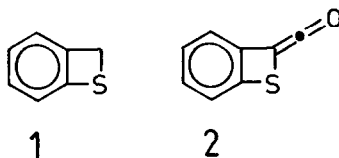


ELUCIDATION OF THERMAL REACTIONS BY VARIABLE TEMPERATURE PHOTOELECTRON SPECTROSCOPY. A NEW SYNTHESIS OF BENZOTHIETE AND FIRST DIRECT EVIDENCE FOR TRANSIENT BENZOTHIETE KETENE ¹

Reinhard Schulz and Armin Schweig
Fachbereich Physikalische Chemie der Universität Marburg
Hans-Meerwein-Straße, D-3550 Marburg-1, W.-Germany

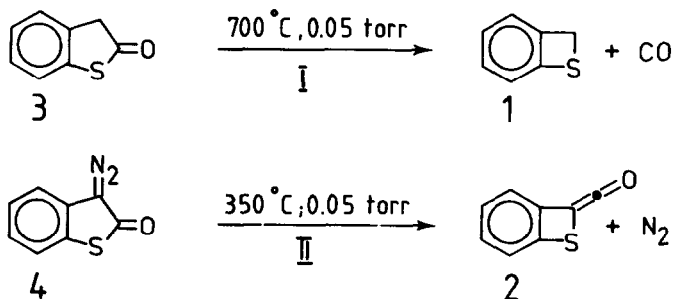
Abstract: An efficient synthesis (80% yield) of benzothiete has been found and transient benzothiete ketene has been detected using the technique of variable temperature photoelectron spectroscopy.

Benzothiete **1** was obtained by flash vacuum pyrolysis (1000°C, 45% yield) of benzo[b]thiophen-1,1-dioxide ² and is fairly stable at room temperature. Its ketene derivative **2** was suggested as a transient intermediate during the photolysis of 3-diazo-benzo[b]thiophen-2-one ³. We wish now to record the first spectral detection of **2** and a new flash vacuum thermal synthesis of **1** (700°C, 80% yield).



Both results were attained through variable temperature photoelectron spectral (VTPES) ⁴ studies of appropriate organic precursors, namely benzo[b]thiophen-2(3H)-one (**3**) ⁵ and 3-diazo-benzo[b]thiophen-2-one (**4**) ⁶.

The decomposition reactions carried out in the reactor of the PE spectrometer are summarized below.



Both reactions were complete at the temperatures indicated. The PE spectra of precursors and products are shown in Fig.1.

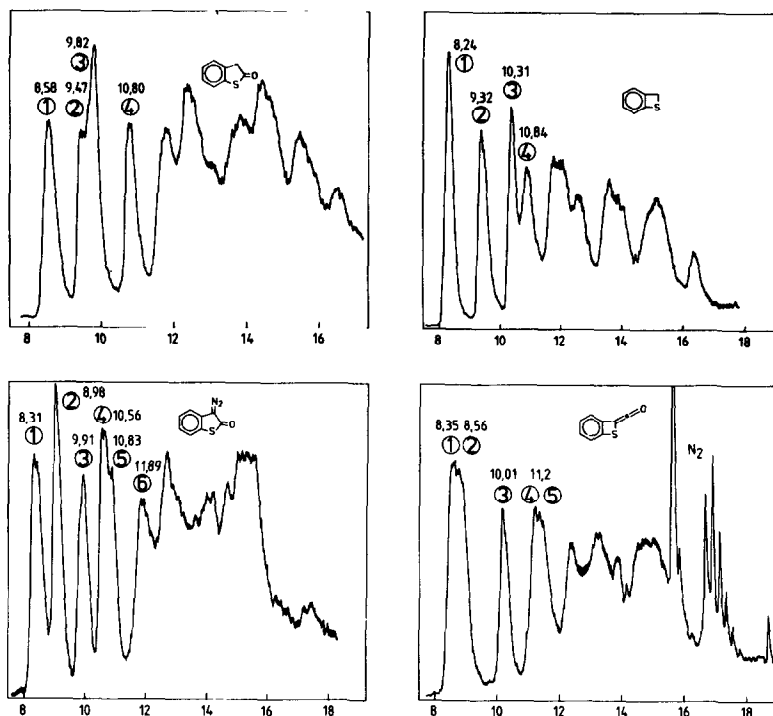


Figure 1: He-I PE spectra of benzo[b]thiophen-2(3H)-one (3), 3-diazo-benzo[b]thiophen-2-one (4), benzothiete (1) and the benzothiete ketene 2. The ionization potentials (in the abscissa) are in eV and the numbers associated with each band refer to vertical ionization potentials. Assignments are based on PERTCI⁸ calculations, the changes of spectra when going from He-I to He-II excitation and the ionizations of suitably chosen reference systems, and are as follows: 1: ① $2A''(\pi)$, ② $2A''(\pi)$, ③ $2A''(\pi)$, ④ $2A'(\sigma)$; 2: ① $2A''(\pi)$, ② $2A''(\pi)$, ③ $2A''(\pi)$, ④ $2A''(\pi)$, ⑤ $2A'(\sigma)$; 3: ① $2A''(\pi)$, ② $2A''(\pi)$, ③ $2A'(n_o)$, ④ $2A''(\pi)$; 4: ① $2A''(\pi)$, ② $2A''(\pi)$, ③ $2A'(n_o)$, ④ $2A''(\pi)$, ⑤ $2A''(\pi)$, ⑥ $2A'(\sigma)$.

Reaction I was repeated in a flash vacuum pyrolysis (FVP) apparatus (stainless steel tube 20x0.6 cm reactor, 700°C, 0.1 torr) and the pyrolysate investigated by NMR and IR spectroscopy as well as mass spectrometry. According to the ¹H-NMR analysis the pyrolysate consists of almost pure benzothiete (1) in 80% yield and a trace (4%) of the precursor 3. All spectroscopic data obtained for 1 agree with those of ref.2. The PE spectrum of a sample of the pyrolysate shown

in Fig.1 matches the corresponding "in situ" recorded spectrum. Thus the identity of the VTPES product of reaction I is most directly proved.

The improved benzothiete synthesis described above is potentially suitable for generating substituted benzothietes as well.

Reaction II shows that highly sensitive benzothiete systems may also be produced. The structure of the decomposition product is clearly established from the comparison of its observed ionization potentials and those calculated for 2 and its non-cyclic valence isomer 6 (cf.Fig.2). The theoretical data are based on MNDO⁷ optimized structural data and large scale PERTCI⁸ calculations using CNDO/S⁹ and MNDO wavefunctions.

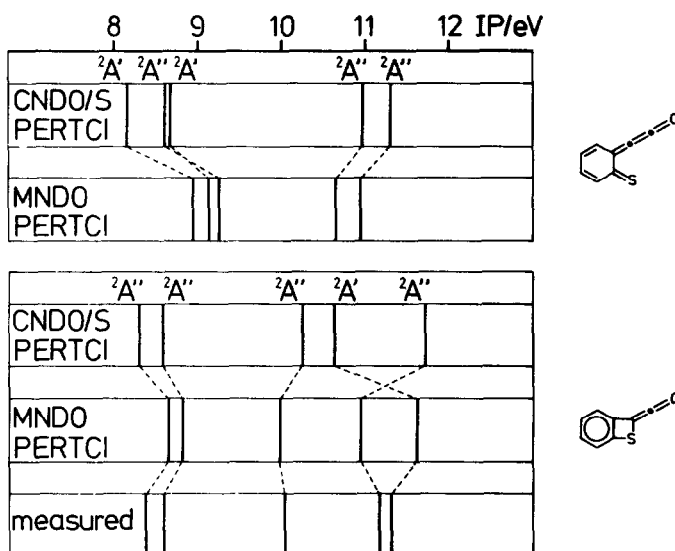
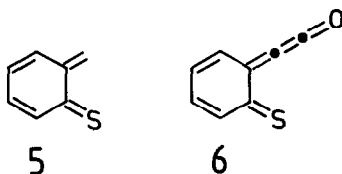


Figure 2: Measured vertical ionization potentials of the product of reaction II vs. calculated PERTCI⁸ vertical ionization potentials of compounds 2 and 6 (all ionization potentials in eV).

To conclude, the results of the foregoing experiments show that both 2 and 1 exhibit no tendency to exist or partially exist (under the experimental conditions applied) in their non-cyclic thiocarbonyl forms 5 and 6.



This is in concordance with MNDO data that predict 1 (2) to be more stable than 5 (6) by 9 (16) kcal/mol¹⁰.

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