HETEROCYCLES, Vol. 30, No. 1, 1990

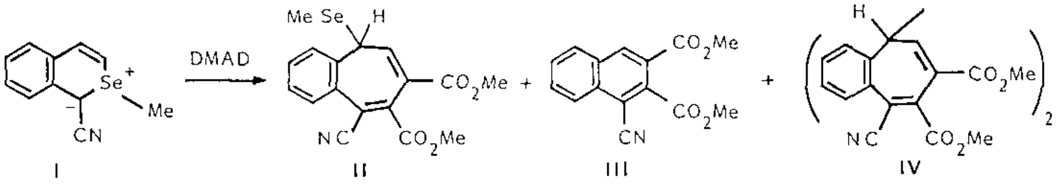
NOVEL REACTION OF A STABLE SELENANAPHTHALENE, 1-CYANO-2-METHYL-2-SELENANAPHTHALENE WITH ELECTROPHILES

Mikio Hori*, Tadashi Kataoka, Hiroshi Shimizu, Kazuhiro Tsutsumi, and Mitsuhiro Yoshimatsu
Gifu Pharmaceutical University, 6-1 Mitahora-higashi
5-chome, Gifu 502, Japan

Abstract-Reactions of 1-cyano-2-methyl-2-selenanaphtharene (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-selenanaphtalene, 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.

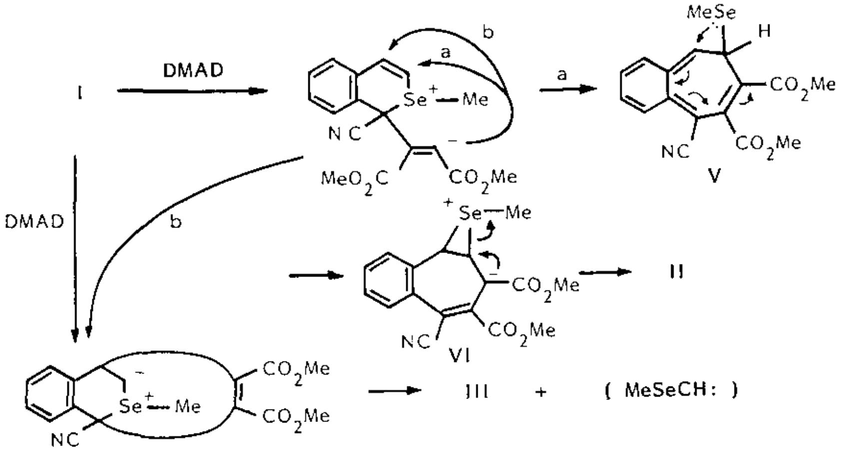
The reaction of ylide I with dimethyl acetylenedicarboxylate (DMAD) in benzene at room temperature gave a benzocycloheptene derivative II in 61% yield.[3] The reaction in sulfolane afforded a naphthalene derivative III (37%) together with the benzocycloheptene II (17%), while the reaction in acetonitrile 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 ^{1}H-nmr spectrum showed a characteristic broad signal due to a methine proton (H-5) of the 5H-benzocycloheptene ring.[5] The ^{13}C-nmr spectrum exhibited the C-5 signal at δ 40.0 as a doublet. The structure 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 ^{1}H-nmr spectrum showed



Scheme 1

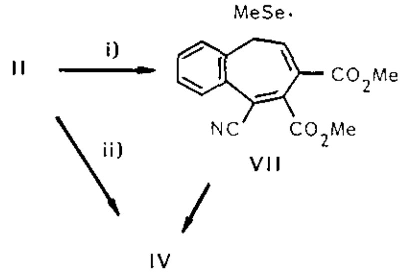
absence of the methylseleno group. The ^{13}C-nmr spectrum exhibited the C-5 signal at δ 40.9 as a doublet and the C-4 signal at δ 120.7 as a doublet.

Scheme 2 shows the plausible mechanism for the formation of the benzocycloheptene II and the naphthalene III.



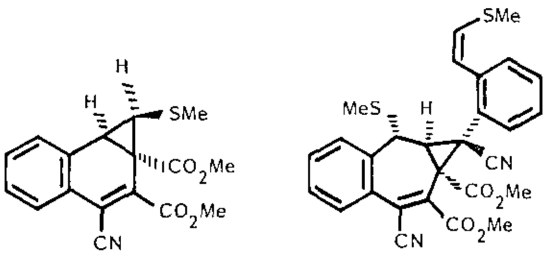
Scheme 2

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-tolueneselenosulfonate^6 in 80% yield (Scheme 3). These experiments show that a



Reagents: i, AIBN or p-TolSO$_2$SePh, hν ;
ii, (O)

Scheme 3



VIII

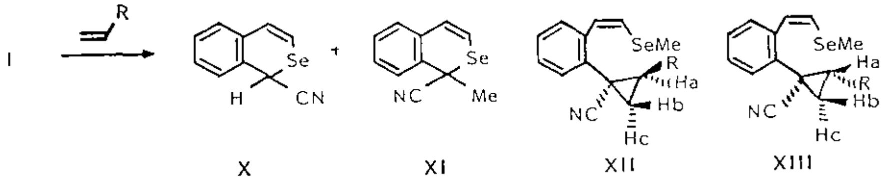
IX

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 attemped 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 thianaphtalene 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



R:CN XIIa(29%) XIIIa(53%)
R:CO_2Me XIIb(18%) XIIIb(33%)
R:COMe XIIc(37%) XIIIc(55%)

Scheme 5

sulfones, but reacted with mono-substitued 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 $C_{14}H_{12}N_2Se$ corresponding to a 1:1-adduct of the ylide and acrylonitrile. In the ^{1}H-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 ^{13}C-nmr spectrum showed the cyclopropane carbons at δ 13.8 (doublet), 19.4 (singlet), and 20.3 (triplet). The ^{1}H-nmr spectrum of XIIIa was so complex that chemical shifts and coupling constants of the cyclopropane ring protons could not be determined exactly. The ^{13}C-nmr spectrum exhibited the cyclopropane carbons at δ 13.5, 20.9, and 21.0. The trans-1,2-dicyano compound XIIa gradually isomerized in $CDCl_3$ to the stable cis-isomer XIIIa at room temperture. 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.

REFERENCES

1 J. Stackhouse, G. E. Senkler Jr., B. E. Maryanoff, and K. Mislow, J. Am. Chem. Soc., 1974, 96, 7835.

2 M. Hori, T. Kataoka, H. Shimizu, K. Tsutsumi, and K. Imaoka, Heterocycles, 1987, 26, 2365.

3 ^{1}H-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).

4 M. Hori and T. Kataoka, Yuki Gosei Kagaku Kyokai Shi, 1987, 45, 232. M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, H. Ogura, H. Takaynagi, Y. Iitaka, and H. Koyama, J. Chem. Soc., Perkin Trans. 1, 1988, 1885.

5 W. Tochtermann, G. Schabel, and A. Mannschreck, Ann. Chem., 1968, 711, 88. B. Foehlisch, C. Fischer, and W. Rogler, Chem. Ber., 1978, 111, 213.

6 T. G. Back and S. Collins, Tetrahedron Lett., 1980, 2215.

7 J. D. Graham and M. T. Rogers, J. Am. Chem. Soc., 1962, 84, 2249. B. M. Trost and H. C. Arndt, J. Org. Chem., 1973, 38, 3140.

8 A. De Mesmaeker, L. Vertommen, R. Merenyi, and H. G. Viehe, Tetrahedron Lett., 1982, 23, 69.

Received, 14th August, 1989