

Alkylation of Heteroaromatic Bases with Diphenylselenium Diacyloxylate

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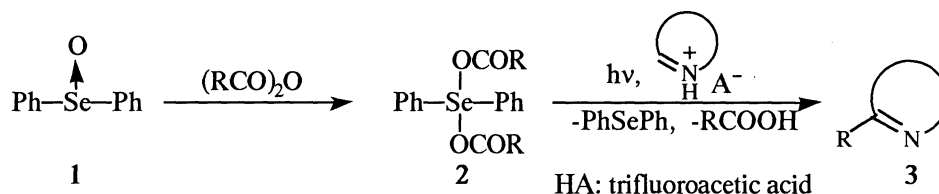
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Heteroaromatic bases were alkylated with selenuranes, which were formed by the reaction of diphenylselenoxide and carboxylic anhydrides, under photoirradiation conditions. This reaction was presumed to proceed via a radical pathway accompanying decarboxylation.

Preparation of hypervalent selenium compounds has been well studied along with hypervalent tellurium and sulfur compounds.¹⁾ Among them, tetravalent selenium compounds such as diarylselenium bis(trifluoroacetate), $\text{Ar}_2\text{Se}(\text{OCOCF}_3)_2$, have been used as an oxidant under mild conditions.²⁾ Recently, Suárez et al.³⁾ reported that diphenylselenurane reacts with alcohols in the presence of iodine to generate alkoxy radical which intramolecularly abstracts hydrogen atom from non-activated carbons through a six-membered ring transition state (Barton reaction). However, little attention has been focussed to the selenurane chemistry as a reagent.

As a part of our study directed toward alkylation of heteroaromatic bases with hypervalent heteroatom compounds, especially in relation to synthetic applications to nucleosides,⁴⁾ we have studied the alkylation of heteroaromatic bases with selenurane compounds. We report herein the first study on the alkylation of heteroaromatic bases with diphenylselenium diacyloxylate under photochemical conditions.

Selenurane **2** was obtained by the reaction of selenoxide **1** with the corresponding carboxylic anhydride.⁵⁾ The selenuranes may be also isolated,⁶⁾ though their stabilities depend on the acyloxy group of **2**. Thus, selenurane **2** slowly decomposed to diphenylselenium hydroxy acyloxylate, if R group is primary and secondary. The selenurane was thus used without isolation. The alkylation of heteroaromatic bases was carried out in dichloromethane under irradiation with 400 W high pressure mercury lamp at about 30 °C.



The results are shown in Table 1. Lepidine, quinoline, and quinoxaline were alkylated in moderate yields. The by-products, diphenylselenide and carboxylic acid were obtained quantitatively. The reactivity of alkyl group decreased in the order of tertiary>secondary>primary. When THF was used as a solvent instead of CH_2Cl_2 in entry 1, the yield of 2-(1-adamantyl)-4-methylquinoline decreased to 35% and 2-(2-tetrahydrofuryl)-4-methylquinoline was obtained as a by-product. Thus, we propose the radical reaction mechanism based on the result of product analysis by gas chromatography as follows: initially, homolytic bond cleavage of Se-O bond in diphenylselenium bis(1-adamantanecarboxylate)⁶⁾ occurred to give 1-adamantyl radical via immediate

Table 1. Alkylation of Heteroaromatic Bases with 2

Entry	Heteroaromatic base	2 (R-)	3 (Product)	Yield/%
1	lepidine	1-adamantyl	2-(1-adamantyl)-4-methylquinoline	82
2	"	"	"	77a)
3	quinoline	"	2-(1-adamantyl)quinoline	60b)
4	quinoxaline	"	2-(1-adamantyl)quinoxaline	34
5	lepidine	cyclohexyl	2-(cyclohexyl)-4-methylquinoline	63
6	"	β -phenylpropionyl	2-(phenethyl)-4-methylquinoline	14
7	"	1-methyl-1-cyclohexyl	2-(1-methyl-1-cyclohexyl)-4-methylquinoline	80
8	quinoline	cyclohexyl	cyclohexylquinoline (2:4 = 3:1)	40

a) Isolated selenurane 2⁶⁾ (R=1-adamantyl) was used. b) The yield of 4-(1-adamantyl)quinoline was trace.

decarboxylation of 1-adamantanecarboxylate radical. When CH₂Cl₂ was used as a solvent, the adamantyl radical reacted with lepidine to give the adamantylated compound 3. However, in THF solvent the adamantyl radical abstracted the hydrogen atom from THF, resulting in the formation of adamantane and 2-tetrahydrofuryl radical. Then the produced tetrahydrofuryl radical alkylated lepidine to give 2-(2-tetrahydrofuryl)-4-methylquinoline (4.1%). Furthermore, 1,1'-bisadamantyl (coupling product), diphenyldiselenide, and adamantylbenzene were also obtained in 1.4%, 12.4%, and 1.2% yields, respectively. Another evidence for generation of adamantyl radical is that adamantane was obtained in 6.5% yield, when the selenurane was reacted in the presence of 5 equivalents of 1,4-cyclohexadiene, together with alkylated compound 3 in 40% yield. When the concentration of the reaction mixture was lower than that in usual radical reaction (0.03 M for the selenurane), the yield increased. Studies on the detailed reaction mechanism and further applications are under way in this laboratory.

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- 6) Diphenylselenium bis(1-adamantanecarboxylate): Mp 156.1 - 157.5 °C (decompd., THF/ *n*-pentane); ¹H-NMR (500 MHz, CDCl₃, TMS) δ 1.59-1.91 (m, 30H, adamantyl) 7.44-7.49 (m, 6H, Ph-*m*, *p*) 7.73-7.75 (m, 4H, Ph-*o*); ¹³C-NMR (67.8 MHz, CDCl₃, TMS) δ 28.1 (CH) 36.5 (CH₂) 38.9 (CH₂) 41.1 (C) 126.4 (Ar) 129.0 (Ar) 130.4 (Ar) 141.2 (Se-C) 181.5 (C=O); ⁷⁷Se-NMR (51.39 MHz, CDCl₃, neat Me₂Se) δ 673.7; IR (Nujol) ν 1680, 1650, 1320, 1266, 1248, 800, 757, 680 cm⁻¹; Anal. Found: C, 68.60; H, 6.96%. Calcd for C₃₄H₄₀O₄Se: C, 69.02; H, 6.81%.

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