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THERMAL AND PHOTOCHEMICAL REACTIONS OF 1,4-DITHIINE AND DERIVATIVES

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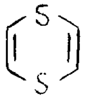
Summary Thermally, dithiines may react as dienophiles in [2+4]-cycloadditions. Photochemically, they afford [2+2]-cyclodimerization products in the absence of oxygen; in its presence, they are degraded to CO_2 and H_2S among other photooxidation products. CT-complexes occur with tetracyanoethylene, maleic anhydrides and acetylenes, but no stable products are formed, neither thermally nor photochemically.

Thermal reactions of cyclic thioenol ethers with tetracyanoethylene (TCNE) produce [2+2]-cycloadducts via deeply colored CT-complexes [1]; with dimethyl acetylenedicarboxylate (DA), yellowish CT-complexes and [2+3]-cycloadducts, i.e. sulfonium ylid intermediates are formed which undergo either a retro-cycloaddition to starting materials or a fragmentation to stable products [2].

Addition of 1,4-dithiine (1), 2,5-diphenyldithiine (2), 2,3;5,6-bis[trimethylene]1,4-dithiine (3), 1,4-dithiene (4), and oxathiene (5) to toluene solutions of TCNE, maleic anhydride, dimethylmaleic anhydride, or of acetylenes such as DA, dimethyl propiolate, methyl phenylpropiolate, diphenylacetylene, and 1,2-bis(ethylthio)-acetylene, yield colored CT-complexes but no thermal conversion products whatsoever. More than 98% of the starting material may, therefore, be recovered from the reaction mixtures.

Only with a reactive diene such as 2,5-dimethyl-3,4-diphenylcyclopentadienone (6) [3] reacts 1 as a dienophile to afford the [2+4]-cycloaddition product 7 [95% yield in toluene; m.p. 175°C; IR (KBr): 1770 cm^{-1}, trans-annular $>C=O$; ^1H-NMR ($CDCl_3$): δ = 1.35 (s, 6H of 2CH_3-groups); 3.85 (s, 2H_a); 6.72(s, 2H_b); 7.15 (m, 10H of 2 phenyl groups].



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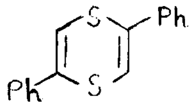

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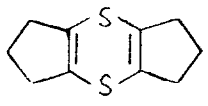

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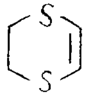

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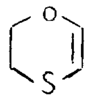

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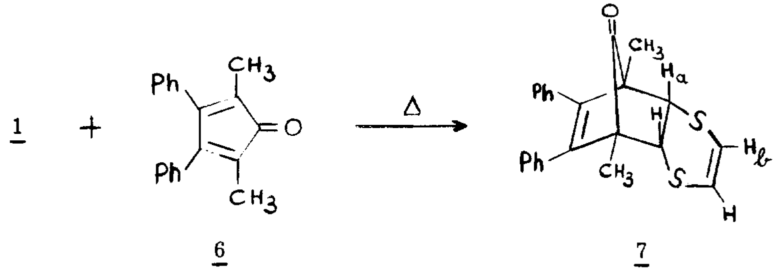
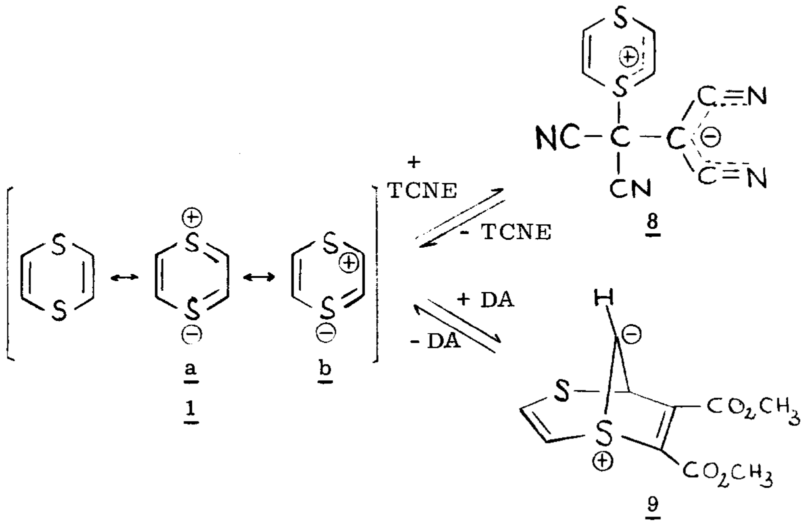
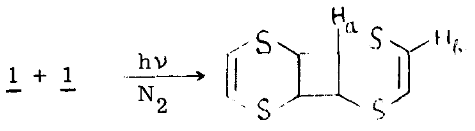


Tetrathioethylenes exhibit a similar inertness toward TCNE and DA indicating a considerable contribution of dipolar structures to their ground-states[4]. Similarly, dipolar structures a and b contribute to the ground-states of 1 and 2[5] significantly. The π-electron distribution in 1 (as well as in the other dithiine derivatives) may thus prevent [2+2]-cycloadditions with electrophiles such as TCNE and DA but may favor the (reversible) formation of dipoles 8 and 9, respectively. As with 3,4-dihydro-2H-thiopyrans[2], the [2+3]-cycloaddition of 1 to DA would then represent a dead-end pathway since the retro-reaction of 9 should be favored energetically over the fragmentation into thiirene and dimethyl 2,3-thiophenedicarboxylate.



Irradiation (λ_{exc} = 254 or 300 nm) of dithiine (1, λ_{max}^{EtOH} = 254 (sh), lgε = 3.66; 262, lgε = 3.70; 271 (sh), lgε = 3.62) in degassed solvents such as cyclohexane, benzene, dioxane, ether, methylene chloride, and acetone results in the formation of the [2+2]-photodimer 10 which precipitates readily from the irradiated solutions. 10 is slightly soluble in chloroform from which it may be recristallized: 80% yield; sublimation at 270°C; IR (KBr): 1540 cm^{-1}, C=C in cyclic thioethers; ^{1}H-NMR (CDCl$_3$): δ = 4.27 (s, 4 H$_a$), 6.60 (s, 4 H$_b$); MS (70 eV): m/e = 232 (M$^+$), 116 (M$^+$/2). No further products are observed.



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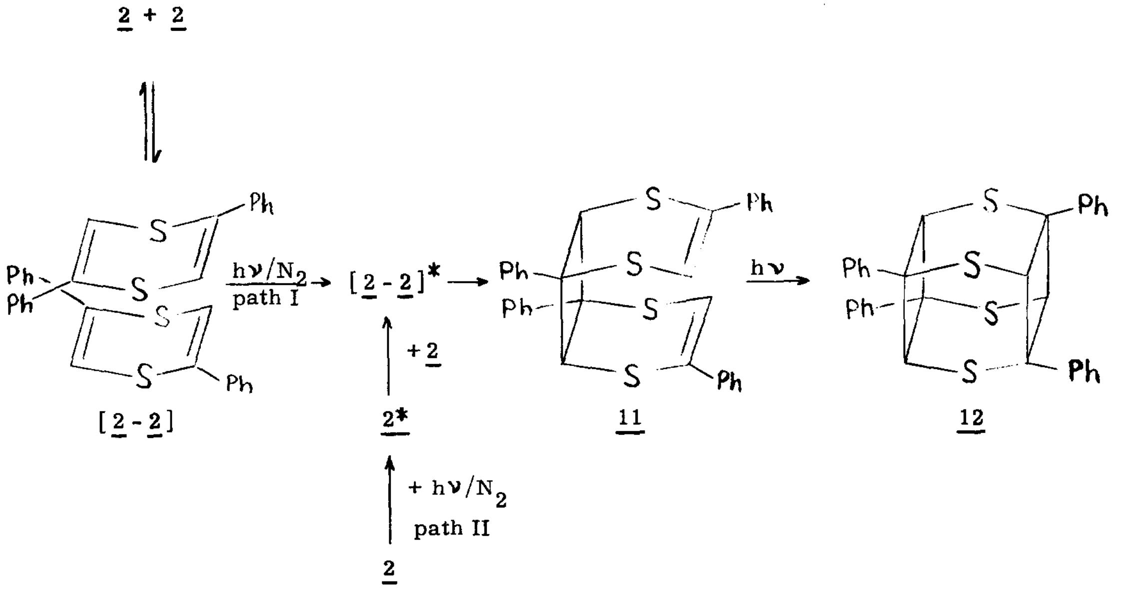
Irradiation of 2,5-diphenyldithiine (2, λ_{max}^{EtOH} = 261, lg ε = 4.34; 309 nm, lg ε = 3.93) under the same conditions leads to a precipitate insoluble in all common solvents. Elemental analysis and mass spectra indicate a photodimer: 75% yield; sublimation at 340°C; C 71.60 (71.54), H 4.51 (4.47), S 23.88 (23.97), theoretical values in parenthesis; MS (70 eV): m/e = 536 (M^+), 268 ($M^+/2$). ^{1}H-NMR spectra at room temperature or elevated temperatures cannot be taken.

The same photodimer was recently observed by Kobayashi and Ohi [6] who inferred a cage structure 12 with a 1,3-disposition of the phenyl groups from mass spectra.

The observation of product 10 from 1 may cast some doubt on the cage-structure of the photodimer from 2. Provided, however, that the latter dimer does possess cage-structure 12, it should be formed in a consecutive two-photon process with the syn-cyclobutane derivative 11 as a precursor which, in turn, is formed in a stereospecific as



well as in a regiospecific [2+2]-photocycloaddition reaction, either via a "sandwich"-like ground-state complex ([2-2]) (path I) or via a "sandwich"-like excimer ([2-2]*) (path II), with the phenyl groups in staggered orientations. The fact that 1 does not form a cage-dimer may then be due either to 10 being the anti-cyclobutane derivative or to the dithioethylene moiety being a much less effective chromophore at the exciting wavelengths in comparison with the dithiostyrene unit in 11.

Dithiine derivative 3 (λ_{max}^{EtOH} = 230, lgε = 3.93; 295 nm, lgε = 3.31) turns out to be photochemically inert, probably because syn- as well as anti-[2+2]-photodimerization is prevented sterically by the trimethylene moieties of 3.

Irradiation of 1 and 2 in the presence of the above-mentioned (donor- or acceptor-substituted) acetylenes in degassed solutions afford only the photodimers 10 and 12, respectively. Increasing concentrations of DA decrease the yields of the photodimers; if DA is used as a solvent, photodimerizations of 1 and 2 are entirely suppressed.

2,5-Diphenyldithiine (2) is a stable solid if stored in a sealed test-tube in the dark. If exposed to light and air, however, it turns into a viscous red oil out of which benzoic acid grows in long colorless needles. Thus, if 2 is irradiated in solution in the presence of oxygen, benzoic acid (and some benzaldehyde, its precursor), carbon dioxide, and hydrogen sulfide are formed according to

$$\underline{2} + 4\,O_2 + 4\,H_2O \xrightarrow{h\nu} 2\,PhCO_2H + 2\,CO_2 + 2\,H_2S + 2\,H_2O_2$$

but no photodimer of 2 is found. Under similar conditions, 1 yields CO_2 and H_2S besides the photodimer 10.

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