The Photodimerisation of Some Unsaturated Cyclic Sulphones.

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Thionaphthen 1 : 1-dioxide (I) in benzene solution is converted by sunlight into a stable dimer, m. p. 330—331°, which is considered to contain a central *cyclo*butane structure as in (VII) or (VIII). The sulphones of 3-bromo- and 3 : 4-dimethyl-thiophen similarly give high-melting crystalline dimers presumably of the same type, but intractable oils are formed from the three non-cyclic sulphones investigated containing the $\cdot SO_2\cdot CH{:}CH\cdot$ group.

It has been noted in this Department that crystalline thionaphthen 1 : 1-dioxide (I) undergoes a change when exposed to light. It is now found that in benzene solution the pure dioxide, m. p. 142°, is completely converted by long exposure to sunlight into a sparingly soluble crystalline dimer, m. p. 330—331°. The stability of this towards oxidising and reducing agents shows the absence of a double bond, and therefore structures of type (IV) are untenable. Though the monomer cannot be isolated when the dimer is heated, the latter in boiling butyl phthalate (b. p. 338—340°) slowly decomposes forming sulphur dioxide and fluorescent 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (III). The precursor of this is considered to be the dimer (II), which is accepted (Bordwell, McKellin, and Babcock, *J. Amer. Chem. Soc.*, 1951, **73**, 5566; Davies, Gamble, and Savige, *J.*, 1952, 4678) as the unisolated intermediate adduct in the conversion of (I) into (III) by heat. The photodimer cannot be (II), which on steric grounds is inherently unstable,* and from analogy with related, though simpler, structures (Davies and James, *J.*, 1954, 16; Bailey and Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1938) would be expected to lose the sulphur bridge easily. The conversion of the photodimer into (III) is evidently due, at the boiling point of butyl phthalate, to dissociation of the photodimer into (I), which when heated readily gives (III).

Since no dimerisation of 2 : 3-dihydrothionaphthen 1 : 1-dioxide is brought about by illumination even for two months under the above conditions, the 2 : 3-double bond in (I) seems responsible for its self-addition. Polar molecules are known to add to this bond (Challenger and Clapham, *J.*, 1948, 1615; Bordwell and McKellin, *J. Amer. Chem. Soc.*, 1950, **72**, 1985), and it is also known that in some sulphur-free compounds electrophilic groups (usually CO and CO_2H) activate double bonds which are not only polarised but also take part in photodimerisation. The latter phenomenon has been reviewed by Mustafa (*Chem. Reviews*, 1952, **51**, 1), and perhaps the nearest formal analogy with (I) is 2-methyl-3-phenylindanone, the two photodimers of which are accepted as being the dimethyldiphenyltruxones (V) and (VI). Numerous photodimers from monomers containing the $C{:}C\cdot CO$ group are accepted as containing the *cyclo*butane ring, for which, however, the main chemical evidence is the absence of a double bond in the photodimers, and their easy dissociation by heat. But for the case of stilbamidine $[NH_2\cdot C\cdot({:}NH)\cdot C_6H_4\cdot CH{:}]_2$, not mentioned by Mustafa, proof exists that its dimer contains the *cyclo*butane ring (Fulton and Dunitz, *Nature*, 1947, **160**, 161).

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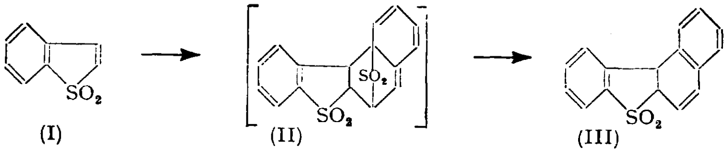
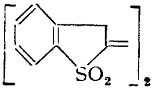
* We are indebted to a Referee for drawing this to our attention.

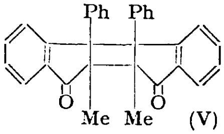
The rejection of the theoretically possible structures (II) and (IV), and analogy with the photodimers reviewed by Mustafa, makes it likely that the single photodimer obtained from (I) contains a *cyclo*butane ring. The photodimer would then be (VII) or (VIII), and it is unfortunate that attempts to obtain direct experimental evidence for either structure have failed. Fission with alkaline reagents cannot be effected, and desulphurisation with Raney nickel in boiling ethanol to produce ethylbenzene is ambiguous. A diphenyl*cyclo*butane was expected, and though this is apparently not known to suffer hydrogenolysis, it may nevertheless have done so even more thoroughly than does ethyl*cyclo*butane under more drastic conditions in the presence of platinised carbon (Kazanskii and Yu. Lukina, *Doklady Akad. Nauk U.S.S.R.*, 1950, **74**, 263; *Chem. Abs.*, 1951, **45**, 2879), or alternatively the dimer (despite the relatively low temperature) may have dedimerised to yield (I) which is desulphurised to give ethylbenzene.



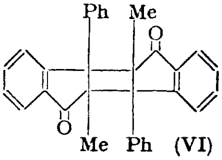
(I) (II) (III)



(IV)

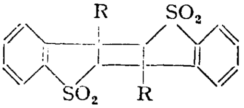


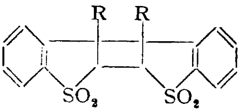
(V)



(VI)

(VII)





(VIII)

3-Bromothionaphthen 1 : 1-dioxide was photodimerised in order to ascertain whether angular (VII; R = Br) or linear (as VIII; R = Br) dimerisation was favoured. Since the bromine atom in 3-bromo-2 : 3-dihydrothionaphthen 1 : 1-dioxide is very reactive, sodium iodide could be expected to react with the photodimer if it were (VIII; R = Br) to cause complete loss of halogen with the formation of a double bond (cf. Finkelstein, *Ber.*, 1910, **43**, 1530), behaviour which would not take place with the isomer (VII; R = Br). However, sodium iodide does not react with the photodimer, of which the successful debromination by zinc and acetic acid does not indicate the structure. Both this dimer and that of (I) are non-fluorescent and are stable to heat and oxidising agents.

3 : 4-Dimethylthiophen 1 : 1-dioxide also gives a high-melting crystalline photodimer, the stability of which to permanganate at room temperatures indicates that it contains no exocyclic methylene group. Moreover, the behaviour of the compound at its melting point recalls that of a number of substances shortly to be described, which contain the $\cdot SO_2\cdot C{:}C$ group in a ring. The structure of this photodimer is being further studied in connection with that of the monomer and related monomers, about which there is confusion in the literature (Bailey and Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1933).

Though in the only cases investigated photodimerisation occurs smoothly when the $\cdot SO_2\cdot CH{:}CH\cdot$ is in a ring, intractable oils are obtained after the irradiation by moderate sunlight for three weeks of benzene solutions of phenyl vinyl sulphone, styryl *p*-tolyl sulphone, and 3-bromo-1-phenylsulphonylprop-1-ene (Culvenor, Davies, and Savige, *J.*, 1949, 2205).

EXPERIMENTAL

Preparation of the Sulphones.—Thionaphthen, oxidised as described by Davies, Gamble, and Savige (*J.*, 1952, 4679) except that the oxidising mixture was heated on the water-bath for 1 hr. instead of over a flame, again gave the same yields of 9-thia-3 : 4-benzofluorene 9 : 9-

dioxide, m. p. 233—234°, and thionaphthen 1 : 1-dioxide, m. p. 142°. 3-Bromothionaphthen (Komppa, *J. prakt. Chem.*, 1929, **122**, 1319) was similarly converted into 3-bromothionaphthen 1 : 1-dioxide, m. p. 183·5—184° (Bordwell and Albisetti, *J. Amer. Chem. Soc.*, 1948, **70**, 1559). 2 : 3-Dihydrothionaphthen 1 : 1-dioxide, and its 3-bromo-derivative (made by the action of hydrogen bromide on thionaphthen 1 : 1-dioxide) were prepared as described by Bordwell and McKellin (*loc. cit.*). 3-Bromo-2 : 3-dihydrothionaphthen 1 : 1-dioxide is not only readily dehydrobrominated to regenerate the parent thionaphthen 1 : 1-dioxide when refluxed for 1 hr. with pyridine in benzene, but also when refluxed with sodium iodide in acetone, the solution, diluted with water, being then kept for a week at room temperature.

3 : 4-Dibromo-3 : 4-dimethylthiophen 1 : 1-dioxide (van Zuydewijn, *Rec. Trav. chim.*, 1938, **57**, 445) (2 g.) and pyridine (5 ml.) in benzene (20 ml.) were refluxed for 2 hr., then filtered from pyridine hydrobromide. The residual 3 : 4-dimethylthiophen 1 : 1-dioxide from the filtrate crystallised from water (yield, 0·8 g. of needles or plates, m. p. 120°), and then from ethanol (m. p. 120·5—121°) (Found : C, 50·2; H, 5·5; S, 21·9. Calc. for $C_6H_8O_2S$: C, 50·0; H, 5·6; S, 22·2%). This process is essentially that of Savige (Thesis, Melbourne, 1951), who also showed that this sulphone is identical (mixed m. p.) with that formed by the interaction of 3 : 4-dimethylthiophen and hydrogen peroxide.

Formation of the Photodimers.—An almost saturated solution of the sulphone in benzene in a silica flask was exposed to direct sunlight for many days. The irradiation products crystallised and though almost insoluble in common solvents, were recrystallised from a large amount of boiling acetone.

The dimerisation of the strongly fluorescent thionaphthen sulphone to the non-fluorescent dimer was readily followed, and moreover the isolation of any unchanged monomer in the preliminary experiments was easily effected by crystallisation from water. Much of the irradiation products from the sulphones crystallised in an almost pure condition on the walls of the flask, and crystallisation of the residues after evaporation of the benzene gave no other dimers.

Thionaphthen 1 : 1-dioxide (10 g.) was not completely dimerised after a week's exposure to sunlight, but after 20 days gave the *dimer* which crystallised (5·0 g.; m. p. 330—331°) from a large volume of acetone. The same m. p. was obtained when the unrecrystallised material was sublimed at 260—270°/1 mm. The dimer is insoluble in water, sparingly soluble in hot acetic acid and other low-boiling organic solvents, and moderately soluble in boiling ethylene glycol, from which it separates in small needles [Found : C, 57·7; H, 3·7; S, 19·5%; *M* (cryoscopic in *p*-bromophenol), 335, 353. $(C_8H_6O_2S_2)_2$ requires C, 57·9; H, 3·6; S, 19·3%; *M*, 332].

The dimer was unaffected by potassium permanganate in boiling acetone for 8 hr., by hydrogen peroxide in hot glacial acetic acid, or by lithium aluminium hydride in tetrahydrofuran. No fission occurred on 20 hours' refluxing in ethanolic sodium hydroxide, or in the use of sodamide and piperidine (Bradley, *J.*, 1938, 458) or sodium amalgam (Dably, Kenyon, and Mason, *J.*, 1952, 4881). The dimer dissolved unchanged in hot concentrated nitric acid, but was converted by hot mixed concentrated sulphuric and fuming nitric acids into an insoluble nitrogenous compound which could not be purified. The dimer slowly dissolved in boiling butyl phthalate, sulphur dioxide was evolved, and after 3 hours' refluxing the solution on cooling deposited crystals of 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (III), m. p. and mixed m. p. with an authentic specimen, 181—182° (cf. Davies, Gamble, and Savige, *loc. cit.*).

Conversion of the Thionaphthen Sulphone Dimer into Ethylbenzene.—A suspension of the dimer (1·0 g.), Raney nickel (30 g.; prepared as described by Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013) in ethanol (100 c.c.) and acetone (100 c.c.) was refluxed for 5 hr., then diluted with water (500 c.c.), and distilled until the ethanol was removed. This distillate was again diluted with water (500 c.c.), and the ethanolic azeotrope formed two layers when diluted with water (200 c.c.). The upper layer, when dried ($CaCl_2$) and evaporated, yielded ethylbenzene (0·1 g.; b. p. 133—135°), oxidised by potassium permanganate to benzoic acid (m. p. and mixed m. p. 120—121°).

3-Bromothionaphthen 1 : 1-dioxide (3·0 g.), exposed to sunlight for 30 days, gave a sparingly soluble *dimer* which was recrystallised (1·2 g.; m. p. 314—315°) from acetone or more conveniently from ethylene glycol (needles) [Found : C, 38·9; H, 2·1; S, 13·5%; *M*, 470, 452. $(C_8H_5O_2SBr)_2$ requires C, 39·2; H, 2·0; S, 13·1%; *M*, 490]. It was recovered unchanged after refluxing with sodium iodide in acetone and in acetonylacetone. When refluxed with zinc dust and acetic acid for 3 hr. it gave a bromine-free product (in amount too small for analysis) which crystallised from ethylene glycol in non-fluorescent rods, m. p. >360°, which slowly became light buff after exposure to air.

Irradiation of 3 : 4-dimethylthiophen 1 : 1-dioxide (1·0 g.) in sunlight for 28 days yielded the non-fluorescent *dimer* (0·6 g.), m. p. 290—291° (decomp.) [Found : C, 50·1; H, 5·5; S, 22·2%; *M*, 295, 310. $(C_6H_8O_2S)_2$ requires C, 50·0; H, 5·6; S, 22·2%; *M*, 288]. It crystallises from acetone and *cyclo*hexanone in compact prisms of high refractive and dispersive power. At the m. p., which varies somewhat with the rate of heating, there is sudden evolution of sulphur dioxide, and a xylene solution of the yellowish-brown residue had a weak yellow fluorescence. The dimer is appreciably soluble in cold water, and neither this solution nor one in acetone decolorised dilute potassium permanganate solutions in 5 min. at room temperature.

The three crystalline photodimers obtained in this work are too insoluble in camphor for their molecular weights to be obtained by the Rast process. *p*-Bromophenol has been used instead (by F. C. J.).

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