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Photocycloaddition of acetylselenophene to double bond containing substrates

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Abstract

Upon direct irradiation with light of wavelength between 290 and 320 nm, 2-acetylselenophene in the presence of olefinic substrates exhibits three types of behavior. Namely, it undergoes [2 + 2] cycloaddition reactions involving the C=C bond of the olefinic compound and the acetyl-substituted selenophene C=C bond, oxetane formation involving the carbonyl group present in the selenophene moiety and the C=C bond of the olefinic compound. Third, but not less important, it acts as a photosensitizer. This versatile behavior is discussed and compared with that of several thiophene analogs. © 2001 Published by Elsevier Science B.V.

Keywords: 2-Acetylselenophene; 2,3-Dimethyl-2-butene; 2,3-Dimethylmaleic anhydride; Oxetane; Photocycloaddition

1. Introduction

In the course of several investigations, carried out in this laboratory, concerning photoadditions of methylmaleic anhydride derivatives to furan and to several thiophene derivatives sensitized by benzophenone, the corresponding [2 + 2] cycloaddition products have been isolated [1–9]. Furthermore, Cantrell [10,11] has found that irradiation of both 2-benzoyl and 2-acetylthiophene in an excess of 2,3-dimethyl-2-butene (tetramethylethylene) results in [2 + 2] cycloaddition of the olefin to one of the double bonds of the thiophene ring. This has been explained by the fact that the mode of excitation of the thiophene derivatives is probably of π, π^* type.

It should also be pointed out that some ketones are capable of adding to the double bond of maleic anhydride yielding an oxetane in the same form of aldehyde to cyclic olefin with electronic control of stereoselectivity [12–14]. Some authors suggested that in carbonyl compounds excited via π, π^*, oxetane formation though inefficient may proceed as an S_1 (n,π^*) reaction [15–18]. Finally, there was the question as to whether benzophenone would be needed as the sensitizer, as has been the case for the majority of this type of reactions carried out in this laboratory [1–8] or if 2-acetylselenophene would act as its own sensitizer.

In view of all these facts and considerations, it appeared interesting to investigate the photochemical reactions of 2-acetylselenophene in the presence of tetramethylethylene and 2,3-dimethylmaleic anhydride and compare its behavior with that of its thiophene analogs.

2. Experimental

Selenophene, tetramethylethylene and 2,3-dimethylmaleic anhydride were purchased from Aldrich (Steinheim, Germany). All analytical or high performance liquid chromatography (HPLC) grade solvents were obtained from Merck (Darmstadt, Germany). The preparation of 2-acetylselenophene was carried out by heating a solution of 3.0 ml of selenophene and 1.75 ml of acetic anhydride at 70°C for 30 min. The solution was removed from the heat source and 0.15 ml of 85–89% orthophosphoric acid was added to it. An exothermic reaction occurred, the solution was refluxed for 2 h, and after allowing it to cool to room temperature 10 ml of water were added. The organic phase was washed with a sodium carbonate solution and dried over magnesium sulfate. The red liquid was purified through a silica gel column (hexane/ethylene chloride (4:1)). The first fraction (1.51 ml of a greenish-yellow liquid) was identified as 2-acetylselenophene (yield 78%). The purity was 99% as determined by ^{1}H NMR. The product was identical to that synthesized by Maria et al. [19].

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2.1. Photochemical reactions

Equimolar quantities (0.346 mol) of acetylselenophene and tetramethylethylene (or 2,3-dimethylmaleic anhydride) were irradiated at room temperature for 72 h in 100 ml methanol. This was carried out with a Rayonet photochemical reactor equipped with 16 phosphor lamps with emission between 290 and 320 nm (23 mW/cm^2 of irradiance) as measured with a model of UVX Digital Radiometer after 1 h of continued illumination, under an argon atmosphere. The photoreaction was also carried out in isopropanol as solvent. The last results (products, yields and ratios) were similar to those obtained with methanol (analyzed by GC mass).

After irradiation the solvent was evaporated at reduced pressure (14 Torr) at room temperature, the residue purified by column chromatography (silica gel) using dichloromethane–methanol mixture (5:1 (v/v)) as elutant, and the photoproducts were isolated by preparative TLC chromatography (silica gel Merck 60 F_{254}) or alternatively by preparative HPLC. HPLC used in all experiments described herein was a Waters Delta Prep 4000 equipped with a 3.9×300 mm Porasil 10 μm column using a CH_2Cl_2/MeOH binary solvent system. The isolated products **1**–**5** were analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy (Bruker Aspect 3000, 300 MHz), FTIR (Nicolet DX V 5.07) and MS (Carlo Erba/Kratos MS25RFA).

2.2. Photocycloaddition products

2.2.1. Ketone **1**

Yield (%, ratio): 32%, 56; (b.p. 52°C, 2 mm), $R_f = 0.32$. IR (KBr): ν = 3095, 3075, 2960, 1700, 1392, 1375, 850 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz): δ = 7.42 (dd, 1H, $J_{5,4}$ = 5.0 Hz, $J_{5,3}$ = 1.2 Hz, 5H), 7.38 (dd, 1H, $J_{4,5}$ = 5.0 Hz, $J_{4,3}$ = 3.0 Hz, 4H), 3.75 (dd, 1H, $J_{3.4}$ = 3.0 Hz, $J_{3,5}$ = 1.2 Hz, 3H), 2.60 (s, 3H, 6H), 1.54 and 1.45 (s, 3H each, 8CH_3), 1.23 and 1.12 (s, 3H each, 7CH_3). ^{13}C NMR (CD_3OD, 100 MHz): δ = 206 (s, C=O-6), 133 (d, CH-5), 130 (d, CH-4), 66 (s, C-2), 55 (s, C-8), 52 (d, CH-3), 29 (s, C-7), 27 (q, CH_3CO), 22 (q, $(CH_3)_2$–C-8), 19 (q, $(CH_3)_2$–C-7). MS: m/z (%) = 216 (35), 215 (20, parent — CH_3CO, parent not observed), 201 (55), 199 (30), 159 (40), 73 (10), 43 (50), 39 (12).

2.2.2. Oxetane **2**

Yield (%, ratio): 22%, 44; (b.p. 60°C, 2 mm, with decomposition), $R_f = 0.66$. IR (KBr): ν = 3040, 3020, 2885, 1390, 1370, 1039 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz): δ = 8.50 (5H), 8.30 (3H) and 8.02 (5H) (3H, AMX), 1.63 (s, 3H, 6CH_3), 1.31 and 1.27 (s, 3H each, 8CH_3), 1.26 and 1.23 (s, 3H each, 7CH_3). ^{13}C NMR (CD_3OD, 100 MHz): δ = 155 (s, C-2), 142 (d, CH-5), 134 (d, CH-4), 122 (d, CH-3), 78 (s, C-8), 70 (s, C-6), 56 (s, C-7), 21 (q, $(CH_3)_2$–C-8), 17 (q, CH_3–C-6), 15 (q, $(CH_3)_2$–C-7). MS: m/z (%) = 199 (100, parent — acetone, parent not observed), 184 (45), 169 (14), 115 (70), 91 (30), 79 (15), 65 (20), 45 (18), 39 (15).

2.2.3. Ketone **3**

Yield (%, ratio): 15%, 14; (m.p. = 118°C), $R_f = 0.33$. IR (KBr): ν = 3092, 3073, 2962, 1790, 1740, 1725, 845 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz): δ = 7.90 (dd, $J_{5,4}$ = 5.8 Hz, $J_{5.3}$ = 1.2 Hz, 1H, CH-5), 7.54 (dd, $J_{4,5}$ = 5.8 Hz, $J_{4,3}$ = 3 Hz, 1H, CH-4), 4.31 (m, $J_{3,4}$ = 3 Hz, $J_{3,5}$ = 1.2 Hz, 1H, CH-3), 2.05 (S, 3H, CH_3–CO), 1.56 (s, 3H, CH_3-8), 1.22 (s, 3H, CH_3-7). ^{13}C NMR (CD_3OD, 100 MHz): δ = 203 (s, C=O-6), 180 (s, C=O), 173 (s, C=O), 133 (d, CH-5), 131 (d, CH-4), 62 (s, C-2), 59 (s, C-8), 45 (s, C-7), 41 (d, CH-3), 26 (q, CH_3-6), 14 (q, CH_3-8), 13 (q, CH_3-7). MS: m/z (%) = parent not observed, 174 (80), 159 (70), 131 (14), 127 (100), 54 (26).

2.2.4. Oxetane **4**

Yield (%, ratio): 28%, 32; (m.p. = 38–40°C, decomposition), $R_f = 0.60$. IR (KBr): ν = 3090, 3072, 2960, 1792, 1740, 1394, 1372, 1038 cm^{-1}. ^{1}H NMR (CD_3OD, 300 MHz): δ = 8.44 (dd, $J_{5,4}$ = 6 Hz, $J_{5,3}$ = 1 Hz, 1H, CH-5), 7.97 (dd, $J_{4,5}$ = 6 Hz, $J_{4,3}$ = 4 Hz, 1H, CH-4), 7.41 (dd, $J_{3,4}$ = 4 Hz, $J_{3,5}$ = 1 Hz, 1H, CH-3), 2.57 (s, 3H, CH_3-8), 2.05 (s, 3H, CH_3-6), 1.93 (s, 3H, CH_3-7). ^{13}C NMR (CD_3OD, 100 MHz): δ = 172 (s, C=O), 168 (s, C=O), 154 (s, C-2), 140 (d, CH-5), 132 (d, CH-4), 130 (d, CH-3), 85 (s, C-8), 71 (s, C-7), 69 (s, C-6), 19 (q, CH_3-8), 17 (q, CH_3-6), 14 (q, CH_3-7). MS: m/z (%) = parent not observed, 175 (30), 174 (25), 127 (100), 54 (45), 43 (35).

2.2.5. Dimer **5**

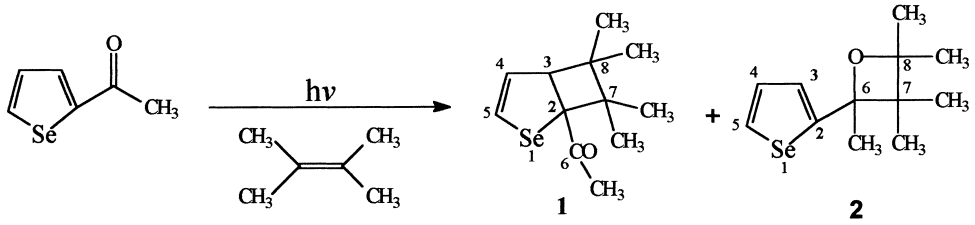
Yield (%, ratio): 32%, 54; (m.p. = 380°C [20,21], $m.p._{obs.}$ = 379–381°C, decomposition), R_f = 0.72. ^{1}H NMR (CD_3OD, 300 MHz): δ = 1.58 (s, 3H, CH_3). ^{13}C NMR (CD_3OD, 100 MHz): δ = 172 (s, C=O), 54 (s, C–C), 13 (s, CH_3).

3. Discussions

Upon direct irradiation of 2-acetylselenophene in the presence of tetramethylethylene afforded the [2 + 2] cycloaddition product **1** involving the C=C bond of the olefinic compound and the acetyl-substituted selenophene C=C bond, as well as oxetane **2** (Scheme 1).

On the other hand, in the presence of 2,3-dimethylmaleic anhydride, 2-acetylselenophene, under the same conditions, yields the [2 + 2] cycloaddition product **3**, oxetane **4** involving the carbonyl group of the substituted heterocycle and the double bond of the anhydride, and also the dimer of the anhydride **5** (Scheme 2).

In previous work, where [2 + 2] cycloaddition reactions between heterocyclic systems and maleic anhydride derivatives were studied, the presence of a sensitizer, namely benzophenone was required for the photoreaction to proceed.



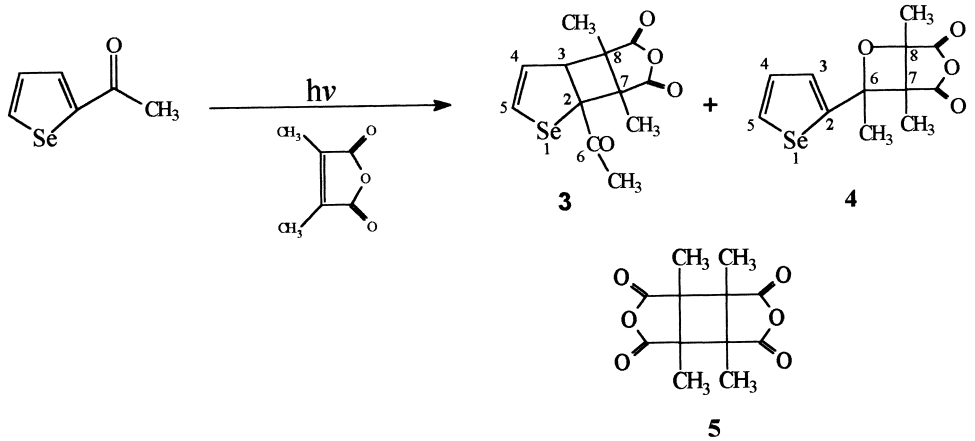
Scheme 1.

In the present investigation it was found that, as it was observed before for 2-benzoylthiophene [9], the use of benzophenone as a sensitizer was not necessary. Therefore, 2-acetylselenophene plays the dual role of reactant and sensitizer.

The choice of methanol, a protic solvent, as the reaction medium had the purpose of covering the whole spectrum of photochemical reactions known for this type of compound including photoreduction by hydrogen abstraction from the solvent. No photoreduction products were isolated. In order to assert this statement the reaction was also carried out in 2-propanol, a standard solvent to test for photoreduction of carbonyl compounds, obtaining the same result as in the previous experiment. Furthermore, the reactions were carried out in benzene, one of the current solvents used in oxetane synthesis and in [2 + 2] photocycloaddition of the type studied in this laboratory. The products obtained in all of these trials were the same.

As a photosensitizer, 2-acetylselenophene only acted upon 2,3-dimethylmaleic anhydride producing its dimer. No dimer of tetramethylethylene was found. In view of the results obtained it is tempting to establish the similarities and the differences between 2-acetylselenophene and its thiophene analogs. None of the heterocycles (2-benzoylthiophene, 2-acetylthiophene and 2-acetylselenophene) are prone to yield photoreduction products by hydrogen abstraction from protic solvents if the suggestion based on phosphorescence data [22] that their lowest excited state is of the π, π^* type is taken into account. In the reaction with benzophenone *n*, π^* excitation produces a deficiency of one electron on the oxygen atom to which a new bond must be formed. In these compounds where the π, π^* excitation occurs, the half empty orbital is delocalized over the entire system involving the heterocyclic nucleus. If such is the case, it is possible that charge transfer complexes or exciplexes, in these cases, may be easily formed between one of the two C=C bonds in the heterocyclic ring and the C=C bond of the olefinic substrates which collapse to the [2 + 2] cycloaddition product. In fact, in our experience, UV-spectral evidence for the formation of charge transfer complexes between methylmaleic anhydrides and thiophene was found. Furthermore, application of NMR methods and further analysis of the results by a Foster adaptation of the Benesi–Hildebrand equation [23] allowed to determine the equilibrium constants of the systems methylmaleic anhydride derivative thiophene with their complex [24]. Qualitatively it has also been observed that the UV-spectrum of selenophene and 2,3-dimethylmaleic anhydride in cyclohexane appear on new peak at 290 nm, different from those of the heterocycle (250 nm) and the anhydride (255 nm).

Regarding the stereo- and regio-selectivity of the reaction between 2-acetylselenophene and 2,3-dimethylmaleic anhydride to form the [2 + 2] cycloaddition product it is worth noting that in contrast to 2-methylthiophene [4] and 2-methylselenophene [25] where the addend goes to the unsubstituted double bond in the ring, in 2-acetylselenophene



Scheme 2.

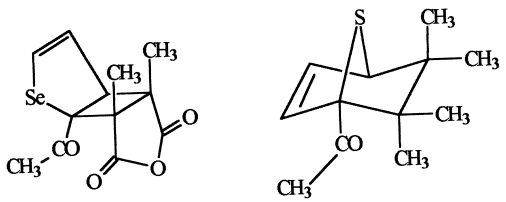
the [2 + 2] cycloaddition to the heteroaromatic ring takes place at the double bond bearing the acetyl group. The same type of regio-selectivity was observed in 2-benzoylthiophene [9].

The possible involvement of exciplexes may answer unequivocally the question of orientation in the cycloaddition reaction. Griesbeck and Stadtmüller [13] who have devoted a great deal of attention to the formation of regioisomers in the Paterno–Büchi reactions suggest that regio-selectivity could be determined by the pre-orientation of the substrates which would be influenced by several factors, including steric, electronic and solvent effects.

The stereochemistry of the [2 + 2] cycloaddition product between 2-acetylselenophene and 2,3-dimethylmaleic anhydride could be assigned on the basis of an analogy to that proposed before for adducts with the same carbon skeleton which were elucidated by means of selective $^{13}C\{^1H\}$ NOE experiments [26]. Thus, all the [2+2] cycloaddition products studied here, analogous to the one presently under investigation have anti-configuration (compound **6** in Scheme 3).

Formation of the oxetanes may be rationalized by the fact that, as it is well known, the triplet lifetime of compounds possessing T_1 (π, π^*) states is commonly found to be much longer than that of compounds with T_1 (n, π^*) states. This effect presumably counterbalances the low reactivity of these states. Of the two frontier orbital mechanisms commonly accepted for the formation of the biradical precursors of oxetanes, perhaps, the more feasible in this case would be a LUMO–LUMO interaction in which the half-occupied π^* carbonyl orbital interacts with the unoccupied π^* MO of an electron-deficient alkene.

The lack of sensitization of the double bond in tetramethylethylene to form the dimer (octamethylcyclobutane) by way of a triplet obtained by energy transfer from a sensitizer is one of the various, e.g. of non-conjugated acyclic olefins whose triplet is generally believed to quickly deactivate so that the bimolecular dimerization cannot compete. According to Arnold and Abraitys [27], photodimerization of tetramethylethylene requires direct irradiation into π, π^* singlet. On the other hand, 2,3-dimethylmaleic anhydride is an excellent quencher ($K_q = 13.03 \times 10^{-8}\,M^{-1}\,s^{-1}$) of triplet ketones with T_1 about 69 kcal/mol. More or less abundance of dimer depends, to a greater extent, on the concentrations of heterocycle relative to that of the anhydride [24].



6 **7**

Scheme 3.

In contrast to 2-acetylfuran and 2-acetylthiophene which yield 2,4-cycloaddition products (Diels Alder) (compound **7** in Scheme 3), in the present investigation no such products were found. It may presumably be due to the size of the selenium atom, which is larger than sulfur and thus the former is too large to be held at the bridgehead of the bicyclic structure, as it is the case with O, N and to a lesser extent sulfur. In our experience, in [3 + 4] cycloadditions stable bicyclic compounds with Se and even Te at the bridgehead were obtained [28]. The mass spectrum of the dimer of the anhydride has been previously reported [20,21] and that of the [2 + 2] cycloaddition product follows the same type of fragmentation previously reported for analogous compounds [29].

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