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Sir:

It is very well known that the derivatives of the common five-membered heterocycles, furan (1), pyrrole (2) and thiophene (3) undergo 2 + 2 photochemically induced cycloaddition reactions. However, selenophene has not, heretofore, been used as a substrate for photochemically excited species in 2 + 2 cycloaddition reactions.

Keeping in mind that the  $\pi$  electron density localized at the heteroatom decreases in the series: furan > thiophene > selenophene, that citraconic anhydride adds smoothly to furan (1) and to thiophene (4) and that 2,3-dimethylmaleic anhydride adds, as well, to thiophene (3) in sensitized reactions, it was decided to investigate the reactivity of selenophene as a substrate for 2,3-dimethylmaleic anhydride in a benzophenone photosensitized reaction.

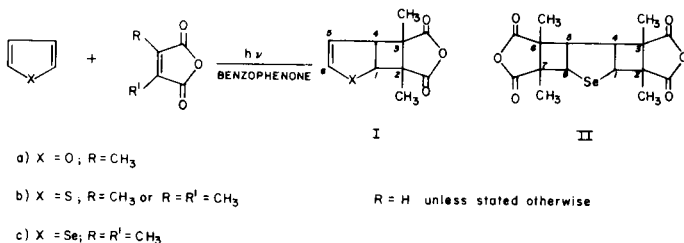


Figure 1

In this manner, equimolar quantities of 2,3-dimethylmaleic anhydride (0.02 mole) and selenophene (0.02 mole) were dissolved in dried benzene and irradiated with a Hanovia 450 watt lamp, in the presence of benzophenone (0.04 mole) for 15 hours at 20° with nitrogen bubbling through the solution before and during the irradiation. After 1 hour irradiation white crystals start to appear on the walls of the reaction vessel. At the end of the irradiation the crystals were collected on a filter, washed with benzene and crystallized from a mixture benzene-acetone; the product (Ic) was isolated in 75% yield, m.p. 170°. Structure Ic was assigned to the main product, namely the substance that remains on the filter after washing with benzene. The assignment was made on the basis of its nmr spectrum which exhibits the following resonances (acetone d<sub>6</sub>):  $\delta$  1.43 (s, 3, 2-CH<sub>3</sub>), 1.30 (s, 3, 3-CH<sub>3</sub>), 5.05 (d, 1, J<sub>1,4</sub> = 9.38 Hz, 1-H), 4.20 (qq, 1, J<sub>4,1</sub> = 9.38; J<sub>4,5</sub> = 3.50; J<sub>4,6</sub> = 2.00 Hz, 4-H), 6.00 (q, 1, J<sub>5,4</sub> = 3.50; J<sub>5,6</sub> = 6.38 Hz, 5-H), 7.00 (dd, 1, J<sub>6,4</sub> = 2.00 Hz, 6-H). The assignments of the chemical shifts for the different protons were made by analogy to those obtained for the thiophene adducts (5).

Furthermore, the analogy between the selenophene

compound and the corresponding thiophene derivatives can be made extensive to the coupling constants in such a way that the *anti* Stereochemistry III may be inferred for compound Ic. NOE studies (5) of the adducts obtained from different thiophene derivatives and methylmaleic anhydrides, showed that the *anti* configuration is the preferred one for these molecules.

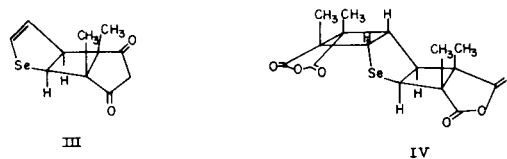


Figure 2

Since the chemical shifts for the methyl groups are virtually the same in both the selenophene and the corresponding thiophene adduct (6) or even in some adducts derived from methylthiophenes (5) they are presumably located in the same position in relation to the double bond between carbon atoms 5 and 6 in both types of molecules because, if the selenophene adduct were *syn*, the chemical shifts of its methyl groups should have different values from those observed. The reason for this being that they would no longer be under the anisotropic influence of the above-mentioned double bond. In the thiophene derivatives the methyl groups can be so close to the vinyl protons that the nuclear overhauser effect values between the 3-methyl group and the vinylic proton at C-5 can range from 8 to 15% (5).

The second compound formed in the irradiation, namely the one that goes into the benzene used for washing the crude product is a substance where two molecules of 2,3-dimethylmaleic anhydride add to one selenophene nucleus II. Furthermore, it was found that when Ic is sublimed under vacuum at 100° or even less (*e.g.* 70°) and the nmr of the sublimate is measured, the resonances corresponding to Ic disappear and those considered to belong to the less important (II) photoproduct are enhanced and are the only ones visible on the chart. Therefore, when samples of Ic were sent for elemental analysis (7), they cannot withstand the normal routine vacuum manipulations previous to the analysis and as a consequence, the results do not fit the elemental composition of Ic but instead they agree with that for II (*Anal.* (Compound II) Calcd. for C<sub>16</sub>H<sub>16</sub>O<sub>6</sub>Se: C, 50.13; H, 4.17; O, 25.06; Se, 20.83.

Found: C, 50.18; H, 4.25; O, 24.94; Se, 20.76). The nmr spectrum of II exhibits the following resonances:  $\delta$  4.70 (d, d, 2,  $J_{1,4} = 4.5$ ,  $J_{8,5} = 4.5$  Hz 1-H and 8-H), 3.80, 3.88 (d, d, 2,  $J_{4,1} = 4.5$ ,  $J_{5,8} = 4.5$  Hz, 4-H and 5-H), 1.25, 1.32, 1.40, 1.53 (s, s, s, s, 12, 4 methyl groups).

From the nmr spectrum we may presumably assign the stereochemistry of this molecule as shown (IV). The two partially superimposed doublets centered at 4.70 ppm correspond to the two protons on both sides of the selenium atom and the two doublets at 3.80 and 3.88 correspond to the two protons at carbon atoms 4 and 5. If a model of the molecule is built it is possible to observe that the four protons around the five-membered ring 1-H, 4-H, 5-H and 8-H are all chemically different from each other and the same thing may be said about the four methyl groups; thus we obtain the one singlet for each methyl group and one doublet for each proton around the central ring; protons 1-H and 4-H are coupled with each other  $J = 4.5$  Hz and protons 5-H and 8-H are likewise coupled with each other  $J = 4.5$  Hz. The model is useful for visualizing that the dihedral angle between protons at carbon atoms 4 and 5 is very close to  $90^\circ$  and therefore  $J_{4,5} = 0$ . An analogous nmr argument was previously applied in this laboratory to a similar molecule (2). Any other possible configurations give structures with some element of symmetry that would produce a different nmr spectrum.

The structural assignments based on nmr arguments are supplemented by the mass spectral data  $m/e$  for Ic 258 (M) 25%, 132 ( $C_4H_4Se$ , 100%) 126 ( $C_6H_6O_3$ , 33%). Both selenophene (8) and 2,3-dimethylmaleic anhydride (9) give their own fragmentation patterns; ms:  $m/e$  for IV 348 (M) 9%, 258  $C_{10}H_{10}O_3Se$  (7%), 132 ( $C_4H_4Se$ , 100%) 126 ( $C_6H_6O_3$ , 5%). Both selenophene and 2,3-dimethylmaleic anhydride give their own fragmentation patterns. The selenophene and 2,3-dimethylmaleic anhydride fragments are presumably formed by a retro Diels-Alder mechanism (10). In addition to low resolution mass spectrometric

analysis a sample of Ic was sent for high resolution mass spectrometry (7). The presence of a very low intensity (0.03%) molecular ion  $m/e$  384 corresponding to II as well as a mass fragment at  $m/e$  257.9803  $C_{10}H_{10}O_3Se$  (3.51%) is one more piece of evidence to show that Ic when subjected to high vacuum goes into II with addition of one more molecule of 2,3-dimethylmaleic anhydride.

Attempts to prepare an oxetane from selenophene and benzophenone have failed so far. Irradiation of selenophene in the presence of benzophenone in benzene solution afforded unreacted benzophenone after 8 hours of irradiation.

#### REFERENCES AND NOTES

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- (7) Elemental Analyses: F. Pascher, *Microanalytisches Laboratorium*, Bonn, Germany. The nmr spectra were measured with a Varian 390 spectrometer, TMS as an internal standard. Abbreviations in brackets denote singlet (s) doublet (d), and quartet (q), followed by the integration. The mass spectra were performed in a Dupont 21492B. The high resolution mass spectra were performed in an AEI MS-30 mass spectrometer at the Venezuelan Petroleum Institute (INTEVEP).
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