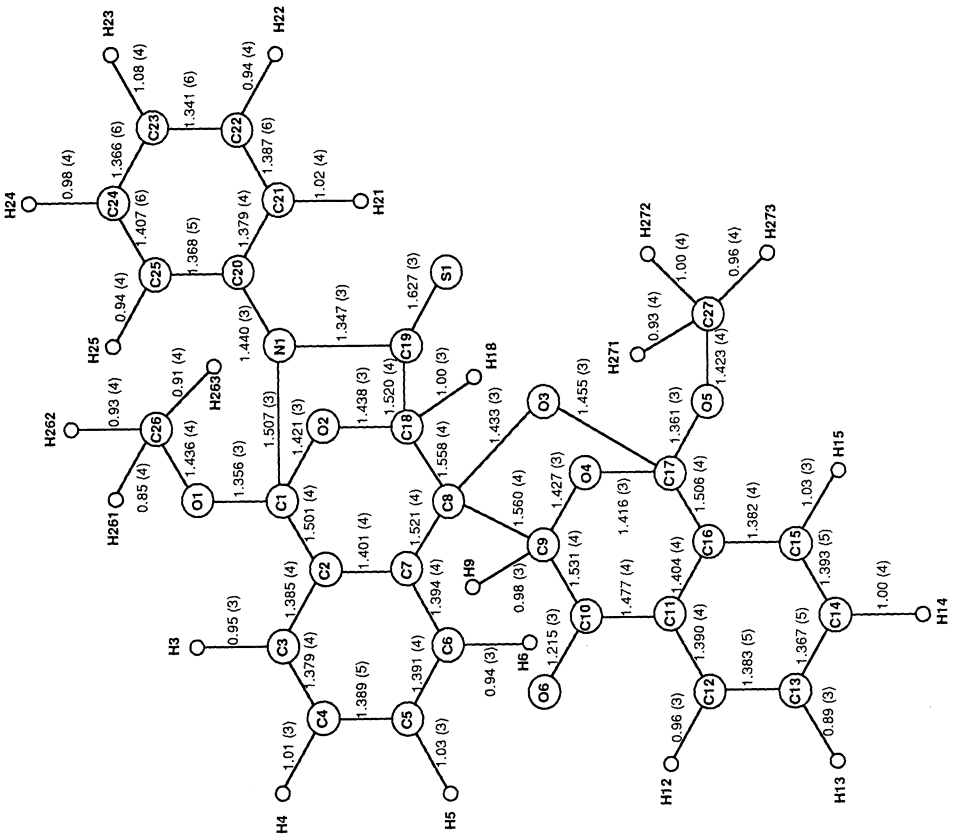


Fig. 6. Bond angles of the 2 : 1-adduct **9Bc**.

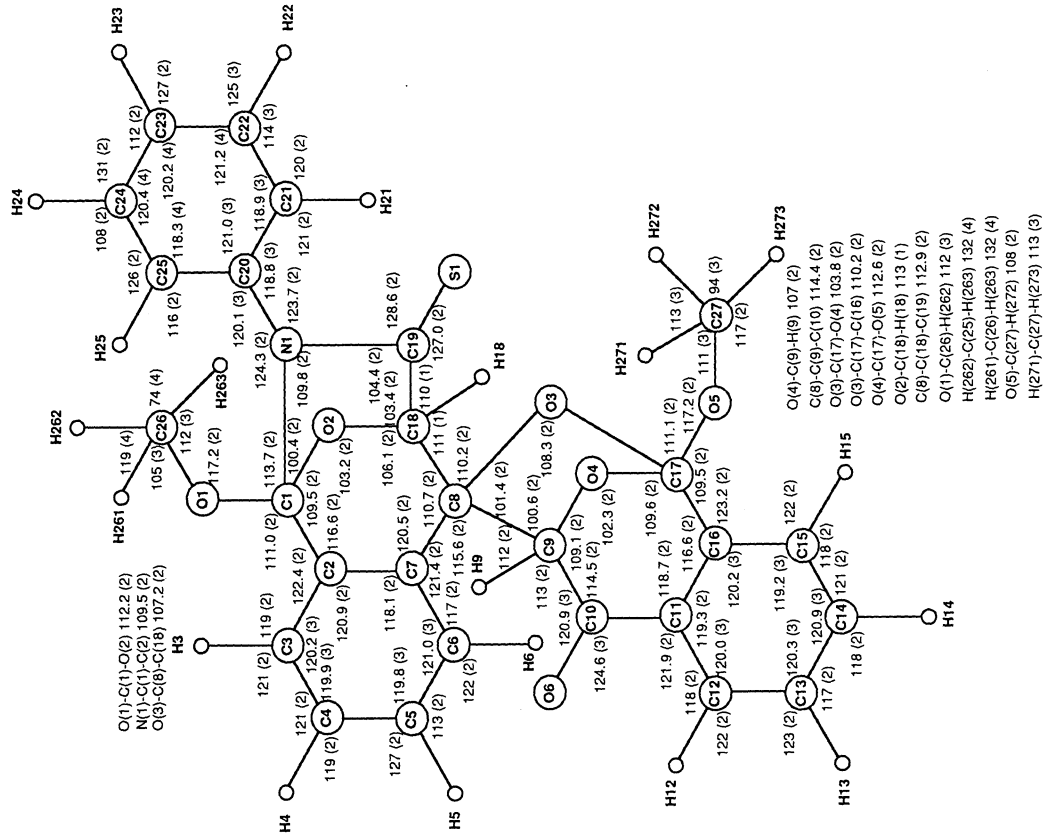


Fig. 5. Bond lengths of the 2 : 1-adduct **9Bc**.

Table 3. Atomic Coordinates and Thermal Parameters of **9Bc**

Atom	x	y	z	B_{eq}
S(1)	0.31678(7)	0.02354(4)	0.93850(6)	4.26
O(1)	0.2475(2)	−0.2641(1)	1.0539(2)	3.67
O(2)	0.3669(1)	−0.1681(1)	1.1395(2)	3.23
O(3)	0.2999(1)	0.0364(1)	1.2351(1)	2.88
O(4)	0.4586(1)	0.0156(1)	1.3491(2)	3.31
O(5)	0.4147(2)	0.1456(1)	1.2819(2)	4.04
O(6)	0.3340(2)	−0.1181(1)	1.5285(2)	4.36
N(1)	0.2469(2)	−0.1256(1)	0.9866(1)	2.98
C(1)	0.2602(2)	−0.1855(1)	1.0891(2)	2.95
C(2)	0.1852(2)	−0.1639(1)	1.1776(2)	2.71
C(3)	0.0923(2)	−0.2071(2)	1.1860(2)	3.40
C(4)	0.0217(2)	−0.1811(2)	1.2621(3)	4.14
C(5)	0.0428(2)	−0.1104(2)	1.3287(3)	4.28
C(6)	0.1370(2)	−0.0678(2)	1.3219(2)	3.41
C(7)	0.2102(2)	−0.0941(1)	1.2472(2)	2.70
C(8)	0.3156(2)	−0.0499(1)	1.2430(2)	2.83
C(9)	0.3983(2)	−0.0571(2)	1.3582(2)	3.07
C(10)	0.3491(2)	−0.0556(2)	1.4758(2)	3.15
C(11)	0.3189(2)	0.0262(2)	1.5141(2)	3.21
C(12)	0.2778(3)	0.0389(2)	1.6216(2)	4.00
C(13)	0.2450(3)	0.1159(2)	1.6507(3)	4.50
C(14)	0.2517(3)	0.1795(2)	1.5737(3)	4.50
C(15)	0.2919(2)	0.1685(2)	1.4650(3)	3.91
C(16)	0.3277(2)	0.0923(2)	1.4368(2)	3.03
C(17)	0.3775(2)	0.0750(2)	1.3245(2)	3.09
C(18)	0.3715(2)	−0.0807(2)	1.1357(2)	2.94
C(19)	0.3095(2)	−0.0601(2)	1.0144(2)	3.07
C(20)	0.1597(2)	−0.1269(2)	0.8905(2)	3.21
C(21)	0.1801(3)	−0.1488(2)	0.7771(3)	4.96
C(22)	0.0969(3)	−0.1472(2)	0.6835(3)	6.33
C(23)	−0.0020(3)	−0.1250(2)	0.7018(4)	6.41
C(24)	−0.0226(3)	−0.1029(3)	0.8137(4)	7.37
C(25)	0.0601(3)	−0.1020(2)	0.9107(3)	5.58
C(26)	0.3183(2)	−0.2948(2)	0.9740(3)	5.28
C(27)	0.4788(3)	0.1393(2)	1.1870(3)	5.03

a) $B_{eq}=(4/3)\{a^2B_{11}+b^2B_{22}+c^2B_{33}+ac\cos\beta(B_{13}/2)\}$.

on an ACOS-S900 computer at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University using "The Universal Crystallographic Computing Systeim-Osaka." Table 3 lists the final atomic coordinates and thermal parameters with their estimated standard deviations. Lists of structure factors, anisotropic thermal parameters, H-atom parameters and best planes is deposited as Document No. 8994 at the Office of the Editor of Bull. Chem. Soc. Jpn. The bond distances and angles are given in Figs. 5 and 6.

Molecular Structure of 9Bc. The results of the X-ray structure analysis indicate that **9Bc** has a structure similar to the 2 : 1-adduct **5** between **2** and aryl isocyanate,[6] and that the structure is consistent with the NMR-data. The CPK-model inspection shows that the approach of **2** to the carbonyl group of the 1 : 1-adduct **8A** to give **9Bc** is stereochemically the most favorable one.

The X-ray study indicates that the aromatic proton **Ha** locates close to the benzene ring **A**: the perpendicular drawn from **Ha** to the plane of benzene ring **A** has a length 2.55 Å, and the distance from the foot of the perpendicular to the center of ring **A** is 1.87 Å. The

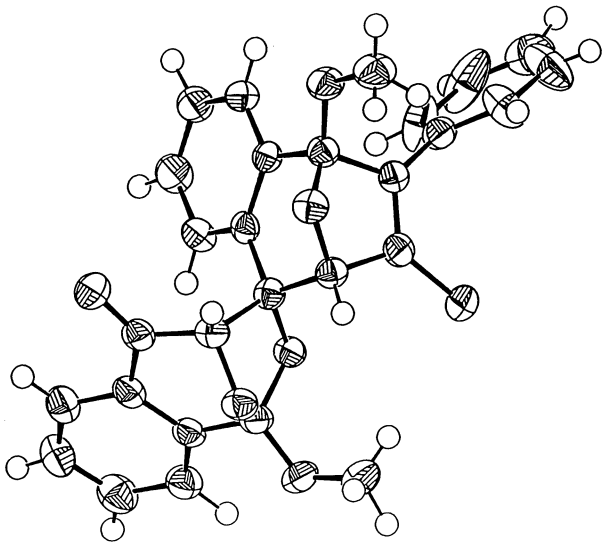


Fig. 7. ORTEP drawing of the 2 : 1-adduct **9Bc**.

estimated value of the high field shift of the **Ha** according to the Johnson–Bovey's ring current effect is 0.84 ppm.[9] This may explain the signal of **Ha** at δ=6.35—6.37.

Experimental

All melting points were measured on a Yanagimoto Melting Point Apparatus and were not corrected. The IR spectra were taken on a Perkin–Elmer, model 983 in KBr mull. The ^{1}H and ^{13}C NMR spectra were recorded with JEOL GSX-400 (400 MHz), GX-500 (500 MHz) and Bruker AM-360 (360 MHz) Spectrometers in a $CDCl_3$ solution using TMS as an internal standard. A Varian EM-390 Spectrometer was also used for ^{1}H NMR measurements.

Materials. Methyl 2-diazoacetylbenzoate (**1**) was prepared by the procedure described in the previous paper.[2]

Phenyl isothiocyanate and methyl isothiocyanate were purified just before use by distillation of the commercial reagents. Other aryl isothiocyanates were prepared by the reaction of ethyl chloroformate with triethylammonium aryldithiocarbamate formed by the reaction of arylamine, carbon disulfide and triethylamine.[12] *p*-ClC_6H_4NCS: 53% yield, mp 46.0—47.8 °C; *p*-$CH_3C_6H_4NCS$: 70% yield, bp 125 °C/20 Torr (1 Torr=133.322 Pa); *p*-$CH_3OC_6H_4NCS$: 72%, bp 152 °C/18 Torr.

Benzene was purified by distillation after reflux for a few days over CaH_2 and stored over molecular sieves 4A.

General Procedure of the Decomposition of 1 in the Presence of Isothiocyanates. The $Cu(acac)_2$-catalyzed decomposition of **1** was carried out according to the procedure described in the previous paper.[3-5] A benzene solution of **1** was added dropwise into a benzene solution of two molar equivalents of isothiocyanates and catalytic amount of $Cu(acac)_2$ under reflux at 80 °C. The reaction mixture was heated until no more N_2 was evolved (about one hour) and then separated by medium pressure preparative silica gel column chromatography using benzene–hexane as an eluent.

Catalytic decomposition of **1** (3.0 mmol) in the presence of *p*-methoxyphenyl isothiocyanate (6.0 mmol) according to the general procedure gave 3 : 1- **11a** and 4 : 1-adduct **12a**.

3 : 1-Adduct **11a**: 19 mg (yield 3.0%); colorless crystals; mp 172.1—174.5 °C; IR (KBr) 1710 (C=O), 1603, 1510, 1456, 1403, 1290, 1252, 1219, 1166, 1110, 1056, 1036, 972, 934, 768, 745, 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.88—6.46 (m, 14H, ArH), 6.10—6.08 (m, 1H, ArH), 5.96—5.94 (m, 1H, ArH), 5.37 (s, 1H, CH), 5.32 (s, 1H, CH), 5.24 (s, 1H, CH), 4.06 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.74 (C=S), 190.68 (C=O), 159.73, 142.49, 137.26, 134.41, 133.72, 130.77, 130.16, 129.69, 129.29, 129.09, 128.87, 128.34, 128.01, 127.59, 125.95, 125.81, 123.34, 123.17, 121.95, 120.49, 119.99, 114.66, 114.39, 90.18 (CH), 88.53 (CH), 87.16 (CH), 81.47 (spiro C), 79.83 (spiro C), 55.32 (OCH_3), 51.46 (OCH_3), 51.46 (OCH_3), 51.27 (OCH_3), 50.33 (OCH_3).

4 : 1-Adduct **12a**: 32 mg (yield 4.9%), colorless solid; mp 181.5—183.4 °C; IR (KBr) 1710 (C=O), 1602, 1509, 1457, 1400, 1362, 1292, 1280, 1254, 1222, 1168, 1112, 1095, 1044, 1035, 969, 939, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.85—6.45 (m, 21H, ArH), 6.08—6.05 (m, 1H, ArH), 5.79—5.77 (m, 1H, ArH), 5.71—5.69 (m, 1H, ArH), 5.32 (s, 1H, CH), 5.23 (s, 1H, CH), 5.22 (s, 1H, CH), 5.19 (s, 1H, CH), 4.02 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.75 (C=S), 190.93 (C=O), 159.71, 142.68, 137.50, 136.66, 134.42, 133.51, 132.30, 130.99, 130.18, 129.79, 129.64, 129.07, 128.92, 128.68, 128.35, 128.04, 127.39, 125.82, 123.43, 122.73, 122.34, 121.75, 120.59, 120.00, 114.75, 114.37, 90.36 (CH), 88.57 (CH), 88.42 (CH), 86.92 (CH), 82.45 (spiro C), 81.50 (spiro C), 79.61 (spiro C), 55.31 (OCH_3), 51.37 (OCH_3), 51.28 (OCH_3), 50.57 (OCH_3), 50.02 (OCH_3); MS (FAB) $(M+2)^+$=869.

Catalytic decomposition of **1** (3.0 mmol) in the presence of *p*-methylphenyl isothiocyanate (6.0 mmol) gave 2 : 1- **9Bb**, 3 : 1- **11b**, and 4 : 1-adduct **12b**, and 5 : 1-adduct **13b**.

2 : 1-Adduct **9Bb**: 28 mg (yield 3.7%); colorless crystals; mp 199.1—200.7 °C; ^1H NMR ($CDCl_3$) δ=7.93—6.70 (m, 9H, ArH), 6.52—6.50 (m, 2H, ArH), 6.37—6.34 (m, 1H, ArH), 5.42 (s, 1H, CH), 5.34 (s, 1H, CH), 4.14 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ=195.36 (C=S), 190.72 (C=O), 142.47, 139.19, 134.78, 134.48, 132.81, 130.88, 130.15, 129.92, 129.44, 128.24, 127.51, 127.33, 126.03, 123.66, 122.85, 120.63, 114.66, 88.79 (C-H), 88.46 (C-H), 78,83 (spiro C), 51.79 (OCH_3), 51.56 (OCH_3), 21.23 (CH_3). Found: C, 66.81; H, 4.68; N, 2.70%. Calcd for $C_{28}H_{23}NO_6S$: C, 67.05; H, 4.62; N, 2.79%.

3 : 1-Adduct **11b**: 24 mg (yield 3.5%); colorless crystals; mp 208.0—209.2 °C (recrystallized from benzene-hexane); IR (KBr) 2954, 2854, 1710 (C=O), 1604, 1510, 1455, 1397, 1289, 1218, 1163, 1109, 1094, 1056, 1037, 973, 935, 889, 850, 766, 745, 730, 708, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.88—6.81 (m, 12H, ArH), 6.47—6.45 (m, 2H, ArH), 6.10—6.08 (m, 1H, ArH), 5.96—5.94 (m, 1H, ArH), 5.38 (s, 1H, CH), 5.32 (s, 1H, CH), 5.24 (s, 1H, CH), 4.07 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3); MS (*m*/*z*) 677 (2%, M^+), 645 (1%, M^+—S), 515 (1%), 499 (10%), 469 (2%), 454 (4%), 253 (2%), 339 (35%), 307 (3%), 278 (3%), 221 (4%), 177 (21%), 163 (100%), 133 (20%), 104 (17%), 77 (12%), 44 (31%). Found: C, 67.96; H, 4.84; N, 2.03%. Calcd for $C_{38}H_{31}NO_9S$: C, 67.34; H, 4.61; N, 2.07%.

4 : 1-Adduct **12b**: 34 mg (yield 5.3%); colorless crystals; mp 245.8—248.3 °C; IR (KBr) 2951, 2853, 1710, (C=O), 1603, 1509, 1455, 1394, 1311, 1292, 1259, 1221, 1165, 1117, 1093, 1045, 972, 938, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.85—6.72 (m, 15H, ArH), 6.45—6.43 (m, 2H, ArH), 6.08—6.06 (m, 1H, ArH), 5.79—5.77 (m, 1H, ArH), 5.71—5.69 (m, 1H, ArH), 5.32 (s, 1H, CH), 5.235 (s, 1H, CH), 5.230 (s, 1H, CH), 5.16 (s, 1H, CH), 4.00 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ=195.57 (C=S), 190.86 (C=O), 142.67, 139.06, 137.51, 136.66, 134.38, 133.56, 132.94, 132.30, 130.99, 130.18, 129.81, 129,63, 129.03, 128.93, 128.67, 128.34, 127.62, 127.38, 125.84, 123.42, 122.71, 122.34, 121.74, 120.59, 120.00, 119.75, 114.81, 90.43 (CH), 88.58 (CH), 88.44 (CH), 86.92 (CH), 82.44 (spiro C), 81.50 (spiro C), 79.62 (spiro C), 51.37 (OCH_3), 51.29 (OCH_3), 50.56 (OCH_3), 50.01 (OCH_3), 21.22 (CH_3). Found: C, 67.16; H, 4.68; N, 1.68%. Calcd for $C_{48}H_{37}NO_{12}S$: C, 67.68; H, 4.38; N, 1.64%.

5 : 1-Adduct **13b**: 11 mg (yield 1.8%); colorless crystals; ^1H NMR ($CDCl_3$) δ=7.83—6.91 (m, 18H, ArH), 6.45—6.43 (m, 2H, ArH), 6.07—6.05 (m, 1H, ArH), 5.79—5.77 (m, 1H, ArH), 5.71—5.69 (m, 1H, ArH), 5.55—5.53 (m, 1H, ArH), 5.292 (s, 1H, CH), 5.290 (s, 1H, CH), 5.22 (s, 1H, CH), 5.20 (s, 1H, CH), 5.14 (s, 1H, CH), 4.00 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3).

Catalytic decomposition of **1** (4.0 mmol) in the presence of phenyl isothiocyanate (6.0 mmol) gave 2 : 1- **9Bc**, 3 : 1- **11c**, and 4 : 1-adduct **12c**.

2 : 1-Adduct **9Bc**: 31 mg (yield 3.2%); pale yellow crystals; mp 209.3—211.5 °C (recrystallized from benzene-hexane); IR (KBr) 1710 (C=O), 1600, 1495, 1456, 1400, 1293, 1247, 1218, 1158, 1110, 1081, 1049, 976, 927, 765, 738, 669 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.94—7.71 (m, 3H, ArH), 7.60—7.55 (m, 1H, ArH), 7.36—7.25 (m, 3H, ArH), 7.11—6.99 (m, 3H, ArH), 6.66—6.64 (m, 2H, ArH), 6.37—6.35 (m, 1H, ArH), 5.43 (s, 1H, CH), 5.35 (s, 1H, CH), 4.14 (s, 1H, OCH_3), 3.78 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.34 (s, C=S), 190.72 (s, C=O), 142.43 (s), 135.53, 134.80, 134.43, 130.13, 129.96, 129.51, 129.18, 129.07, 128.88, 128.28, 127.75, 127.34, 126.06, 123.66, 122.81, 120.64, 114.75, 88.82 (dd, $^3J_{CH}$=2.4 Hz, CH), 88.46 (dd, $^3J_{CH}$=2.6 Hz, CH), 78.83 (s, spiro C), 51.79 (q, OCH_3), 51.59 (q, OCH_3). Found: C, 66.62; H, 4.39; N, 2.91%. Calcd for $C_{27}H_{21}NO_6S$: C, 66.52; H, 4.34; N, 2.87%.

3 : 1-Adduct **11c**: 36 mg (yield 4.1%); colorless solid; mp 235.3—237.6 °C; IR (KBr) 2953, 2923, 2853, 1710 (C=O), 1602, 1493, 1455, 1404, 1328, 1289, 1257, 1218, 1162, 1097, 1071, 1036, 1013, 973, 932, 904, 872, 848, 763, 743, 728, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.85—6.58 (m, 15H, ArH), 6.11—6.08 (m, 1H, ArH), 5.97—5.95 (m, 1H, ArH), 5.39 (s, 1H, CH), 5.32 (s, 1H, CH), 5.24 (s, 1H, CH), 4.07 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.55 (s, C=S), 190.68 (s, C=O), 142.49, 137.27, 135.69, 134.43, 133.76, 130.77, 130.19, 129.75, 129.32, 129.15, 129.01, 128.89, 128.35, 127.91, 127.65, 125.99, 125.83, 123.36, 123.19, 121.93, 120.52, 120.00, 114.8, 90.34 (dd, $^3J_{CH}$=2.3 Hz, CH), 88.54 (dd, $^3J_{CH}$=2.9 Hz, CH), 87.21 (dd, $^3J_{CH}$=3.5 Hz, CH), 81.48 (sdd, $^2J_{CH}$=2.9 Hz, $^2J_{CH}$=4.1 Hz, spiro C), 79.87 (sdd, $^2J_{CH}$=2.9 Hz, $^2J_{CH}$=4.7 Hz, spiro C), 51.47 (q, OCH_3), 51.33 (q, OCH_3), 50.34 (q, OCH_3); MS (*m*/*z*) 633 (0.55%), 499 (11%), 455 (3%), 339 (30%), 324 (6%), 177 (23%), 176 (24%), 163 (100%), 133 (21%), 104 (20%), 77 (19%). Found: C, 66.84; H, 4.64; N, 2.02%. Calcd for $C_{37}H_{29}NO_9S$: C, 66.96; H, 4.40; N, 2.21%.

4 : 1-Adduct **12c**: 53 mg (yield 6.4%); colorless crystals; mp 236.0—238.8 °C; IR (KBr) 3010, 2953, 2851, 1711 (C=O), 1603, 1495, 1456, 1394, 1312, 1291, 1259, 1221, 1165, 1117, 1094, 1045, 1036, 970, 940, 902, 763, 735, 692 cm^{-1}; ^1H NMR ($CDCl_3$)

δ=7.86—6.39 (m, 18H, ArH), 6.08—6.06 (m, 1H, ArH), 5.80—5.77 (m, 1H, ArH), 5.71—5.69 (m, 1H, ArH), 5.33 (s, 1H, CH), 5.237 (s, 1H, CH), 5.230 (s, 1H, CH), 5.20 (s, 1H, CH), 4.02 (s, 3H, OCH_3), 3.70 (s 3H, OCH_3), 3.42 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.55 (s, C=S), 190.90 (s, C=O), 142.67, 137.49, 136.64, 135.69, 134.40, 133.53, 132.29, 130.98, 130.19, 129.83, 129.64, 129.09, 129.00, 128.69, 128.41, 128.35, 127.67, 122.41, 125.87, 125.82, 123.85, 122.72, 122.34, 121.72, 120.61, 120.00, 119.76, 114.93, 90.50 (dd, $^3J_{CH}$=2.9 Hz, CH), 88.57 (dd, $^3J_{CH}$=3.0 Hz, CH), 88.45 (ddd, $^3J_{CH}$=2.8 Hz, $^3J_{CH}$=2.5 Hz, CH), 86.92 (dt, $^3J_{CH}$=3.4 Hz, CH), 82.44 (st, $^2J_{CH}$=3.4 Hz, spiro C), 81.50 (sdd, $^2J_{CH}$=4.2 Hz, $^2J_{CH}$=3.8 Hz, spiro C), 79.63 (sdd, $^2J_{CH}$=5.0 Hz, $^2J_{CH}$=4.2 Hz, spiro C), 51.37 (q, OCH_3), 51.32 (q, OCH_3), 50.56 (q, OCH_3), 50.00 (q, OCH_3); MS (*m*/*z*) 839 (0.08%, M^++1), 675 (3%), 499 (7%), 455 (10%), 422 (4%), 396 (5%), 339 (14%), 176 (16%), 163 (100%), 133 (15%), 104 (11%), 77 (14%); MS (FAB) $(M+1)^+$=839. Found: C, 67.42; H, 4.05; N, 1.35%. Calcd for $C_{47}H_{36}NO_{12}S$: C, 67.30; H, 4.33; N, 1.67%.

Catalytic decomposition of **1** (3.0 mmol) in the presence of *p*-chlorophenyl isothiocyanate (6.0 mmol) gave 2 : 1- **9Bd**, 4 : 1- **12d**, and 5 : 1-adduct **13d**.

2 : 1-Adduct **9Bd**: 88 mg (yield 11.2%); colorless crystals; mp 193.5—194.1 °C (recrystallized from benzene–hexane); IR (KBr) 2953, 2851, 1709 (C=O), 1601, 1491, 1456, 1391, 1329, 1291, 1246, 1217, 1159, 1111, 1081, 1049, 1037, 1026, 1014, 976, 956, 930, 916, 891, 874, 843, 821, 784, 769, 748, 735, 710, 682, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.93—7.82 (m, 2H, ArH), 7.75—7.55 (m, 2H, ArH), 7.26—7.22 (m, 2H, ArH), 7.11—6.98 (m, 3H, ArH), 6.62—6.58 (m, 2H, ArH), 6.36—6.34 (m, 1H, ArH), 5.42 (s, 1H, CH), 5.33 (s, 1H, CH), 4.13 (s, 1H, OCH_3), 3.76 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.53 (s, C=S), 190.61 (s, C=O), 142.35 (s), 134.99 (s), 130.08 (s), 129.99 (d), 129.63 (d), 129.51 (d, *p*-ClAr), 129.08 (d, *p*-ClAr), 128.86 (s), 128.38 (d), 127.41 (d), 126.04 (d), 123.65 (d), 122.69 (d), 120.66 (s), 114.76 (s), 88.87 (dd, $^3J_{CH}$=3.0 Hz, CH), 88.09 (d, $^3J_{CH}$=0 Hz, CH), 78.76 (st, $^2J_{CH}$=1.65 Hz, spiro C), 51.75 (q, OCH_3), 51.67 (q, OCH_3); MS (*m*/*z*) 521 (5.4%, M^+), 489 (5%), 457 (3.6%), 425 (13%), 339 (36%), 177 (13%), 176 (17%), 163 (100%), 147 (10%), 133 (14%), 75 (10%). Found: C, 62.13; H, 3.86; N, 2.72%. Calcd for $C_{27}H_{20}NO_6SCl$: C, 62.13; H, 3.86; N, 2.68%.

4 : 1-Adduct **12d**: 90 mg (yield 13.7%); colorless crystals; mp 227.0—229.3 °C; IR (KBr) 3071, 3001, 2953, 2853, 1710 (C=O), 1603, 1491, 1456, 1384, 1311, 1292, 1260, 1221, 1165, 1117, 1094, 1045, 1016, 971, 939, 889, 873, 852, 808, 763, 749, 721, 708, 694, 679, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.86—7.83 (m, 1H, ArH), 7.62—7.45 (m, 4H, ArH), 7.28—7.15 (m, 5H, ArH), 7.02—6.73 (5H, ArH), 6.55—6.51 (m, 2H, Cl-ArH), 6.07 (dd, *J*=7.9 Hz, *J*=0.7 Hz, 1H, ArH),5.78 (dd, *J*=8.1 Hz, *J*=0.7 Hz, 1H, ArH), 5.71 (dd, *J*=7.9 Hz, *J*=0.7 Hz, 1H, ArH), 5.32 (s, 1H, CH), 5.231 (s, 1H, CH), 5.227 (s, 1H, CH), 5.19 (s, 1H, CH), 4.01 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.80 (s, C=S), 190.86 (s, C=O), 142.64 (s), 137.43 (s), 136.55 (s), 134.89 (s), 134.41 (s), 134.13 (s), 133.21 (s), 132.23 (s), 130.96 (s), 130.18 (s), 130.15 (s), 129.88 (d), 129.65 (d), 129.43 (d), 129.20 (d), 129.12 (d), 129.07 (d), 128.75 (d), 128.70 (d), 128.39 (d), 128.35 (d), 127.53 (d), 125.87 (d), 125.83 (d), 123.43 (d), 122.73 (d), 122.32 (d), 121.61 (d), 120.63 (s), 120.00 (s), 119.77 (s), 114.94 (s), 90.51 (dd, $^3J_{CH}$=2.9 Hz, CH), 88.56 (dd, $^3J_{CH}$=3.3 Hz, CH), 88.39 (dd, $^3J_{CH}$=2.9 Hz, CH), 86.90 (dd, $^3J_{CH}$=2.9 Hz, CH), 82.39 (s, spiro C), 81.47 (s, spiro C), 79.57 (s, spiro C), 79.57 (s, spiro C), 51.35 (q, 2×OCH_3), 50.54 (q, OCH_3), 49.96 (q, OCH_3). Found: C, 64.71; H, 4.15; N, 1.63%. Calcd for $C_{47}H_{36}O_{12}NSCl$: C, 64.57; H, 4.15; N, 1.60%.

5 : 1-Adduct **13d**: 59 mg (yield 9.4%); colorless crystals; mp 252.0—253.6 °C; MS (FAB) $(M+1)^+$ =1050; IR (KBr) 2954, 2853, 1711 (C=O), 1631; 1492, 1455, 1394, 1314, 1291, 1222, 1166, 1094, 1047, 1035, 971, 942, 874, 763, 721, 685 cm^{-1} ^1H NMR ($CDCl_3$) δ=7.85—6.51 (m, 20H, ArH), 6.06—6.04 (m, 1H, ArH), 5.77—5.75 (m, 1H, ArH), 5.70—5.68 (m, 1H, ArH), 5.53—5.51 (m, 1H, ArH), 5.29 (s, 1H, CH), 5.24 (s, 1H, CH), 5.23 (s, 1H, CH), 5.14 (s, 1H, CH), 5.11 (s, 1H, CH), 3.98 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3). Found: C, 65.25; H, 4.40; N, 1.42%. Calcd for $C_{57}H_{44}NO_{15}SCl$: C, 65.17; H, 4.22; N, 1.33%.

Catalytic decomposition of **1** (3.0 mmol) in the presence of *p*-nitrophenyl isothiocyanate (6.0 mmol) according to the procedure described above gave two types of 2 : 1-adducts **9Be** and **10e** together with a 3 : 1-adduct **11e**.

2 : 1-Adduct **9Be**: 160 mg (yield 20.0%); yellow crystals; mp 169.4—170.1 °C (recrystallized from benzene–hexane); IR (KBr) 1709 (C=O), 1601, 1525 (N=O), 1346 (N=O), 1292, 1247, 1217, 1050, 1013, 974, 929, 844, 770, 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.14—6.83 (m, 11H, ArH), 6.44—6.26 (m, 1H, ArH), 5.40 (s, 1H, CH), 5.29 (s, 1H, CH), 4.10 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=195.55 (s, C=S), 190.50 (s, C=O), 147.27 (s), 142.21 (s), 141.28 (s), 134.96 (d), 133.88 (s), 130.10 (d), 129.99 (d), 129.93 (d), 128.87 (s), 128.60 (d), 123.65 (d), 122.42 (d), 120.72 (s), 115.14 (s), 89.08 (dd, $^3J_{CH}$=2.4 Hz, CH), 88.33 (dd, $^3J_{CH}$=2.8 Hz, CH), 78.74 (s, spiro C), 51.85 (q, OCH_3), 51.71 (q, OCH_3); MS (*m*/*z*) 532 (6%, M^+), 500 (2%, M^+−S), 356 (13%), 339 (20%), 323 (10%), 309 (7%), 296 (6%), 189 (6%), 176 (26%), 163 (100%), 149 (9%), 133 (27%), 104 (29%), 77 (14%), 76 (17%).

2 : 1-Adduct **10e**: 45 mg (yield 5.6%); yellow crystals; mp 169.2—170.0 °C (recrystallized from benzene–hexane); IR (KBr) 1702 (C=O), 1598, 1514 (N=O), 1502, 1457, 1349 (N=O), 1290, 1269, 1236, 1205, 1152, 1098, 1083, 1050, 1038, 986, 957, 854, 762, 739, 703, 656 cm^{-1}; ^1H NMR ($CDCl_3$) δ=8.08—7.34 (m, 10H, ArH), 6.79—6.75 (m, 2H, ArH), 5.15 (s, 1H, CH), 4.98 (s, 1H, CH), 3.94 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ=189.58 (s, C=O), 189.33 (s, C=O), 146.44 (s), 144.80 (s), 143.19 (s), 141.96 (s), 135.30 (d), 134.03 (d), 129.68 (d), 129.22 (d), 128.16 (s), 127.54 (s), 127.49 (d), 126.70 (d), 124.77 (d), 124.44 (d), 123.38 (d), 121.21 (d), 117.76 (s), 122.22 (s), 88.86 (dd, $^3J_{CH}$=2.6 Hz, CH), 88.13 (dd, $^3J_{CH}$=3.3 Hz, CH), 79.92 (st, $^2J_{CH}$=1.7 Hz, spiro C), 53.38 (q, OCH_3), 50.57 (q, OCH_3); MS (*m*/*z*) 532, (0.75%, M^+), 356 (16%), 339 (4%), 324 (8%), 309 (4%), 176 (54%), 163 (100%), 133 (25%), 104 (20%), 77 (18%). Found: C, 60.97; H, 3.87; N, 5.22%. Calcd for $C_{27}H_{20}N_2O_8S$: C, 60.90; H, 3.79; 5.26%.

3 : 1-Adduct **11e**: 90 mg (yield 12.7%); yellow crystals; mp 182.5—185.8 °C (recrystallized from benzene–hexane); IR (KBr) 1709 (C=O), 1602, 1524, (N=O), 1455, 1383, 1345, (N=O), 1291, 1258, 1218, 1162, 1056, 1036, 971, 934, 767; ^1H NMR ($CDCl_3$) δ=8.14—6.83 (m, 14H, ArH), 6.11—6.08 (m, 1H, ArH), 5.97 —5.95 (m, 1H, ArH), 5.40 (s, 1H, CH), 5.31 (s, 1H, CH), 5.23 (s, 1H, CH), 4.05 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.14 (s, 3H, OCH_3);^{13}C NMR ($CDCl_3$) δ=195.80 (s, C=S), 190.56 (s, C=O), 147.28 (s), 142.33 (s), 141.50 (s), 137.05 (s), 134.50 (d), 133.21 (s), 130.63 (s), 130.16 (s), 130.13 (s), 129.96 (d), 129.81 (d), 129.55 (d), 129.43 (d), 129.01 (d), 128.34 (d),

127.96 (d), 125.99 (d), 125.83 (d), 124.47 (d), 123.33 (d), 123.16 (d), 121.51 (d), 120.62 (s), 120.02 (s), 115.26 (s), 90.56 (dd, $^3J_{CH}$=2.9 Hz, CH), 88.46 (dd, $^3J_{CH}$=2.9 Hz, CH), 87.13 (dd, $^3J_{CH}$=2.9 Hz, CH), 81.37 (s, spiro C), 79.79 (s, spiro C), 51.54 (q, OCH_3), 51.42 (q, OCH_3), 50.21 (q, OCH_3); MS (FD) (M^+)=708.

Catalytic decomposition of **1** (3.0 mmol) in the presence of methyl isothiocyanate (6.0 mmol) according to the general procedure gave 2 : 1- **9Bf** and 3 : 1-adduct **11f**.

2 : 1-Adduct **9Bf**: 10 mg (yield 1.6%); colorless crystals; mp 213.5—216.0°C (recrystallized from benzene–hexane); IR (KBr) 2955, 2923, 2853, 1709 (C=O), 1600, 1482, 1388, 1323, 1289, 1243, 1159, 1107, 1080, 1046, 1028, 978, 929, 883, 840, 787, 767, 741, 712, 669, 653 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.91 (dt, J=7.7 Hz, J=0.6 Hz, 1H, ArH), 7.80 (dd, J=7.7 Hz, J=0.6 Hz, 1H, ArH), 7.69 (td, J=7.7 Hz, J=1.3 Hz, ArH), 7.54 (td, J=7.7 Hz, J=1.1 Hz, 1H, ArH), 7.35 (dd, J=7.7 Hz, J=1.3 Hz, 1H, ArH), 7.18 (td, J=7.7 Hz, J=1.1 Hz, 1H, ArH), 6.96 (td, J=7.7 Hz, J=1.3 Hz, 1H, ArH), 6.26 (dd, J=7.7 Hz, J=0.6 Hz, 1H, ArH), 5.31 (s, 1H, CH), 5.26 (s, 1H, CH), 4.12 (s, 3H, OCH_3), 3.16 (s, 3H, OCH_3), 2.81 (s, 3H, NCH_3); ^{13}C NMR ($CDCl_3$) δ=193.26 (sdq, $^2J_{CH}$=3.7 Hz, $^3J_{CH}$=1.8 Hz, C=S), 190.70 (st, $^2J_{CH}$=$^3J_{CH}$=3.7 Hz, C=O), 142.49 (s, ArC), 134.73 (d, ArCH), 133.61 (s, ArC), 130.16 (s, ArC), 129.89 (d, ArCH), 129.45 (d, ArCH), 128.95 (s, ArC), 128.48 (d, ArCH), 127.78 (d, ArCH), 125.99 (d, ArCH), 123.59 (d, ArCH), 121.65 (d, ArCH), 120.53 (s, C), 113.09 (s, C), 88.49 (dd, $^3J_{CH}$=2.5 Hz, CH), 88.39 (dd, $^3J_{CH}$=2.8 Hz, CH), 78.44 (s, spiro C), 51.68 (q, OCH_3), 50.95 (q, OCH_3), 28.63 (q, NCH_3); MS (m/z) 425 (20%, M^+), 323 (12%), 262 (12%), 189 (45%), 176 (48%), 163 (100%), 133 (25%), 77 (13%). Found: C, 62.11; H, 4.85; N, 3.09%. Calcd for $C_{22}H_{19}NO_6S$: C, 62.72; H, 4.50; N, 3.29%.

3 : 1-Adduct **11f**: 6 mg (yield 1.0%); IR (KBr) 2953, 2853, 1708 (C=O), 1602, 1460, 1387, 1288, 1258, 1230, 1161, 1110, 1092, 1072, 1054, 1038, 974, 936, 882, 848, 819, 765, 745, 734, 702, 678, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.87—6.77 (m, 10H, ArH), 6.08 (d, J=7.8 Hz, 1H, ArH), 5.88 (d, J=8.0 Hz, 1H, ArH), 5.28 (s, 1H, CH), 5.26 (s, 1H, CH), 5.16 (s, 1H, CH), 4.05 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 2.78 (s, 3H, NCH_3); ^{13}C NMR ($CDCl_3$) δ=193.31 (sd, $^2J_{CH}$=3.7 Hz, $^3J_{CH}$=1.8 Hz, C=S), 190.66 (st, $^2J_{CH}$=$^3J_{CH}$=3.5 Hz, C=O), 142.53 (s, ArC), 137.31 (s, ArC), 134.40 (d, ArCH), 132.87 (s, ArC), 130.80 (s, ArC), 130.27 (s, ArC), 130.25 (d, ArCH), 130.23 (s, ArC), 129.72 (d, ArCH), 129.24 (d, ArCH), 129.11 (d, ArCH), 128.84 (d, ArCH), 127.87 (d, ArCH), 125.96 (d, ArCH), 125.80 (d, ArCH), 123.35 (d, ArCH), 123.14 (d, ArCH), 120.68 (d, ArCH), 120.41 (s, C), 119.99 (s, C), 113.17 (s, C), 89.99 (dd, $^3J_{CH}$=2.8 Hz, CH), 88.56 (dd, $^3J_{CH}$=2.8 Hz, CH), 87.14 (dd, $^3J_{CH}$=2.8 Hz, CH), 81.46 (s, spiro C), 79.74 (std, $^2J_{CH}$=3.4 Hz, $^3J_{CH}$=1.2 Hz, spiro C), 51.68 (q, OCH_3), 50.81 (q, OCH_3), 50.37 (q, OCH_3), 28.58 (q, NCH_3).

References

1) a) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **16**, 572 (1977); b) M. Hamaguchi and T. Ibata, *Tetrahedron Lett.*, **1974**, 4475; c) M. Békhazi and J. Werkentin, *J. Am. Chem. Soc.*, **105**, 1289 (1983); d) A. Padwa, S. P. Carter, H. Nimmesgerm, and P. D. Stull, *J. Am. Chem. Soc.*, **110**, 2894 (1988), and references cited therein.

2) K. Ueda, T. Ibata, and M. Takebayashi, *Bull. Chem. Soc. Jpn.*, **45**, 2779 (1972).

3) T. Ibata, K. Jitsuhiro, and Y. Tsubokura, *Bull. Chem. Soc. Jpn.*, **54**, 240 (1981).

4) T. Ibata and K. Jitsuhito, *Bull. Chem. Soc. Jpn.*, **52**, 3582 (1979).

5) a) T. Ibata and J. Toyoda, *Chem. Lett.*, **1983**, 1453. b) T. Ibata and J. Toyoda, *Bull. Chem. Soc. Jpn.*, **58**, 1787 (1985).

6) T. Ibata, J. Toyoda, M. Sawada, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1986**, 1267.

7) T. Ibata and H. Nakano, *Chem. Express*, **1989**, 93; T. Ibata and H. Nakano, *Bull. Chem. Soc. Jpn.*, **64**, 771 (1991).

8) T. Ibata and J. Toyoda, *Bull. Chem. Soc. Jpn.*, **59**, 2489 (1986).

9) J. Toyoda, T. Ibata, H. Tamura, K. Ogawa, T. Nishino, and M. Takebayashi, *Bull. Chem. Soc. Jpn.*, **58**, 2212 (1985).

10) P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J-P. Declercq, and M. M. Woolfson, "MULTAN 80. A System of Computer Programs for Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univs. of York, England and Louvain, Belgium (1980).

11) C. E. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

12) S. R. Sandler and W. Karo. "Organic Functional Group Preparation," Academic Press, New York (1968), Vol.1, p. 313.