Reaction of Selenobenzophenones with Olefins. Formation of 1*H*-2-Benzoselenopyrans. Reaction of 1*H*-2-Benzoselenopyrans with Diazoalkanes

Kentaro Okuma,* Yuji Koga, Kazuki Kojima, Kosei Shioji, Haruo Matsuyama,† and Yoshinobu Yokomori‡

Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-0180, Japan, Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan, and Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239-0811, Japan

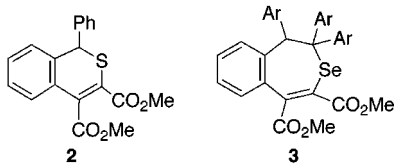
Received October 26, 1999

Selenobenzophenone reacts as a diene with dimethyl acetylenedicarboxylate (DMAD) to lead to dimethyl 1*H*-1-diphenylmethyl-1-phenyl-2-benzoselenopyran-3,4-dicarboxylate (**5c**) in moderate yield; the initial [4 + 2] cycloaddition is followed by the addition of another 1 mol equiv of selenobenzophenone. The reaction might proceed through carbene insertion of the primary cycloadduct. On the other hand, 4,4′-dimethoxyselenobenzophenone combines as a diene with DMAD furnishing dimethyl 1*H*-1-*p*-methoxyphenyl-6-methoxy-2-benzoselenopyran-3,4-dicarboxylate (**4a**). The reaction of benzoselenopyran derivative (**4**) with diaryldiazomethanes afforded another type of carbene insertion product.

Introduction

The reaction of selenocarbonyl compounds is of current interest.[1] In the past decades, the synthesis of many stable selenocarbonyl compounds has been realized by taking advantage of the steric protection afforded by bulky substituents, and the chemistry of these compounds has been extensively studied.[2] Some electronically stabilized selenocarbonyl compounds have been isolated by taking advantage of the mesomeric effect due to heteroatoms such as nitrogen and sulfur or coordination to transition metals.[3] We have also succeeded in the isolation of selenobenzophenones (**1**).[4] The reactivity of selenobenzophenones is interesting because they act as dienes or dienophiles toward olefins. Erker and coworkers have also reported the unique stereochemistry of the [4 + 2] cycloaddition of **1** with 2,4-hexadienes.[5] Thiobenzophenone is well-known to react with DMAD to afford the corresponding [4 + 2] cycloadduct (**2**).[6] We have reported that the reaction of selenobenzophenones with DMAD gave benzoselenepin derivatives (**3**).[7] However, in the course of pursuing the reactivity of these derivatives, some ambiguous results in the structure of **3** were revealed (Scheme 1).

Scheme 1



2 **3**

These results prompted us to investigate the precise mechanism of this reaction. In this paper, we disclose the full details of the reaction of **1** with olefins, correction of structure **3**, and X-ray crystallographic analysis of the adducts.

Results and Discussion

Selenocarbonyl compounds are generally difficult to isolate, whereas 4,4′-dimethoxyselenobenzophenone (**1a**) can be isolated as its monomeric form.[4] We first tried the reaction of **1a** with DMAD. Treatment of **1a** with DMAD at room temperature in benzene gave colorless crystals of dimethyl 1*H*-1-*p*-methoxyphenyl-6-methoxy-2-benzoselenopyran-3,4-dicarboxylate (**4a**) in 66% yield (Scheme 2).

† Tokyo Metropolitan University.
‡ National Defense Academy.

(1) For reviews, see (a) Guziec, Jr., F. S. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley, New York, 1987; p 277. (b) Guziec, F. S., Jr.; Guziec, L. J. In *Comprehensive Organic Functional Transformations*; Katritzky, A. R., M-Cohn, O., Rees, C. W., Pattenden, G., Eds.; Pergamon: Cambridge, 1995; Vol. 3, 3.09. For recent reports, see (c) Fischer, H.; Kalbas, C.; Stumpf, R. *Chem. Ber.* **1996**, *129*, 1169. (d) Shimada, K.; Yamaguchi, M.; Sasaki, T.; Ohnishi, K.; Takikawa, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2235. (e) Murai, T.; Kakami, K.; Itoh, N.; Kanda, T.; Kato, S. *Tetrahedron* **1996**, *52*, 2839. (f) Chesney, A.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. *Chem. Commun.* **1997**, 2293. (g) Zhou J.; Chen, R. Y. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2917. (h) Purseigle, F.; Dubreuil, D.; Marchand, A.; Pradere, J. P.; Goli, M.; Toupet, L. *Tetrahedron* **1998**, *54*, 2545. (i) Back, T. G.; Dyck, B. P.; Parvez, M. *J. Org. Chem.* **1995**, *60*, 4657. (j) Fischer, H.; Treier, K.; Troll, C. *Chem. Ber.* **1995**, *128*, 1149. (k) Back, T. G.; Dyck, B. P.; Parvez, M. *J. Org. Chem.* **1995**, *60*, 703. (l) Shimada, K.; Oikawa, S.; Nakamura, H.; Takikawa, Y. *Chem. Lett.* **1995**, 135. (m) Yong, D. N.; Serguiski, P.; Detty, M. R. *J. Org. Chem.* **1998**, *63*, 5716.

(2) (a) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079. (b) Okazaki, R.; Kumon, N.; Inamoto, N. *J. Am. Chem. Soc.* **1989**, *11*, 5949. (c) Takeda, N.; Tokitoh, N.; Okazaki, R. *Tetrahedron* **1997**, *53*, 12167.

(3) (a) Reid, D. H.; Webster, R. G.; Mckenzie, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2334. (b) Michael, J. P.; Reid, D. H.; Rose, B. G.; Speirs, R. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1494. (c) Fischer, H.; Zeuner, S.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 726. (d) Fischer, H.; Seuner, S.; Alt, H. G. *J. Organomet. Chem.* **1985**, *289*, C21. (e) Fischer, H.; Zeuner, S.; Gerbing, U.; Riede, J.; Kreiter, C. G. *J. Organomet. Chem.* **1989**, *377*, 105.

(4) (a) Okuma, K.; Kojima, K.; Kaneko, I.; Ohta, H. *Chem. Lett.* **1991**, 1053. (b) Okuma, K.; Kojima, K.; Kaneko, I.; Tsujimoto, Y.; Ohta, H.; Yokomori, Y. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2151.

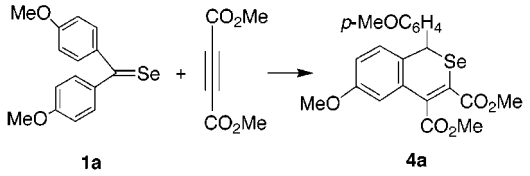
(5) Wilker S.; Erker, G. *J. Am. Chem. Soc.* **1995**, *117*, 10922.

(6) (a) Ohno, A.; Koizumi, T.; Ohnishi, Y. *Bull. Chem. Soc., Jpn.* **1971**, *44*, 2511. (b) Gotthardt H.; Nieberl, S. *Liebigs Ann. Chem.* **1980**, 867. (c) Rapp J.; Huisgen, R. *Tetrahedron* **1997**, *53*, 961.

(7) Okuma, K.; Kojima, K.; Kaneko, I.; Ohta, H. *Tetrahedron Lett.* **1992**, *33*, 1333.

10.1021/jo991679w CCC: $19.00
Published on Web 03/09/2000

Scheme 2



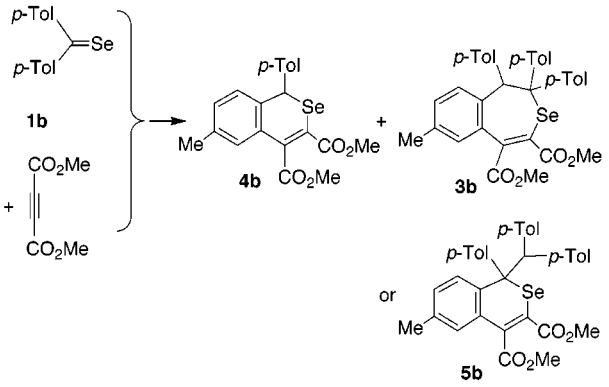
This result is similar to that of thiobenzophenone;[6] selenobenzophenone acts as a diene toward DMAD. The initial [4 + 2] cycloaddition is followed by 1,3-prototropy to give **4a**.

We then tried the reaction of 4,4′-dimethylselenobenzophenone (**1b**) with DMAD; **1b** is relatively unstable and is easily oxidized to give the corresponding benzophenone. Thus, the reaction was carried out in a one-pot operation of di-*p*-tolylmethylenetriphenylphosphorane with elemental selenium, followed by the addition of DMAD. Interestingly, treatment of 4,4′-dimethylselenobenzophenone (**1b**) with DMAD resulted in the formation of two different adducts. One was the normal [4 + 2] cycloadduct (**4b**). The other adduct was found not to be the normal [4 + 2] cycloadduct but a 2:1 adduct by spectroscopic, MS, and elemental analysis. ^{1}H NMR of this adduct shows four tolyl methyl (2.25, 2.26, 2.27, and 2.29 ppm), two methoxy (3.73 and 3.75 ppm), one methine (5.02 ppm), and 15 aromatic protons. ^{13}C NMR shows four tolyl methyl (20.9, 20.9, 21.0, and 21.1 ppm), two methoxy (52.6 and 52.7 ppm), one quaternary (58.9 ppm), one methine (59.4 ppm), and 19 olefinic and aromatic, and two ester carbonyl (165.6 and 168.5 ppm) carbons. In our previous communication, we have shown that this adduct may be dimethyl 1,2-dihydro-1,2,2-tri-*p*-tolyl-3-benzoselenepin-4,5-dicarboxylate (**3b**).[7]

However, the structure of **3b** was deemed incorrect for the following two reasons. If the reaction proceeded through a tetraarylethylene intermediate formed from selenobenzophenone with phosphorus ylide, the tetraphenylethylene further reacts with selenium to give an episelenide intermediate, which finally reacted with DMAD to afford **3**. However, the reaction of tetra-*p*-tolylethylene with elemental selenium in the presence of DMAD recovered the starting materials almost quantitatively. Krafft and Meinke reported the isolation of a selenofluorenone dimer whose regioselectivity was confirmed by zinc dust reduction.[8] We applied this method to the reduction of **3b**. Zinc dust reduction of **3b** in acetic acid led to the formation of **4b** instead of a ring-opened product, suggesting that the structure of this adduct would not be **3b**. Another possible structure of this adduct would be dimethyl 1*H*-1-(4,4′-dimethyldiphenylmethyl)-1-tolyl-2-benzoselenopyran-3,4-dicarboxylate (**5b**) (Scheme 3). The exact structure was finally confirmed by single-crystal X-ray diffraction. An X-ray crystallographic structure of the adduct (**3b** or **5b**) has an exocyclic diarylmethyl group, thus confirming the structure to be **5b**.[9]

We then carried out the reaction of selenobenzophenone (**1c**) with DMAD; **1c** is relatively unstable and easily dimerizes to give diselenetane. Thus, the reaction was carried out by adding diphenylmethylenetriphenylphosphorane with elemental selenium followed by

Scheme 3



Scheme 4

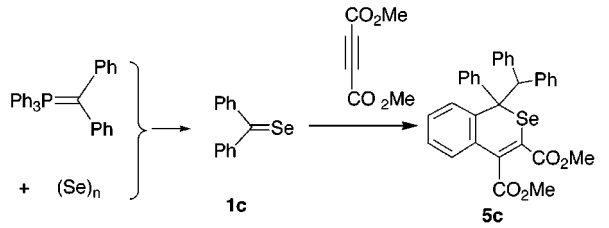
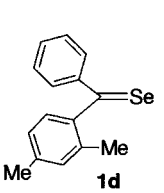
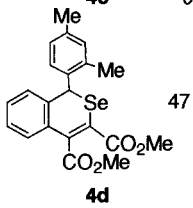
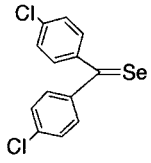
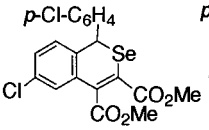
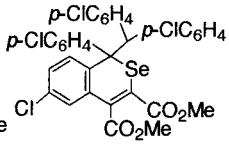


Table 1. Reaction of Selenobenzophenones (1) with DMAD

Entry	1	Products (Yield /%) 4		5	
1	**1a**	**4a**	71	**5a**	0
2	**1b**	**4b**	23	**5b**	54
3	**1c**	**4c**	0	**5c**	62
4	 **1d**	 **4d**	47	**5d**	0
5	 **1e**	 **4e**	9	 **5e**	12

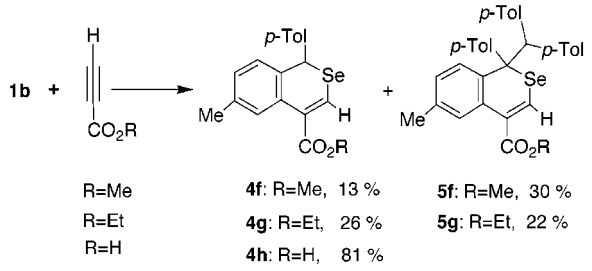
the addition of DMAD. Interestingly, only the colorless crystals of the 2:1 cycloadduct (**5c**) were isolated in 71% yield (Scheme 4). Other reactions were carried out in a similar manner (Table 1).

Generally, electron-rich selenobenzophenones such as **1a** and **1d** gave the normal cycloadducts (entries 1 and 4). On the other hand, normal or electron-deficient selenobenzophenones gave both cycloadducts (entries 3 and 5).

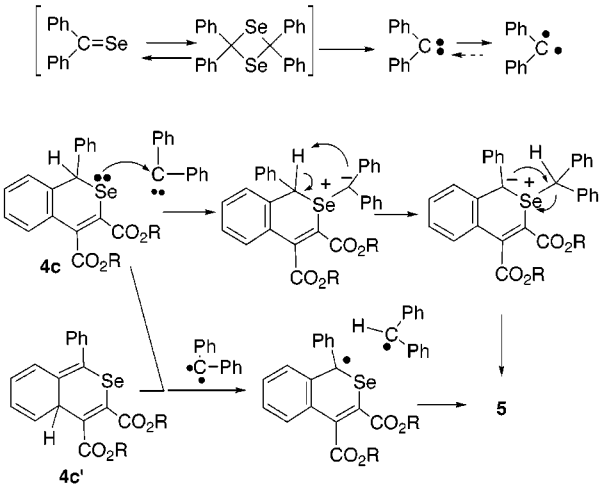
How do we account for the formation of **5**? Compound **5** might be formed by the addition of 2 molar amounts of **1** with DMAD. Tokitoh et al. reported that the thermolysis of triselenastannolane gave selenobenzophenone, which reacted with DMAD to give only the normal cycloadduct (**4c**).[10]

(8) Meinke, P. T.;. Krafft, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 8679.
(9) The X-ray crystallographic analyses of **5b** and **13** were carried out by using Enraf-Nonius CAD4 diffractometer. Full details were shown in Supporting Information.

Scheme 5



Scheme 6

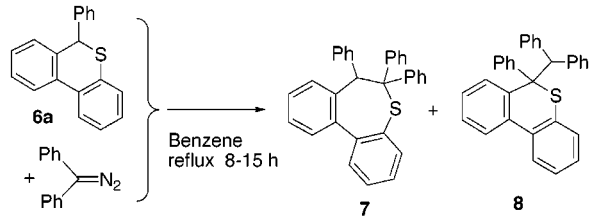


When the reaction was carried out by using alkyl propiolates instead of DMAD, the corresponding cycloadducts (**4f**, **4g**, **5f**, and **5g**) were obtained regioselectively (Scheme 5). When propiolic acid was used as a substrate in toluene for 2 h at 60 °C, compound **4h** was obtained in 81% yield. When isolated 4,4′-dimethylselenobenzophenone **1b** was reacted with DMAD, **4b** and **5b** were obtained in 11 and 32% yields, respectively, which suggested that phosphorus ylide or elemental selenium did not affect the formation of **5b**. Noteworthy is that the reaction of **1b** with methyl propiolate in the presence of 5 equiv of acetic acid led to the formation of **4f** as the sole product in 35% yield. Thus, acid would prevent the formation of **5**.

These results suggested that the cycloadduct **4** was further attacked by a carbenoid produced from an additional selenobenzophenone or its dimer. The produced carbenoid might attack the selenium of **4** to give the corresponding selenonium ylide, which abstracts the α-hydrogen of the ylide to form another selenonium ylide. Stevens rearrangement of the rearranged ylide finally afforded the 2:1 adduct **5**. The formation of a triplet carbene is another possibility, which abstracts the α-hydrogen of **4** or γ-hydrogen of primary cycloadduct **4′** to afford the radical intermediate, which finally recombines to give **5** (Scheme 6).

Recently, we have isolated the thiobenzophenone–benzyne adducts, one of which (**6a**) was identical with that of the product independently prepared by Benati et al.[11] They reported that **6a** reacted with diphenyldiazomethane to afford benzothiepin (**7**) and *exo*-diphenylmethylbenzothiopyran (**8**) in 26 and 13% yields, respectively.[12] Thus, two types of carbene insertion might proceed in this case (Scheme 7).

Scheme 7



Scheme 8

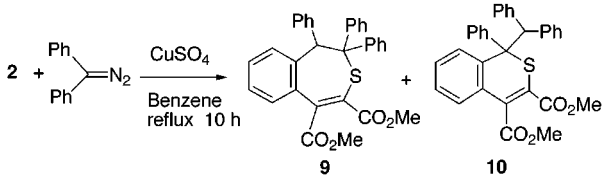
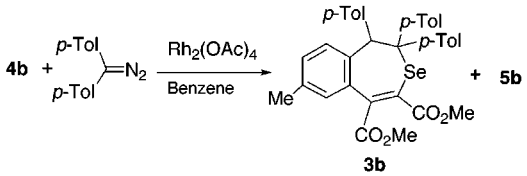


Table 2. Reaction of 2 and 4 with Diaryldiazomethane[a]

2 or **4b**	diaryl-diazomethane	catalyst	products (yields/%) **3** or **9**	**5** or **10**	recovered **2** or **4b** (%)
2	$Ph_2C{=}N_2$	none	**9**: 0	**10**: 0	**2**: 86
2	$Ph_2C{=}N_2$	$CuSO_4$	**9**: 10	**10**: 12	**2**: 32
2	$Ph_2C{=}N_2$	$Rh_2(OAc)_4$	**9**: 14	**10**: 8	**2**: 35
4b	*p*-$Tol_2C{=}N_2$	none	**3b**: 0	**5b**: 0	**4b**: 88
4b	*p*-$Tol_2C{=}N_2$	$CuSO_4$	**3b**: 0	**5b**: 0	**4b**: 85
4b	*p*-$Tol_2C{=}N_2$	$Rh_2(OAc)_4$	**3b**: 14	**5b**: 1	**4b**: 46

[a] All reactions were carried out in refluxing benzene.

Scheme 9



We applied this method to the reaction of **2** with diaryldiazomethane. An attempted reaction of **2** with diazomethane resulted in almost complete recovery of **2**, suggesting that the reactivity of **2** might be lower than that of **6a**. After several trials, we finally found that the reaction of benzothiopyran **2** with diphenyldiazomethane in the presence of $CuSO_4$ afforded two adducts, which were found to be benzothiepin derivative (**9**) and *exo*-diphenylmethyl derivative (**10**) (Scheme 8).

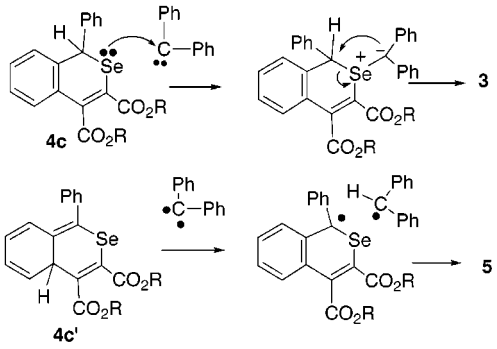
If the same reaction occurs in the case of selenobenzophenone, carbene formation from selenobenzophenone would be a good route to **5**. An attempted reaction of **4b** with ditolyldiazomethane by using copper(II) sulfate resulted in complete recovery of the starting **4b**. By using rhodium(II) acetate in place of copper sulfate, this reaction provided the corresponding benzoselenepin (**3b**) in 14% yield along with *exo*-benzhydrylbenzoselenopyran (**5b**, 1%). Unreacted **4b** was recovered in 46% yield (Table 2, Scheme 9). The structure of **3b** was confirmed by spectroscopic, MS, and elemental analysis.

(10) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1993**, 407.

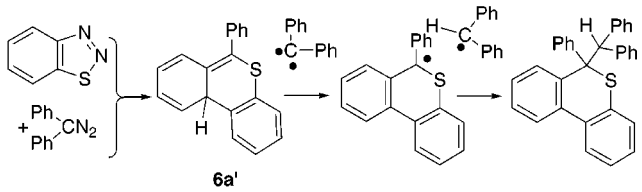
(11) (a) Okuma, K.; Shirokawa, T.; Yamamoto, T.; Kitamura, T.; Fujiwara, Y. *Tetrahedron Lett.* **1996**, *37*, 8883. (b) Benati, L.; Montevecchi, P. C.; Spagnolo, P.; Tundo, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1544.

(12) Benati, L.; Montevecchi, P. C.; Spagnolo P. *J. Chem. Soc., Perkin Trans. 1* **1982**, 917.

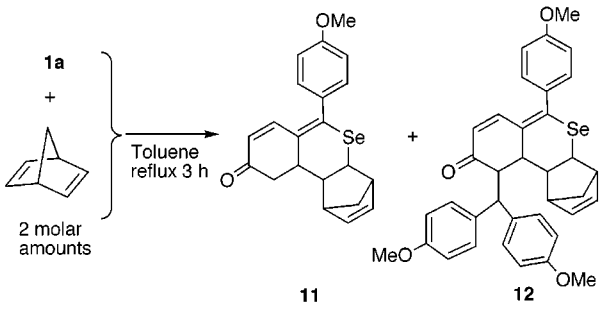
Scheme 10



Benati et al.



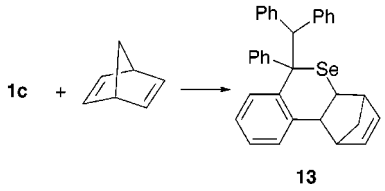
Scheme 11



When copper(II) sulfate was used as a catalyst in the reaction of **2** with diphenyldiazomethane, the product ratio (**9**:**10**) was 5:6, whereas the ratio was changed to 7:4 by using rhodium(II) acetate as a catalyst, suggesting that the cause of the product-ratio-deviation was dependent on the carbenoid complex used. Considering these two results, it is seen that singlet carbenoids play a main role in the formation of **3** and **9**. The reason only one product **5c** is obtained in the reaction of **1c** with DMAD would be that the reaction proceeded through the triplet carbene insertion of primary 4 + 2 adduct **4c′**. Benati et al. suggested a similar mechanism by the reaction of 1,2,3-benzothiadiazole with diphenydiazomethane (Scheme 10).[11]

The reaction of **1a** with 2,5-norbornadiene is further confirmation of the carbene insertion mechanism. Treatment of **1a** and 2,5-norbornadiene in refluxing toluene resulted in the formation of the demethylated cycloadduct (**11**) and another type of 2:1 adduct (**12**) in 26 and 8% yields, respectively (Scheme 11). The structure of **11** was confirmed by spectroscopic, MS, and elemental analyses. ^{1}H NMR of **12** shows three methoxy (3.74, 3.75, and 3.86 ppm), one methylene (1.40 and 1.69 ppm), seven methine (1.86, 2.73, 2.75, 3.07, 3.42, 3.51, and 4.18 ppm), four olefinic (5.60, 6.05, 6.17, and 7.01 ppm), and twelve aromatic protons. ^{13}C NMR of **12** shows one methylene (42.7 ppm), seven methine, three methoxy (55 ppm around), eighteen olefinic and aromatic, and one carbonyl (201.6 ppm) carbons. Compound **12** would be a triplet carbene insertion product; the initial formation of [4 + 2] cycloadduct followed by 1,3-prototropy and demethylation afforded **11**, which was further attacked by a triplet carbenoid to give **12**.

Scheme 12



We also found that the reaction of **1c** with norbornadiene gave exclusively the 2:1 adduct. Treatment of **1c** with 2,5-norbornadiene at room-temperature resulted in the formation of *exo*-methylbenzoselenopyran (**13**), a similar product of **1c** with DMAD (Scheme 12). The structure of **13** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystallographic analysis.[9]

In summary, we have succeeded in the cycloaddition reaction of **1** with DMAD and 2,5-norbornadiene. The formation of 1-diarylmethylene-1*H*-2-benzoselenopyrans might proceed through diaryl carbenes as radical intermediates.

Experimental Section

General. All chemicals were obtained from commercial suppliers and used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254), and flash column chromatography was performed with silica (Merck, 70−230 mesh). NMR spectra (^{1}H at 400 MHz; ^{13}C at 100 MHz) were recorded in $CDCl_3$ solvent, and chemical shifts are expressed in ppm relative to internal TMS.

Material. 4,4′-Dimethoxyselenobenzophenone (**1a**) and 4,4′-dimethylselenobenzophenone (**1b**) were obtained by the reaction of diarylmethylenetriphenylphosphoranes with elemental selenium.[4]

Reaction of 1a with DMAD. To a solution of **1a** (0.090 g, 0.30 mmol) in toluene (10 mL) was added DMAD (0.184 mL, 1.5 mmol) in one portion. After being stirred for 10 h at room temperature, the reaction mixture was concentrated to afford a pale brown oil, which was chromatographed on silica gel (elution with 4:1 hexane/ethyl acetate). Compound **4a** was isolated 0.089 g (66%). **4a**: orange crystals: mp 45−46 °C. ^{1}H NMR ($CDCl_3$) δ = 3.77 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 3.95 (s, 3 H, OMe), 5.25 (s, 1 H, CH with Se−H satellite, J_{Se-H}=20 Hz), 6.82 (d, 2 H, J = 7 Hz, Ar), 6.92 (m, 1 H, Ar), 6.99 (m, 2 H, Ar), 7.13 (d, 2 H, J = 7 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 41.2 (CH), 52.9 (OMe), 53.0 (OMe), 55.3 (OMe), 55.5 (OMe), 113. 0, 114.1, 116.1, 124.6, 126.1, 128.3, 129.3, 132.4, 133.1, 138.7, 158.8, 159.0, 165.3 (COO), 168.5 (COO). Anal. Calcd for $C_{21}H_{20}O_6Se$: C, 56.38. H, 4.59%. Found: C, 56.43; H, 4.96%.

Reaction of 1b with DMAD. To a suspension of 4,4′-dimethyldiphenylmethyltriphenylphosphonium tetrafluoroborate (1.09 g, 2.0 mmol) in toluene (50 mL) was added butyllithium (1.5 mL in hexane, 10% w/v, 2.1 mmol) at room temperature. After being stirred for 20 min, elemental selenium (0.39 g, 6.0 mmol) was added to this red suspension in one portion. After refluxing for 30 min, DMAD (0.55 mL, 4.5 mmol) was added to this bright green suspension. After refluxing for 5 h, the reaction mixture was filtered and concentrated to afford a pale brown oil, which was chromatographed over silica gel by elution with hexanes−ethyl acetate (4:1). Triphenylphosphine selenide (0.60 g, 1.7 mmol), colorless oil of **4b** (0.20 g, 0.48 mmol), and colorless crystals of **5b** (0.33 g, 0.48 mmol) were obtained. Compound **5b**; colorless crystals; mp 173−175 °C. ^{1}H NMR ($CHCl_3$) δ = 2.25 (s, 3H, Me), 2.25 (s, 3 H, Me), 2.27 (s, 3H, Me), 2.29 (s, 3 H, Me), 3.73 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 5.02 (s, 1 H, CH), 6.50 (d, 2 H, J = 8 Hz, Ar), 6.86 (br, 4 H, Ar), 6.91 (d, 2 H, J = 8 Hz, Ar), 6.97

(d, 2 H, J = 8 Hz, Ar), 7.06 (d, 2H, J = 8 Hz, Ar), 7.37 (d, 1 H, J = 8 Hz, Ar), 7.47 (d, 2 H, J = 8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 20.90 (Me), 20.93 (Me), 20.99 (Me), 21.04 (Me), 52,65 (OMe), 52.73 (OMe), 58.79 (C), 59.36 (CH), 124.78, 127.83, 128,14, 128.32, 128.44, 128.65, 129.99, 130.23, 130.79, 130.99, 133.04, 135.50, 136.06, 136.34, 136.50, 138.51, 138.82, 139.01, 139.34, 163.53 (C=O), 168.53 (C=O). HRMS: Found: *m*/*z* 610.1572. Calcd for $C_{36}H_{34}O_4{}^{78}Se$ (M^+): *m*/*z* 610.1622. Anal. Calcd for $C_{36}H_{34}O_4Se$: C, 70.93; H, 5.62%. Found: C, 70.81; H, 5.57%.

Zinc Dust Reduction of 5b. To a solution of **5b** (0.30 g, 0.5 mmol) in acetic acid (5 mL) was added zinc dust (0.13 g, 2.0 mmol) in one portion at room temperature. After refluxing for 48 h, the suspension was filtered, poured into water (20 mL), and extracted with dichloromethane (10 mL × 3). The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and concentrated to give an orange oil, which was subjected to silica gel chromatography by elution with dichloromethane to give a orange oil of **4b** (0.043 g, 0.10 mmol).

Reaction of 1c with DMAD. To a solution of diphenylmethylenetriphenylphosphorane (0.436 g, 1 mmol) in benzene (20 mL) was added elemental selenium (0.316 mg, 4 mmol) in one portion. After refluxing for 30 min, DMAD (0.28 g, 2 mmol) was added to this suspension. After being refluxed for 1 h, the reaction mixture was filtered and concentrated to afford a pale brown oil, which was chromatographed over silica gel by elution of hexanes−ethyl acetate (4:1). Triphenylphosphine selenide (0.26 g, 0.75 mmol) and colorless crystals of **5c** (0.144 g, 0.26 mmol) were obtained.

Reaction of 1b with Methyl propiolate in the Presence of Acetic Acid. To a solution of 4,4′-dimethyldiphenylmethyltriphenylphosphonium tetrafluoroborate (2.72 g, 5.0 mmol) in toluene (50 mL) was added butyllithium (3.4 mL in hexane, 15% w/v, 5.5 mmol) at room temperature. After being stirred for 20 min, elemental selenium (1.58 g, 20 mmol) was added in one portion to this red suspension. After refluxing for 30 min, the suspension turned to bright green. To this suspension, acetic acid (1.50 g, 25 mmol) and methyl propiolate (0.84 g,10 mmol) was added. After being refluxed for 48 h, the reaction mixture was filtered and concentrated to afford a pale brown oil, which was chromatographed over silica gel by elution of hexanes−ethyl acetate (4:1). Triphenylphosphine selenide (1.20 g, 3.4 mmol) and colorless oil of **4f** (0.97 g, 1.75 mmol) were obtained. Compound **4f** was identical with the authentic sample.

Reaction of 2 with Diphenyldiazomethane in the Presence of $CuSO_4$. To a boiling solution of **2** (0.46 g, 1.5 mmol) and $CuSO_4$ (7 mg, 0.044 mmol) in benzene (10 mL) was added diphenyldiazomethane (0.44 g, 2.3 mmol). After refluxing for 12 h, excess benzene was distilled off and the residue was chromatographed over silica gel by elution with hexanes−ethyl acetate (4:1) afforded starting **2** (0.16 g, 0.48 mmol), **9** (0.075 g, 0.15 mmol), and **10** (0.09 g, 0.18 mmol). Separation of **9** and **10** is so difficult that all of **9** and **10** could not be isolated.

Compound **9**: yellow oil. ^{1}H NMR ($CHCl_3$) δ = 3.50 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 5.34 (s, 1 H, CH), 6.82 (m, 3 H, Ar), 7.09−7.36 (m, 14 H, Ar), 7.51 (d, 2 H, J = 7 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 52.46 (OMe), 52.72 (OMe), 55.99 (CH), 79.31 (C), 125.92, 125.98, 126.14, 126.35, 126.85, 127.29, 127.49, 127.57, 127.76, 128.26, 129.55, 130.41, 130.65, 131.46, 135.12, 138.93, 140.96, 142.45, 145.27, 165.56 (C=O), 166.64 (C=O). HRMS: Found: *m*/*z* 506.1537. Calcd for $C_{32}H_{26}O_4S$ (M^+): *m*/*z* 506.1552. Compound **10**: yellow oil. ^{1}H NMR ($CHCl_3$) δ = 3.72 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 5.15 (1 H, s, CH), 6.62 (d, 3 H, J = 7 Hz, Ar), 7.02−7.31 (m, 14 H, Ar), 7.46 (d, 2 H, J = 7 Hz, Ar, 7.68 (d, 2 H, J = 7 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 52.69 (OMe), 52.97 (OMe), 59.25 (CH), 59.66, 125.80, 125.95, 126.40, 126.79, 126.98, 127.07, 127.12, 127.17, 127.66, 128.24, 128.50, 129.41, 130.88, 130.94, 131.35, 136.40, 136.89, 139.93, 141.06, 141.69, 164.30 (C=O), 167.60 (C=O). HRMS: Found: *m*/*z* 507.1605. Calcd for $C_{32}H_{26}O_4S$ ($M+1^+$): *m*/*z* 507.1606.

Reaction of 2 with Diphenyldiazomethane in the Presence of $Rh_2(OAc)_4$. To a refluxing solution of **2** (0.31 g, 1.0 mmol) and rhodium acetate (0.004 g, 0.05 mmol) in benzene (10 mL) was added dropwise a solution of diphenyldiazomethane (0.29 g, 1.5 mmol) in benzene (5 mL). After refluxing for 0.5 h, the reaction mixture was filtered and evaporated to give pale brown oily crystals, which was subjected to column chromatography by elution with hexane−dichloromethane then dichloromethane−ethyl acetate to give diphenyl azine (0.14 g, 0.38 mmol), **9** (0.07 g, 0.14 mmol), and **10** (0.037 g, 0.08 mmol). Starting **2** (0.11 g, 0.35 mmol) was recovered. Separation of **9** and **10** is so difficult that all of **9** and **10** could not be isolated.

Reaction of 4b with Di-*p*-tolyldiazomethane in the Presence of $Rh_2(OAc)_4$. To a refluxing solution of **4b** (0.179 g, 0.5 mmol) and rhodium acetate (0.004 g, 0.05 mmol) in benzene (8 mL) was added dropwise a solution of ditolyldiazomethane (0.29 g, 1.5 mmol) in benzene (25 mL). After being refluxed for 0.5 h, the reaction mixture was filtered and evaporated to give pale brown oily crystals, which were subjected to column chromatography by elution with hexane−dichloromethane then dichloromethane−ethyl acetate to give di-*p*-tolyl azine (0.357 g, 0.75 mmol), **3b** (0.043 g, 0.075 mmol), and **5b** (0.003 g, 0.005 mmol). Starting **4b** (0.082 g, 0.23 mmol) was recovered. Compound **5b** is identical with the authentic sample. Compound **3b**: pale yellow oil: ^{1}H NMR ($CHCl_3$) δ = 2.20 (s, 3 H, Me), 2.25 (s, 3 H, Me), 2.32 (s, 3 H, Me), 2.37 (s, 3 H, Me), 3.57 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 5.24 (s, 1 H, CH), 6.74 (d, 2H, J = 7 Hz, Ar), 6.86−7.05 (m, 8H, Ar), 7.31 (d, 2 H, J = 7 Hz, Ar), 7.42 (d, 1 H, J = 7 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 20.99 (Me), 21.03 (Me), 21.14 (Me), 21.24 (Me), 52.63 (OMe), 52.96 (OMe), 54.61, 54.65 (CH), 127.53, 127.62, 127.97, 128.53, 129.10, 129.61, 130.50, 131.58, 131.75, 131.79, 135.56, 135.70, 136.44, 136.70, 136.98, 137.52, 140.63, 143.52, 166.41 (C=O), 167.19 (C=O). HRMS: Found: *m*/*z* 610.1709. Calcd for $C_{36}H_{34}O_4{}^{80}Se$ (M^+); *m*/*z* 610.1622. Anal. Calcd for $C_{36}H_{34}O_4Se$: C, 70.93; H, 5.62%. Found: C, 70.53; H, 5.84%.

Reaction of 1a with 2,5-Norbornadiene. To a solution of **1a** (0.154 g, 0.5 mmol) in toluene was added 2,5-norbornadiene (0.18 g, 2.0 mmol) in one portion. After refluxing for 4 h, the reaction mixture was concentrated to afford pale brown crystals, which was chromatographed over silica gel by elution of hexanes−ethyl acetate (4:1). Yellow oil of **11** was obtained in 26% yield (0.053 g, 0.13 mmol). **11**: Yellow oil: ^{1}H NMR ($CHCl_3$) δ = 1.64 (br d, 1 H, J = 9 Hz, CH_2), 1.90 (dd, 1 H, J = 8 and 10 Hz, CH), 2.36 (d, 1 H, J = 9 Hz, CH_2), 2.80 (br d, 1 H, J = 16 Hz, CH), 2.90 (m, 2 H, CH_2), 3.00 (d, 1H, J = 8 Hz, CH_2), 3.03 (br s, 1 H, CH_2), 3.47 (dd, 1 H, J = 2 and 8 Hz, CH_2), 3.84 (s, 3 H, OMe), 5.79 (d, 1 H, J = 10 Hz, CH=), 6.11 (dd, 1 H, J = 3 and 6 Hz, CH=), 6.23 (dd, 1 H, J = 3 and 6 Hz, CH=), 6.93 (d, 2 H, J = 8 Hz, Ar), 7.06 (d, 1 H, J = 10 Hz, CH=), 7.42 (d, 2 H, J = 8 Hz, Ar). ^{13}C NMR ($CDCl_3$) δ = 40.45, 43.90, 45.56, 45.65, 47.20, 47.55, 50.35, 52.05, 55.26, 113.50, 122.16, 130.86, 131.27, 135.00, 135.64, 138.61, 141.71, 150.07, 160.08, 198.83 (C=O). HRMS: Found: *m*/*z* 385.0708. Calcd for $C_{21}H_{21}O_2{}^{80}Se$ ($M + 1^+$): 385.0706. Elemental analysis was carried out by using its hydrazone. mp 230−232 °C. Found: C, 57.16; H, 4.30; N, 9.65%. Calcd for $C_{27}H_{24}N_4O_5Se$: C, 57.55; H, 4.29; N, 9.94%. Compound **12** was obtained in 8% yield (0.012 g, 0.02 mmol). **12**: Yellow crystals; mp 209−210 °C: ^{1}H NMR ($CHCl_3$) δ = 1.40 (d, 1 H, J = 9 Hz, C*H*H), 1.69 (d, 1 H, J = 9 Hz, C*H*H), 1.86 (dd, 1 H, J = 8 and 10 Hz, CH), 2.73 (br s, 1 H, CH), 2.75 (d, 1 H, J = 12 Hz, CH), 3.07 (br s, 1 H, CH), 3,42 (br d, 1 H, J = 7 Hz, CH), 3.51 (d, 1 H, J = 12 Hz, CH), 3.74 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 3.86 (s, 3 H, OMe), 4.18 (d, 1 H, J = 12 Hz, CH), 5.60 (d, 1 H, J = 10 Hz, CH=), 6.05 (dd, 1 H, J = 3 and 6 Hz, CH=), 6.17 (dd, 1 H, J = 3 and 6 Hz, CH=), 6.80 (d, 2 H, J = 8 Hz, Ar), 6.83 (d, 2 H, J = 8 Hz, Ar), 6.94 (d, 2 H, J = 8 Hz, Ar), 7.01 (d, 1 H, J = 10 Hz, CH=), 7.22 (d, 2 H, J = 8 Hz, Ar), 7.27 (d, 2 H, J = 8 Hz, Ar), 7.47 (d, 2 H, J = 8 Hz, Ar).). ^{13}C NMR ($CDCl_3$) δ = 42.67 (CH_2), 45.18 (CH), 46.76 (CH), 49.10 (CH), 50.49 (CH), 51.02 (CH), 54.97 (OMe), 55.10 (OMe), 55.25 (OMe), 55.31 (OMe), 55.81 (CH), 113.49, 113.56, 113.86, 121.28, 128.61, 128.71, 131.02, 131.42, 133.70, 134.33, 134.44, 135.92, 138.55, 139.95, 151.68, 157.75, 157.85, 160.23, 201.60 (C=O). HRMS: Found: *m*/*z*

610.1613. Calcd for C_{36} $H_{34}O_4{}^{80}Se$ (M^+): *m*/*z* 610.1622. Anal. Found: C, 70.58; H, 5.61%. Calcd for $C_{36}H_{34}O_4Se$: C, 70.93; H, 5.62%.

Reaction of 1c with 2,5-Norbornadiene. To a suspension of diphenylmethyltriphenylphosphonium bromide (2.55 g, 5.0 mmol) in toluene (50 mL) was added a solution of butyllithium (3.5 mL, 10% w/v, 5.5 mmol) in hexane at room temperature. After being stirred for 1 h, elemental selenium (1.18 g, 15 mmol) was added in one portion to this red suspension. After refluxing for 5 min, the red suspension turned to a bright green suspension of selenobenzophenone. 2,5-Norbornadiene (3.8 mL, 35 mmol) was added to this suspension and refluxed for 20 h. The reaction mixture was filtered and evaporated to give brown oily crystals, which were extracted with hexane three times. The residue was recrystalized from methanol to afford triphenylphosphine selenide (0.852 g, 2.5 mmol). The combined extracts were chromatographed over silica gel by elution with hexane−dichloromethane (9:1) to give triphenylphosphine selenide (0.17 g, 0.5 mmol) and the adduct **13** (0.553 g, 1.1 mmol, 44%). Tetraphenylethylene (0.35 g, 1.05 mmol) and benzophenone (0.18 g, 1.0 mmol) were obtained. **13**: colorless crystals; mp 186−187 °C. ^{1}H NMR ($CHCl_3$) δ = 1.28 (d, 1 H, J = 8 Hz, C*H*H),1.54 (br, 1 H, CH), 1.94 (d, 1 H, J = 8 Hz, CH), 2.60 (d, 1 H, J = 7 Hz, CH), 2.67 (s, 1 H, CH), 3.14 (s, 1 H, CH), 5.08 (s, 1 H, CH), 5.97 (m, 1 H, CH), 6.22 (m, 1 H, CH), 6.78−7.67 (m, 19 H, Ar). ^{13}C NMR ($CDCl_3$) δ = 36.14, 40.55, 49.12, 53.18, 54.96, 61.69, 124.29, 125.97, 126.08, 126.22, 126.33, 127.05, 127.32, 127.49, 130.36, 130.76, 131.09, 131.38, 131.60, 135.09, 137.91, 142.17, 142.41, 143.09, 143.21, 146.12. Anal. Calcd for $C_{33}H_{28}Se$: C, 78.71; H, 5.60%. Found: C, 78.86; H, 5.33%.

Supporting Information Available: Spectral data of compounds **4b**, **4d**, **4e**, **4f**, **4g**, **4h**, **5c**, **5e**, **5f**, and **5g**; text giving full details of the X-ray structure of **5b** and **13** including the tables of crystal sata, structure refinements, atomic coordination parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991679W