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PHOTOREACTION OF 2,5-DIPHENYL-1,4-DITHIIN

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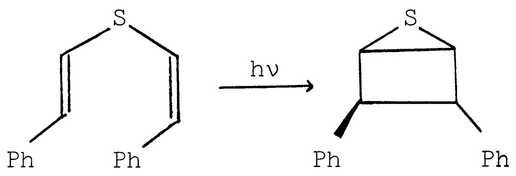
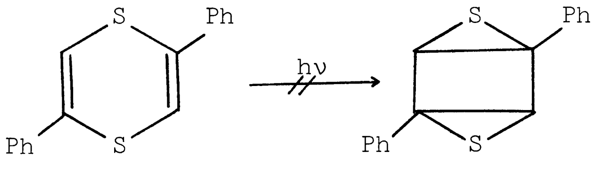
Irradiation of an ethereal solution of 2,5-diphenyl-1,4-dithiin afforded two types of dimer without formation of the products resulting from intramolecular photocyclization. The photodimers were shown to be a *cis, syn*-half-closed dimer and an *anti*-cage dimer.

It has been reported1) that *cis, trans*-distyryl sulfide undergoes facile cyclization on irradiation to *trans*-2,3-diphenyl-5-thiabicyclo[2.1.0]pentane. In connection with this fact, we have investigated the photochemistry of 2,5-diphenyl-1,4-dithiin (I). It was anticipated that intramolecular [2+2] photocyclization would occur affording a highly strained 3,6-dithiatricyclo[3.1.0.0^{2,4}]hexane system.

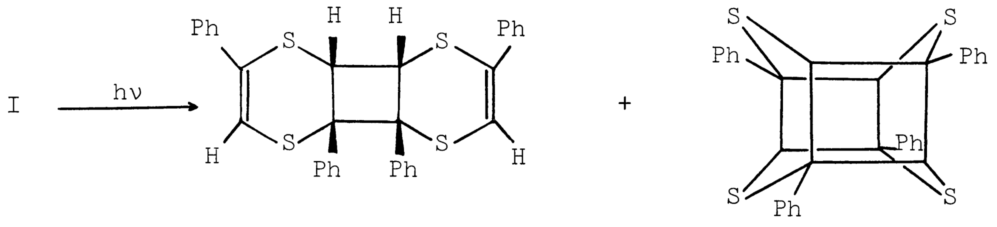




(I)

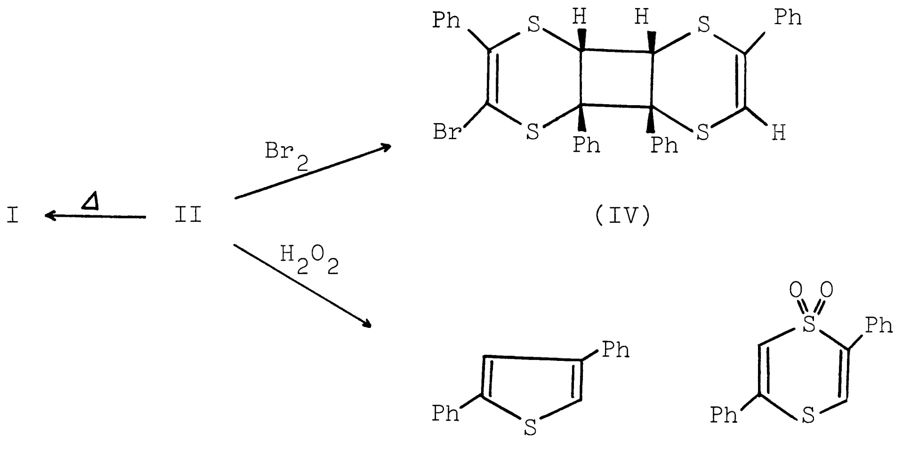
The irradiation of an ethereal solution of I (0.043 M) by means of a 100 W high pressure mercury lamp with Pyrex filter for 15 hours gave a half-closed dimer (II) and a cage dimer (III) in 2.5 % and 13 % yields, respectively. Contrary to the expectation, no intramolecular cyclization products were obtained.

The structure of II, colorless needles2), mp 198 °C(decomp.), was deduced from its spectral and chemical evidence. The mass spectrum of II, m/e: 268(M^+/2), 236(M^+/2-S), was practically identical with that of I, which, coupled with the molecular weight determined by cryoscopy in bromoform, suggested the dimeric



(II) (III)

structure of II. The nmr spectrum of II, showing a singlet peak at δ 5.07 (2H) ascribed to the newly formed cyclobutane protons and a multiplet at δ6.9-7.5 (22H) assigned to the phenyl protons overlapped with two olefinic protons, indicated that the dimer is the half-closed type. Chemical evidence for the dimeric structure was also provided by its thermal reversal to I: when II was heated at melting point, it was converted to I in almost quantitatively. For the half-closed-type dimer, four isomers are possible according to combination of *syn* or *anti* and *cis* or *trans* fusions. In order to elucidate the full stereostructure, II was treated with one molar amount of bromine in chloroform to yield a monobromide IV, mp 190 °C (decomp.), m/e: 348, 346 (M^+ of brominated I), and 268 (M^+ of I). In the nmr spectrum of IV the signals of cyclobutane protons were splitted to AB quartet at δ 5.13 with coupling constant of 9.3 Hz. Thus, it was revealed that methine protons in cyclobutane ring are situated at 1,2-positions and not at 1,3-positions. If the latter were the case, they should appear as two singlets. Moreover, the observed coupling constant 9.3 Hz may be compared with the coupling constant 10.4 Hz for *cis* protons



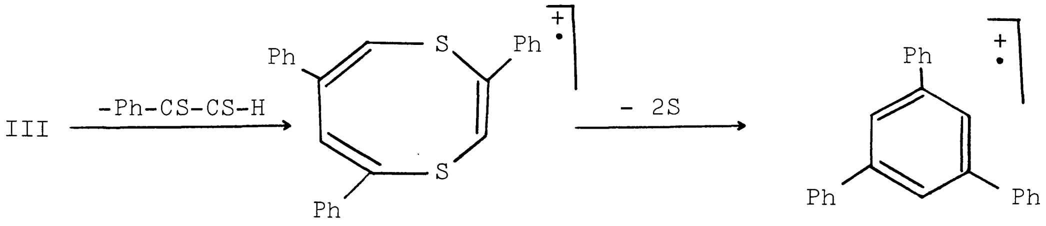
(IV)

(V) (VI)

rather than 4.9 Hz for *trans* protons[3]. Thus, the structure of II was determined to be a *cis*,*syn*-half-closed dimer.

Upon treatment with one molar amount of hydrogen peroxide in chloroform-acetic acid solution at 0 °C, II was converted to 2,4-diphenylthiophene (V), mp 120-121 °C (lit.[4] 121 °C), in 26 % yield and I in 40 % yield. On the other hand, with two molar amounts of hydrogen peroxide 2,5-diphenyl-1,4-dithiin-1,1-dioxide (VI), mp 152 °C (lit.[5] 152-154 °C), ir: 1280, 1120 cm^{-1}, nmr: δ 6.84(1H, s), 7.07(1H, s), 7.3-7.7(10H, m), was obtained in 21 % yield together with 28 % of I. The formation of V would be reasonably interpreted by the facile cyclobutane ring opening of a monosulfoxide of II to 2,5-diphenyl-1,4-dithiin-1-oxide and I. The former should be unstable and decompose to give V, as it is known[6] that I is transformed to V *via* monosulfoxide by the oxidation with hydrogen peroxide. When excess hydrogen peroxide was used, II would yield a monosulfone which also decomposed to afford VI and I.

With regard to the structure of III, which sublimes at *ca.* 350 °C, no available informations could be obtained except for elemental analysis and mass spectrum, because III was hardly soluble in the common organic solvents. The mass spectrum of III displayed a molecular ion peak at m/e 536 and, below 268 (M$^+$/2), corresponded to that of the monomer I except for individual peak intensities. The most remarkable feature of the mass spectrum of III is appearance of prominent peaks at m/e 370 and 306. The former fragment would be assigned to a fragment ion of triphenyl 1,4-dithiocin (VII), which may arise from M$^+$ by expulsion of Ph-CS-CS-H and would easily lose two sulfur atoms to afford the stable ion of 1,3,5-triphenylbenzene (m/e 306)[7]. The absence of peaks at m/e 294 and 446 corresponding to the fragment ions of M$^+$-(Ph-CS-CS-Ph) and M$^+$-(H-CS-CS-H), respectively, strongly suggests that III should be assigned to *anti* but not *syn* dimer.



(VII)

It is interesting to note that the both photodimers are *cis*-configuration: two rings of monomer component lie the same side of the cyclobutane ring resulting from sandwich-like overlapping of two I molecules. These facts suggest that an excimer participates in the process of the photodimerization. The detailed investigations on the mechanistic aspects of this photodimerization are now in progress.

References

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