

A CONVENIENT SYNTHESIS OF SELENONIUM YLIDES¹⁾

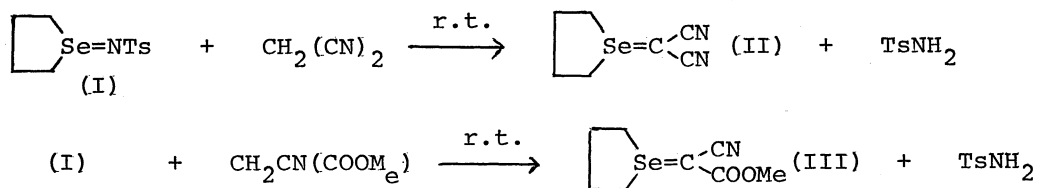
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The treatment of selenonium N-p-toluenesulfonimides and selenoxides except diphenyl selenoxide with active methylene compounds readily afforded the corresponding stable selenonium ylides in relatively high yields.

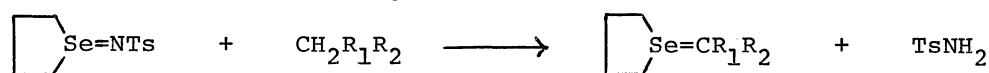
In connection with sulfonium ylides, much attention has been paid to selenonium ylides²⁾ and very recently Ibragimov and coworkers have prepared several of them from the corresponding selenium dihalides and active methylene compounds in the presence of a base.³⁾ In view of the interest of such compounds we would like to present another valuable method of synthesizing some stable alkyl and aryl selenonium ylides from the corresponding selenonium N-p-toluenesulfonimides or selenoxides.

Synthesis from Selenonium Imides: tetramethylene selenonium N-p-toluenesulfonimide (I: 304 mg, 1 mmol) was treated with an equimolar amount of, for example, malononitrile or methyl cyanoacetate in dried CHCl_3 at room temperature. After the solution had stood overnight, the solvent was evaporated in vacuo and the resulting residue was washed with Et_2O to remove the produced p-toluenesulfonamide and recrystallized from CHCl_3 - Et_2O , yielding, as white solids, tetramethylene selenonium dicyanomethylide (II: mp 91-93°C, 163 mg, 82%) or tetramethylene selenonium cyanomethoxycarbonylmethylide (III, mp 125-126°C, 206 mg, 89%). On the basis of the elemental analyses, and the ir and nmr spectra, the structure of these materials were confirmed to have the following formulas.



Meanwhile, the reactions of I with other methylene compounds were examined by following disappearance of the nmr peak due either to the CH₃ protons in I or to the CH₂ protons in methylene compounds employed. Table I collects the results of the reactions.

Table I. The Reactions of I with One Equivalent of Methylene Compounds in CDCl₃ at Room Temperature.

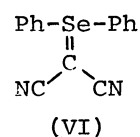
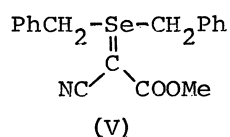
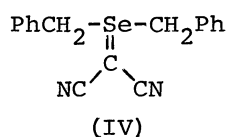


R ₁	R ₂	Initial relative rate	Yield ^{a)} of ylide(%)	pK _a for CH ₂ R ₁ R ₂
CN	CN	18	quant.	11
CN	COOMe	4.2(4.4) ^{b)}	quant.(quant.)	9
COMe	COMe	1.1	89	9
COOMe	COOMe	1.0	25	13
SO ₂ Ph	SO ₂ Ph	very slow	54.5	---
H	NO ₂	no reaction	0	10

a) After 15 days. b) Figures in parentheses are values for the reaction of tetramethylene selenoxide.

As the table shows, the initial rates for methylene compounds fall in the order: (NC)₂CH₂ > NCCH₂COOMe > MeCOCH₂COMe > MeOOCCH₂COOMe > PhSO₂CH₂SO₂Ph > CH₃NO₂ and no linear correlation was obtained between the dissociation constants, pK_a, and the initial rates for methylene compounds; the stabilities of selenonium ylides formed seem to play an essential role in determining the reactivity order of methylene compounds.

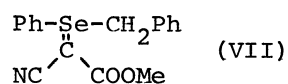
Furthermore, by the use of the same procedure as that described above, dibenzyl (IV: mp 136.5-137.5°C, yield 70.0 % and V: mp 133-134°C, yield 82.5 %) ⁴⁾ and diphenyl (VI: mp 118-122°C, yield 62.6 %) selenonium ylides depicted below were also obtained from the corresponding N-p-toluenesulfonimides.



Synthesis from Selenoxides: a few selenonium ylides could also be synthesized

by treating the corresponding selenoxides with desired methylene compounds with or without addition of a desiccating agent; thus, an equimolar mixture of tetramethylene selenoxide (151 mg, 1 mmol) and either malononitrile or methyl cyanoacetate was dissolved in dried CHCl_3 . After the solution was kept at room temperature for 12 hr, removal of the solvent and then recrystallization of the resulting residue from $\text{CHCl}_3\text{-Et}_2\text{O}$ afforded II (195 mg, 84 %) or III (133 mg, 67 %). Similarly, dibenzyl selenoxide easily gave the corresponding selenonium ylides, IV and V, in 72 and 75 % yields, respectively.

The reaction of phenyl benzyl and diphenyl selenoxides was fairly slow even with the most reactive malononitrile. Therefore, in order to accomplish the reaction, such a desiccating agent as sodium sulfate or magnesium sulfate must be added to the reaction mixture. Thus, phenyl benzyl selenoxide reacted with methyl cyanoacetate and afforded the anticipated phenyl benzyl selenonium cyanomethoxycarbonylmethylide (VII: mp 133-134°C)⁵⁾ in 68 % yield. However, the reaction of



diphenyl selenoxide with methylene compounds was found to be markedly different in reaction modes from that of phenyl benzyl selenoxide; thus, the reaction with malononitrile afforded 53.4 % of the reduction product, i.e., diphenyl selenide as a main product along with a poor amount of the expected selenonium ylide (VI: 6.6 %), whereas that with methyl cyanoacetate yielded no ylide but the reduction product only. Detailed features of this reduction are now being examined.

References

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- 4) (IV): Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{Se}$: C, 62.77; H, 4.31; N, 8.62%. Found: C, 62.37;

H, 4.19; N, 8.27%. IR(KBr): 2150(C≡N), 1270, 760, and 690 cm^{-1} .

(V): Calcd. for $\text{C}_{18}\text{H}_{17}\text{NO}_2\text{Se}$: C, 60.33; H, 4.78; N, 3.91%. Found: C, 60.70, H, 4.50; N, 3.77%. NMR(CDCl_3): 3.67(s, 3H), 4.45(q, 4H), 7.41(s, 10H) ppm. IR(KBr): 2150(C≡N), 1630(C=O), 1320, and 1170 cm^{-1} .

- 5) (VII): Calcd. for $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{Se}$: C, 59.31; H, 4.39; N, 4.07%. Found: C, 59.02; H, 4.27; N, 4.03%. NMR(CDCl_3): 3.76(s, 3H), 3.38-3.92(q, 2H), 7.42 and 7.65 (s,s, 10H). IR(KBr): 2160(C≡N), 1640(C=O), 1450, 1350, and 745 cm^{-1} .

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