The adsorbability of chloraminophenamide [a=6.45×10^{-4} (mol/g), b=4.19×10^{4} (l/mol)] was similar to that of hydrochlorothiazide. Thus, it seemed likely that the adsorbability of trichlormethiazide, *etc.*, was larger than the values shown in Fig. 2. In conclusion, the present results supported the previous finding that there is a relationship between adsorbability and relative diuretic activity.

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Photolysis and Thermolysis of 3-Diazothiochroman-4-one and Related Compounds

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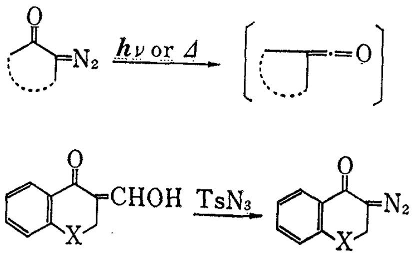
The photochemical and thermal reactions of 3-diazothiochroman-4-one (**2a**), 3-diazochroman-4-one (**2b**), 3-diazo-1-methyl-1,2,3,4-tetrahydroquinolin-4-one (**2c**), and 2-diazo-1-tetralone (**2d**) were investigated. Wolff rearrangement was observed with **2a**, **2c**, and **2d** only under photolytic conditions. In the case of **2a**, migration of the thioether group competed with the above reaction.

Keywords——tosyl azide; α-diazoketone; episulfonium ylide; carbene; Wolff rearrangement; participation of thioether; dimerization

Wolff rearrangement of cyclic α-diazoketones has been utilized as a method for ring contraction (Chart 1).[2] In view of the known susceptibility of diazo compounds substituted at the β-position with sulfur to undergo carbenic rearrangement of the thioether group,[3] it seemed of interest to investigate the photochemical and thermal behavior of cyclic α-diazoketones having a sulfur atom at the γ-position. One such molecule is 3-diazothiochroman-4-one (**2a**), which could undergo either phenyl migration (Wolff rearrangement) or rearrangement of the thioether group, or both. We present the results of a study of the photochemical and thermal reactions of **2a**. For comparison, the behavior of the related compounds **2b**—**d** is also described.



1a—**d** **2a**—**d**

a: X=S; **b**, X=O;
c, X=NMe; **d**, X=CH$_2$

Chart 1

The starting α-diazoketones **2a**—**d** were synthesized by treatment of the known α-hydroxymethyleneketones **1a**—**d** with tosyl azide in ether in the presence of diethylamine.[4] All the compounds showed two strong infrared (IR) absorption bands at 2070—2080 cm^{-1} (N$_2$) and 1620—1630 cm^{-1} (C=O).

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Irradiation of 3-diazothiochroman-4-one (**2a**) in methanol for 5 hr afforded a Wolff rearrangement product **3**[5] and a dimeric product **4**, mp 170—171°, in 24 and 8% yields, respectively. In sharp contrast, when it was refluxed in methanol in the presence of silver oxide **2a** gave exclusively **4** in 44% yield. The proposed structure of **4** is based on the spectroscopic data: the parent ion in its mass spectrum (MS) appears at *m/e* 324, indicating that **4** is dimeric. The IR spectrum shows a carbonyl band at 1710 cm^{-1}, and the ultraviolet (UV) spectrum (in EtOH) of **4** exhibits maxima at 239 (log ε 4.50), 262 (3.71), 271 sh (3.68), 294 (3.45), and 370 nm (3.05). This closely resembles the combined UV spectrum of 2-benzyl-3-benzyloxybenzo[*b*]thiophene (**10**) and 2,2-dibenzylbenzo[*b*]thiophen-3(2H)-one (**9**), prepared from benzo[*b*]thiophen-3(2H)-one 1,1-dioxide (**5**) as illustrated in Chart 2. The nuclear magnetic resonance (NMR) spectrum of **4** shows a complex multiplet between δ 2.0 and 2.3 (4 H). It was concluded, therefore, that **4** is a Diels–Alder dimer[6,7] of 2-methylidenebenzo[*b*]thiophen-3(2H)-one (**11**), which may arise by a 1,2-shift of the arylthio group[3] as indicated in Chart 2.

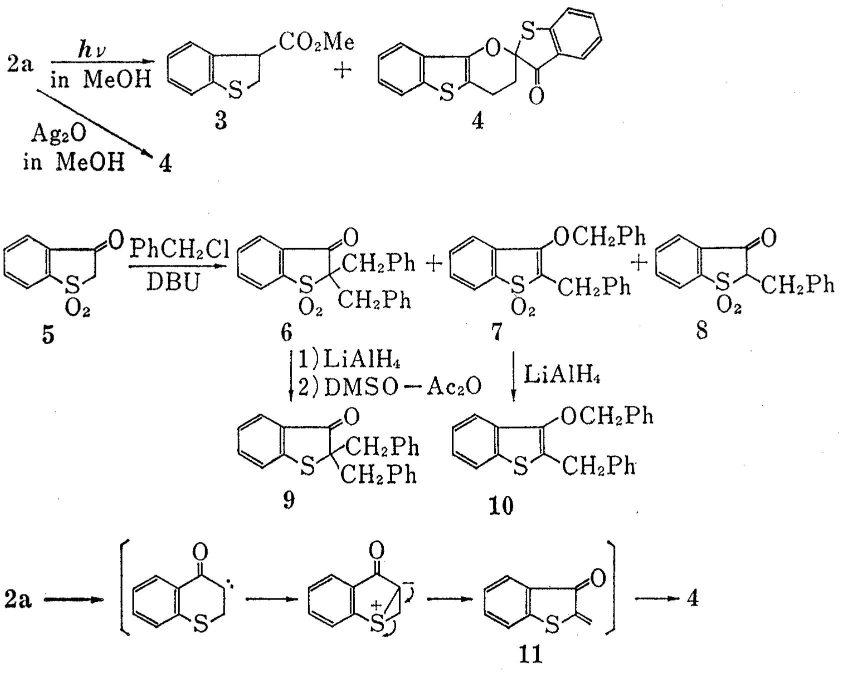

Chart 2

3-Diazochroman-4-one (**2b**), when irradiated in methanol, gave a complex mixture. However, thermolysis of **2b** afforded 4-chromenone (**12**)[8] in 42% yield, due to migration of the β-hydrogen atom. Irradiation of 3-diazo-1-methyl-1,2,3,4-tetrahydroquinolin-4-one

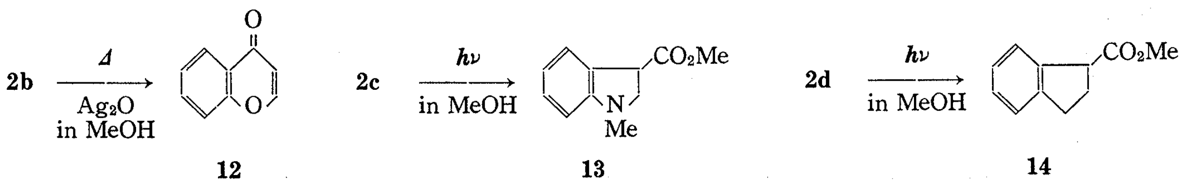

Chart 3

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(**2c**) in methanol for 3 hr again afforded a complex mixture, from which a Wolff rearrangement product **13**[5] was isolated in 8% yield. Thermolysis of **2c** gave no isolable products. Irradiation of 2-diazo-1-tetralone (**2d**) in methanol for 5 hr gave a Wolff rearrangement product **14**[5] in 44% yield, whereas thermolysis of **2d** gave only an intractable mixture.

In summary, Wolff rearrangement was observed with **2a**, **2c**, and **2d** only under photolytic conditions. In the case of **2a**, rearrangement of the thioether group competed with the above reaction, reflecting the ability of the thioether group to participate in a carbenic center.[3]

Experimental[9]

General Procedure for the Preparation of α-Diazoketones 2a—d——A solution of diethylamine (30 mmol) in ether (20 ml) was added dropwise to a solution of an α-diazoketone (15 mmol) and tosyl azide (15 mmol) in ether (40 ml) with stirring. The reaction mixture was stirred at room temperature for 1—4 hr then poured into H_2O (20 ml). The organic layer was separated and the aqueous layer was extracted with ether (50 ml). The combined extract was washed with H_2O, dried ($MgSO_4$), and concentrated. The residue was purified by passage through a short column of silica gel. In this manner, 3-diazothiochroman-4-one (**2a**) (2.11 g, 75%) was obtained from **1a**[10] (2.85 g). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2080 (N_2), 1610 (CO). NMR ($CDCl_3$) δ: 4.06 (2H, s), 7.0—8.2 (4H, m). 3-Diazochroman-4-one (**2b**) (290 mg, 61%) was obtained from **1b**[11] (487 mg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2070 (N_2), 1630 (CO). NMR ($CDCl_3$) δ: 5.14 (2H, s), 6.8—8.0 (4H, m). 3-Diazo-1-methyl-1,2,3,4-tetrahydroquinolin-4-one (**2c**) (1.82 g, 82%) was obtained from **1c**[12] (2.3 g). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2080 (N_2), 1630 (CO). NMR ($CDCl_3$) δ: 2.94 (3H, s), 4.33 (2H, s), 6.7—8.6 (4H, m). 2-Diazo-1-tetralone (**2d**) (2.2 g, 56%) was obtained from **1d**[13] (4.0 g). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2070 (N_2), 1620 (CO). NMR ($CDCl_3$) δ: 3.02 (4H, s), 7.0—8.2 (4H, m).

Photolysis of 2a——A solution of **2a** (300 mg, 1.6 mmol) in absolute MeOH (36 ml) was irradiated for 5.5 hr, then concentrated. The residue was purified by column chromatography on silica gel. Elution with benzene gave **3** (74 mg, 24%) as an oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730 (CO). NMR ($CDCl_3$) δ: 3.74 (3H, s), 3.28—4.44 (3H, m), 6.85—7.4 (4H, m). MS *m/e*: 193 (M^+). Further elution with benzene gave **4** (22 mg, 8%) as yellow needles, mp 170—171°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710 (CO). NMR ($CDCl_3$) δ: 2.0—2.3 (4H, m), 7.1—7.9 (8H, m). UV (EtOH) nm (log ε): 239 (4.50), 262 (3.71), 271 sh (3.68), 294 (3.40), 303 (3.45), 370 (3.05). MS *m/e*: 324 (M^+), 162. *Anal.* Calcd for $C_{18}H_{12}O_2S$: C, 66.64; H, 3.73. Found: C, 66.50; H, 3.60.

Thermolysis of 2a——A mixture of **2a** (400 mg, 2.1 mmol) and silver oxide (100 mg) in absolute MeOH (15 ml) was refluxed with stirring for 5 hr. The solution was filtered and the filtrate was concentrated. The residue was purified by column chromatography on silica gel with benzene to give **4** (150 mg, 44%).

2,2-Dibenzylbenzo[*b*]thiophen-3(2H)-one 1,1-Dioxide (6) and 2-Benzyl-3-benzyloxybenzo[*b*]thiophene 1,1-Dioxide (7)——A solution of benzo[*b*]thiophen-3(2H)-one 1,1-dioxide (**5**)[14] (3.5 g, 19 mmol), benzyl chloride (5.08 g, 40 mmol), and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) (6.04 g, 40 mmol) in benzene (60 ml) was refluxed for 5 hr. The solution was washed with dil. HCl and H_2O, dried ($MgSO_4$), and concentrated. The residue was dissolved in MeOH and left overnight. The resulting white solid was collected to give **6** (2.8 g). The mother liquor was concentrated and chromatographed on silica gel with benzene to give additional **6** (1 g, 55% total yield). Further elution with the same solvent gave **7** (1.4 g, 22%), and finally 2-benzylbenzo[*b*]thiophen-3(2H)-one 1,1-dioxide (**8**) (0.85 g, 16.5%). Compound **6** gave mp 139—140° (from MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710 (CO), 1300, 1150 (SO_2). NMR ($CDCl_3$) δ: 3.36, 3.52 (2H each, ABq, *J*=14 Hz), 7.0—7.9 (14H, m). *Anal.* Calcd for $C_{22}H_{18}O_3S$: C, 72.90; H, 5.00. Found: C, 72.83; H, 4.90. Compound **7** gave mp 102—104° (from MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1630, 1300, 1160. NMR ($CDCl_3$) δ: 4.00 (2H, s), 5.18 (2H, s), 7.1—7.85 (14H, m). *Anal.* Calcd for $C_{22}H_{18}O_3S$: C, 72.90; H, 5.00. Found: C, 72.88; H, 4.87. Compound **8** gave mp 122—123° (from MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720 (CO), 1320, 1150 (SO_2). NMR ($CDCl_3$) δ: 3.2—3.7 (2H, m), 4.05—4.2 (1H, m), 7.1—8.1 (4H, m). *Anal.* Calcd for $C_{15}H_{12}O_3S$: C, 66.15; H, 4.44. Found: C, 66.01; H, 4.50.

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[9] All melting points are uncorrected. The IR spectra were determined with a JASCO IRA-1 spectrophotometer, UV spectra with a Hitachi 124 spectrophotometer, and NMR spectra with a Hitachi R-20 instrument, with tetramethylsilane as internal standard. Irradiation was carried out in a quartz vessel with a high-pressure mercury lamp.

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2,2-Dibenzylbenzo[*b*]thiophen-3(2H)-one (9)——A solution of **6** (3 g) in ether (50 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (4.5 g) in ether (90 ml), and the reaction mixture was stirred at 25° for 5 hr. The excess hydride was hydrolyzed with 10% HCl and the organic layer was separated. The aqueous layer was extracted with ether. The combined extract was washed with H_2O, dried ($MgSO_4$), and concentrated to give an oily product (2.7 g), which was dissolved in acetic anhydride (20 ml) and dimethylsulfoxide (30 ml). The mixture was stirred at room temperature overnight, poured into ice-water, stirred for 2 hr, and then extracted with *n*-hexane. The extract was washed with H_2O several times, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel with benzene–*n*-hexane (1: 2) to give **9** (1.2 g, 44%), mp 129—131° (from MeOH). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1680 (CO). NMR ($CDCl_3$) δ: 3.10, 3.24 (2H each, ABq, $J=14$ Hz), 6.9—7.9 (14H, m). UV (EtOH) nm (log ε): 239 (4.19), 260 (3.52), 370 (3.09). *Anal.* Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49. Found: C, 79.66; H, 5.49.

2-Benzyl-3-benzyloxybenzo[*b*]thiophene (10)——A mixture of **7** (100 mg, 0.3 mmol) and $LiAlH_4$ (32 mg) in ether (30 ml) was stirred at room temperature for 0.5 hr. The excess hydride was decomposed by addition of a saturated solution of Rochelle salt. The ether layer was separated, washed wtih H_2O, dried ($MgSO_4$), and concentrated. The residue was passed through a short column with benzene to give **10** (64 mg) as colorless crystals, mp 96.5—98.5°. NMR ($CDCl_3$) δ: 4.03 (2H, s), 5.06 (2H, s), 6.8—7.9 (14H, m). UV (EtOH) nm (log ε): 234 (4.50), 241 sh (4.35), 265 (3.85), 291 (3.55), 301 (3.44). *Anal.* Calcd for $C_{22}H_{18}OS$: C, 79.96; H, 5.49. Found: C, 79.68; H, 5.39.

Thermolysis of 2b——A mixture of **2b** (156 mg, 1 mmol) and silver oxide (62 mg) in MeOH (16 ml) was refluxed with stirring for 4 hr. The reaction mixture was filtered and the filtrate was concentrated. The residue was purified by column chromatography on silica gel with benzene to give **12** (55 mg, 42%), mp 55—56° (lit.[5] mp 59°). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1640. NMR ($CDCl_3$) δ: 6.28 (1H, d, $J=7.5$ Hz), 7.15—8.2 (4H, m), 7.78 (1H, d, $J=7.5$ Hz).

Photolysis of 2c——A solution of **2c** (300 mg, 1.6 mmol) in absolute MeOH (30 ml) was irradiated for 3 hr and concentrated. The residue was purified by column chromatography on silica gel with benzene–EtOAc (4: 1) to give **13** (25 mg, 8%) as an oil.[5] IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1735 (CO). NMR ($CDCl_3$) δ: 2.77 (3H, s), 3.76 (3H, s), 3.4—4.3 (3H, m), 6.4—7.5 (4H, m).

Photolysis of 2d——A solution of **2d** (300 mg, 1.7 mmol) in MeOH (30 ml) was irradiated for 5 hr, then concentrated. The residue was purified by column chromatography on silica gel with benzene–EtOAc (2: 1) to give **14** (134 mg, 44%) as an oil.[5] IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1730 (CO). NMR ($CDCl_3$) δ: 2.15—2.6 (2H, m), 2.85—3.2 (2H, m), 3.70 (3H, s), 3.9—4.2 (1H, m), 6.95—7.5 (4H, m).

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Isolation of O-Demethyllycoramine from Bulbs of *Lycoris radiata* HERB.

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The bulbs of *Lycoris radiata* HERB. (Amaryllidaceae) were found to contain a new phenolic base, O-demethyllycoramine (O-demethyldihydrogalanthamine) (**3**), as well as previously isolated alkaloids, such as pretazettine (**1**), lycorine (**4**), lycoramine (**5**), lycorenine (**6**), demethylhomolycorine (**7**), hippeastrine (**8**), and homolycorine (**9**). The structure of **3** was confirmed by demethylation of lycoramine (**5**) with pyridine hydrochloride.

Keywords——O-demethyllycoramine; pretazettine; lycoramine; lycorenine; demethylhomolycorine; hippeastrine; homolycorine; Amaryllidaceae; pyridine hydrochloride

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