

NOVEL REACTION OF A STABLE SELENANAPHTHALENE, 1-CYANO-2-METHYL-2-SELENANAPHTHALENE WITH ELECTROPHILES

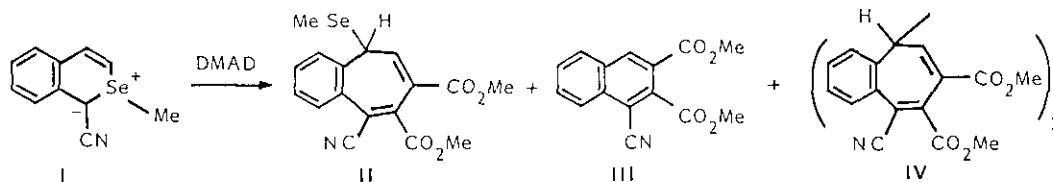
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Abstract—Reactions of 1-cyano-2-methyl-2-selenanaphthalene (I) with dimethyl acetylenedicarboxylate gave benzocycloheptene derivatives, II and IV, and naphthalenedicarboxylate III, while olefinic electrophiles such as acrylonitrile, methyl acrylate, and methyl vinyl ketone reacted with I to afford the cyclopropane derivatives, XII and XIII.

Mislow et al. reported generation of 1-pentafluorophenyl-2-methyl-2-selenanaphthalene, but could not stably isolate it.¹ We have first synthesized the stable selenanaphthalene, 2-cyano-1-methyl-4-phenyl-1-selenanaphthalene.² Now we succeeded in synthesizing its isomer, 1-cyano-2-methyl-2-selenanaphthalene (I) and found the interesting reactivities toward electrophiles. This paper presents the reactions of the selenanaphthalene with some electrophiles.

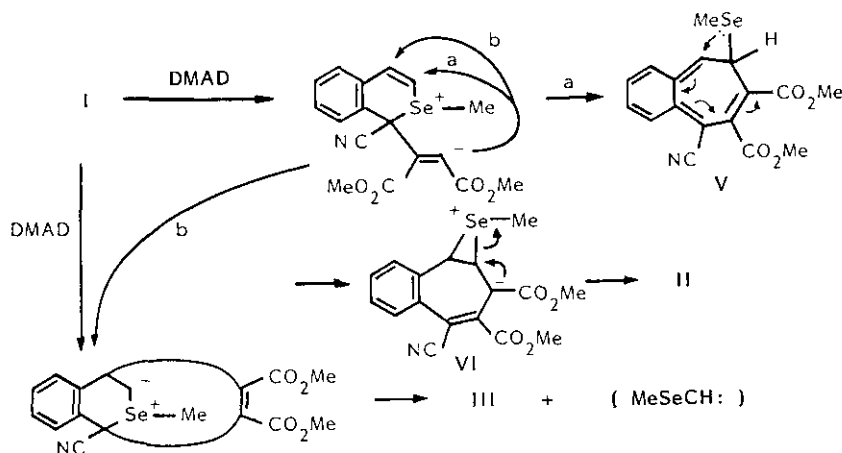
The reaction of ylide I with dimethyl acetylenedicarboxylate (DMAD) in benzene at room temperature gave a benzocycloheptene derivative II in 61% yield.³ The reaction in sulfolane afforded a naphthalene derivative III (37%) together with the benzocycloheptene II (17%), while the reaction in acetonitrile gave II (17%) and a bisbenzocycloheptene derivative IV (56%).³ The structure of the benzocycloheptene II was elucidated by comparison of its spectral data with those of the corresponding sulfur compound.⁴ The ¹H-nmr spectrum showed a characteristic broad signal due to a methine proton (H-5) of the 5H-benzocycloheptene ring.⁵ The ¹³C-nmr spectrum exhibited the C-5 signal at δ 40.0 as a doublet. The struc-



Scheme 1

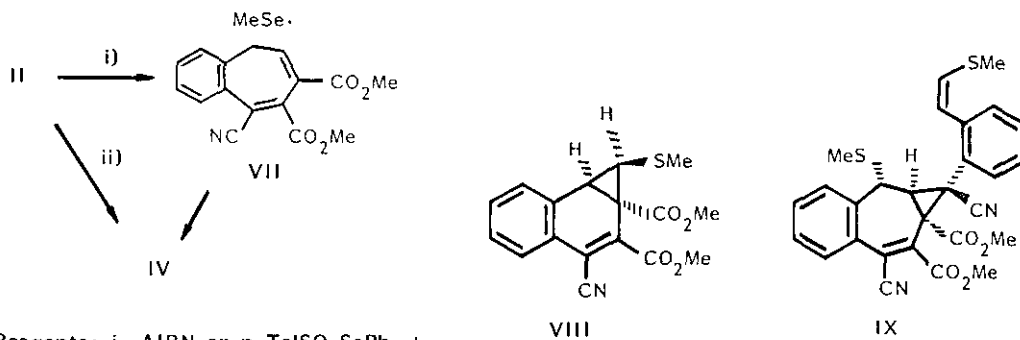
ture of III was determined by comparison of its spectral data with those of the authentic sample produced by the reaction of corresponding thianaphthalene with DMAD.⁴ The structure of the bisbenzocycloheptene IV was estimated by a molecular formula, $C_{32}H_{24}N_2O_8$ shown by an exact mass spectrum. The ¹H-nmr spectrum showed

absence of the methylseleno group. The ^{13}C -nmr spectrum exhibited the C-5 signal at δ 40.9 as a doublet and the C-4 signal at δ 120.7 as a doublet. Scheme 2 shows the plausible mechanism for the formation of the benzocycloheptene II and the naphthalene III.



Scheme 2

In order to elucidate the mechanism for the formation of bisbenzocycloheptene IV, some experiments shown in Scheme 3 were examined. We assumed that oxidative elimination of the methylseleno group would be the first step for the formation of bisbenzocycloheptene IV. However, the bisbenzocycloheptene IV was not formed by the treatment of the benzocycloheptene II with air, oxygen or *m*-chloroperbenzoic acid. Next we examined the reaction of the benzocycloheptene II with certain radical sources. Treatment of the compound II with 0.1 equiv. of azobisisobutyronitrile (AIBN) afforded the bisbenzocycloheptene IV in 30% yield. The compound IV was also formed by the photochemical reaction with Se-phenyl *p*-tolueneselenosulfonate⁶ in 80% yield (Scheme 3). These experiments show that a



Reagents: i, AIBN or *p*-TolSO₂SePh, hv;
ii, O

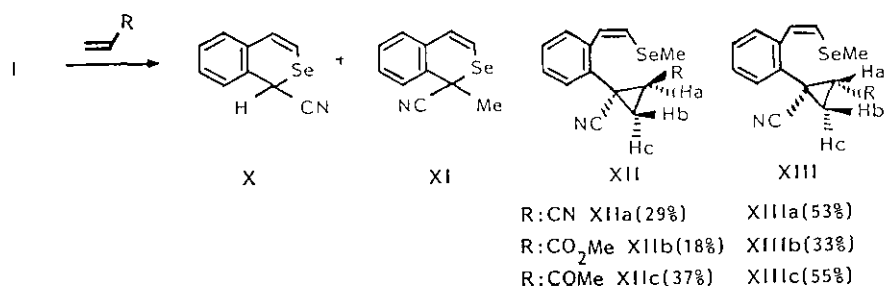
Scheme 3

Scheme 4

radical attacks the methylseleno group of the compound II and resulting radical VII is dimerized to the bisbenzocycloheptene IV. Some more experiments were attempted to clarify the radical species which initiate the radical reaction of II in the reaction of selenanaphthalene I and DMAD. However, we could not find the radical species so far.

Reactions of the selenanaphthalene I with DMAD were considerably different from those of the corresponding thianaphthalene.⁴ The bisbenzocycloheptene IV was not obtained from the reaction of the thianaphthalene. On the contrary, the thianaphthalene gave the dihydrocyclopropa[a]naphthalene VIII and the tetrahydrobenzo-[a]cyclopropa[d]cycloheptene IX but the selenanaphthalene did not produce the corresponding selenium analogues. Although the thianaphthalene did not react with the electron-deficient olefins, the differences in reactivity of the selenanaphthalene and thianaphthalene toward DMAD mentioned above led us to examine the reaction of the selenanaphthalene I with olefins.

The selenanaphthalene I did not react with styrene, dimethyl fumarate, and vinyl



Scheme 5

sulfones, but reacted with mono-substituted olefins such as acrylonitrile, methyl acrylate, and methyl vinyl ketone to afford cyclopropane derivatives (Scheme 5). Reaction with acrylonitrile afforded r-1,t-2-dicyano-1-[2-(cis-2-methylselenovinyl)phenyl]cyclopropane XIIa and cis-1,2-di-cyano isomer XIIIa. The exact mass spectral data of XIIa and XIIIa indicate a molecular formula of C₁₄H₁₂N₂Se corresponding to a 1:1-adduct of the ylide and acrylonitrile. In the ¹H-nmr spectrum, the cyclopropane ring protons (Ha, Hb, Hc) were observed as each doublet at δ 2.52 (J=6, 9Hz), 2.10 (J=6, 6Hz) and 1.96 (J=9, 6Hz), respectively. Assignment of the signals was made on the basis of relative chemical shifts and coupling constants. The cis coupling of cyclopropane ring protons is larger than the trans coupling.⁷ The ¹³C-nmr spectrum showed the cyclopropane carbons at δ 13.8 (doublet), 19.4 (singlet), and 20.3 (triplet). The ¹H-nmr spectrum of XIIIa was so complex that chemical shifts and coupling constants of the cyclopropane ring protons could not be determined exactly. The ¹³C-nmr spectrum exhibited the cyclopropane carbons at δ 13.5, 20.9, and 21.0. The trans-1,2-di-

cyano compound XIIa gradually isomerized in CDCl_3 to the stable cis-isomer XIIIa at room temperature. Viehe and his coworkers have reported the cis-trans isomerization of cyano-substituted cyclopropanes.⁸ Methyl acrylate and methyl vinyl ketone reacted with I to afford the cis-trans mixtures of the cyclopropane derivatives XIIb, XIIIb, and XIIc, XIIIc, respectively. Their structures were determined by the spectral data in a similar way to XIIa.

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- 3 ¹H-Nmr data for II, IV, XIIa, XIIIa. II: (270 MHz)(CDCl_3) δ 1.94 (3H, s, 8-SeMe), 3.69 (3H, s, OMe), 3.86 (3H, s, OMe), 4.75 (1H, br s, 5-H), 7.26-7.51 (4H, m, olefinic H and ArH), 7.93 (1H, d, J = 7.3 Hz, ArH). IV: (270 MHz) (DMSO-d_6) δ 3.69 (3H, s, 7-OMe), 3.91 (3H, s, 8-OMe), 4.19 (1H, br s, 5-H), 6.88-7.96 (5H, m, olefinic H and ArH). XIIa: (270 MHz)(CDCl_3) δ 1.96 (1H, dd, J = 9 Hz, J = 6 Hz, Hc), 2.10 (1H, dd, J = 6 Hz, J = 6 Hz, Hb), 2.20 (3H, s, SeMe), 2.52 (1H, dd, J = 6 Hz, J = 9 Hz, Ha), 6.91 (1H, d, J = 10 Hz, vinylic H), 7.13 (1H, d, J = 10 Hz, vinylic H), 7.24-7.61 (4H, m, ArH). XIIIa: (270 MHz)(CDCl_3) δ 1.84-1.92 (1H, m, Hb), 2.08-2.14 (2H, m, Ha and Hc), 2.21 (3H, s, SeMe), 6.92 (1H, d, J = 10 Hz, vinylic H), 7.10 (1H, d, J = 10 Hz, vinylic H), 7.12-7.49 (4H, m, ArH).
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