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# anti-9,18-DIMETHYL-2,11-DISELENA[3.3]METACYCLOPHANE - A CORRECTION TO THE LITERATURE. THE SELENOXIDE ELIMINATION APPLIED TO THE SYNTHESIS OF DIMETHYLDIHYDROPYRENE.

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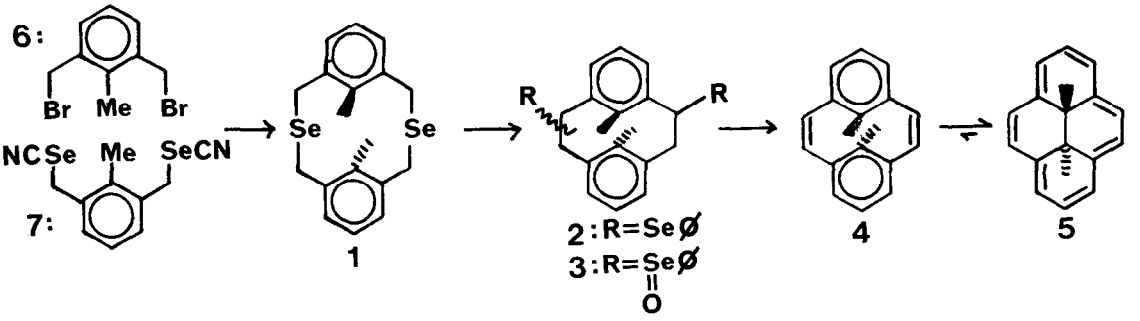
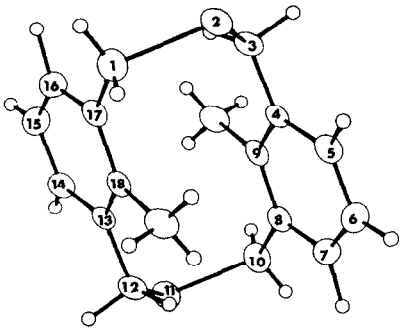
Summary: The previously reported title compound was incorrect. The now obtained sample was characterised by X-ray structure determination, $^{1}H$ and $^{13}C$ nmr spectra and via a selenoxide elimination into the known 15,16-dimethyldihydropyrene.

In 1980, we[1] reported that the reaction of 2,6-bis(bromomethyl)toluene with sodium selenide gave the dimer, supposedly anti-9,18-dimethyl-2,11-diselena[3.3]metacyclophane, 1, as well as trimer. Both of these compounds had the same melting point, 186°, yet gave different $^{1}H$nmr spectra. One gave clear trimer peaks at m/e 594 in its mass spectrum, while the other gave (as far as we could see) only peaks consistent with the dimer at m/e 396. It should be noted that the trimer also gave very strong peaks at m/e 396. We therefore assigned one of these compounds the structure of 1. We noted however that after benzyne induced Stevens rearrangement[2], which should have yielded 2, followed by conversion to the selenoxide 3 and elimination, no metacyclophane-diene 4 or dihydropyrene 5 was obtained. As a result of a study of $^{77}Se$ nmr spectra of a number of selenacyclophanes, we had cause to remake a sample of 1. However, Misumi[3] has more recently shown that much better yields of selenacyclophanes can be obtained by coupling a bromide and a selenacyanate in the presence of $NaBH_4$ than via the sodium selenide coupling, and thus this was the route used. Indeed coupling of bromide 6[4] with selenacyanate 7[5] in ethanol/THF with $NaBH_4$ yielded up to 55% of the authentic anti-selenaphane 1, mp 215-216°C. Since the melting point and



$^1$Hnmr spectrum obtained were different from that which we previously reported, we immediately obtained an X-ray structure determination[6] of this sample. This confirmed that the recently obtained sample was the dimer; the ORTEP drawing of 1 is shown in Figure 1.

Figure 1: An ORTEP drawing of anti-selenaphane 1 and its $^1$H and $^{13}$C nmr data.




$^1$Hnmr data for 1.

7.32 ($AB_2$, 4H, H-5,7,14,16)
7.07 ($AB_2$, 2H, H-6,15)
3.77 (s, 8H, H-1,3,10,12)
1.31 (s, 6H, 9,18-$CH_3$).

$^{13}$Cnmr data for 1.

138.9(C-9,18), 136.3(C-4,8,13,17)
130.7(C-5,7,14,16), 126.0(C-6,15)
23.7($CH_2$), 15.1($CH_3$).

The internal methyl protons of 1 at δ 1.31 are thus in the same shielded region as those for the analogous thiacyclophane, δ 1.30[7] and not as previously reported at δ 1.77. In the mother liquors from the recrystallization of 1, a small amount of the syn-isomer of 1 could be seen with internal methyl protons at δ 2.43 (those of the analogous thiacyclophane are at δ 2.54)[7], though we have not yet obtained this isomer free of the anti-isomer. Clearly then the selenacyclophanes behave as far as the internal methyl protons are concerned in the same way as the well documented[7] thia-analogues. The $^{77}$Se chemical shift of 1 appears at -765 ppm relative to 19.0915 MHz, and does not change on lowering of temperature, unlike the syn-selenaphanes, consistent with one selenium atom pointing towards each aromatic ring, as they do in the crystal structure.

Reaction of 1 with benzyne generated from benzenediazonium-2-carboxylate yielded 65% of the ring contracted Steven's product 2, which with m-CPBA in $CHCl_3$ at room temperature for 12h forms the bis-selenoxide, which on elimination by heating in toluene for 12h with $Et_3N$ gave 40% of trans-15,16-dimethyldihydropyrene 5 (via the cyclophane-diene 4). This serves not only to further prove the structure of 1, but for the first time shows that the selenoxide elimination[8] can be applied to metacyclophanedienes and hence to their valence tautomers the dihydropyrenes.

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NOTES AND REFERENCES.

1. R.H. Mitchell, Can. J. Chem., 1980, 58, 1398-1406.
2. T. Otsubo and V. Boekelheide, Tetrahedron Letters, 1975, 16, 3881-3884.
3. H. Higuchi and S. Misumi, Tetrahedron Letters, 1982, 23, 5571-5574.
4. R.H. Mitchell and V. Boekelheide, J. Am. Chem. Soc., 1974, 96, 1547-1557.
5. Obtained from 6 with KSeCN in $Me_2CO$, mp 178-179°C; $^1$Hmr δ 7.2-7.3(ArH), 4.35($CH_2$), 2.40($CH_3$).
6. The crystal system was monoclinic, space group $P2_1/C$ (No.14), with a=7.614(2)Å, b=13.028(4)Å, c=8.161(2)Å, β=106.89(2)°, $D_{meas.}$=1.68 g.cm$^{-3}$, $D_{calc.}$=1.689 g.cm$^{-3}$, Z=2 molecules per cell. Measurements were made on a Picker 4-circle diffractometer, automated with a PDP11 computer. The structure was solved by direct methods and refined by least squares to R=0.0434 and $R_w$= 0.0480 for 1355 observations (2θ=0-50°, W=1/($\sigma^2$(F)+0.001F$^2$)) and 131 parameters (9 anisotropic atoms and 10 isotropic H atoms). The aromatic rings are slightly non-planar (max. dev. 0.032Å), with the mean planes of the two rings parallel by symmetry. The structural details will be published elsewhere.
7. R.H. Mitchell, Org. Chem.,(Academic Press) 1983, 45I, 239-310.
8. H.J. Reich, Accts. Chem. Res., 1979, 12, 22-30.

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