Photochemistry of Heterocyclic Compounds. VII.[1] Photochemical Reaction of 2,5-Diphenyl-1,3,4-oxadiazole with Benzo[*b*]thiophenes

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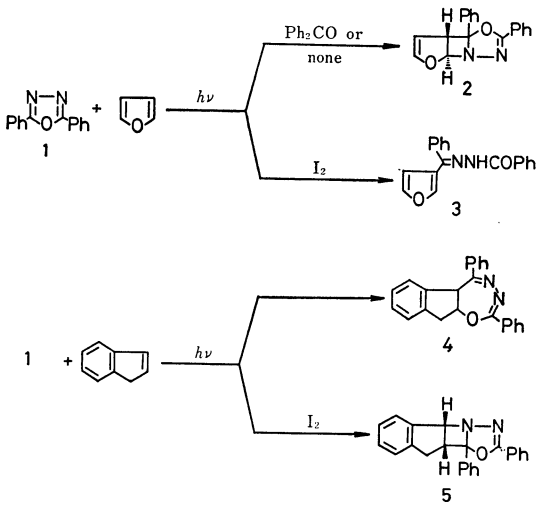
Irradiation of 2,5-diphenyloxadiazole **1** with benzothiophene **6a** gives 3-benzoylbenzothiophene **7**, its benzoylhydrazone **8**, and/or the oxadiazepine **9**; the yields depended on the nature of solvents. With benzophenone as a sensitizer, the photochemical reaction of **1** with **6a** forms the [2+2] cycloadduct **12**. It is found that **9** is photochemically dissociated to **1** and **6a**. In the case of 2-methylbenzothiophene **6b**, 3-benzoyl-2-methylbenzothiophene benzoylhydrazone **18** is formed, and with benzophenone as a sensitizer the [2+2] cycloadduct **19** is obtained. In the absence or presence of benzophenone, however, irradiation of **1** with 3-methylbenzothiophene **6c** gives the [2+2] cycloadduct **20**. The photochemical reaction of **1** with **6a** or **6b** in the presence of iodine gives the corresponding 3-benzoylbenzothiophene, **7** or **21**, and benzoylhydrazone, **8** or **18**, respectively. In the case of **6c**, however, the [2+2] cycloadduct **23** is formed, together with 2-benzoyl-3-methylbenzothiophene **22**. Mechanistic considerations of these reactions are also described.

Although [2+2] photocycloadditions of olefins to other olefins[2] and to ketones[3] are well characterized, only a few examples of similar photocycloadditions to the carbon-nitrogen double bonds appeared in the literature.[4-8] Previously, we reported some novel photoproducts from the photochemical reactions of 2,5-diphenyl-1,3,4-oxadiazole (**1**) with furan[4] and indene[5] in the absence or presence of iodine as depicted in Scheme 1. The [2+2] cycloadduct **2** is formed *via* the interation between a triplet excited state of **1** and furan, and the formation of the benzoylhydrazone **3** is attributable to the reaction of **1** with cyclobutadiene oxide (probably its iodine complex) produced from the photochemical interaction between furan and iodine. On the other hand, the reaction to afford the oxadiazepine **4** starts with a singlet excited state of indene, and the [2+2] cycloadduct **5** is produced *via* the photochemical reaction of **1** with σ-complex between indene and iodine.

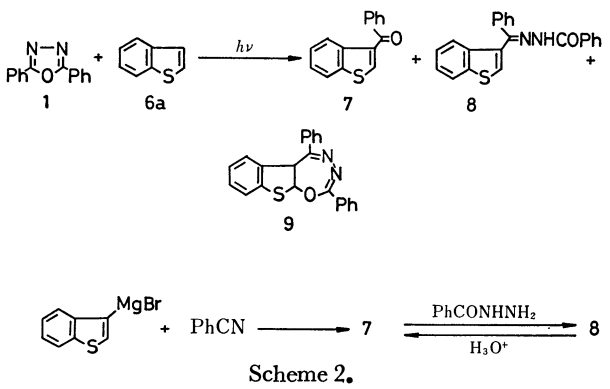


Scheme 1.

It has been reported that upon irradiation with olefins[9] and acetylenes[10] benzo[*b*]thiophene gave the cycloadducts. Thus we were interested in the photochemical reaction of **1** with benzo[*b*]thiophene. We now report here on the photochemical reactions of **1** with benzo[*b*]thiophene and its methyl derivatives under various conditions.

Results and Discussion

Photochemical Reaction in the Absence of Iodine. Irradiation of a solution of the oxadiazole **1** and benzo[*b*]thiophene (**6a**) in benzene below 15 °C afforded 3-benzoylbenzo[*b*]thiophene (**7**), its benzoylhydrazone **8**, and the 1:1 cycloadduct **9**. The results in various solvents are shown in Table 1; the yields of the products depended on the nature of solvent. Structural elucidation of **7** and **8** was accomplished on the basis of their spectral data as well as of identification with authentic samples prepared by the routes depicted in Scheme 2.



Scheme 2.

From the following evidence, the 1:1 adduct **9** was assigned to be 2,5-diphenyl-5a,10a-dihydro[1]benzothieno[3,2-*f*][1,3,4]oxadiazepine whose ring system is the same as that of **4**. The IR spectrum and chemical behavior of **9** are similar to those of the oxadiazepine **4**. The 1:1 adduct **9** is thermally labile and on being heated readily isomerized to the benzoylhydrazone **8** in benzene. Reduction of **9** with sodium borohydride afforded the dihydro compound whose structure was assigned to be 2,5-diphenyl-4,5,5a,10a-tetrahydro[1]-benzothieno[3,2-*f*][1,3,4]oxadiazepine (**10**), but not the 2,3,5a,10a-tetrahydro compound **10'**. The NMR spectrum of **10** exhibits methine proton signals at δ 4.67

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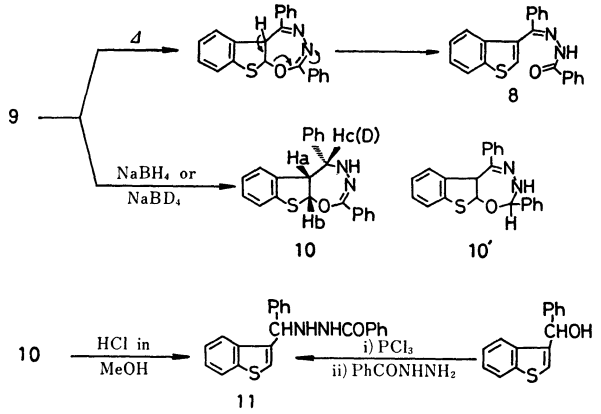
(H_a, t, J=8 Hz), 6.23 (H_b, d, J=8 Hz) and 6.32 (H_c, d, J=8 Hz), besides aromatic and NH proton signals. In the NMR spectrum of **10**-d_1 which was prepared by reduction of **9** with sodium borohydride-d_4, the doublet at δ 6.32 does not appear, and two doubles (J=8 Hz) are displayed at δ 4.67 and 6.25. On treatment with hydrochloric acid in methanol at room temperature, **10** was converted into 1-benzoyl-2-[α-(3-benzo[*b*]thienyl)-benzyl]hydrazine (**11**), which was identical with an authentic sample (Scheme 3).



Scheme 3.

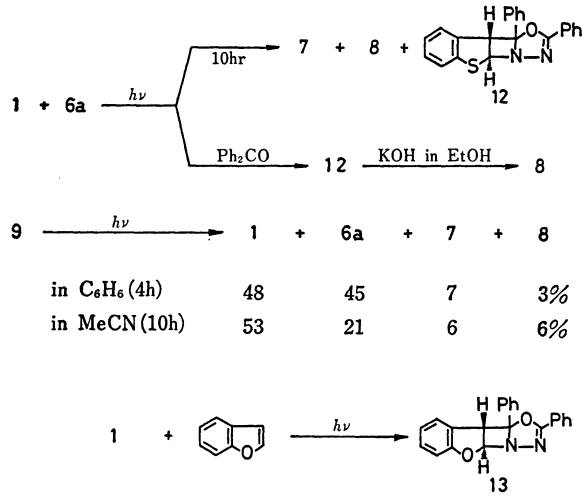
Previously,[5] we have reported that the oxadiazepine **4** is the *cis*-fused adduct, and that three methine hydrogens in the dihydro compound of **4** are situated *cis* each other. Although the NMR spectrum of **9** could not be measured owing to its insolubility in solvents and to its lability, it was deduced that **9** would be also the *cis*-fused adduct on the basis of stereochemistry of **10**. In analogy with the dihydro compound of **4**, we assumed that the moiety –N–N=C$\langle^{O}_{Ph}$ in the seven-membered cyclic ring of **10** is coplanar. An inspection of the Dreiding models of **10** indicates that the dihedral angles, θ_{ab} between H_a and H_b, and θ_{ac} between H_a and H_c, are *ca.* 25° respectively, when the hydrogens H_a, H_b, and H_c are situated *cis* each other. The observed J_{ab} and J_{ac} values are 8 Hz which is compatible with the calculated value (6.7 Hz) when θ is 25°.[11]

Table 1. Photochemical reaction of **1** with **6a** in various solvents

Solvent	Irradiation time, h	Products, %		
		7	**8**	**9**
Hexane	1	trace	—	69
Dioxane	1	6	—	21
Benzene	1	5	trace	24
Diethyl ether	1	2	—	47
Tetrahydrofuran	1	4	—	21
Acetonitrile	1	1	3	—
Acetonitrile	10	2	5	—

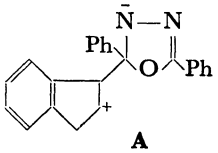
Irradiation of **1** with **6a** in benzene for 10 h did not give the oxadiazepine **9**, but instead a new 1 : 1 adduct **12** was obtained in 8% yield, together with small quantities of **7** and **8** and with recovery of **1** and **6a**. Photolysis of the oxadiazepine **9** in benzene or acetonitrile afforded the oxadiazole **1**, benzothiophene **6a**, benzoylbenzothiophene **7**, and 1 : 1 adduct **12** (Scheme 4). Thus, it can be concluded that the oxadiazepine **9** is photochemically dissociated to the starting materials **1** and **6a**, along with a partial isomerization to **8**. On treatment with ethanolic potassium hydroxide, the 1 : 1 adduct **12** isomerized to **8**. On the basis of the above fact and spectral data, **12** was assigned to be the *trans* [2+2] cycloadduct, 4,4a,9b,9c-tetrahydro-2,9c-diphenyl[1]benzothieno[3',2': 3,4]azetidino[2,1-*b*][1,3,4]oxadiazole.

In the benzophenone photosensitized reaction of **1** with **6a**, the [2+2] cycloadduct **12** was formed as the sole product. Both electronic absorption spectra of **1** and **6a** show absorptions around 310 nm, while that of benzo[*b*]furan displays no appreciable absorption above 290 nm. When a solution of **1** and benzo[*b*]-furan in benzene was irradiated with a high-pressure mercury lamp or with monochromatic light (313 nm), the *trans* [2+2] cycloadduct **13** was obtained. Thus, it may concluded that the reaction for the formation of **12** starts with a triplet excited state of **1**.



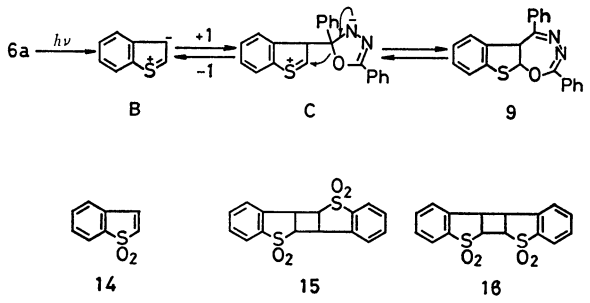
Scheme 4.

In a previous paper[5] we suggested that the reaction producing the oxadiazepine **4** starts with a singlet state of indene, and the subsequent interaction with **1** forms the betaine intermediate **A** which gives **4**. The plausible



A

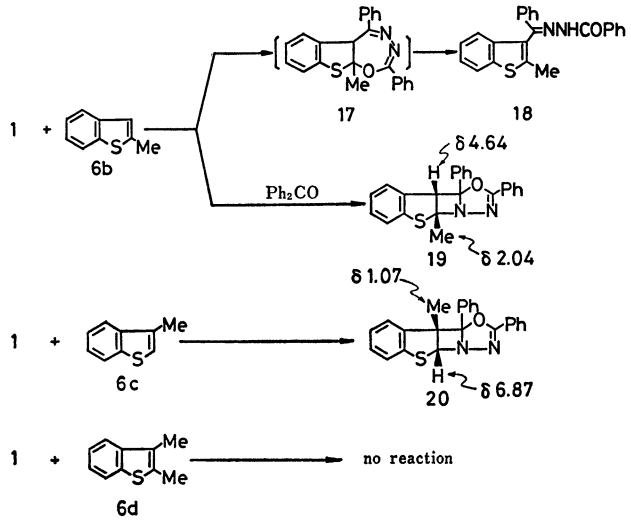
pathway for the formation of **9** is outlined in Scheme 5. By the absorption of light **6a** is excited to the polar species **B** proposed in the photochemical reaction of **6a**.[10] This is followed by interaction with **1** to give the betaine intermediate **C** like **A**, and subsequent ring opening of **C** with concurrent ring closure affords **9**.



Scheme 5.

The following result suggests a significant contribution of **B** to the formation of **9**. Benzo[*b*]thiophene 1,1-dioxide (**14**) cannot form an excited species such as **B**. The 1,1-dioxide **14** failed to add **1**, but instead underwent a cinnamic acid type dimerization to give a mixture of two isomeric dimers **15** and **16**.

Although the photochemical reaction of **1** with **6a** in acetonitrile did not give the oxadiazepine **9** (Table 1), irradiation in ethyl ether containing acetonitrile (5 mol to **6a**) afforded the oxadiazepine **9** in 38% yield; this fact indicates that acetonitrile does not act as an inhibitor for the formation of **9**. Thus it may be viewed that the primary photoadduct **9** is readily dissociated to the starting materials in a polar solvent such as acetonitrile.



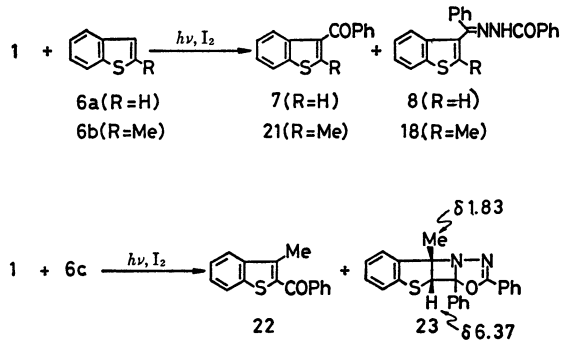
Scheme 6.

Next, we investigated the photochemical reaction between **1** and methylbenzo[*b*]thiophenes. Without or with benzophenone as the sensitize, irradiation of **1** with 2-methylbenzo[*b*]thiophene (**6b**) afforded 3-benzoyl-2-methylbenzo[*b*]thiophene benzoylhydrazone (**18**) or [2+2] cycloadduct **19**, respectively. The benzoylhydrazone **18** might be interpreted as arising *via* the oxadiazepine **17**, but no **17** was detected in the reaction mixture. On the other hand, the photochemical reaction of **1** with 3-methylbenzo[*b*]thiophene (**6c**) did not give the corresponding oxadiazepine nor benzoylhydrazone, but instead the [2+2] cycloadduct **20** was formed in 13% yield; this fact means that the polarized species of **6c** such as **B** does not contribute to the reaction, because of the electron-donating 3-methyl group. With benzophenone as the sesitizer, the [2+2] cycloadduct **20** was obtained in 33% yield. Upon irradiation, however, 2,3-dimethylbenzo[*b*]thiophene (**6d**) did not react with **1** (Scheme 6). Structures of the photoproducts, **18**—**20**, were established by the spectral data. The stereochemistry of **19** and **20** will be described later.

It is reasonable to conclude that the reactions producing the [2+2] cycloadducts **19** and **20**, as well as the [2+2] cycloadduct **12**, start with a triplet excited state of **1**.

Photochemical Reaction in the Presence of Iodine. Irradiation of **1** with **6a** or **6b** in the presence of iodine (20 mol % to **1**) in benzene afforded the corresponding 3-benzoylbenzothiophene **7** (16%) or **21** (1%), and benzoylhydrazone **8** (50%) or **18** (15%), respectively. These results appear to be similar to that of the reaction with furan in the presence of iodine (Scheme 1). In the reaction of **1** with **6c** under similar conditions, however, a new [2+2] cycloadduct **23** was obtained, together with 2-benzoyl-3-methylbenzo[*b*]thiophene (**22**) (Scheme 7). The benzoyl compounds **21** and **22** were identical with the respective authentic samples prepared from the Friedel-Crafts benzoylation of **6b** and **6c**.

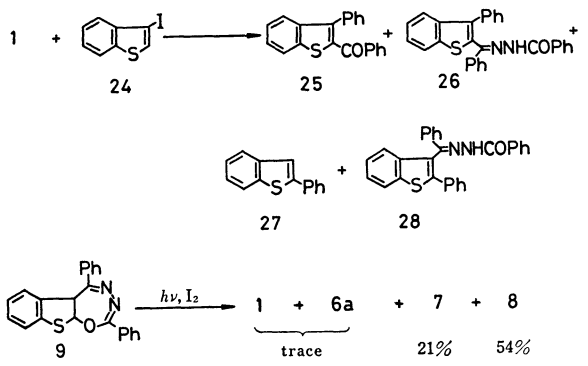
On the basis of the following spectral data, **23** was assigned to be 4,4a,9a,9b-tetrahydro-2,9b-diphenyl-4a-methyl[1]benzothieno[2',3': 3,4]azetidino[2,1-*b*][1,3,4]-oxadiazole, whose structure corresponds to the reversed adduct of **20**. The IR spectrum of **23** is very similar to that of **20**. The chemical shift of methine proton in **23** is comparable to that (δ 6.45) of the methine adjacent to the nitrogen atom in the [2+2] cycloadduct **5**, but not compatible with that in **20**. The methyl proton signal in **23** appears at a higher field than that in **19**, but at a lower field than that in **20**. The stereochemistry of **23** will be also described later.



Scheme 7

It is known that **6a** undergoes electrophilic substitution with bromine to yield 3-bromobenzo[*b*]thiophene.[12] Thus, we investigated the possibility of the formation of **8** from the photochemical reaction of **1** with 3-iodobenzo[*b*]thiophene (**24**). As shown in Scheme 8, irradiation of **1** with **24** in benzene gave 2-benzoyl-3-phenylbenzo[*b*]thiophene (**25**), its benzoylhydrazone **26**, 2-phenylbenzo[*b*]thiophene (**27**), and 3-benzoyl-2-phenylbenzo[*b*]thiophene (**28**); no **7** and **8** were formed. The benzoylhydrazone **26** may be interpreted as arising *via* interaction between **1** and 3-phenylbenzo[*b*]thiophene which formed from the pho-

tochemical reaction of **24** with the solvent (benzene). It has been reported that the treatment of 3-phenylbenzothiophene with iodine does not give the 2-isomer **27**,[13] but with hydrogen fluoride 3-phenyl derivative isomerizes to **27**.[14] The formation of **27** seems to be attributable to the isomerization of 3-phenyl derivative with hydrogen iodide generated *in situ*.



Scheme 8.

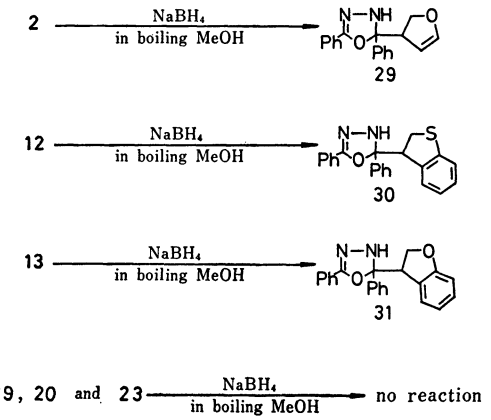
As mentioned above, the oxadiazepine **9** is photochemically dissociated to the starting materials. However, we found that iodine inhibited the photochemical dissociation of **9**. Irradiation of **9** in the presence of iodine afforded 3-benzoylbenzothiophene **7** and its benzoylhydrazone **8**, together with traces of **1** and **6a** (Scheme 8). It is noteworthy that the yields of **7** and **8** are almost equal to those in the direct irradiation of **1** with **6a** in the presence of iodine. In addition, upon irradiation of **9** in the presence of 2,5-di(*p*-tolyl)-1,3,4-oxadiazole **7** and **8** were formed in 18 and 50% yields respectively, but no 3-(*p*-toluoyl)benzothiophene and its *p*-toluoylhydrazone were formed. Thus, the formation of **8** in the direct irradiation of **1** with **6a** in the presence of iodine may be interpreted as arising *via* isomerization of the primary adduct **9** with iodine.[15]

The photochemical reaction of **1** with **6c** in the presence of iodine is comparable to that of **1** with indene producing the [2+2] cycloadduct **5**. Although mechanistic considerations are still speculative, a potential pathway for the formation of **23** is outlined in Scheme 9, which is similar to that previously proposed for the formation of **5**.[5] The photochemical reaction of **6c** with iodine yields the complex **E** *via* **D**. Subsequent interaction between **E** and **1** forms the intermediate **F**, which undergoes ring closure with loss of iodine to produce the [2+2] cycloadduct **23**.

*Stereochemistry of [2+2] Cycloadducts **19**, **20**, and **23**.* It is difficult to learn the stereochemistry of [2+2] cycloadducts **19**, **20**, and **23** from inspection of their NMR spectra. We have inadvertently found that the reduction of [2+2] cycloadducts with sodium borohydride can be used to distinguish between the *cis*- and *trans*-adducts.

Reduction of the *trans* [2+2] cycloadduct **2** with sodium borohydride in boiling methanol gave the corresponding dihydro compound, 2-(2,3-dihydro-3-furyl)-2,5-diphenyl-2,3-dihydro-1,3,4-oxadiazole (**29**).

Similarly, *trans* [2+2] cycloadducts, **12** and **13**, afforded the corresponding dihydro compounds, **30** and **31**, respectively. However, the *cis* [2+2] cycloadduct **5** remarkably resisted toward reduction under similar conditions; **5** was recovered quantitatively.



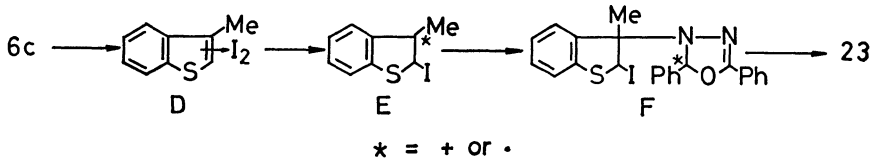
Scheme 10.

The above facts indicate that *trans* [2+2] cycloadducts, **2**, **12**, and **13**, are susceptible to reductive cleavage with sodium borohydride owing to their ring strain, and that this method can be used to diagnose the stereochemistry of [2+2] cycloadducts, **19**, **20**, and **23**. The cycloadducts, **19**, **20**, and **23**, as well as **5**, did not undergo reductive cleavage with sodium borohydride (Scheme 10). Thus, **19**, **20**, and **23** may be assigned to the corresponding *cis*-adducts respectively.

Experimental

All melting and boiling points are uncorrected. The IR spectra were measured in KBr disks, and NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet and an ionization energy of 70 eV. Unless otherwise stated, irradiations were performed with Pyrex-filtered light from a 300-W high-pressure mercury lamp (Taika HLV-B) below 15 °C in a nitrogen atmosphere. Irradiation with monochromatic light (313 nm) was performed with a 100-W high-pressure mercury lamp (Riko UVL-100P) utilizing the potassium biphthalate aqueous solution[16] as a filter.

*Photochemical Reaction of 2,5-Diphenyl-1,3,4-oxadiazole (**1**) with Benzo[b]thiophene (**6a**).* A solution of 1.11 g (5×10^{-3} mol) of **1** and 2.01 g (1.5×10^{-2} mol) of **6a**[17] in 250 ml of benzene was irradiated for 1 h. The solvent from the



Scheme 9.

mixture was removed *in vacuo* to afford a residue, which was triturated with 30 ml of diethyl ether giving pale yellow needles. Filtration gave 0.43 g (24%) of oxadiazepine **9**, mp 172—173 °C, which was subjected to microanalysis without further purification. IR 1607, 1560 cm^{-1} ($\nu_{C=N}$); mass spectrum *m/e* 356 (M^+), 253 (M^+-PhCN), 251 (M^+-PhCO), 236 ($M^+-PhCONH$), 223, 222, 221, 189, 121, 105, 77. Found: C, 73.88; H, 4.43; N, 7.70%. Calcd for $C_{22}H_{16}N_2OS$: C, 74.14; H, 4.53; N, 7.86%.

The ether filtrate was evaporated *in vacuo*, and the residue was chromatographed on alumina using hexane and benzene as eluents. From the hexane elution 1.76 g (88%) of **6a**, and from the hexane–benzene (1:1) elution 60 mg (5%) of 3-benzoylbenzo[*b*]thiophene (**7**) and traces of the benzoylhydrazone **8** were obtained respectively. The benzene elution gave 0.48 g (43%) of **1**.

7: yellow oil; IR (neat) 1645 cm^{-1} ($\nu_{C=O}$). This compound was identical with an authentic sample prepared by the reaction described below.

8: colorless needles, mp 172—173 °C; IR 3340 (ν_{NH}), 1640 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 7—8 (15H, m, aromatic protons), 9.05 (1H, br, N**H**); mass spectrum *m/e* 356 (M^+), 251 (M^+-PhCO), 236 ($M^+-PhCONH$), 233 ($PhO{\equiv}\overset{+}{N}NH-COPh$), 222, 221, 181, 121 ($[PhCO-NH_2]^+$), 105, 77. Found: C, 74.18; H, 4.36; N, 7.73%. Calcd for $C_{22}H_{16}N_2OS$: C, 74.14; H, 4.53; N, 7.86%. This compound was identical with an authentic sample prepared from **7** and benzoylhydrazine.

Similar photochemical reactions were carried out in various solvents, and the results are given in Table 1.

3-Benzoylbenzo[b]*thiophene (7).* A solution of 2.0 g of benzonitrile in 20 ml of diethyl ether was added to a solution of 3-benzo[*b*]thienylmagnesium bromide which was prepared *in situ* from 3-bromobenzo[*b*]thiophene[12] (3.3 g) and metallic magnesium (0.55 g) in 20 ml of diethyl ether, at 0 °C. The reaction mixture was stirred at room temperature for 1 h, and then refluxed for 30 min. After the mixture was stirred with 1 ml of concd hydrochloric acid, the ether layer was evaporated *in vacuo*, and the residue was chromatographed on alumina using benzene as an eluent to give 0.4 g (11%) of **7**.

Isomerization of Oxadiazepine 9. A suspension of 0.3 g of **9** in 30 ml of benzene was refluxed for 3 h. The solvent from the mixture was removed *in vacuo*, and the residue was triturated with small amounts of diethyl ether to give 0.29 g (97%) of benzoylhydrazone **8**.

Reduction of Oxadiazepine 9 with Sodium Borohydride. A suspension of 0.2 g of **9** in 40 ml of methanol was stirred with 0.1 g of sodium borohydride at room temperature for 1 h. The reaction mixture was poured into 100 ml of water, giving 0.2 g (*ca.* 100%) of crystals. Recrystallization from methanol afforded the dihydro compound **10**, mp 187—188 °C, as colorless needles. IR 3320 (ν_{NH}), 1650 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 4.67 (1H, t, >C**H**, J=8 Hz), 6.23, 6.32 (each 1H, d, >C**H**, J=8 Hz), 6.5—7.8 (14H, m, aromatic protons), 8.0 (1H, br, N**H**); mass spectrum *m/e* 358 (M^+), 356 (M^+-H_2), 224 ($[PhCH{=}NNHCOPh]^+$), 223, 147 (224—Ph), 134, 121 ($[PhCONH_2]^+$), 105, 91, 89, 77. Found: C, 73.75; H, 4.86; N, 7.80%. Calcd for $C_{22}H_{18}N_2OS$: C, 73.77; H, 5.06; N, 7.82%.

Similarly, reduction of **9** with sodium borohydride-d_4 in methanol-d_1, and recrystallization of the product from methanol afforded the dihydro compound **10**-d_1, mp 184—185 °C, as colorless needles. NMR ($CDCl_3$) δ 4.67, 6.25 (each 1H, d, >C**H**, J=8 Hz), 6.5—7.8 (14H, m, aromatic protons), 8.1 (1H, br, N**H**); mass spectrum *m/e* 359 (M^+), 358, 357 (M^+-H_2), 356, 225 ($[PhCD{=}NNHCOPh]^+$), 224, 148 (225^+-Ph), 134, 121, 105, 92, 90.

1-Benzoyl-2-[α-(3-benzo[b]*thienyl)benzyl]hydrazine (11).*

i) A solution of 1.35 g of **10** in 20 ml of methanol was stirred with 2 ml of concd hydrochloric acid at room temperature for 10 h. The reaction mixture was evaporated *in vacuo*, and the residue was triturated with 20 ml of diethyl ether, giving 0.95 g (70%) of crystals. Recrystallization from methanol afforded the hydrazine **11**, mp 165—166 °C, as colorless prisms. IR 3300, 3240 (ν_{NH}), 1650 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 4.74, 8.0 (each 1H, br, N**H**), 5.75 (1H, s, >C**H**), 7.0—8.0 (15H, m, aromatic protons); mass spectrum *m/e* 358 (M^+), 237 ($M^+-PhCONH_2$), 208 ($[PhCH{=}N{-}N{=}CH-Ph]^+$), 189, 178, 134, 121, 105, 91, 89, 77. Found: C, 73.60; H, 4.87; N, 7.87%. Calcd for $C_{22}H_{18}N_2OS$: C, 73.77; H, 5.06; N, 7.82%.

A similar treatment of the dihydro compound **10**-d_1 afforded the hydrazine **11**-d_1, mp 164—166 °C, in 80% yield. NMR ($CDCl_3$) δ 4.74, 8.0 (each 1H, br, N**H**), 7.0—8.0 (15H, m, aromatic protons); mass spectrum *m/e* 359 (M^+), 237, 236, 225, 224, 209, 190, 180, 178, 148, 134, 122, 105, 92, 77.

ii) A solution of 0.14 g of 3-benzoylbenzothiophene **7** in 20 ml of methanol was stirred with 50 mg of sodium borohydride at room temperature for 30 min. The reaction mixture was poured into 50 ml of water, and the aqueous solution was acidified with hydrochloric acid, and then extracted with chloroform. The extract was concentrated *in vacuo*, and the residue was chromatographed on silica gel using chloroform as an eluent to give 90 mg (64%) of 3-benzo[*b*]thienylphenylmethanol as pale yellow oil. IR (neat) 3300—3400 cm^{-1} (ν_{OH}); NMR (CCl_4) δ 3.75 (1H, br, O**H**), 5.62 (1H, s, >C**H**), 6.9—7.8 (10H, m, aromatic protons); mass spectrum *m/e* 240 (M^+), 233 (M^+-OH), 221, 163 (M^+-Ph), 161, 135, 105, 77.

After 70 mg of the alcohol was heated with 2 ml of phosphorus trichloride under reflux for 1 h, excess phosphorus trichloride from the mixture was removed *in vacuo*. The residue was treated with 0.1 g of benzoylhydrazine to give crystals, which on recrystallization from methanol gave 10 mg of the hydrazine **11**, mp 165—166 °C.

Irradiation of Oxadiazepine 9. A suspension of 1.0 g of **9** in 250 ml of benzene was irradiated for 4 h. The solvent from the mixture was removed *in vacuo*, and the residue was chromatographed on alumina. From the hexane elution 0.17 g (45%) of benzothiophene **6a**, and from the hexane–benzene (1:1) 50 mg (7%) of benzoylbenzothiophene **7** were obtained respectively. Finally, 30 mg (3%) of the [2+2] cycloadduct **12** and 0.3 g (48%) of oxadiazole **1** were separated from the benzene elution.

12: colorless prisms, mp 187—188 °C. IR 1645 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 4.85, 6.97 (each $1H^2$ d, >C**H**, J= 2.5 Hz), 7.1—8.0 (14H, m, aromatic protons); mass spectrum *m/e* 356 (M^+), 253 (M^+-PhCN), 251 (M^+-PhCO), 237 ($M^+-PhCNO$), 210, 164, 134, 121, 105, 77. Found: C, 74.05; H, 4.31; N, 7.71%. Calcd for $C_{22}H_{16}N_2OS$: C, 74.14; H, 4.53; N, 7.86%.

A similar irradiation of **9** was performed in acetonitrile for 10 h, and the yields of products are given in Scheme 4.

Isomerization of the [2+2] Cycloadduct 12. A solution of 0.2 g of **12** in 30 ml of ethanol was stirred with 0.1 g of potassium hydroxide at 60—70 °C for 1 h. The reaction mixture was poured into 50 ml of water, and neutralized with 10% hydrochloric acid to give crystals. Recrystallization from methanol afforded 20 mg (10%) of the benzoylhydrazone **8**.

Photochemical Reaction of Oxadiazole 1 with Benzothiophene 6a in the Presence of Benzophenone. A solution of 1.11 g (5×10^{-3} mol) of **1**, 2.01 g (1.5×10^{-2} mol) of **6a**, and 0.45 g (2.5×10^{-3} mol) of benzophenone in 250 ml of benzene was irradiated for 10 h. The solvent from the mixture was removed *in*

vacuo, and the residue was chromatographed on silica gel using benzene and then chloroform as eluents. The first elution gave 1.25 g of a mixture of **6a** and benzophenone. From the second and third elutions, 0.25 g (14%) of the [2+2] cycloadduct **12**, and 0.65 g (59%) of 1 were isolated respectively.

*Photochemical Reaction of Oxadiazole **1** with Benzo*[b]*furan.* *i*) A solution of 1.11 g (5×10^{-3} mol) of **1** and 1.77 g (1.5×10^{-2} mol) of benzofuran[18] in 250 ml of benzene was irradiated for 10 h. The solvent from the mixture was removed *in vacuo*, and the residue was chromatographed on alumina using benzene as an eluent, giving 0.93 g (53%) of benzofuran, 0.22 g (13%) of the [2+2] cycloadduct **13**, and 0.85 g (77%) of **1**.

13: colorless prisms, mp 216—218 °C. IR 1670 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 4.68 (1H, m, >C**H**), 7.03 (1H, d, >C**H**, J=1.0 Hz), 6.8—7.9 (14H, m, aromatic protons); mass spectrum *m/e* 340 (M^+), 312 (M^+-CO), 311, 237 ($M^+-PhCNO$), 207 (312^+-PhCO), 194, 178, 118, 105, 77. Found: C, 77.63; H, 4.67; N, 8.26%. Calcd for $C_{22}H_{16}N_2O$: C, 77.63; H, 4.74; N, 8.23%.

A similar photochemical reaction in diethyl ether for 10 h afforded 0.15 g (9%) of **13**, together with recovery of **1** (47%) and benzofuran (56%).

ii) A solution of 1.11 g of **1** and 1.77 g of benzofuran in 600 ml of benzene was irradiated with monochromatic light (313 nm) for 30 h. A similar treatment afforded 50 mg (3%) of **13**, together with 0.82 g (74%) of **1** and 1.2 g (68%) of benzofuran.

Irradiation of Benzo[b]*thiophene 1,1-Dioxide (**14**) in the Presence of Oxadiazole **1**.* A solution of 1.9 g (1.1×10^{-2} mol) of **14**[19] and 1.11 g (5×10^{-3} mol) of **1** in 250 ml of diethyl ether was irradiated for 10 h. Filtration gave 0.74 g (39%) of crystals. Recrystallization from chloroform gave colorless needles, mp>300 °C, which were a mixture of the head to tail dimer **15**[20] and head to head dimer **16**[20] by inspection of the IR spectrum.

The filtrate was evaporated *in vacuo* to afford 1.92 g of a mixture of **1** and the dimers.

*Photochemical Reaction of Oxadiazole **1** with 2-Methylbenzo*[b]*thiophene (**6b**).* *i) Without Benzophenone*: A solution of 1.11 g (5×10^{-3} mol) of **1** and 2.22 g (1.5×10^{-2} mol) of **6b**[21] in 250 ml of diethyl ether was irradiated for 10 h. The solvent from the mixture was removed *in vacuo*, and the residue was chromatographed on alumina using benzene and then chloroform. From the benzene elution, 0.97 g (44%) of **6b**, and 0.61 g (55%) of **1** were recovered. The benzene–chloroform elution afforded 0.29 g (16%) of 3-benzoyl-2-methylbenzo[*b*]thiophene benzoylhydrazone (**18**), mp 125—126 °C, as colorless prisms. IR 3240 (ν_{NH}), 1675 cm^{-1} ($\nu_{C=O}$), NMR ($CDCl_3$) δ 2.40 (3H, s, C**H**$_3$), 7.0—8.2 (14H, m, aromatic protons), 9.0 (1H, br, N**H**); mass spectrum *m/e* 370 (M^+), 265 (M^+-PhCO), 250 ($M^+-PhCONH$), 249, 235 ($M^+-PhCONHNH$), 234, 223 ($PhC\equiv\overset{+}{N}NHCOPh$), 221, 147, 105, 77. Found: C, 74.47; H, 5.01; N, 7.33%. Calcd for $C_{23}H_{18}N_2OS$: C, 74.58; H, 4.90; N, 7.56%.

ii) With Benzophenone: A solution of 1.11 g of **1**, 2.22 g of **6b**, and 0.275 g (1.5×10^{-3} mol) of benzophenone in 250 ml of benzene was irradiated for 10 h. The solvent from the mixture was removed *in vacuo*, and the residue was chromatographed on alumina. From the benzene elution, 1.40 g of a mixture of **6b** and benzophenone, and 0.1 g (5%) of the [2+2] cycloadduct **19** were isolated, and the chloroform elution gave 0.67 g (60%) of **1**.

19: colorless prisms, mp 204—205 °C. IR 1645 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 2.04 (3H, s, C**H**$_3$), 4.64 (1H, s, >C**H**), 7.0—8.0 (14H, m, aromatic protons); mass spectrum *m/e* 370 (M^+), 267 (M^+-PhCN), 265 (M^+-PhCO), 237 (265^+-N_2), 235, 223, 221, 148, 105, 77. Found: C, 74.52; H, 4.75; N, 7.71%. Calcd for $C_{23}H_{18}N_2OS$: C, 74.58; H, 4.90; N, 7.56%.

*Photochemical Reaction of Oxadiazole **1** with 3-Methylbenzo*[b]*thiophene (**6c**).* *i) Without Benzophenone*: A solution of 2.22 g (10^{-2} mol) of **1** and 4.44 g (3×10^{-2} mol) of **6c**[22] in 250 ml of diethyl ether was irradiated for 10 h. The reaction mixture was concentrated *in vacuo*, and the residue was chromatographed on alumina using benzene and benzene–chloroform as eluents. From the benzene elution, 2.7 g (61%) of **6c** and 65 mg (2%) of the [2+2] cycloadduct **20** were isolated, and the benzene–chloroform elution gave 0.68 g (31%) of **1**.

20: colorless prisms, mp 267—268 °C. IR 1645 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 1.07 (3H, s, C**H**$_3$), 6.87 (1H, s, >C**H**), 7.0—8.1 (14H, m, aromatic protons); mass spectrum *m/e* 370 (M^+), 267 (M^+-PhCN), 265 (M^+-PhCO), 237 (265^+-N_2), 224, 221, 147, 105, 77. Found: C, 74.43; H, 4.87; N, 7.57%. Calcd for $C_{23}H_{18}N_2OS$: C, 74.58; H, 4.90; N, 7.56%.

A similar photochemical reaction in benzene affords the [2+2] cycloadduct **20** in 13% yield.

ii) With Benzophenone: A solution of 1.11 g (5×10^{-3} mol) of **1**, 2.22 g (1.5×10^{-2} mol) of **6c**, and 0.28 g (1.5×10^{-3} mol) of benzophenone in 250 ml of benzene was irradiated for 10 h. A similar work-up afforded 1.17 g of a mixture of **6c** and benzophenone, 0.61 g (33%) of **20**, and 0.52 g (47%) of **1**.

Photochemical Reaction in the Presence of Iodine. *i) Reaction with Benzothiophene **6a***: A solution of 2.0 g (9×10^{-3} mol) of oxadiazole **1**, 4.0 (3×10^{-2} mol) of **6a**, and 0.46 g (1.8×10^{-3} mol) of iodine in 500 ml of benzene was irradiated for 20 h. The solvent from the mixture was removed *in vacuo*, and chromatographic separation of the residue on alumina using benzene and then chloroform as eluents afforded 2.9 g (73%) of **6a**, 0.35 g (16%) of 3-benzoylbenzothiophene **7**, 0.21 g (11%) of **1** (from the benzene elution), and 1.59 g (50%) of the benzoylhydrazone **8** (from the benzene–chloroform elution).

*ii) Reaction with 2-Methylbenzothiophene **6b***: A solution of 1.11 g (5×10^{-3} mol) of **1**, 2.22 g (1.5×10^{-2} mol) of **6b**, and 0.25 g (10^{-3} mol) of iodine in 250 ml of benzene was irradiated for 10 h. A similar work-up afforded 15 mg (1%) of 3-benzoyl-2-methylbenzo[*b*]thiophene (**21**) and 0.28 g (15%) of the benzoylhydrazone **18**, together with recovery of 0.6 g (54%) of **1** and 1.05 g (47%) of **6b**.

The compound **21**, mp 73—74 °C, was identical with an authentic sample prepared from the Friedel-Crafts benzoylation of **6b**.

*iii) Reaction with 3-Methylbenzothiophene **6c***: A solution of 1.11 g of **1**, 2.22 g of **6c**, and 0.25 g of iodine in 250 ml of benzene irradiated for 10 h. A similar work-up afforded 75 mg (6%) of 2-benzoyl-3-methylbenzo[*b*]thiophene (**22**) and 0.15 g (8%) of the [2+2] cycloadduct **23**, together with recovery of 0.98 g (44%) of **6c** and 0.21 g (19%) of **1**. The compound **22**, mp 67—68 °C, was identical with an authentic sample prepared from the Friedel-Crafts benzoylation of **6c**.

23: colorless prisms, mp 152—153 °C; IR 1640 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 1.83 (3H, s, C**H**$_3$), 6.37 (1H, s, >C**H**), 6.9—8.1 (14H, m, aromatic protons); mass spectrum *m/e* 370 (M^+), 267 (M^+-PhCN), 265 (M^+-PhCO), 237 (265^+-N_2), 224, 223, 222, 165, 149, 148, 105, 77. Found C, 74.23; H, 4.56; N, 7.36%. Calcd for $C_{23}H_{18}N_2OS$: C: 74.58; H, 4.90; N, 7.56%.

*Photochemical Reaction of Oxadiazole **1** with 3-Iodobenzo*[b]*thiophene (**24**).* A solution of 1.11 g (5×10^{-3} mol) of **1** and 0.73 g (2.8×10^{-3} mol) of **24**[23] in 250 ml of benzene was irradiated for 10 h. The solvent from the mixture was removed *in vacuo*, and the residue was chromatographed on alumina using hexane, benzene, and then chloroform as eluents. From the hexane elution, 0.15 g (21%) of **24** and

40 mg (7%) of 2-phenylbenzo[*b*]thiophene (**27**) were obtained. From the benzene elution, 65 mg (7%) of 2-benzoyl-3-phenylbenzo[*b*]thiophene (**25**) and 0.59 g (53%) of **1** were isolated, and finally the chloroform elution gave 15 mg (1%) of 3-benzoyl-2-phenylbenzo[*b*]thiophene benzoylhydrazone (**28**) and 0.22 g (18%) of 2-benzoyl-3-phenylbenzo[*b*]thiophene benzoylhydrazone (**26**).

25: colorless prisms, mp 105—106 °C; IR 1630 cm^{-1} ($\nu_{C=O}$); mass spectrum *m/e* 314 (M^+), 286 (M^+-CO), 237 (M^+-Ph), 209 (M^+-PhCO), 165 ($M^+-PhCOS$), 105, 77. Found: C, 80.20; H, 4.50%. Calcd for $C_{21}H_{14}OS$: C, 80.24; H, 4.49%. This compound was identical with an authentic sample prepared from the Friedel-Crafts benzoylation of 3-phenylbenzo[*b*]thiophene.[14]

26: colorless prisms, mp 177—178 °C; IR 3160 (ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 7.0—8.2 (19H, m, aromatic protons), 8.5 (1H, br, N**H**); mass spectrum *m/e* 432 (M^+), 327 (M^+-PhCO), 311 ($M^+-PhCONH_2$), 297 ($M^+-PhCONHNH$), 223 ($PhC{\equiv}\overset{+}{N}NHCOPh$), 105, 77. Found: C, 77.62; H, 4.63; N, 6.42%. Calcd for $C_{28}H_{20}N_2OS$: C, 77.76; H, 4.66; N, 6.48%. Hydrolysis of **26** with hydrochloric acid in boiling ethanol for 1 h afforded **25** in 28% yield.

27: colorless needles, mp 177—178 °C (lit,[14] mp 174—175 °C); IR 1600, 1480, 1440, 1420 cm^{-1}; mass spectrum *m/e* 178 (M^+-S), 176, 165 (M^+-CHS), 134, 92, 77.

28: colorless needles, mp 183—184 °C; IR 3360 (ν_{NH}), 1690 cm^{-1} ($\nu_{C=O}$); mass spectrum *m/e* 432 (M^+), 327 (M^+-PhCO), 311 ($M^+-PhCONH_2$), 297 ($M^+-PhCONHNH$), 223, 105, 77. Found: C, 77.29; H, 4.59; N, 6.49%. Calcd for $C_{28}H_{20}N_2OS$: C, 77.76; H, 4.66; N, 6.48%.

*Irradiation of Oxadiazepine **9** in the Presence of Iodine.* *i)* A suspension of 0.5 g (1.4×10^{-3} mol) of **9** in 250 ml of benzene was irradiated with 0.107 g (30 mol% to **9**) for 3 h. The solvent from the mixture was removed *in vacuo*, and chromatographic separation afforded traces of **6a**, 70 mg (21%) of **7** (from the benzene elution), traces of **1** and 0.27 g (54%) of **8** (from the chloroform elution).

ii) A suspension of 0.5 g of **9** in 250 ml of benzene irradiated in the presence of 0.107 g of iodine and 0.7 g (2.8×10^{-3} mol) of 2,5-di(*p*-tolyl)-1,3,4-oxadiazole for 3 h. A similar work-up afforded 60 mg (18%) of **7** and 0.25 g (50%) of **8**, together with recovery of 0.62 g (89%) of ditolyloxadiazole.

Reduction of the [2+2] Cycloadducts with Sodium Borohydride. A solution of 0.2 g of the [2+2] cycloadduct **2** in 20 ml of methanol was refluxed with 0.1 g of sodium borohydride for 3 h. The solvent from the mixture was removed *in vacuo*, and 30 ml of water was added to the residue to give crystals, which on recrystallization from methanol afforded 30 mg (15%) of the dihydro compound **29**, mp 142—143 °C, as colorless prisms. IR 3240 (ν_{NH}), 1620 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 2.9—3.9 (3H, m, C**H**$_2$ and N**H**), 4.8, 6.7 (each 1H, m, =C**H**), 5.1 (1H, m, >C**H**), 6.9—7.9 (10H m, aromatic protons); mass spectrum *m/e* 292 (M^+), 290, 263 (M^+-CHO), 261, 187 (M^+-PhCO), 185, 170, 159, 157, 145, 128, 115, 105, 77. Found: C, 74.11; H, 5.48; N, 9.30%. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58%.

Similar reductions of the [2+2] cycloadducts **12** and **13** with sodium borohydride in boiling methanol for 1 h afforded the corresponding dihydro compounds **30** and **31** in 28 and 40% yields respectively.

30: colorless prisms, mp 152—153 °C; IR 3260 (ν_{NH}), 1620 cm^{-1} ($\nu_{C=N}$); NMR ($CDCl_3$) δ 3.20 (1H, dd, H**C**H, J=6, 12 Hz), 3.6 (1H, br, N**H**), 3.70 (1H, dd, HC**H**, J=7, 12 Hz), 4.18 (1H, dd, >C**H**, J=6, 7 Hz), 7.0—8.0 (14H, m, aromatic protons); mass spectrum *m/e* 358 (M^+), 356, 253 (M^+-PhCO), 212, 211, 210, 165, 121, 105, 77. Found: C, 73.76; H, 5.04; N, 7.93%. Calcd for $C_{22}H_{18}N_2OS$: C, 73.73; H, 5.06; N, 7.82%.

31: colorless prisms, mp 182—183 °C; IR 3220 (ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 3.25 (1H, dd, H**C**H, J=4, 12 Hz, when exchanged with D_2O, this signal changed to a doublet with J=12 Hz), 3.74 (1H, dd, HC**H**, J=6, 12 Hz), 4.10 (1H, d, >C**H**, J=6 Hz), 4.6 (1H, m, N**H**), 6.7—7.9 (14H, m, aromatic protons); mass spectrum *m/e* 342 (M^+), 340, 237 (M^+-PhCO), 222, 220, 207, 194, 165, 105, 77. Found: C, 77.13; H, 5.17; N, 8.16%. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18%.

The [2+2] cycloadducts, **5**, **19**, **20**, and **23**, were inert with similar reduction.

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