Monatshefte für Chemie 125, 1153–1158 (1994)

Monatshefte für Chemie
Chemical Monthly
© Springer-Verlag 1994
Printed in Austria

Photocycloaddition of 2,3-Dimethylmaleimide to Selenophene and 3,4-Dimethylselenophene

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Summary. The benzophenone sensitized photocycloaddition of 2,3-dimethylmaleimide to selenophene and 3,4-dimethylselenophene was carried out first to generalize the photoaddition reaction of methylmaleic anhydride derivatives to selenophene, using this time the nitrogen analogue, and second to reexamine the composition of the product mixture formed in the reaction. It was found that in adition to the 1:1 adduct isolated in previous investigations, three geometrical isomers may be proposed for the 2:1 adduct (two molecules of maleimide of one of selenophene or its methyl derivative).

Keywords. Photocycloaddition; Selenophene;Dimethylmaleimide; Benzophenone photosensitized cycloaddition.

Photocycloaddition von 2,3-Dimethylmaleimid an Selenophen und 3,4,-Dimethylselenophen

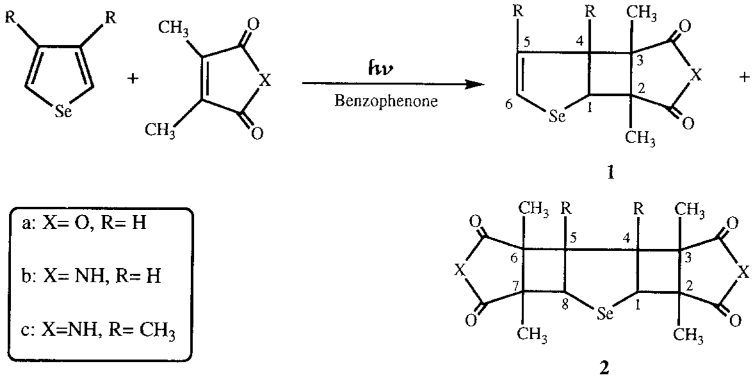
Zusammenfassung. Die benzophenonsensitivierte Photocycloaddition von 2,3-Dimethylmaleimid an Selenophen und 3,4-Dimethylselenophen wurde durchgeführt, um erstens die Photoadditionsreaktionen von Methylmaleinsäureanhydridderivaten an Selenophen allgemein zu studieren und um zweitens die Zusammensetzung der bei der Reaktion gebildeten Produktgemische erneut zu untersuchen. Zusätzich zu dem bei früheren Arbeiten gefundenen 1:1-Addukt werden drei geometrische Isomere für das 2:1 – Addukt (2 Moleküle Maleimid und 1 Molekül Selenophen oder 3,4-Dimethylselenophen) vorgeschlagen.

Introduction

It is well known that the derivatives of the common five-membered heterocycles, furan, pyrrole, and thiophene undergo 2 + 2 photocycloaddition reactions. However, selenophene has been used only in few cases [1] as a substrate for photochemically excited species in 2 + 2 cycloadditions reactions. Compounds **1a** and **2a** were reported by this laboratory as the only products of the benzophenone sensitized photocycloaddition of 2,3-dimethylmaleic anhydride to selenophene.

Their structure and stereochemistry were determined by their ^{1}H NMR and mass spectral data on the basis of previous experience with analogous compounds [2–4].

In order to extend this reaction to the nitrogen analogues of 2,3-dimethylmaleic anhydride, the photoaddition reaction was carried out using 2,3-dimethylmaleimide



Scheme 1

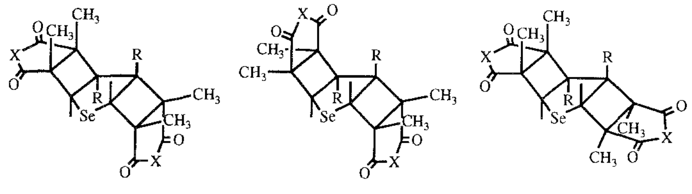
as the substrate for selenophene and 3,4-dimethylselenophene. The reaction with selenophene, as well as with 3,4-dimethylselenophene, takes place as expected, giving the corresponding single (1:1) (**1b** and **1c**) and the double adduct (2 molecules of maleimide to 1 of selenophene) (**2b** and **2c**) as observed before for 2,3-dimethylmaleic anhydride.

The ^1H NMR spectrum of **2a** exhibits the following resonances: 4.70 (2 × d, $J_{1,4} = 4.5$ Hz, $J_{8,5} = 4.5$ Hz, 2H, H1 and H8), 3.80, 3.88 (2 × d, 2H, H4 and H5), 1.25, 1.32, 1.40, 1.53 (4 × s, 12H, $CH_3 - 2,3,6,7$). From this spectrum the structure and the stereochemistry of **2** was unequivocally assigned [1]. The two partially superimposed doublets centered at 4.70 correspond to the two protons on both sides of the selenium atom and the two doublets at 3.80 and 3.88 ppm correspond to the two protons at carbons 4 and 5. The four siglets at 1.25, 1.32, 1.40, and 1.53 ppm were assigned to the four methyl groups. From a molecular model one can dednce that the four protons around the five-membered ring and the four methyl groups are all chemically different from each other. The model is also useful for visualizing that the dihedral angle between protons at carbon atoms 4 and 5 is very close to 90° and hence $J_{4,5} = 0$. Therefore, from this argument is may be inferred that the molecule is not symmetric (it has neither a plane nor an axis of symmetry) and that each proton around the central five-membered ring appears as a doublet since each one of them is only coupled to its neighbor on the same side of the ring. This spectrum agrees very well with the *syn-anti* (**Ia**) (Figure 1) structure already reported [1]. At that time it was thought that the double adduct **2a** (2 molecules of the anhydride to 1 of selenophene) consisted of pure isomer **Ia** and there was no idea of the existence of a mixture of isomers since the ^1H NMR spectrum exhibited very sharp resonances for all protons in the molecule.

Results and Discussion

When 2,3-dimethylmaleimide was irradiated in a benzophenone photosensitized reaction in the presence of selenophene or 3,4-dimethylselenophene, the nitrogen analogs of **1a** and **2a**, namely **1b**, **2b** and **1c**, **2c**, were obtained. Their NMR spectra – with slight differences in chemical shifts and coupling constants–fit well for structures exactly the same as assigned for **1a** and **2a** except for the fact that the doublets corresponding to the four protons (1, 4, 5 and 8) around the central ring in **2b** were noted to be slightly broadened as compared to the corresponding ones in the dimethylmaleic anhydride derivative. The reason for this efffect is not obvious. Nevertheless, this fact indicated that perhaps there may be formed more than one isomer. In order to find out if this assumption could be substantiated, a ^{13}C NMR spectrum of the 2,3-dimethylmaleimide-selenophene derivative (**2d**) was recorded and the following relevant information was obtained. The carbonyl groups exhibit four resonances between 179 and 182 ppm. Between 10 and 16 ppm there are four resonances, which can be assigned to the four methyl groups. So far, nothing deviates from what should be expected if the product were adduct **I** as reported [1]; however, the four carbon atoms of selenophene ring should exhibit only four resonances while actually eight resonances appear between 47 and 56 ppm which is the appropriate region for this type of carbon atoms. To explain this fact has to postulate the existance of at least two more isomers. The *syn-anti* structure **I** previously proposed has no elements of symmetry; hence, it is unsymmetric and therefore the four carbon atoms around the central ring exhibit four different resonances. The other two possible structures that may be proposed have an axis of symmetry. One of them would be the *anti-anti* isomer (**III**) in which the carbon atoms of the selenophene ring should exhibit two different resonances with respect to those corresponding to **I** (*anti-syn*). On the other hand in the *syn-syn* isomer (**II**) where the two NH groups are closer to the selenium atom, the four carbon atoms of the selenophene ring should also give two resonances with chemical shifts different from the other six resonances already assigned; in this way, all eight resonances are accounted for. All the chemical shifts proposed for the carbonyl and the methyl groups carbon atoms agree well with the resonances in their respective regions of the spectrum as stated above. Finally, the noncarbonylic carbon atoms of the maleimide rings are chemically equivalent in all cases and therefore the resonances between 47 and 56 ppm may be assigned to them. The stereochemistry proposed for the three geometrical isomers fitting the ^{13}C NMR spectral data are depicted in Fig. 1. A *syn-syn* isomer with the two maleimide rings on the same side of the molecule is not possible because of the very high steric hindrance caused by these two groups. In general, any other isomer where protons 4 and 5 are not *trans* is not likely because in that case the resonances for these two protons would not be doublets since they would be coupled with each other in addition to the coupling with their neighbor on the same side of the molecule.

In view of these findings, the ^{13}C NMR spectrum of **2a** was recorded and appeared to be virtually the same as that of **2b** as expected. That is, it has the same number of resonances with about the same values for the chemical shifts except for the fact that



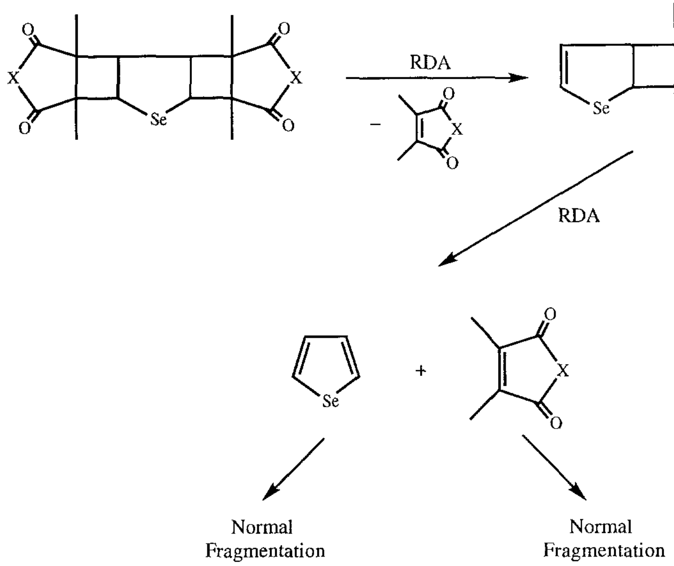
I II III

a: X= O, R= H

b: X= NH, R= H

c: X=NH, R= CH_3

Fig. 1



Scheme 2

the carbonyl carbon atoms of the former exhibit four resonances between 175.6 and 178.0 ppm. Therefore, for that adduct structures **Ia**, **IIa** and **IIIa** can be postulated.

The mass spectra revealed that all the cycloaddition products were first degraded via a *retro*-Diels-Alder processes, as reported previously for analogous compounds [1–5] to the initial components selenophene and maleimide, each of which subsequently unerwent its own characteristic fragmentation [6, 7]. Consequently, the mass spectra of the adducts virtually consist of the sum of the two spectra corresponding to the starting materials (Scheme 2).

Further studies on benzophenone photosensitized photocycloaddition of various maleic anhydride analogues such as substituted maleimides and citraconimides to other selenophene and selenophthene [2] derivatives are in progress. Full details of the synthesis and structure of the isomers will be reported at a later date.

Experimental

Melting points were measured with a Kofler apparatus and are uncorrected. IR spectra were obtained in KBr with a FT-IR Nicolet DX V 5.07. All ^{1}H NMR and ^{13}C NMR spectra were measured at approximately 30° with a Varian 390 Spectrometer (90 MHz), a Bruker WP 60 and a Bruker Aspect 3000 (300 MHz) NMR spectrometer. TMS served as an internal standard, the solvent was deuterated dimethylsulfoxide (*DMSO*-d_6). The mass spectra were determined in a Dupont 21492B Spectrometer. Selenophene was prepared by the method of *Gronowitz* and *Frejd* [8] modified by *Vargas* [2] and 3,4-Dimethylselenophene by the method of *G. Barbey* and *G. Dian* [9].

2,3-Dimethylmaleic anhydride (Aldrich) was used without further purification, 2,3-dimethyl maleimide was prepared by a standard method [10].

Photochemical Reactions

Equimolar quantities of the heterocycle (0.01 mole) and of 2,3-dimethylmaleic anhydride or amide (0.01 mole) in addition to 3.6 g of benzophenone (0.02 mole) were dissolved in 250 ml of dry benzene and irradiated with a Hanovia 450 W medium pressure lamp for 8 hours at 20 °C under a nitrogen atmosphere in a quarz apparatus fitted with a pyrex filter sleeve. In all experiments after about 3 hours of exposure to light small crystals begin to appear on the walls of the irradiation apparatus. At the end of the irradiation the crystals were filtered and washed with petroleum ether. Separation of the products and further purification was performed by chromatography on neutral alumina. They were eluted from the column with benzene-acetone (3 : 1). When adduct **2b** is sublimed, adduct **1b** is obtained in pure form [11].

Products

Adduct **1b**: yield, 90% (acetone/petroleum ether-1 : 1); m.p. 175 °C; IR (cm^{-1}): 3250 (N–H), 1750 (C=O), 1500 (CH$_3$); ^{1}H NMR (ppm): 9.00 (s, 1 H, N–H), 7.80 (2d, $J_{6,5}$ = 5.0, 1 H, 6–CH), 6.20 (q, J = 2.0, 1 H, 5–CH), 5.00 (d, $J_{4,1}$ = 9.3, 1 H, 1–CH), 420 (2q, $J_{5,4}$ = 3.0, 1H, 4–CH), 1.50 (s, 3 H, 3–CH$_3$) 1.20 (s, 3 H, 2–CH$_3$); MS (m/z (%)): 257 (M$^+$, 2), 132 (100), 125 (52); anal: calcd. for $C_{10}H_{11}NO_2Se$: C 46.69, H 4.28, N 5.44, Se 31.13; found: C 46.40, H 4.18, N 5.25, Se 31.02.

Adduct **1c**: yield, 90% (benzene); m.p. 99–101 °C (d); I R (cm^{-1}).: 1758, 1674 (C=O), 3219 (NH), 3087 (CH), 1473–1459 (CH3), 1399, 1355; ^{1}H NMR (ppm): 4.25 (s, 1 H, 1–H), 1.34 (s, 3 H, 2–H$_3$), 1.32 (s, 3 H, 3–CH$_3$), 1.25 (s, 3 H, 4–CH$_3$), 1.67 (s, 3 H, 5–CH$_3$), 6.17 (d, $J_{1,6}$ = 1.4, 1 H, 6–H); ^{13}C NMR (ppm): 182.36 (C=O), 180.53 (C=O), 63.48 (1–C), 49.82 (2–C), 53.44 (3–C), 55.97 (4–C), 117.01 (5–C); 138.29 (6–C), 12.30 (2–CH$_3$), 14.68 (3–CH$_3$), 16.72 (4–CH$_3$), 21.71 (5–CH$_3$); MS (m/z (%): 285 (M$^+$, 20), 125 (90), 54 (80), 39 (60), 160 (100), 145 (16), 79 (60); anal.: calcd. for $C_{12}H_{15}NO_2Se$: C 50.71, H 5.32, O 11.26, N 4.93, Se 27.78; found: C 50.7, H 5.32, O 11.27, N 4.93, Se 27.00.

Adduct **2a**: ^{1}H NMR (ppm): 4.70 (dd, $J_{1,4} = J_{8,5} = 4.5$, 2 H, 1–H and 8–H), 3.80–3.88 (dd, $J_{4,1} = J_{5,8}$ = 4.5, 2 H, 4–H and 5–H), 1.53, 1.40, 1.32, 1.25 (4 × s, 12 H, CH$_3$); ^{13}C NMR (ppm): 178.09 (C=O), 177.24 (C=O), 176.82 (C=O) 176.59 (C=O), 55.67 (*C*–CH$_3$) 54.45 (CH-ring), 54.09 (CH-ring), 53.78 (CH-ring), 52.56 (CH-ring), 52.14 (CH-ring), 51.83 (CH-ring), 50.37 (CH-ring), 47.87 (CH-ring), 14.60 (CH$_3$), 14.30 (CH$_3$), 12.80 (CH$_3$), 10.70 (CH$_3$); anal: calcd. for $C_{16}H_{16}0_6Se$: 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.

Adduct **2b**: yield, 70% (acetone/petroleum ether-1 : 1); m.p. 295 °C (d); IR (cm^{-1}): 3470 (N–H), 1770 (C=O), 1340 (CH$_3$); ^{1}H NMR (ppm): 9.00 (s, 1 H, N–H), 4.70–4.40 (2d, $J_{1,4}$ = 7.0, 2 H, 1–H, 8–H), 3.70–3.50 (2d, $J_{5,8}$ = 7.0, 2 H, 4–H, 5–H), 1.45–1.15 (4s, 12 H, CH$_3$); ^{13}C NMR (ppm): 182.79 (C=O), 182.30 (C=O), 181.32 (C=O), 180.17 (C=O), 55.73 (*C*–CH$_2$) 55.12 (CH-ring), 53.78 (CH-ring), 53.42 (CH-ring), 52.99 (CH-ring), 51.23 (CH-ring), 50.00 (CH-ring), 49.58 (CH-ring), 47.63 (CH-ring), 16.70 (CH$_3$), 14.30 (CH$_3$), 12.70 (CH$_3$), 10.70 (CH$_3$); MS (m/z (%)): 257 (M$^+$ – imide, 2), 132 (85), 125 (100); anal.: calcd. for $C_{16}H_{18}N_2O_4Se$: C 50.40, H 4.67, N 7.35, Se 20.71; found: C 50.00, H 4.45, N 7.28, Se 21.05.

Adduct **2c**: yield, 60% (acetone/petroleum ether-1 : 1); m.p. 250 °C (d); IR (cm^{-1}).: 1733–1723 (C=O), 3102, 835.4 (CH), 1378–1328 (CH3), 3234 (NH); ^{1}H NMR (ppm): 11.66 (s, 2 H, NH), 4.19 (s, 2 H, 1–H, 8–H), 1.17 (s, 6 H, 2–CH$_3$, 7–CH$_3$), 1.14 (s, 6 H, 3–CH$_3$, 6–CH$_3$), 1.60 (s, 6 H, 4–CH$_3$, 5–CH$_3$); ^{13}C NMR (ppm): 181.45 (C=O), 62.72 (1–C), 49.75 (2–C), 54.98 (3–C), 55.93 (4–C), 12.29 (2–CH$_3$), 14.30 (3–CH$_3$), 21.22 (4–CH$_3$); MS (m/z (%)): 285 (M$^+$, 5) 160 (100), 145 (22), 125 (52), 79 (65), 54 (60), 39 (70).

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[11] Satisfactory analytical data (C, H, N, Se) were obtained for the reported compounds

Received January 21, 1994. Accepted January 26, 1994

Verleger: Springer-Verlag KG, Sachsenplatz 4–6, A-1201 Wien. – Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, A-1010 Wien und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. – Redaktion: Währinger Straße 38, A-1090 Wien. – Satz und Umbruch: Thomson Press Ltd., New Delhi, India. – Offsetdruck: Eugen Ketterl Gesellschaft m.b.H., Schopenhauerstraße 45, A-1180 Wien. – Verlagsort: Wien. – Herstellungsort: Wien. – Printed in Austria.