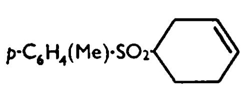
# 83. *Thionaphthen* 1 : 1-*Dioxide as a Dienophil.*

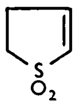
By W. Davies and Q. N. Porter.

Thionaphthen 1 : 1-dioxide forms adducts with anthracene, *cyclo*pentadiene, 3 : 4-dimethylthiophen 1 : 1-dioxide, tetracene, and 1-vinylnaphthalene, and the reaction is useful for the synthesis of polycyclic thiophen derivatives. So far the dioxide has not reacted as a diene with typical dienophils.

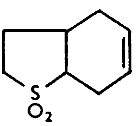
Though the Diels–Alder reaction has been widely used in the synthesis of cyclic compounds (for reviews see ref. 1), little work has been done with unsaturated sulphones as dienophils. Alder, Rickert, and Windemuth [2] have shown that *p*-tolylsulphonylethylene adds butadiene to give 4-*p*-tolylsulphonyl*cyclo*hexene (I). Similarly 2 : 3-dihydrothiophen 1 : 1-dioxide (II) adds butadiene and *cyclo*pentadiene to give the thionaphthen derivatives (III) and (IV) respectively.[2, 3] On the other hand Melles [4] has investigated the reaction of a number of derivatives of thiophen 1 : 1-dioxide as dienes. He has shown that dioxides of type (V) function as dienes (with loss of sulphur dioxide) with maleic anhydride to give, first, a *cyclo*hexadienedicarboxylic anhydride (VI), which then often reacts further with maleic anhydride to give the bis-adduct. More recently, thionaphthen 1 : 1-dioxide and its benzo-derivatives have been shown to act as both diene and dienophil in self-condensation reactions, to give derivatives of 9-thiafluorene.[5]



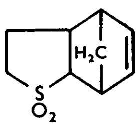
(I)



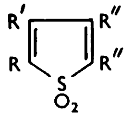
(II)



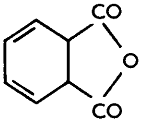
(III)



(IV)



(V)



(VI)

It is now found that thionaphthen 1 : 1-dioxide reacts as a dienophil with a number of dienes, and that this is a convenient reaction for the synthesis of condensed thiophen derivatives. Thus the dioxide and *cyclo*pentadiene at 170° in xylene (sealed tube) give the adduct (VII). With anthracene, best in large excess, it gives similarly the adduct (VIII). The temperature employed (170°) is that at which self-condensation of the dioxide usually occurs, and as this was not observed it appears that anthracene is more reactive as a diene than the dioxide. Equimolecular quantities of thionaphthen 1 : 1-dioxide and tetracene at 140° give a quantitative yield of the adduct (IX). The greater reactivity of tetracene compared with anthracene is in accord with its lower *p*-localisation energy as calculated by Brown.[6]

1-Vinylnaphthalene adds to thionaphthen 1 : 1-dioxide at 115°, to give 75% of the tetrahydronaphthothiafluorene dioxide (X). Initial formation of the isomer (XI) would be expected. Related compounds are isomerised by hydrogen chloride in acetic acid,[7] whereas the product here was unaffected by such treatment, indicating that isomerisation had accompanied the initial reaction, perhaps because the reaction temperature was higher than that used for the maleic anhydride–vinylnaphthalene reaction.[7] Since an unsymmetrical dienophil has been used, there is an ambiguity in the structure of the product.

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[1] Norton, *Chem. Rev.*, 1942, **31**, 319; Kloetzel, "Organic Reactions," Wiley, New York, 1954, Vol. IV, p. 1; Holmes, *op. cit.*, p. 60; Butz and Rytina, *op. cit.*, Vol. V, p. 136.

[2] Alder, Rickert, and Windemuth, *Ber.*, 1938, **71**, 2451.

[3] Bailey and Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1936.

[4] Melles, *Rec. Trav. chim.*, 1952, **71**, 869.

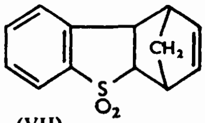
[5] (*a*) Bordwell, McKellin, and Babcock, *J. Amer. Chem. Soc.*, 1951, **73**, 5566; Davies *et al.*, *J.*, 1952, 4678; 1955, 1565; (*b*) 1956, 2609.

[6] Brown, *J.*, 1950, 691.

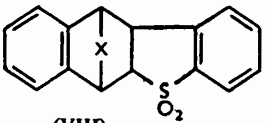
[7] Cohen and Warren, *J.*, 1937, 1315.

Bachmann and Deno[8] found that in reactions of 1-vinylnaphthalene with a number of unsymmetrical unsaturated acids and vinyl ketones the products are those expected from the Hudson–Robinson principle,[9] that is, that the most nucleophilic carbon atom of the diene (in this case the terminal carbon atom of the vinyl group) becomes attached to the most electrophilic carbon atom of the dienophil. Application of the rule to this case would suggest the structure (XII) for the adduct; however, the structure is actually (X), as is proved by reduction of the sulphonyl group with lithium aluminium hydride and dehydrogenation of the unpurified tetrahydro-derivative (XIII) to naphtho(1′ : 2′-3 : 4)-9-thiafluorene (XIV).

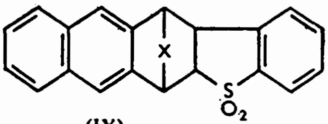
Removal of sulphur from this compound gave surprisingly an octahydrophenylphenanthrene. This appears to be the first case in which Raney nickel desulphurisation is accompanied by ring hydrogenation of a phenanthrene derivative, and is probably due to the highly active catalyst (W4). If the course of hydrogenation is similar to that of phenanthrene with a copper chromite catalyst,[10] the product is probably 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-1-phenylphenanthrene (XV). The compound was dehydrogenated with selenium to 1-phenylphenanthrene (XVI), m. p. 79—80°, identical with a sample synthesised from 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene and phenylmagnesium bromide.[11] The 2-isomer,[12] m. p. 196—197°, would have been formed if the compound (XII) had resulted from the original Diels–Alder reaction.



(VII)

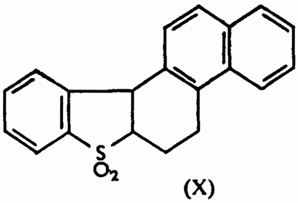


(VIII)

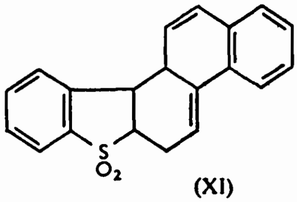


(IX)

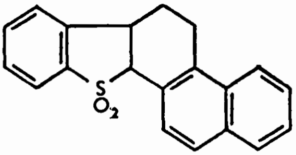
X = o-$C_6H_4$<



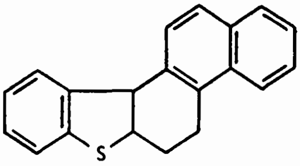
(X)



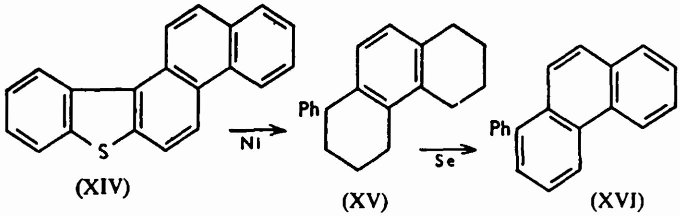
(XI)



(XII)



(XIII)



(XIV) (XV) (XVI)

1-Vinylnaphthalene also adds to 4 : 5-benzothionaphthen 1 : 1-dioxide, to give the compound (XVII). On the other hand 2-vinylnaphthalene is unreactive towards thionaphthen 1 : 1-dioxide, all conditions so far investigated giving only the homopolymer of the diene. It is pertinent that Cohen and Warren[7] obtained only 6% of adduct from this diene and maleic anhydride compared with 32% from the 1-isomer. Di*cyclo*hex-1-enyl

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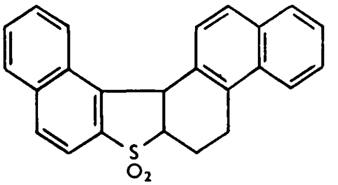
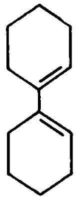
[8] Bachmann and Deno, *J. Amer. Chem. Soc.*, 1949, **71**, 3062.
[9] Hudson and Robinson, *J.*, 1941, 715.
[10] Kamp and Mosettig, *J. Amer. Chem. Soc.*, 1935, **57**, 1107.
[11] Bachmann and Wilds, *ibid.*, 1938, **60**, 624.
[12] Newman, *J. Org. Chem.*, 1944, **9**, 518.

(XVIII) also gives no adduct with thionaphthen 1 : 1-dioxide; this is surprising since it is reactive towards maleic anhydride and *p*-benzoquinone [13] and also sulphur dioxide.[14]

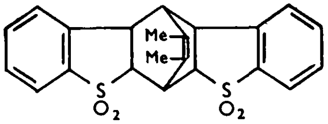
It is now found that 3 : 4-dimethylthiophen 1 : 1-dioxide adds to thionaphthen 1 : 1-dioxide, to give the bis-adduct (XIX) or (XX). Despite the use of excess of thionaphthen 1 : 1-dioxide it was not possible to isolate the monoadduct (XXI) which is apparently a more reactive diene than 3 : 4-dimethylthiophen 1 : 1-dioxide itself.



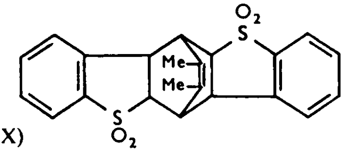
(XVII)



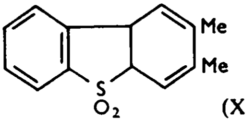
(XVIII)



(XIX)



(XX)



(XXI)

Thionaphthen 1 : 1-dioxide is inert as a diene towards maleic anhydride, ethyl acetylenedicarboxylate, and *p*-benzoquinone, even at the self-condensation temperature of the dioxide. This may be contrasted with the ready condensation of the thiophen 1 : 1-dioxides with maleic anhydride observed by Melles.[4] It is possible that steric factors preclude sufficiently close approach of the dienophils to thionaphthen 1 : 1-dioxide for reaction to occur.

The adducts of thionaphthen 1 : 1-dioxide are characterised by stability to heat, as they do not dissociate at 300°, in contrast to the adducts of many dienes with maleic anhydride; [1] this is apparently associated with the sulphonyl group, since reduction with lithium aluminium hydride of the adduct of anthracene and thionaphthen 1 : 1-dioxide gives a thia-compound which rapidly decomposes at 250° into anthracene and thionaphthen. The stability of the present adducts with thionaphthen 1 : 1-dioxide also contrasts with the instability of the adduct of sulphur dioxide with butadiene, which dissociates at 140°.[15]

Extensions of the reaction to produce molecules of interest in the study of carcinogenesis are being examined, and a number of products are being tested in the Pathology Department of the University of Melbourne.

## EXPERIMENTAL

*Preparation of Dienes.*—*cyclo*Pentadiene, b. p. 41—42°, was prepared by cracking " di*cyclo*pentadiene " at 160°, and separating the monomer by fractionation.

1-Vinylnaphthalene, b. p. 132—134°/17 mm., was prepared (73% yield) by distilling the crude product from 1-naphthylmagnesium bromide and acetaldehyde.[16]

*2-Vinylnaphthalene.* 2-Acetylnaphthalene,[17] m. p. 54°, b. p. 174—176°/18 mm., was reduced to 1-β-naphthylethanol, m. p. 71—72°, with aluminium *iso*propoxide,[18] the yield being highest (86%) with 20% excess of aluminium *iso*propoxide. 2-Vinylnaphthalene, m. p. 66°, b. p. 136—138°/17 mm., was prepared (65%) by dehydration as described for the 1-isomer.

3 : *4-Dimethylthiophen* 1 : 1-*dioxide.* The dioxide, m. p. 119—120°, was prepared (63%) by

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[13] Barnett and Lawrence, *J.*. 1935, 1104.

[14] Backer, Strating, and Huisman, *Rec. Trav. chim.*, 1941, **60**, 381.

[15] Van Zuydewijn, *ibid.*, 1937, **56**, 1047.

[16] Berger, *Bull. Soc. chim. France*, 1906, **35**, 338.

[17] Baddeley, *J.*, 1949, S 99.

[18] Lund, *Ber.*, 1937, **70**, 1520.

bromination and dehydrobromination of 2 : 5-dihydro-3 : 4-dimethylthiophen 1 : 1-dioxide (" 2 : 3-dimethylbutadiene sulphone ") as described by Savige.[19] It was also prepared by the hydrogen peroxide oxidation of 3 : 4-dimethylthiophen.[20] Melles and Backer [21] report m. p. 114° for the sulphone obtained by the perbenzoic acid oxidation of 3 : 4-dimethylthiophen.

*Di*cyclo*hex-*1-*enyl.* *cyclo*Hexanone was reduced to the pinacol as described by Barnett and Lawrence.[13] It is not mentioned by them that it is essential to cool the mixture after reduction commences, to prevent the reaction from becoming uncontrollable. Dehydration of the pinacol by Gruber and Adams's method [22] gave di*cyclo*hex-1-enyl, b. p. 246—248° (65%).

*Reaction of Dienes with Thionaphthen* 1 : 1-*Dioxide.*—(a) *With* cyclo*pentadiene.* *cyclo*Pentadiene (1·0 ml.) and thionaphthen 1 : 1-dioxide (1·2 g.) in xylene (6·0 ml.) were heated at 170—180° (sealed tube) for 10 hr. The product that separated on cooling was crystallised from benzene, giving 4a : 9b-*dihydro*-1 : 4-*methanodibenzothiophen* 5 : 5-*dioxide* (cf. Ring Index No. 1743) (VII) as needles, m. p. 157—158° (0·9 g., 56%) (Found : C, 67·4; H, 5·5. $C_{13}H_{12}O_2S$ requires C, 67·2; H, 5·2%).

(b) *With anthracene.* Anthracene (3·56 g.) and thionaphthen 1 : 1-dioxide (1·66 g.) were refluxed in *o*-dichlorobenzene (30 ml.) for 15 hr. The cooled solution deposited anthracene (1·54 g.), and the filtrate on dilution with light petroleum (120 ml.) gave 5a : 11a-*dihydro*-6 : 11-p-*benzenobenzo*[b]*thiophanthrene* 5 : 5-*dioxide* (cf. R.I. 2502) (VIII), prisms (from benzene), m. p. 253—254° (2·85 g., 83%) (Found : C, 76·7; H, 4·8. $C_{20}H_{16}O_2S$ requires C, 76·7; H, 4·65%).

This adduct (1·9 g.) was extracted (Soxhlet) into tetrahydrofuran (120 ml.) containing lithium aluminium hydride (2·0 g.) for 9 hr. The excess of hydride was destroyed with moist ether, and inorganic material dissolved with dilute hydrochloric acid. The dried ($MgSO_4$) organic layer gave an oil (1·5 g.), readily soluble in benzene, less so in alcohol and light petroleum. The oil (0·8 g.) was heated at 250°, thionaphthen, b. p. 215—220°, m. p. and mixed m. p. 31—32°, distilling off. The residue in the flask, crystallised from benzene, gave anthracene, m. p. and mixed m. p. 215—216°.

(c) *With tetracene.* A suspension of tetracene (0·46 g.) in a solution of thionaphthen 1 : 1-dioxide (0·33 g.) in xylene (15·0 ml.) was refluxed until dissolution was complete (9 hr.). The product that separated on cooling gave prisms (from benzene) of 5a : 13a-*dihydro*-6 : 13-*benzenodibenzo*[b, h]*thiophanthrene* 5 : 5-*dioxide* (cf. R.I. No. 3128) (IX), m. p. 280—281° (0·75 g., 94%) (Found : C, 79·1; H, 4·6. $C_{26}H_{18}O_2S$ requires C, 79·2; H, 4·6%).

(d) *With* 3 : 4-*dimethylthiophen* 1 : 1-*dioxide.* This dioxide (0·2 g.) and thionaphthen 1 : 1-dioxide (0·23 g.) were refluxed in xylene (3·0 ml.) until a copious precipitate was formed (2 hr.), sulphur dioxide being evolved. The product was crystallised from benzene, giving prisms of the *bis-adduct* (XIX or XX), m. p. 345—346° (0·21 g.) (Found : C, 64·4; H, 4·9. $C_{22}H_{20}O_4S_2$ requires C, 64·1; H, 4·8%).

(e) *With* 1-*vinylnaphthalene.* The diene (2·0 g.), thionaphthen 1 : 1-dioxide (2·0 g.), and quinol (0·04 g.) were refluxed in toluene (14 ml.) for 10 hr. The product that separated on cooling was crystallised from benzene, giving prisms of 1 : 2 : 10 : 11-*tetrahydronaphtho*-(1′ : 2′-3 : 4)-9-*thiafluorene* 9 : 9-*dioxide* (X), m. p. 276—277° (2·9 g., 75%) (Found : C, 75·3; H, 5·1. $C_{20}H_{16}O_2S$ requires C, 75·0; H, 5·0%). This was unchanged when refluxed for 2 hr. in glacial acetic acid saturated with dry hydrogen chloride.

*Preparation of Naphtho*(1′ : 2′-3 : 4)-9-*thiafluorene* (XIV).—The adduct (X) (2·0 g.) was extracted (Soxhlet) into a solution of lithium aluminium hydride (2·0 g.) in dry tetrahydrofuran (100 ml.) for 10 hr. Excess of hydride was destroyed with moist ether and inorganic material was dissolved with dilute hydrochloric acid. The dried organic layer ($MgSO_4$) on evaporation gave an oil (1·66 g.), presumably the compound (XIII), which was heated with selenium (1·7 g.) at 300° for 5 hr. The cooled solution was extracted with hot alcohol and after decolorisation (charcoal) gave pale yellow needles of the *naphthothiafluorene* (XIV), m. p. 168·5—169° (1·3 g.) (Found : C, 84·4; H, 4·3. $C_{20}H_{12}S$ requires C, 84·4; H, 4·2%).

This compound was oxidised to the *dioxide*, needles (from benzene), m. p. 277·5—278° (Found : C, 76·3; H, 3·9. $C_{20}H_{12}O_2S$ requires C, 75·95; H, 3·8%), when it (0·25 g.) was heated on the water-bath for 1 hr. with 30% hydrogen peroxide (1·5 ml.) in acetic acid (3·0 ml.).

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[19] Savige, Thesis, Melbourne, 1951, p. 88.

[20] Shephard, Henne, and Midgley, *J. Amer. Chem. Soc.*, 1934, **56**, 1355.

[21] Melles and Backer, *Rec. Trav. chim.*, 1953, **72**, 315.

[22] Gruber and Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 2555.

*Removal of Sulphur from Naphtho*(1′ : 2′-3 : 4)-9-*thiafluorene.*—The compound (XIV) (3·0 g.) and Raney nickel W4 (30 g.) were stirred under reflux in ethanol (250 ml.) for 10 hr. Concentration of the filtrate from the Raney nickel gave an oil (2·3 g.) which was distilled giving pale yellow 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-1-*phenylphenanthrene* (XV), b. p. 193—196°/0·4 mm. (1·8 g.) (Found : C, 91·7; H, 8·4. $C_{20}H_{22}$ requires C, 91·6; H, 8·4%).

The octahydro-compound (0·5 g.) and selenium (0·75 g.) were gently refluxed for 4 hr. The cooled mixture was extracted with benzene and the extract chromatographed on alumina. The colourless band with blue fluorescence in ultraviolet light gave an oil which on trituration with methanol gave 1-phenylphenanthrene (XVI), prisms, (0·28 g.) (from methanol), m. p. 79—80°, undepressed when admixed with a genuine sample, m. p. 79—80°, prepared (85% yield) from 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene.[11]

1-*Vinylnaphthalene and* 4 : 5-*Benzothionaphthen* 1 : 1-*Dioxide.*—The dioxide [5b] (0·4 g.), 1-vinylnaphthalene (0·4 g.), and quinol (0·01 g.) were refluxed in toluene (3·0 ml.) for 2 hr. After cooling, the crystalline product was recrystallised from benzene, giving prisms of 1 : 2 : 10 : 11-*tetrahydro*-9-*thia*-5 : 6-*benzonaphtho*(1′ : 2′-3 : 4)*fluorene* 9 : 9-*dioxide* (XX), m. p. 233·5—234° (0·46 g.) (Found : C, 77·6; H, 4·5. $C_{24}H_{18}O_2S$ requires C, 77·8; H, 4·8%).

2-*Vinylnaphthalene and Thionaphthen* 1 : 1-*Dioxide.*—The compounds were heated under nitrogen in the presence of quinol in acetic acid, toluene, xylene, *o*-dichlorobenzene, and tetralin, and in a sealed tube at 180°, but the only products were a sulphur-free polymer, softening at 140°, very soluble in benzene and insoluble in alcohol and light petroleum, and at 170° and higher temperatures 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide, m. p. 182°, from the self-condensation of the dioxide.

No condensation occurred when di*cyclo*hex-1-enyl and thionaphthen 1 : 1-dioxide were heated under similar conditions.

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