991. The Synthesis of Condensed Heterocyclic Systems. Part I. Use of 2-Vinylthiophen in the Diene Synthesis.

By W. Davies and Q. N. Porter.

2-Vinylthiophen behaves as a moderately active diene with benzoquinone and maleic anhydride. The products give fair yields of 4 : 5-benzothionaphthen and, after dehydrogenation, thionaphthen-4 : 5-dicarboxylic anhydride respectively.

Recognition of the aromatic nature of thiophen has facilitated its substitution for benzene in many well-known condensations and synthetic processes; *e.g.*, reaction with phthalic anhydride[1] gives a tricyclic compound. On the other hand, relatively little synthetic use has been made of the differences, as opposed to the similarities, between thiophen and benzene derivatives: instances of such use are the formation[2] of bicyclic dianhydrides by action of maleic anhydride on the *S*-dioxides of dimethyl- and diphenylthiophen, and the reaction[3] of 3 : 4-dimethylthiophen 1 : 1-dioxide with thionaphthen 1 : 1-dioxide, the latter reacting in this case as a dienophile; other examples are the union[4] of maleic anhydride with 1 : 8 : 1′ : 8′-diacenaphthenothiophen, and with 2-vinylthiophen (I).[5]

The last-mentioned adduct was readily hydrolysed to 4 : 5 : 6 : 7-tetrahydrothionaphthen-4 : 5-dicarboxylic acid (II), the structure of which was proved by its conversion into thionaphthen on dehydrogenation and decarboxylation. The adduct—not previously analysed—has now been obtained in 49% yield and almost quantitatively converted into the dicarboxylic acid (II), m. p. 212°; Scully and Brown's acid was reported to be a mixture (m. p. not given) of *cis*- and *trans*-forms, m. p. 188—189° and 194—195°. The m. p. of some dicarboxylic acids varies according to the method of determination, and it is relevant that only one acid is obtained from the hydrolysis product of the analogous adduct of 3-vinylthionaphthen and maleic anhydride (following paper). Dehydrogenation, with sulphur, of the vinylthiophen adduct gave a 63% yield of thionaphthen-4 : 5-dicarboxylic anhydride. Incidentally, loss, from the acid (II), of the 5-carboxyl group only, either before or after aromatisation, could theoretically yield the still unknown[6] thionaphthen-4-carboxylic acid.

2-Vinylfuran is known to add to maleic anhydride, a tetrahydrocoumaronedicarboxylic anhydride being formed.[7] It is noteworthy that there the strong diene action of the furan ring itself towards maleic anhydride is not in evidence; as with the above more aromatic thiophen derivative the diene system which reacts is in part cyclic and in part exocyclic. Apart from the above two reactions with maleic anhydride, and the addition[8] of benzoquinone to 3-vinylthionaphthen, this use of vinyl heterocyclic compounds has apparently been hitherto neglected.

2-Vinylthiophen reacts slowly with benzoquinone, to give a 43% yield of 4 : 5-benzothionaphthen-1′ : 4′-quinone (III), and so far it has not proved possible to isolate an adduct which has not undergone dehydrogenation by excess of quinone. Lithium aluminium hydride reduces the quinone to 4 : 5-benzothionaphthen in high yield (this method of reduction of 1 : 4-naphthaquinone derivatives has been described for 9-thia-1 : 2-benzofluorene-1′ : 4′-quinone[8] and is of considerable value). Boyland and Manson[9] used

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[1] Hartough and Meisel, "Compounds with Condensed Thiophen Rings," Interscience Pub. Inc., New York, 1954, p. 289.

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

[3] Davies and Porter, following paper.

[4] Clapp, *J. Amer. Chem. Soc.*, 1939, **61**, 2733.

[5] Scully and Brown, *ibid.*, 1953, **75**, 6329.

[6] Badger, Crook, Davies, Farrer, and Kefford, *J.*, 1957, 2624.

[7] Paul, *Bull. Soc. chim. France*, 1943, **10**, 163.

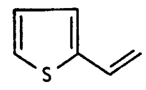
[8] Davies, Porter, and Wilmshurst, *J.*, 1957, 3366.

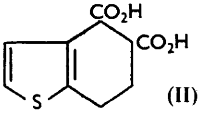
[9] Boyland and Manson, *J.*, 1951, 1837.

lithium aluminium hydride to reduce 1 : 4-naphthaquinone, isolating 1 : 4-dihydroxytetralin and 4-hydroxy-1-tetralone. The former product was then converted into naphthalene by treatment with acid, while the latter gives 1-naphthol under similar conditions. In the present work the excess of lithium aluminium hydride is not only greater than that used by Boyland and Manson, but gradual addition of the quinone to all the lithium aluminium hydride ensures that a very large excess of the latter is present until near the end of the reaction. The analogous products intermediate between the quinone (III) and the thiahydrocarbon have not been isolated but may have been formed. This direct conversion of a quinone into an aromatic compound is often applicable (cf. Davies and Porter [3]).

The time required to produce from quinones a satisfactory yield of adduct shows that 2-vinylthiophen and 3-vinylthionaphthen are more reactive than their isosteres styrene and 1-vinylnaphthalene, probably owing to the lower aromaticity of the heterocyclic isosteres and the consequent greater double-bond character of their 2 : 3-bonds which causes the compounds to approximate more to true dienes. The well-known greater activity of vinylnaphthalenes than of styrene is also paralleled by the superiority of 3-vinylthionaphthen over 2-vinylthiophen. For example, benzoquinone with 2-vinylthiophen gives a 43% yield of the product (III) in 8 hr., but an 80% yield of a similar product from 3-vinylthionaphthen [8] (yields calculated on the vinyl compounds). Moreover, during the preparation of the quinone (III) a bis-adduct from it and another molecule of 2-vinylthiophen is apparently not formed, whereas a 61% yield of the adduct (IV) or (V) is produced in 10 min. under the same conditions from the quinone (III) and 3-vinylthionaphthen. In making these rough comparisons the criterion has been a practical one, namely, the yield of the adduct (or the dehydrogenated adduct) in a reasonable time; the possibility that the true reactivity of the vinyl compound may be masked by its polymerisation or by the thermal dissociation of the adduct or by other factors, has been ignored. Among vinyl compounds this variation of activity in the Diels–Alder reaction with quinones increases the scope of this synthesis.

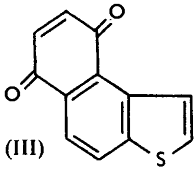
(I)

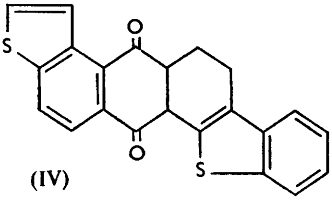




(II)

(III)





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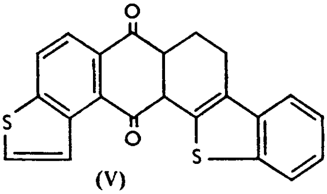

(V)

EXPERIMENTAL

M. p. determinations were made in Pyrex tubes.

2-2′-Thienylethanol.—A solution of 2-thienylmagnesium iodide [from 2-iodothiophen [10] (80 g.) and magnesium (11·0 g.) in ether (175 ml.)] was diluted with dry benzene (175 ml.) and cooled to −10°. Then ethylene oxide (23 g.) in ether (75 ml.) was added with stirring during 30 min. After 12 hr. the solution was distilled until the temperature of the distillate reached 70° (later vigorous decomposition may occur), then refluxed for 2 hr. The cooled solution was decomposed with dilute hydrochloric acid, and the organic layer was separated. The aqueous

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[10] Minnis, *Org. Synth.*, Coll. Vol. II, p. 357.

layer was extracted with ether, and the combined extracts were evaporated and distilled, giving 2-2′-thienylethanol (39 g., 78%), b. p. 112—115°/20 mm. (lit.,[11] b. p. 99—100°/7 mm.).

2-*Vinylthiophen.*—2-2′-Thienylethanol (30 g.) in toluene (30 ml.) was dehydrated with molten potassium hydroxide (130 g.) as described for 3-vinylthionaphthen,[8] but at approx. 100 mm. The product was distilled, giving 2-vinylthiophen, b. p. 77—78°/70 mm. (lit.,[11] b. p. 65·5—66·5°/48 mm.) (17·0 g., 68%). Yields of 28—33% were obtained by chloroethylation of thiophen, followed by dehydrochlorination.[12] 2-Vinylthiophen, stored at 0° over a little quinol, did not polymerise materially in 6 months.

Reactions of 2-*Vinylthiophen.*—(1) *With* p-*benzoquinone.* Freshly sublimed *p*-benzoquinone (4·0 g.) and 2-vinylthiophen (1·3 g.) in acetic acid (15 ml.) were heated on the water-bath for 8 hr. The solvent was removed at reduced pressure and the residue extracted with benzene (3 × 50 ml.). The extracts were concentrated to 5 ml., and the product was extracted with cold ether (35 ml.) (to remove quinol and quinhydrone). The insoluble material was recrystallised from ethanol, giving orange needles of 4 : *5-benzothionaphthen-1′ : 4′-quinone*, m. p. 167—168° (0·88 g., 45%) (Found: C, 67·6; H, 3·0. $C_{12}H_6O_2S$ requires C, 67·3; H, 2·8%).

The quinone (0·4 g.) was extracted (Soxhlet) into lithium aluminium hydride (0·4 g.) in dry tetrahydrofuran (20 ml.) for 10 hr. The excess of hydride was decomposed with moist ether, and inorganic material was dissolved with dilute hydrochloric acid. The organic layer on evaporation gave an oil (0·31 g.) which slowly crystallised. The product from methanol gave plates of 4 : 5-benzothionaphthen, m. p. and mixed m. p. 110—111° (0·20 g., 53%).

The quinone (0·2 g.) and 3-vinylthionaphthen (0·4 g.) in acetic acid (4·0 ml.) were heated on the water-bath for 10 min., yellow crystals separating. The mixture was cooled and filtered, and the solid was washed with a little ether and recrystallised from benzene–ethanol, giving pale yellow needles of the 3 : 4 : 11 : *12-tetrahydrothienothionaphthenoanthraquinone* (IV) or (V), m. p. 209·5—210° (decomp.) (0·22 g., 61%) (Found: C, 70·6; H, 3·8. $C_{22}H_{14}O_2S_2$ requires C, 70·6; H, 3·7%).

(2) *With maleic anhydride.* 2-Vinylthiophen (5·0 g.), maleic anhydride (4·5 g.), and quinol (0·05 g.) in dry benzene (15·0 ml.) were refluxed for 6 hr. Crystals began to separate after 2½ hr. The precipitate from the cooled solution was washed with benzene to remove traces of viscous polymer, and the *adduct* (4·65 g.; m. p. 164—166°) analysed without further purification (Found: C, 58·2; H, 3·6. $C_{10}H_8O_3S$ requires C, 57·7; H, 3·8%). It was very insoluble in non-polar solvents and irreversibly changed by polar solvents. Thus, attempted recrystallisation from acetic acid gave fumaric acid, m. p. and mixed m. p. 284—285° (sealed tube) (Found: C, 41·4; H, 3·5. Calc. for $C_4H_4O_4$: C, 41·1; H, 3·4%).

The preceding adduct (0·8 g.) was warmed on a water-bath for 10 min. with 5N-sodium hydroxide (10 ml.). Acidification of the cooled solution gave the acid (II) (0·83 g., 96%), which crystallised from ethyl acetate in prisms, m. p. 213—214° (decomp.) (Found: C, 53·4; H, 4·7. Calc. for $C_{10}H_{10}O_4S$: C, 53·1; H, 4·4%). This acid was unchanged by refluxing acetic acid containing hydrogen chloride.

The foregoing acid (2·0 g.) and sulphur (0·7 g.) were heated at 208° for 2 hr. The product, recrystallised from carbon tetrachloride (charcoal), gave pale yellow prisms, m. p. 178—178·5°, of *thionaphthen*-4 : *5-dicarboxylic anhydride* (0·62 g., 63%) (Found: C, 58·6; H, 2·3. $C_{10}H_4O_3S$ requires C, 58·8; H, 1·9%).

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[11] Schick and Hartough, *J. Amer. Chem. Soc.*, 1948, **70**, 1646.

[12] Emerson and Patrick, *J. Org. Chem.*, 1948, **13**, 729.