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STEREOSELECTIVE SYNTHESIS OF TRANS OLEFINS BY THE REACTION OF WITTIG REAGENTS WITH SELENIUM. FORMATION OF SELENOCARBONYL COMPOUNDS.

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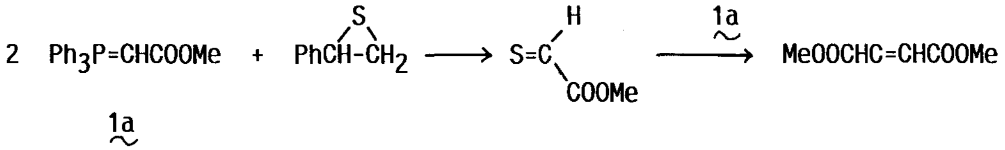
Summary: Wittig reagents were successfully changed to symmetrical olefins when treated with elemental selenium. The reaction proceeds through a selenocarbonyl intermediate, which existence was confirmed by Diels-Alder reaction.

Phosphonium ylides (**1**) have been widely utilized for the synthesis of olefins[1] and also known to react with sulfur to afford thiocarbonyl compounds.[2] However, there is no report on the reaction of **1** with selenium. Recently, we found that the reaction of stable Wittig reagents (**1**) with episulfides afforded alkyl fumarates or maleates in good yields and this reaction might proceed through a thioaldehyde intermediate.[3]



This consideration, in turn, prompted us to investigate the possibility of the formation of selenocarbonyl compounds by the reaction of elemental selenium (**2**) with Wittig reagents. In this communication, we would like to report that the reaction of 1 with selenium gave olefins (**3**) via selenocarbonyl intermediates (**4**) in good yields.

A typical reaction was run as follows: To a solution of triphenylcarboxymethylenephosphorane (**1a**) (10 mmol) in toluene (100 ml) was added a suspension of 2 in toluene. After refluxing for 3 h, the reaction mixture was evaporated and the remaining oil was extracted three times with hexane. The combined extracts were evaporated and roughly chromatographed on silica gel to give dimethyl fumarate (**3a**) in 73.6% yield. Other reactions were carried out in a similar manner (Table 1).

$$2\ \underset{\underset{\sim}{1}}{Ph_3P{=}C(R)R'} + 2\ \underset{\underset{\sim}{2}}{Se} \longrightarrow \underset{\underset{\sim}{3}}{R'(R)C{=}C(R)R'} + 2\ \underset{\underset{\sim}{5}}{Ph_3P{=}Se}$$

Table 1. Reaction of 1 with 2.

Compound			Conditions			Products^{4} Yields (%)		
1	R	R'	Solvent	Temperature	Time	**5**	**3**	trans/cis^{a}
a	H	COOMe	toluene	reflux (°C)	3 (h)	77.6	73.6	trans only
a	H	COOMe	toluene	60	18	75.5	68.0	trans only
b	H	COOEt	toluene	reflux	3	95.5	97.7	trans only
c	H	Ph	toluene	reflux	2	79.0	68.0	4
c	H	Ph	THF	reflux	2	70.5	60.5	8
c	H	Ph	THF	rt	5	67.5	58.0	10
c	H	Ph	toluene	0	8	63.5	50.5	10
d	H	CN	toluene	reflux	3	54.5	52.8	trans only
e	H	COMe	toluene	reflux	3	81.7	56.2	trans only
f	Ph	Ph	toluene	reflux	3	55.0	45.0	-
f	Ph	Ph	toluene	reflux	8	70.5	65.5	-

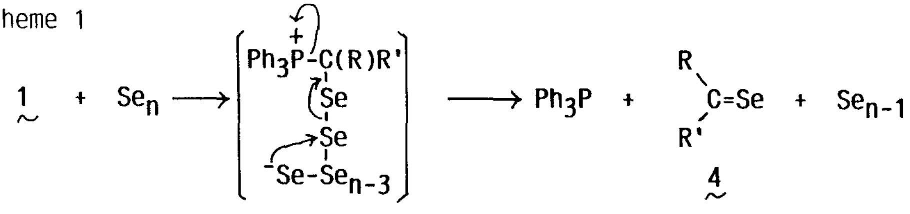
a) The ratio was determined by NMR or capillary GLC.

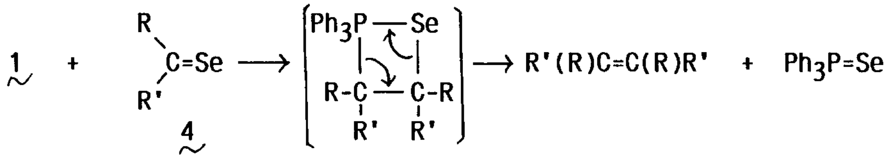
In the case of stable Wittig reagents, relatively severe conditions are necessary to complete the reaction (elevated temperature, longer time). However, the reaction proceeded even at 0°C when **1c** was used as substrate. These results were quite different from those of the reactions of **1** with sulfur. Staudinger and Meyer reported that the cleavage of benzhydrylidenetriphenylphosphorane in the presence of sulfur gave thiobenzophenone and triphenylphosphine sulfide.[2a] Tokunaga and coworkers reported that the reaction of benzylidenetriphenylphosphorane with sulfur gave cyclic polysulfide and a very small amounts of stilbenes and suggested that the reaction might proceed thioaldehyde intermediates.[2c]

Previously, several groups reported the reactions of organophosphorus compounds with elemental selenium. Mikolajczyk and coworkers synthesized vinylphosphonates by the addition of elemental selenium to phosphonate carbanion followed by alkylation and oxidative elimination of the organoselenium moiety.[5] Yoshifuji et al. prepared selenadiphosphiranes and diselenoxophosphorane by the reaction of diphosphenes with elemental selenium.[6] It is also well known that the reaction of triphenylphosphine with selenium gives triphenylphosphine selenide.[7] However, there is no report on the reaction of elemental selenium with Wittig reagents.

In the course of studies on the ring opening reaction of episulfides, we found that the reaction of thioaldehydes with stable phosphonium ylides gave olefins.[3] Similarly, the reaction of **1** with selenium might proceed through selenoaldehyde intermediates as shown below.

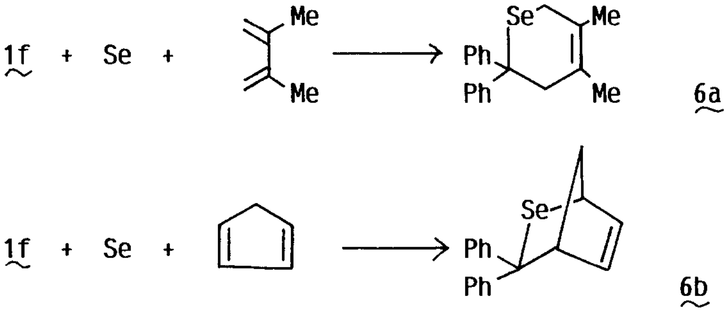
Scheme 1



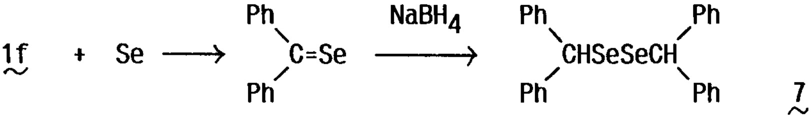


The ylide carbanion attacks elemental selenium to give the corresponding **4**. The resulting **4** further reacts with **1** to afford olefins via a Wittig-like reaction. To confirm the above mechanism, we carried out cycloaddition reactions to trap the selenocarbonyl intermediates. As shown in Scheme 2, Diels-Alder adducts (**6**) were obtained in good yields.[8]

Scheme 2.



We also found that the reduction of **4** with $NaBH_4$ afforded diphenylmethyl diselenide (**7**) in 60% yield.[9] This is another evidence for the formation of diphenylselenoketone.



Selenoketones and selenoaldehydes have been virtually ignored in synthesis, probably due to their high reactivity and difficulty of preparation. Only one isolated report mentions the synthesis of di-t-butylselenoketone and 1,3,3-trimethylnorbornane-2-selenoketone.[10] Recently, Nakayama and coworkers reported the formation α-carbonylselenoketones, which reacted with carbonyl stabilized sulfonium ylides to give 1,3-oxaselenoles in good yields.[11] However, there is no report on the synthesis of selenocarbonyl compounds from Wittig reagents. The present method is the first example of formation of selenoketones and selenoaldehydes from Wittig reagents.

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References

1) Wittig, G.; Schöllkopf, U. Chem. Ber. **1954**, 87, 1318. For reviews, see Emsley, J.; Hall. D. The Chemistry of Phosphorus, Harper & Row Ltd., London, **1955**, pp. 274-298; Johnson, A. W. Ylid Chemistry, Academic Press, New York, **1966**, pp. 132-147; Maercker, A. Organic Reactions, Vol. **14**, John Wiley & Sons, Inc., **1965**, pp. 270-490.

2a) Staudinger, H.; Meyer, J. Helv. Chim. Acta **1919**, 2, 635. 2b) Schönberg, A.; Brosowski, K-H.; Singer, E. Chem. Ber. **1962**, 95, 2144. 2c) Tokunaga, H.; Akiba, K.; Inamoto, N. Bull. Chem. Soc. Jpn. **1972**, 45, 506.

3) Okuma, K.; Yamasaki, Y.; Komiya, T.; Kodera, Y.; Ohta, H. Chem. Lett. **1987**, 357.

4) Products were identified by comparison to authentic samples.

5) Mikolajczyk, M.; Grzejszczak, S.; Korbacz, K. Tetrahedron Lett. **1981**, 22, 3097. Mikolajczyk, M.; Grzejszczak, S.; Chefczynska, A.; Zatorski, A. J. Org. Chem. **1979**, 44, 2967.

6) Yoshifuji, M.; Shibayama, K.; Inamoto, N. Chem. Lett. **1984**, 603. They also reported the reaction of diphosphene with elemental sulfur: Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. J. Chem. Soc., Chem. Commun. **1983**, 862.

7) Michaelis, A. Ann. **1901**, 315, 43.

8) Satisfactory elemental analyses and/or exact mass molecular weights were obtained for all new compounds. Spectral data of **6**: **6a**; pale yellow oil, ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 6H), 2.81 (br s, 2H), 2.92 (br s, 2H), 7.02-7.20 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 20.10, 20.86, 24.76, 47.73, 52.06, 124.66, 126.50, 127.80, 128.01, 128.23, 128.39, 128.56, 128.66, 147.14. **6b**; mp 139-141°C, ^{1}H NMR ($CDCl_3$) δ 2.27 (dt, 1H), 2.37 (d, 1H), 3.80 (br s, 1H), 4.57 (br s, 1 H), 5.47 (dd, 1 H), 6.43 (dd, 1 H), 7.09-7.60 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 50.98, 52.50, 55.31, 126.39, 127.96, 128.34, 128.72, 129.96, 132.73, 133.05, 139.39, 146.22, 149.25; IR (KBr) 3045, 3015, 2990, 1595, 1483, 1440, 1337, 1075, 1035, 1017, 972, 905, 850, 785, 760, 730, 700 (cm^{-1}).

9) Spectral data of **7**: mp 121.5-123 °C; ^{1}H NMR ($CDCl_3$) δ 5.1 (s, 2 H), 7.33 (s, 10 H); ^{13}C NMR ($CDCl_3$) δ 51.90, 127.26, 128.45, 129.04, 141.23; IR (KBr) 3100, 3075, 3040, 1500, 1459, 1090, 1040, 770, 758, 710, 702, 622 (cm^{-1}).

10) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec Jr., F. S. J. Chem. Soc., Chem. Commun. **1975**, 539. Idem, J. Chem. Soc. **1976**, 2079.

11) Nakayama, J.; Sugiura, H.; Hoshino, M.; Kobayashi, H. Tetrahedron Lett. **1985**, 26, 2201.

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