

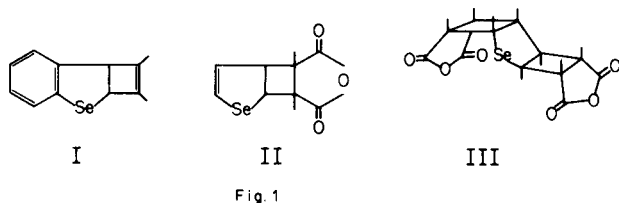
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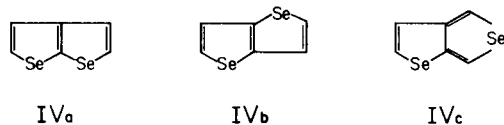
As a continuation of studies carried out in this laboratory [2] on the properties of selenophene and its methyl derivatives as substrates for excited carbonyl compounds and for methylmaleic anhydride derivatives in photosensitized reactions benzo[*b*]selenophene and selenophthene were tested as well. The latter were found to be inert in oxetane formation but good substrates in photosensitized reactions.

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The photochemical cycloaddition of 2,3-dimethylmaleic anhydride to benzo[*b*]thiophene in the presence of benzophenone to form [2 + 2] adducts is well known [3]. On the other hand, the light induced cycloaddition of haloolefins and acetylenes to benzo[*b*]selenophene to give fused benzo[*b*]selenophene cyclobutenes (I) was reported a few years ago [4]. Furthermore, it was possible to carry out in this laboratory the successful photosensitized cycloaddition of 2,3-dimethylmaleic anhydride to selenophene [2] to give a single [2 + 2] adduct to one of the double bonds in the ring and a double [2 + 2] adduct to both double bonds as well, compound II and III respectively.

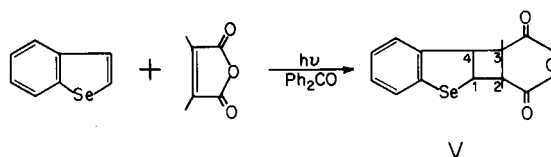


On the basis of these experiences interest arose in attempting the cycloaddition of 2,3-dimethylmaleic anhydride to the different isomeric selenophthenes, IVa, IVb and IVc. However, before performing the reaction with the selenophthenes the cycloaddition was first attempted with benzo[*b*]selenophene. The latter as well as the selenophthenes can be easily obtained as products of the same reaction used for the preparation of selenophene by varying the thermal conditions of the hot tube used in the synthetic procedure [5].



Irradiation of a benzene solution of equimolar quantities of 2,3-dimethylmaleic anhydride and benzo[*b*]selenophene in the presence of benzophenone as the sensitizer yielded a [2 + 2] adduct which was identified by its nmr and mass spectral data. Both of these types of spectra keep a

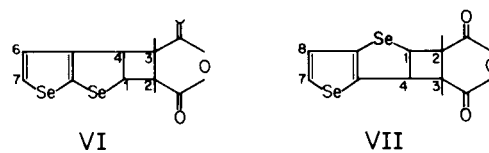
great resemblance with those of the corresponding sulfur analog which was prepared in this laboratory several years ago [3,6] and was now used as a model compound in the identification of the new adducts reported in this paper.



The nmr spectrum of compound V exhibits in addition to the aromatic resonances at 7.50 ppm an AB system where the doublet at 5.00 ppm corresponds to proton at C-1 and the doublet at 4.58 ppm may be assigned to proton at C-4. The former appears downfield compared to the latter due to its proximity to the selenium atom. By analogy to the sulfur compounds described before [3,6] methyl group at C-2 may be assigned the resonance at 1.32 ppm which is the lowest of the two recorded in the methyl group region; the other one located at 1.14 ppm would correspond to methyl group at C-3.

Of the three possible isomeric selenophthenes only a and b were isolated in pure form and therefore, they were the only ones used as substrates in the reaction reported in the present paper.

When isomers IVa and IVb were irradiated in the presence of 2,3-dimethylmaleic anhydride under the same conditions described for the reaction with benzo[*b*]selenophene they yield the corresponding [2 + 2] adducts. Isomer IVa undergoes addition of only one molecule of 2,3-dimethylmaleic anhydride to give compound VI. On the other hand, isomer IVb yields both a single and a double adduct derived from addition of either one or two molecules of the anhydride respectively, compounds VII and VIII.



The structural assignments of compounds VI and VII were made on the basis of the nmr and mass spectral data. Structure VII was inferred from the mass spectral data and the elemental analysis. In compounds VI and VII only the carbon atoms bearing protons were numbered for convenience. The appearance of the nmr spectra of compounds VI and VII is virtually the same as far as the number of resonances exhibited and their multiplicity is concerned. The differences lie in the position of the bands; that is to say, their chemical shifts are slightly different. Protons at C-6 and C-7 in compound VI and protons at C-7 and C-8 in compound VII exhibit an AB system in the aromatic region. Protons at C-1 and C-4 in both compounds exhibit an AB system as well; the two doublets are located at about 5.5 ppm and 4.5 ppm respectively. The methyl groups appear as two resonances at about 1.2 and 1.4 ppm. In all these pairs of protons or of methyl groups the lower field value for the chemical shift has been assigned to the proton or methyl group closer to a selenium atom. This is a gross description of the spectra of the two compounds emphasizing on the similarities. The exact values for the chemical shifts are given in Table I.

Two important features in the chemical shifts of proton at C-1 and methyl group at C-3 point out at the structural differences between the two compounds. Thus, proton at C-1 in compound VII appears at a lower field, 5.65 ppm, than proton at C-1 in compound VI, 5.35 ppm. It is possible that the selenium atom next to proton at C-1 in compound VII may have a stronger deshielding effect on it than what its counterpart in compound VI could exert on the corresponding proton. The close proximity of another selenium atom in the latter may cause a stronger delocali-

zation of its outer electrons thus preventing an efficient anisotropic influence from taking place.

On the other hand, the methyl group at C-3 in compound VII appears at lower field, 1.30 ppm than its analog in compound VI, 1.20 ppm. These values in chemical shift seem reasonable if one considers that this particular methyl group may be closer in space to a selenium atom in compound VII than it would be in compound V. Not having any other evidences for the stereochemistry of these compounds except for the possible analogy of their structures with those of similar sulfur compounds thoroughly studied in this laboratory [6], one could on the basis of this small difference in chemical shift speculate that these compounds may presumably have an *anti* stereochemistry, VIa and VIIa.

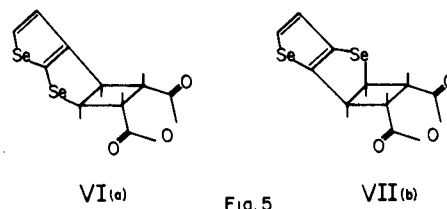


Fig. 5

Due to solubility problems it was not possible to obtain a good nmr spectrum of compound VIII. However, its mass spectrum and the elemental analysis which agrees with that of a tetracarboxylic acid suggest the structure of a double adduct; that is to say, a compound where two molecules of 2,3-dimethylmaleic anhydride have added to the heterocyclic ring.

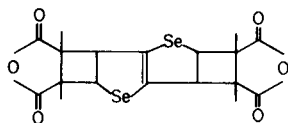
All the elemental analyses for the compounds reported in this paper agree with those calculated for the diacids.

Table I
NMR Data on the Photoadducts

Compound	Protons	Chemical shift (ppm)	Integral and multiplicity	Coupling constants	(Hz)
V	Aromatic	7.30	4 m		
	2-CH ₃	1.32	3 s		
	3-CH ₃	1.14	3 s		
	C-1	5.00	1 d	J _{1,4}	= 8.8
	C-4	4.58	1 d	J _{4,1}	= 8.8
VI	C-7	8.10	1 d	J _{7,6}	= 4.0
	C-6	7.10	1 d	J _{6,7}	= 4.0
	2-CH ₃	1.40	3 s		
	3-CH ₃	1.20	3 s		
	C-1	5.35	1 d	J _{1,4}	= 8.5
VII	C-4	4.50	1 d	J _{4,1}	= 8.5
	C-7	7.10	1 d	J _{7,8}	= 4.7
	C-8	8.15	1 d	J _{8,7}	= 4.7
	2-CH ₃	1.40	3 s		
	3-CH ₃	1.30	3 s		
	C-1	5.65	1 d	J _{1,4}	= 8.5
	C-4	4.50	1 d	J _{4,1}	= 8.5

s, singlet; d, doublet; m, multiplet; acetone d-6, TMS

This fact was observed before for the [2 + 2] adducts of 2,3-dimethylmaleic and citraconic anhydride to thiophene and benzo[*b*]thiophene derivatives. Perhaps, the anhydrides are very easily converted to the acids in the presence of moisture while the samples are sent for analysis. In fact, when the sulfur derivatives are deliberately dissolved in a mixture of acetone water they hydrolyze readily. It was not possible to obtain a good elementary analysis for compound V; perhaps it decomposes while it is being sent for analysis.



VIII

Fig. 6

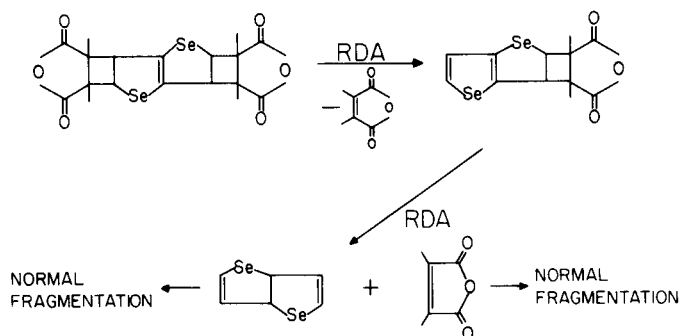
Mass spectra of all the compounds show in addition to the molecular ion the typical retro Diels-Alder fragmentation mechanism observed for this type of adducts to give the starting materials followed by their characteristic fragmentation patterns. The more important mass fragments are given in table II.

Table II

Mass Spectral Data on the Photoadducts *m/e*/%

Compound	M	Fragments				
		a	b	c	d	e
		(M - a)	(M - 2a)	(Se ≡ CH)	(C ₃ H ₃)	
V	308	126	182	-	93	39
	5	5	100		22	25
VI	360	126	236	-	93	39
	20	5	85		30	60
VII	360	126	236	-	93	39
	22	5	85		32	60
VIII	486	126	362	326	43	39
	12	4	13	100	32	60

The mass fragments in this table refer to scheme I.



SCHEME I

EXPERIMENTAL

All the nmr spectra were measured at approximately 30° with a Varian 390 spectrometer, TMS as an internal standard, the mass spectra were determined in a Dupont 21492B spectrometer and the elemental analysis were performed by Franz Pascher, Bonn, Germany.

Benzo[*b*]selenophene and selenophthene were prepared by the method by Gronowitz *et al* [5] for the synthesis of selenophene with slight variations as follows: A pyrex tube (30 × 300 mm) was filled with 20 g (0.253 mole) of powdered selenium (Aldrich) and 100 g of alumina (Fitrol 8 mm, Merck). The tube thus charged was placed in a tube oven (Lindberg 55035) and slow stream of dry nitrogen was passed for an hour until the temperature reached 150-200°. At this point, 2 g of selenium oxide (SeO₂, Aldrich) were introduced in the pyrex tube and the heating continued gradually for an additional hour.

When the desired temperature was reached nitrogen was replaced by acetylene. At 300° benzo[*b*]selenophene is the main product of the reaction; at 380-400° formation of selenophthene is the predominant process and at 450° selenophene is obtained in excellent yield. When acetylene starts to pass through the tube small quantities of air were bled into the system and flashing occurs. The different crude products were purified by distillation under reduced pressure. The *cis* IVa and the *trans* IVb isomers of selenophthene were separated by the method of Umezawa [7].

Photochemical Reactions.

Equimolar quantities of the heterocycle (0.01 mole) and 2,3-dimethylmaleic anhydride (0.01 mole) in addition to 3.6 g of benzophenone (0.02 mole) were dissolved in 50 ml of dry benzene and irradiated with a Hanovia 450 w medium pressure lamp. The irradiation was carried out for 10 hours, at 20°, under nitrogen atmosphere in a quartz apparatus fitted

Table III

Physical Data on the Photoadducts

Compound	MP °C	Yield %	Empirical Formula Diacids	Analyses	Calcd./	Found
				Diacids C	H	Se
V	165	60		-	-	-
VI	160	70	C ₁₂ H ₁₂ O ₄ Se ₂	38.09	3.18	41.79
				38.10	3.15	41.73
VII	167	60	C ₁₂ H ₁₂ O ₄ Se ₂	38.09	3.18	41.79
				38.12	3.14	41.74
VIII	300°	15	C ₁₈ H ₂₀ O ₈ Se ₂	41.37	3.83	30.27
				41.30	3.85	30.30

with a pyrex filter sleeve.

After 6 hours irradiation colored crystals begin to appear on the walls of the irradiation vessel. At the end of the irradiation the crystals were filtered and washed with petroleum ether. Further purification was carried out by chromatographing the photo products over neutral alumina. They were eluted from the column with benzene acetone (3:1).

REFERENCES AND NOTES

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