REACTIONS OF SELENOBENZOPHENONES WITH DIMETHYL ACETYLENEDICARBOXYLATE OR NORBORNADIENE

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Reactions of selenobenzophenones with dimethyl acetylenedicarboxylate or norbornadiene gave benzoselenapyranes or seven-membered cyclic selenides; these reactions might proceed through unusual type of cycloaddition reaction.

The chemistry of thio- and selenocarbonyl compounds is of current interest.¹) The reaction of thiobenzophenones is well studied.²) For example, the reaction of thiobenzophenone with dimethyl acetylenedicarboxylate (DMAD) at room temperature or under irradiation by a Na lamp gave dimethyl 1-H-benzothiopyranedicarboxylate.³) Recently, we have reported the isolation and some reactions of selenobenzophenones (1).⁴) However, to our knowledge, there is no report on the reaction of selenoketones with acetylenedicarboxylate and some bicyclic olefins.

We first tried the reaction of 4, 4'-dimethoxyselenobenzophenone (1a) with DMAD. Treatment of 1a with DMAD at room temperature resulted in the formation of colorless crystals of dimethyl 1-H-benzoselenapyranedicarboxylate (2a) in 66% yield.



However, when unstable selenobenzophenones were used as substrates, the result was quite different from the above. When unsubstituted selenobenzophenone (1b) derived from benzhydrylidenetriphenylphosphorane was used as a starting material, unusual seven-membered bicyclic selenide (3) was obtained in 26 % yield. The results were shown in Table 1.



Table 1. The Reaction of Selenobenzophenones with DMAD,

	Compoun Ar	d 1 Ar'	Conditions Temperature	Time	Solvent	2	Product 3	ts Yield olefin	1/% Ph3P=Se
1a	p-MeOC ₆ H ₂	p-MeOC ₆ H ₄	r t (°C)	5 (hr)	THF	2a 66	3a 0	0	-
1 b	C_6H_5	C_6H_5	гt	5	Toluene	2b 0	3b 26	35	85
1 c	p-McC ₆ H ₅	p-MeC ₆ H ₅	гt	5	Toluene	2c 28	3c 18	50	89
1 d	C_6H_5	2,4-Me ₂ C ₆ H ₃	50	5	Toluene	2d 47	3d 0	44	89

Many reactions of selenoketones with dienes were observed, which resulted in the formation of cycloadducts.⁵⁾ However, there has been no report about the reaction with acetylenic compounds. Selenofluorenone synthesized by Krafft *et al.* from the reaction of the corresponding selenocyanate with triethylamine reacted with dienes or dipolar reagents to afford the corresponding cycloadducts.⁶⁾ They did not mention any reaction with acetylenic compounds due to their low reactivity. However, dimeric selenofluorenone adduct was isolated in the reaction with pyridine N-oxide. Selenofluorenone acted not only as a dienophile but also as a diene and it is the only selenoketone ever reported acting as a diene. The present reaction is the first example of acetylenophilic selenoketone.



Norbornadiene is a strained bicyclic compound and its reactivity is different from that of normal dienes. The reaction of norbornadiene with selenium afforded the unusual cyclic triselenide.⁷) We tried the reaction with selenobenzophenones and found that the products were seven-membered tricyclic compounds (4).



+ (R')RC=CR(R') + Ph₃P=Se

Compound 1			Conditions		Products Yield/%			
R	R'	Se/eq.	Diene or Ene	Temperature	4	Olefin	Ph3P=Se	
Ph	Ph	3	Norbornadiene	reflux	4a 21	18	71	
Ph	Ph	3	Norbornene	reflux	4b 23	22	74	
p-Tol	p-Tol	3	Norbornadiene	reflux	4c 24	20	100	
П	Ph	3	Norbornadiene	reflux	4d 0	65	85	

Table 2. Reaction of Selenobenzophenones with Norbornadiene or Norbornene.

Interestingly, the reaction of thiobenzophenones derived from Wittig reagent and elemental sulfur with norbornadiene afforded the corresponding seven membered tricyclic thioether (21 % yield).

There are two plausible mechanisms which can explain the formation of seven-membered thio- or selenoethers. In one mechanism (path \mathbf{a}), norbornadiene reacts with selenium to afford cyclic triselenide, which is changed to episelenide. The resulting episelenide reacts with tetraphenylethylene in a [4+3] manner to give the seven-membered cyclic selenide. Another route (path \mathbf{b}) is the reaction of an episelenide treated norbornadiene to give the product.

Mechanism



Although we have not obtained experimental evidence, we consider that the reaction most likely proceeds via path **b** since there is no report on the reaction of DMAD with selenium leading to the corresponding tricyclic selenides.

In summary, the reaction of selenobenzophenones with DMAD afforded unusual six- and seven-membered cyclic selenides. Interestingly, the reaction of selenobenzophenones with norbornadiene or norbornene also gave seven-membered cyclic selenides. This is the first example for the reaction of selenobenzophenones with olefins. The present results will provide the new chemistry of selenobenzophenones. Efforts to explore the chemistry of selenobenzophenones and to expand the scope of selenocarbonyl reactivity are continuing in our laboratories.

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- Satisfactory elemental analyses were obtained for all new compounds. Spectral data of 2, 3, and 4: 2a: 8) mp. 45-46 °C, ¹H NMR (CDCl₃) δ =3.77 (s,3H), 3.78 (s, 3H), 3.81 (s, 3H), 3.95 (s, 3H), 5.25 (s, 11I, CH, with Se-H satellite), 6.82 (d, 2H), 6.92 (m, 1H), 6.99 (m, 2H), 7.13 (d, 2H), ¹³C NMR (CDCl₃) δ=41.22 (CH), 52.87 (OMe), 52.96 (OMe), 55.29 (OMe), 55.47 (OMe), 113.00 114.00, 116.15, 124.63, 126.13, 128.36, 129.28, 132.41, 133.14, 138.71 9, 158.85 (ipso), 159.05 (ipso), 165.27 (C=O), 168.47 (C=O). 2c: ¹H NMR (CDCl₃) δ =2.31 (s, 3H), 2.37 (s, 3H), 3.76 (s, 3H), 3.97 (s, 3H), 5.24 (s, 1H, CH, with Se-H satellite), 6.96 (d, 1H), 7.10 (s, 4H), 7.18 (d, 1H), 7.24 (d, 1H). 2d: mp. 64-65 °C, ¹H NMR (CDCl₃) δ =2.26 (s, 3H, Me), 2.38 (s, 3H, Me), 3.72 (s, 3H, OMe), 3.95 (s, 3H, OMe), 5.44 (s, 1H, CH, with Se-H satellite), 6.80-7.46 (m, 7H, Ar). 3b: mp. 194-195 °C, ¹H NMR (CDCl₃) δ =3.70 (s, 3H), 3.75 (s, 3H), 5.11 (s, 1H, CH), 6.61 (d, 2H, Ar), 6.95-7.36 (m, 15H, Ar), 7.49 (d, 1H), 7.64 (d, 2H). 3c: mp. 173-174 °C, ¹H NMR (CDCl₃) δ =2.25 (s, 6H), 2.27 (s, 3H), 2.29 (s, 3H), 3.73 (s, 3H, OMe), 3.75 (s, 3H, OMe), 5.02 (s, 1H, CH), 6.50 (d, 2H, Ar), 6.80-7.10 (m, 10H, Ar), 7.37 (d, 1H, Ar), 7.47 (d, 2H, Ar). 4a; mp. 186-187 °C ¹H NMR (CDCl₃) δ =1.28 (d, 1H), 1.54 (d, 1H), 1.94 (d, 1H), 2.60 (d, 1H), 2.67 (s, 1H), 3.14 (s, 1H), 5.08 (s, 1H), 5.96-5.98 (q, 1H), 6.21-6.23 (q, 1H), 6.78-7.70 (m, 19H, Ar) 4b; mp 172-173 °C ¹H NMR (CDCl₃) δ =1.00 (d, 1H), 1.12 (t, 1H), 1.26 (t, 1H), 1.58 (d, 2H), 1.79 (d, 1H), 1.89 (d, 1H), 2.01 (s, 1H), 2.57 (s, 1H), 2.78 (d, 1H), 5.10 (s, 1H), 6.82-7.68 (m, 19H, Ar). 4c: mp 199.5-200.5 °C ⁻¹H NMR (CDCl₃) δ =1.29 (d, 1H), 1.54 (d, 1H), 1.94 (d, 1H), 2.60 d, 1H), 2.67 (s, 1H), 3.14 (s, 1H), 5.08 (s, 1H), 5.97 (q, 1H), 6.22 (q, 1H), 6.78-7.68 (m, 19H).

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