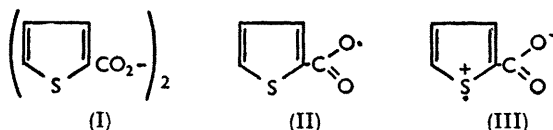


928. *Decomposition Reactions of Heterocyclic Diacyl Peroxides.*
*Part II.*¹ *2-Thenoyl Peroxide.*

By M. C. FORD and DONALD MACKAY.

The compounds formed by the decomposition of 2-thenoyl peroxide (I) in aromatic solvents can be attributed largely to reactions of 2-thenoyloxy-radicals (II). The most regular feature was the production of aryl 2-thenoates, in small yield, by nuclear attack, and in the halogenobenzenes phenyl 2-thenoate was formed, with displacement of the halogen. In toluene and cumene attack occurred preferentially in the side-chain. In solvents lacking side-chain hydrogen, the formation of 2-thenoic anhydride was sometimes observed. In thiophen, 2-thienyl 2-thenoate and 2:2'-dithienyl were produced, the latter providing evidence for the generation of 2-thienyl radicals.

BREITENBACH and KARLINGER^{2a} showed that 2-thenoyl peroxide (I) was an efficient initiator for the polymerisation of styrene. We have now studied the decomposition of this peroxide in various aromatic solvents. In benzene, nitrobenzene, chlorobenzene,



bromobenzene, and iodobenzene, much amorphous material containing combined sulphur was produced, but moderate amounts (0.6—0.9 mole per mole of peroxide) of 2-thenoic acid were formed, together with poor yields of simple neutral products. In a *ca.* 50% solution of naphthalene in benzene a smoother reaction occurred, the naphthalene being attacked preferentially. In toluene and cumene there were very marked increases in the yields both of the acid (1.4 and 2.0 moles respectively) and of simple neutral products, and no complex material was formed. Carbon dioxide estimations showed the production of 0.26 mole in benzene and 0.17 mole in toluene, and in neither solvent was thiophen found among the final products.

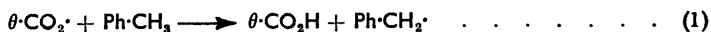
In benzene phenyl 2-thenoate was formed, in the naphthalene-benzene mixture 1-naphthyl 2-thenoate, and in nitrobenzene (in minute yield) *p*-nitrophenyl 2-thenoate. Attack *para* to the substituent in the benzene ring was also observed with both chlorobenzene and bromobenzene, *p*-chlorophenyl and *p*-bromophenyl 2-thenoates being produced. But in these last two solvents the chief product was *phenyl* 2-thenoate, and this ester was again formed when the peroxide was decomposed in iodobenzene. Its production from the halogenobenzenes must have involved attack at the carbon atom already bearing the halogen: in iodobenzene free iodine was liberated, and in bromobenzene hydrogen bromide was evolved; in chlorobenzene combined chlorine was detected in the intractable residues. Considerable amounts of 2-thenoic anhydride were isolated from the decomposition reactions in benzene and chlorobenzene, and smaller amounts in iodobenzene, and in chlorobenzene a little 2-thienyl 2-thenoate was produced.

In toluene substantial amounts of dibenzyl were formed, together with smaller quantities of tolyl 2-thenoates (mainly the *o*-isomer), benzyl 2-thenoate, and 2-benzylthiophen; an acid, C₁₀H₆O₄S₂, believed to be 5-2'-thenoyloxy-2-thenoic acid was also isolated in small yield. In cumene, where the yield of 2-thenoic acid indicated exclusive side-chain attack, dicumyl was the only neutral product isolated.

¹ *J.*, 1951, 824, is to be regarded as Part I of this series.

² Breitenbach and Karlinger, *Sitzungsber. Akad. Wiss. Wien*, (a) 1951, 160 (IIB), 304; (b) 1949, 158 (IIB), 739.

The pattern of the decomposition reactions in toluene (reactions 1—3) clearly shows that the peroxide generates 2-thenoyloxy-radicals ($\theta\cdot\text{CO}_2\cdot$):



The thenoyloxythenoic acid apparently arises either by their attack upon 2-thenoic acid or by a self-interaction process. The analogous 4-1'-naphthoyloxy-1-naphthoic acid is produced when 1-naphthoyl peroxide is decomposed in carbon tetrachloride.³ The scanty evolution of carbon dioxide and the formation of only small amounts of a product, 2-benzylthiophen, attributable to 2-thienyl radicals ($\theta\cdot$) indicate that the thenoyloxy-radicals are rather stable (probably on account of mesomerism: II \longleftrightarrow III), undergoing decarboxylation to only a moderate extent, and the preferential formation of the side-chain products shows that they react typically by hydrogen abstraction, and less readily by nuclear attack.

The reactive nature of the thiophen nucleus present in the substrate probably accounts for the low yields of simple neutral products obtained in solvents lacking easily abstractable hydrogen: the relatively large amounts of 2-thenoic acid formed in these solvents probably arise mainly by hydrogen-transfer processes involving the accumulating complex material (cf. Part I).

The acyloxylation and the halogen displacements were of considerable interest, for acyloxylation of simple aromatic solvents by a diacyl peroxide generally occurs to a negligible extent: only "reactive" substrates (*e.g.*, naphthalene⁴ and anthracene⁵) are benzyloxylation by benzoyl peroxide, simple aromatic solvents being phenylated; the halogen displacements appear to resemble those brought about by chlorine atoms, which displace bromine from aryl bromides, with the formation of aryl chlorides.⁶

The production of 2-thenoic anhydride in three of the first group of solvents, though not in toluene or cumene, suggested that there could be a process, competing with homolytic fission, in which the peroxide was directly reduced (cf. the formation of benzoic anhydride from benzoyl peroxide in the oxidation of triphenylphosphine to triphenylphosphine oxide⁷) and that the accumulating complex sulphur-containing material might be responsible. This view was strengthened by showing that ethyl sulphide also reduced the peroxide to the anhydride; benzoyl peroxide was similarly reduced to benzoic anhydride. Decomposition of 2-thenoyl peroxide in thiophen gave no anhydride; instead, 2-thienyl 2-thenoate was produced in good yield, together with smaller amounts of 2:2'-dithienyl. The decomposition of benzoyl peroxide in thiophen likewise gave 2-thienyl benzoate.

The formation of 2-benzylthiophen in toluene and of 2:2'-dithienyl in thiophen can be attributed to reactions of 2-thienyl radicals. Strong competition by solute molecules is probably responsible for their apparent inability to thienylate the aromatic solvents (cf. phenylation with benzoyl peroxide): for example, hydrogen-transfer processes would lead to thiophen, which would be subject to further attack; the benzylthiophen formed in toluene probably arises in this way, rather than by the direct union of thienyl with benzyl radicals; an independent experiment showed that benzyl radicals (generated⁸ by the interaction of *tert.*-butyl peroxide and toluene) attacked thiophen, and that 2-benzylthiophen was the product. In the affinity it shows for benzyl and acyloxy-radicals thiophen in fact resembles a substrate such as anthracene,^{8,5} and differs from a typical aromatic solvent.

³ Kharasch and Dannley, *J. Org. Chem.*, 1945, **10**, 406.

⁴ Boyland and Sims, *J.*, 1953, 2966.

⁵ Roitt and Waters, *J.*, 1952, 2695.

⁶ Voegtli, Muhr, and Lauser, *Helv. Chim. Acta*, 1954, **37**, 1627.

⁷ Challenger and Wilson, *J.*, 1927, 209; Greenbaum, Denney, and Hoffmann, *J. Amer. Chem. Soc.*, 1956, **78**, 2563.

⁸ Beckwith and Waters, *J.*, 1957, 1001.

EXPERIMENTAL

Solvents.—"AnalaR" benzene was dried over sodium; toluene, thiophen, and ethyl sulphide were fractionated over sodium. Cumene was purified as described by Hey *et al.*⁹ Nitrobenzene was fractionated under reduced pressure. Chlorobenzene and bromobenzene were fractionated and stored over sodium hydroxide. Iodobenzene was shaken with silver powder and redistilled under reduced pressure.

Esters of 2-Thenoic Acid.—Treatment of 2-thenoic acid,¹⁰ m. p. 127—128°, with thionyl chloride gave an almost quantitative yield of the acid chloride, b. p. 77°/10 mm. The following esters (prisms) were prepared under Schotten-Baumann conditions from the appropriate phenol, 2-hydroxythiophen being obtained as described by Hurd and Kreuz:¹¹ *phenyl*, m. p. 54° (Found: C, 64.5; H, 4.05; S, 15.3. C₁₁H₈O₂S requires C, 64.7; H, 3.95; S, 15.7%), *1-naphthyl*, m. p. 80° (Found: C, 70.6; H, 4.05; S, 12.2. C₁₅H₁₀O₂S requires C, 70.8; H, 4.0; S, 12.6%), *p-chlorophenyl*, m. p. 84—84.5° (Found: C, 55.2; H, 3.1; Cl, 14.9. C₁₁H₇O₂ClS requires C, 55.35; H, 3.0; Cl, 14.9%), *p-bromophenyl*, m. p. 85° (Found: C, 46.4; H, 2.7; Br, 28.5. C₁₁H₇O₂BrS requires C, 46.65; H, 2.5; Br, 28.2%), and *2-thienyl 2-thenoate*, straw-coloured, m. p. 54° (Found: C, 51.6; H, 2.9. C₉H₆O₂S₂ requires C, 51.4; H, 2.9%) (all from light petroleum; b. p. 50—60°). The phenyl ester had been prepared by Rhodehamal and Degering,¹² who, however, recorded neither analytical data nor a m. p. *p-Nitrophenyl 2-thenoate*, prepared in pyridine solution, formed needles, m. p. 181°, from methanol (Found: C, 52.8; H, 2.9; N, 5.4. C₁₁H₇O₄NS requires C, 53.0; H, 2.8; N, 5.6%).

2-Thenoyl Peroxide (I).—2-Thenoyl chloride (14 g.) in cyclohexane (20 ml.) was added to a cooled (ice-salt) mixture of 2N-sodium hydroxide (40 ml.) and aqueous hydrogen peroxide (30 vol.; 50 ml.) with vigorous mechanical stirring: the crystalline peroxide separated immediately. Stirring was continued for 15 min. and the product was then collected and dried *in vacuo*. Recrystallisation from benzene by addition of light petroleum (b. p. 30—40°), gave dense colourless prisms (60—65%), m. p. 103° (sharp, with subsequent decomp.) [Found: equiv. (iodometric), 126. Calc. for C₁₀H₆O₄S₂: equiv., 127]; Breitenbach and Karlinger^{2b} record m. p. 92—93° (decomp.).

Decompositions in Aromatic Solvents.—The decompositions in benzene, the halogenobenzenes, and nitrobenzene were carried out in the dark, and an oil-bath was used as the source of heat, for with these solvents the presence of light or the occurrence of superheating led to excessive tar-formation.

Working up consisted in removal of the solvent under reduced pressure (the last traces of nitrobenzene and iodobenzene were eliminated by steam-distillation), followed by extraction of the residue with ether (insoluble polymer being removed at this stage) and separation of the 2-thenoic acid by repeated shaking with 2N-potassium hydrogen carbonate. Except in the case of the toluene decomposition, the acid was obtained pure after recrystallisation from water. After drying (MgSO₄) of the ethereal solution the ether was removed and the neutral residue then treated as described.

Benzene. The peroxide (6.0 g.) was decomposed in benzene (600 ml.) at 75—85° for 48 hr. under nitrogen: 0.26 mole of carbon dioxide per mole of peroxide was evolved (sorption on soda-asbestos). The solvent was removed and the resulting tar extracted with boiling ether; the insoluble residue (0.7 g.), which could be precipitated as a brown amorphous powder (Found: S, 21.3%) from benzene solution by addition of methanol, was not further investigated. The ethereal solution gave 2-thenoic acid (1.9 g.) and neutral material, which when distilled at 0.01 mm. yielded an oil (0.7 g.); chromatography of this on anhydrous magnesium sulphate from light petroleum (b. p. 50—60°) gave phenyl 2-thenoate (0.2 g.), m. p. and mixed m. p. 53° after recrystallisation from light petroleum (Found: C, 64.9; H, 4.0; S, 15.3%), and 2-thenoic anhydride (0.3 g.), m. p. 60.5—61.5° (from light petroleum) (Found: C, 50.5; H, 2.5. Calc. for C₁₀H₆O₃S₂: C, 50.4; H, 2.5%), identical with an authentic specimen.¹³

In another experiment the peroxide (750 mg.) was decomposed in benzene (75 ml.) for 24 hr. and the solvent was distilled through a short column. A portion of the distillate was shaken

⁹ Hey, Pengilly, and Williams, *J.*, 1956, 1463.

¹⁰ Hartough, "Thiophene and its Derivatives," Interscience Publ. Inc., New York, 1952, pp. 503, 505.

¹¹ Hurd and Kreuz, *J. Amer. Chem. Soc.*, 1950, 72, 5543.

¹² Rhodehamal and Degering, *J. Amer. Pharm. Assoc.*, 1942, 31, 281.

¹³ Steinkopf and Ohse, *Annalen*, 1924, 437, 19.

with isatin in concentrated sulphuric acid: the colour response, when compared with that given by standard solutions of thiophen in benzene, showed that the reaction mixture contained <1 mg. of thiophen.

Naphthalene-benzene. The peroxide (1.0 g.) was added to a solution of naphthalene (20 g.) in benzene (20 ml.) at 50° and the whole heated at 80–90° for 10 hr. The mixture gave 2-thenoic acid (0.54 g.) and a gum, which was digested with hot light petroleum (b. p. 50–60°). The petroleum solution was chromatographed on magnesium sulphate; trituration of the eluted oil with light petroleum gave crystals (0.1 g.), which after two recrystallisations from light petroleum afforded 1-naphthyl 2-thenoate, m. p. and mixed m. p. 80°, strongly depressed in admixture with naphthalene.

Nitrobenzene. Decomposition of the peroxide (12 g.) in nitrobenzene (1180 ml.) at 85–95° for 36 hr. gave 2-thenoic acid (2.7 g.) and a dark product, which on trituration with methanol yielded a coloured solid (50 mg.); two recrystallisations from methanol (charcoal) gave *p*-nitrophenyl 2-thenoate, m. p. and mixed m. p. 179–180°.

Chlorobenzene. Decomposition of the peroxide (18 g.) in chlorobenzene (1620 ml.) at 65–75° for 45 hr. gave 2-thenoic acid (6.5 g.) and neutral material, which was distilled at 0.01 mm.: chromatography of the distillate on magnesium sulphate from light petroleum (b. p. 50–60°) solution afforded two oily fractions, A (1.4 g.) and B (1.4 g.).

Fraction A was chromatographed on Norit from light petroleum (b. p. 60–70°); elution with chloroform–light petroleum (1 : 9) gave phenyl 2-thenoate (0.38 g.); recrystallised from light petroleum (b. p. 30–40°) it had m. p. and mixed m. p. 53° (Found: C, 64.9; H, 4.0%). Further elution, with chloroform–light petroleum (2 : 3), gave, in turn, *p*-chlorophenyl 2-thenoate (0.02 g.), m. p. and mixed m. p. 82–83° (from ether–light petroleum), and 2-thienyl 2-thenoate (0.17 g.), m. p. and mixed m. p. 53° (from light petroleum).

Fraction B was obtained crystalline by re-chromatographing it on magnesium sulphate from light petroleum (b. p. 50–60°); recrystallised from light petroleum it had m. p. 59.5°, undepressed in admixture with 2-thenoic anhydride.

In a similar experiment, in which the peroxide (9.0 g., 36 mmoles) gave 0.24 g. (1.2 mmoles) of the phenyl ester, the total combined chlorine (in the crude carboxylic acid and the involatile residues) was found to amount to 0.11 g. (3×10^{-3} g.-atom).

Bromobenzene. (a) Decomposition of the peroxide (15 g.) in bromobenzene (1400 ml.) at 75–80° for 24 hr. gave 2-thenoic acid (6.9 g.) and a dark gum, which was distilled at 0.01 mm.; chromatography of the oily distillate on Norit, with chloroform–light petroleum mixtures, gave phenyl 2-thenoate (0.17 g.) and *p*-bromophenyl 2-thenoate (0.26 g.), m. p. 83° (from methanol): the mixed m. p. with an authentic sample was 84–85°.

(b) A solution of the peroxide (7 g., 28 mmoles) in bromobenzene (100 ml.) was introduced, during 3 hr., into boiling bromobenzene (500 ml.) through which dry nitrogen was passed, and the effluent gases were bubbled through acidified silver nitrate. The mixture was then refluxed for a further hour, the current of nitrogen being maintained. Silver bromide (0.40 g., 2.1 mmoles) collected in the trap. The mixture, worked up as in (a), gave the carboxylic acid (2.6 g.), the phenyl ester (0.57 g., 2.8 mmoles), and a trace of the *p*-bromophenyl ester.

Iodobenzene. A solution of the peroxide (2.5 g., 10 mmoles) in iodobenzene (60 ml.) was added all at once, with vigorous shaking, to iodobenzene (190 ml.) at 150°; the whole was then heated at 150° for 5 min. and cooled. The mixture was deep red, owing to liberation of iodine (1×10^{-3} g.-atom), which was determined by repeated extraction with saturated aqueous potassium iodide and titration of the combined extracts with 0.1N-thiosulphate. The organic layer gave 2-thenoic acid (0.9 g.) and neutral material, which was distilled at 0.05 mm. Chromatography of the distillate on Norit, in the usual way, gave phenyl 2-thenoate (0.12 g., 0.6 mmole), m. p. and mixed m. p. 53°, and a solid (30 mg.) which on recrystallisation (twice) from light petroleum yielded 2-thenoic anhydride, m. p. and mixed m. p. 60–61°.

Toluene. The peroxide (18 g.) was decomposed in toluene (1700 ml.) at 75–85° under nitrogen for 48 hr.; 0.17 mole of carbon dioxide per mole of peroxide was evolved. The acidic material (12.5 g.) obtained, which had a melting-range of 105–110°, was digested with boiling water: the soluble fraction was shown (by sublimation of a portion) to contain 11.0 g. of pure 2-thenoic acid. Trituration of the insoluble fraction with aqueous methanol yielded 5(?)'-2'-thenoyloxy-2-thenoic acid (0.17 g.) as prisms, m. p. 195° (decomp.) (Found: C, 47.3; H, 2.2. $C_{10}H_6O_4S_2$ requires C, 47.2; H, 2.4%); with diazomethane it gave the *methyl ester*, which formed prisms, m. p. 131–132° (decomp.), from light petroleum (b. p. 60–70°) (Found: C,

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49.4; H, 3.3. $C_{11}H_8O_4S_2$ requires C, 49.2; H, 3.0%). Hydrolysis of the acyloxy-acid furnished 2-thenoic acid, together with a highly soluble hydroxythenoic acid, which with aqueous ferric chloride gave an intense vermilion colour, rapidly changing to a dark red precipitate.

The residue from the organic layer was distilled at 0.01 mm., giving two fractions: A (4.5 g.), b. p. 70–80°, which crystallised on cooling, and B (1.5 g.), b. p. 100–150°. Fraction A on recrystallisation from methanol gave dibenzyl, m. p. and mixed m. p. 48–50°. The mother-liquor was evaporated and the residue chromatographed on alumina from light petroleum (b. p. 30–40°); further dibenzyl (2.9 g. in all) was obtained, along with 2-benzylthiophen, which was characterised by conversion into 2-benzyl-5-chloromercurithiophen (0.16 g.), prisms, m. p. and mixed m. p. 184–185° (lit.,¹⁴ 189–191°), from methanol-chloroform (Found: C, 32.5; H, 2.5. Calc. for $C_{11}H_9SHgCl$: C, 32.1; H, 2.2%).

Fraction B was refluxed with potassium hydroxide (4 g.) in alcohol (25 ml.) for 30 min. The alcohol was removed, and water (20 ml.) added: ether-extraction gave an oil (0.4 g.), identified as benzyl alcohol (phenylcarbamate, m. p. and mixed m. p. 76–77°). The alkaline solution yielded 2-thenoic acid (0.7 g.), again purified by sublimation, and phenolic material (0.2 g.); treatment of the latter with α -naphthyl isocyanate gave slightly impure *o*-tolyl α -naphthylcarbamate, m. p. 136° after recrystallisation from light petroleum (b. p. 60–70°), which did not depress the m. p. of an authentic sample, m. p. 142°, and strongly depressed the m. p.s of authentic samples of the *m*- and the *p*-isomer.

In another experiment (1.0 g. of peroxide in 95 ml. of toluene) the effluent nitrogen was passed through a trap at –70°; the solvent was finally distilled through a column at atmospheric pressure, the first runnings being added to the condensate in the trap; the mixture was shown to contain <0.2 mg. of thiophen.

Cumene. Decomposition of the peroxide (3.0 g.) in cumene (300 ml.) at 70–80° under nitrogen for 36 hr. gave 2-thenoic acid (3.0 g.) and a pale yellow oil, which was distilled at 0.6 mm. Chromatography of the distillate (1.2 g.) from light petroleum (b. p. 50–60°) afforded dicumyl (2 : 3-dimethyl-2 : 3-diphenylbutane) (0.24 g.), m. p. and mixed m. p. 117°, after recrystallisation from methanol.

Decomposition of Peroxides in Thiophen.—(a) *2-Thenoyl peroxide.* A solution of the peroxide (3.0 g.) in thiophen (100 ml.) was refluxed for 16 hr. The thiophen was removed, the residue was taken up in ether, and 2-thenoic acid (1.3 g.) was extracted. The organic layer was then evaporated and distilled at 0.02 mm. Trituration of the distillate (1.0 g.) with light petroleum (b. p. 30–40°) gave 2-thienyl 2-thenoate (0.50 g.). The petroleum-soluble fraction was chromatographed on magnesium sulphate, yielding 2 : 2'-dithienyl (0.12 g.), obtained as plates, m. p. 34–35°, from methanol, identical with an authentic sample,¹¹ m. p. 34°, and a further quantity of the ester (0.73 g. in all), m. p. and mixed m. p. 53°, after recrystallisation from light petroleum (b. p. 30–40°).

(b) *Benzoyl peroxide.* A solution of the peroxide (4.0 g.) in thiophen (100 ml.) was refluxed for 24 hr. The thiophen was removed and the residue taken up in ether. Benzoic acid (2.6 g.) was obtained by extraction, and the ether layer was evaporated and distilled at 1 mm. The distillate (0.9 g.) was chromatographed (twice) on magnesium sulphate from light petroleum (b. p. 30–40°) solution, yielding 2-thienyl benzoate¹¹ (0.51 g.), nodules (from light petroleum), m. p. and mixed m. p. 43–44°.

Reduction of Peroxides with Ethyl Sulphide.—(a) *2-Thenoyl peroxide.* The peroxide (3.0 g.) was added in small portions to the sulphide (6 g.); the reaction was exothermic and external cooling (ice) was necessary. The colourless solution was refluxed for 3 min. and concentrated, and gave 2-thenoic acid (1.9 g.); the neutral residue (1.0 g.) on trituration with light petroleum (b. p. 30–40°) gave 2-thenoic anhydride (0.63 g.), m. p. and mixed m. p. 59–60° (from light petroleum).

(b) *Benzoyl peroxide.* In a similar experiment, with benzoyl peroxide (8.0 g.) and ethyl sulphide (16 g.), benzoic acid (5.0 g.) and benzoic anhydride (1.3 g.) were obtained. The latter was purified by chromatography on magnesium sulphate, and had m. p. and mixed m. p. 43°, after recrystallisation from ether-light petroleum.

In neither case was any attempt made to isolate the oxidation products of the sulphide, or other neutral compounds.

Decomposition of tert.-Butyl Peroxide in Toluene-Thiophen.—The peroxide (10 g.), toluene

¹⁴ Steinkopf, *Annalen*, 1921, **424**, 54.

(50 ml.), and thiophen (50 ml.) were refluxed together for 7 days. Concentration of the reaction mixture at atmospheric pressure left a high-boiling residue, which was extracted with light petroleum (b. p. 30—40°); the extract on evaporation and distillation at 10 mm. gave 2-benzylthiophen (0.5 g.), identified by conversion into its 5-chloromercuri-derivative. No dibenzyl was formed.

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