5. 1 : 2-*Dihydro*-2-*thianaphthalene Derivatives. Part II.* Conversion of* 1 : 2-*Dihydro*-1-*keto*-2-*thianaphthalenes into Indanones.*

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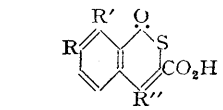
Treatment of 1 : 2-dihydro-1-keto-2-thianaphthalene-3-carboxylic acid and its 7 : 8-dimethoxy- and 4-methyl derivatives with Raney nickel give respectively indan-1-one, 6 : 7-dimethoxyindan-1-one, and 3-methylindan-1-one. The first compound is also obtained by the action of Raney nickel on 1 : 2-dihydro-1-keto-2-thianaphthalene.

In Part I * of this series we described the preparation of rhodanine condensation products of benzoic acids with an *o*-carbonyl function and their conversion by sodium hydroxide into 1 : 2-dihydro-1-keto-2-thianaphthalene-3-carboxylic acids (I). It was further shown that the sulphur atom in the latter compounds was readily eliminated by ammonia and

* Part I, *J.*, 1951, 1213.

primary amines with the formation of *iso*quinoline derivatives. Continuing our studies on the reactions of thianaphthalenes we have examined their desulphurisation by the action of Raney nickel. Use of this reagent for the formation of aldehydes from thiol-esters, R·CO·SR′ ⟶ R·CHO, has been reported by Wolfrom and Karabinos (*J. Amer. Chem. Soc.*, 1946, **68**, 724, 1455; cf. Spero, McIntosh, and Levin, *ibid.*, 1948, **70**, 1907). Desulphurisation of the thio-lactone acid (I; R = R′ = R″ = H) might therefore have been expected to give *o*-formylcinnamic acid (II). In fact the reaction product was a neutral carbonyl compound, isolated as its semicarbazone and its 2 : 4-dinitrophenylhydrazone which proved to be identical with the corresponding derivatives of indan-1-one (III; R = R′ = R″ = H). Wiley and Hobson (*ibid.*, 1949, **71**, 2429) prepared *o*-formyl-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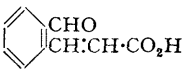
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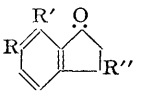
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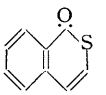
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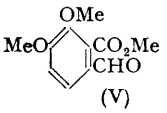
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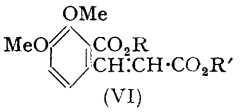
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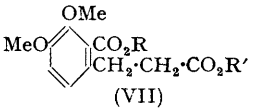
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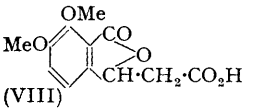
(VIII)

cinnamic acid (II) by the interaction of phthalaldehyde with malonic acid in the presence of pyridine and reported that it lost carbon dioxide readily with the formation of indan-1-one. Reaction of 1 : 2-dihydro-1-keto-2-thianaphthalene (IV) with Raney nickel also gave indan-1-one (III; R = R′ = R″ = H) in fair yield; in this case the intermediate *o*-vinylbenzaldehyde or more probably a related ion cyclises to give (III; R = R′ = R″ = H) by a mechanism similar to that suggested by Wiley and Hobson (*loc. cit.*) for the cyclisation of *o*-formylcinnamic acid; this involves the reaction of the ion formed by decarboxylation of *o*-formylcinnamic acid with the carbonium ion of the carbonyl group rather than with the liberated proton, the latter combining with the carbonyl-oxygen anion. The resulting 1-hydroxyindene is then converted into indan-1-one by a prototropic change.

The general nature of the above desulphurisation reaction has been demonstrated by its application to 1 : 2-dihydro-1-keto-4-methyl- (I; R = R′ = H, R″ = Me) and to 1 : 2-dihydro-1-keto-7 : 8-dimethoxy-2-thianaphthalene-3-carboxylic acid (I; R = R′ = OMe, R″ = H). In the first case the product was 3-methylindan-1-one (III; R = R′ = H, R″ = Me) and, in the second, 6 : 7-dimethoxyindan-1-one (III; R = R′ = OMe, R″ = H), both compounds being isolated as their semicarbazones and 2 : 4-dinitrophenylhydrazones.

6 : 7-Dimethoxyindan-1-one, for comparison with the specimen obtained by the desulphurisation method, was prepared by a modification of the route described by Schöpf, Jackh-Tettweiler, Meyer, Perry-Fehrenbach, and Winterhalter (*Annalen*, 1940, **544**, 77). Condensation of α-methyl opianate (V) (Bain, Perkin, and Robinson, *J.*, 1914, 2392) with malonic acid in pyridine containing piperidine gives 2-carbomethoxy-3 : 4-dimethoxycinnamic acid (VI; R = Me, R′ = H) characterised by the preparation of methyl 2-carbomethoxy-3 : 4-dimethoxycinnamate (VI; R = R′ = Me). Alkaline hydrolysis of (VI; R = Me, R′ = H) gives 2-carboxy-3 : 4-dimethoxycinnamic acid (VI; R = R′ = H) identical with the acid described by Schöpf *et al.* (*loc. cit.*) by the action of alkali on meconin-α-acetic acid (VIII). Crystallisation of 2-carboxy-3 : 4-dimethoxycinnamic acid from dilute hydrochloric acid gives meconin-α-acetic acid; the last compound is also obtained in quantitative yield by fusion of the dicarboxylic acid. Hydrogenation of (VI; R = Me, R′ = H) in the presence of platinum gives β-(2-carbomethoxy-3 : 4-dimethoxyphenyl)propionic acid (VII; R = Me, R′ = H) which on hydrolysis gives β-(2-carboxy-3 : 4-dimethoxyphenyl)propionic acid (VII; R = R′ = H); the latter has been obtained by Schöpf *et al.* (*loc. cit.*) by hydrogenation of 2-carboxy-3 : 4-dimethoxycinnamic acid. Treatment of (VII; R = R′ = H) with acetic anhydride gave 6 : 7-dimethoxyindan-1-one which was identical with the product obtained by desulphurisation of (I; R = R′ = OMe, R″ = H).

Experimental

2-Carbomethoxy-3 : 4-dimethoxycinnamic Acid.—A mixture of α-methyl opianate (10·0 g.), malonic acid (10·0 g.), pyridine (50 c.c.), and piperidine (2 c.c.) was heated for 2 hours on the steam-bath. The cooled reaction mixture was poured into a stirred mixture of ice (150 g.) and hydrochloric acid (100 c.c.; *d* 1·17), and the precipitated solid collected. *2-Carbomethoxy-3 : 4-dimethoxycinnamic acid* (10·0 g., 84%) crystallised from aqueous ethanol as rectangular plates, m. p. 161—162° (Found : C, 59·05; H, 5·7. $C_{13}H_{14}O_6$ requires C, 58·8; H, 5·3%).

Methyl 2-Carbomethoxy-3 : 4-dimethoxycinnamate.—A solution of the acid-ester (2·0 g.) in dry methanol (100 c.c.) containing sulphuric acid (2 c.c.; *d* 1·84) was heated under reflux for 2 hours, and then concentrated under reduced pressure to a bulk of 30 c.c. After the addition of water (200 c.c.) the mixture was extracted with ether (3 × 100 c.c.). The ethereal solution was washed with saturated sodium hydrogen carbonate solution (100 c.c.) and then water (100 c.c.) and dried (Na_2SO_4). The oil (1·7 g.) obtained after removal of the ether crystallised from aqueous methanol to give the *ester* as needles, m. p. 64—66° (Found : C, 59·95; H, 5·8. $C_{14}H_{16}O_6$ requires C, 60·0; H, 5·7%).

2-Carboxy-3 : 4-dimethoxycinnamic Acid.—(*a*) (cf. Schöpf *et al.*, *loc. cit.*). A solution of meconin-α-acetic acid (4·5 g.) in aqueous potassium hydroxide (23 c.c., 50%) was evaporated to dryness on the steam-bath. The residue was dissolved in water (25 c.c.) and the process repeated. Water (50 c.c.) was then added and the solution acidified with hydrochloric acid (2N.) with ice-cooling. The precipitated 2-carboxy-3 : 4-dimethoxycinnamic acid (3·5 g.) separated from water as fine needles, m. p. 171—172° (Schöpf *et al.* record m. p. 178—180°; a mixture with meconinacetic acid had m. p. 158—172°) (Found : C, 57·2; H, 4·9%; equiv., 125. Calc. for $C_{12}H_{12}O_6$: C, 57·1; H, 4·8%; equiv., 126). Light absorption in ethanol : Max. at 2350 (ε = 15,000) and 3000 Å (ε = 18,900).

(*b*) 2-Carbomethoxy-3 : 4-dimethoxycinnamic acid (0·5 g.) in aqueous potassium hydroxide (10 c.c.; 2N.) was heated on the steam-bath for 1 hour. The ice-cooled solution was acidified (Congo-red) with hydrochloric acid (2N.); the precipitate crystallised from water, to give 2-carboxy-3 : 4-dimethoxycinnamic acid (0·35 g.) as fine needles, m. p. 171—172° undepressed by preparation (*a*) (Found : C, 56·6; H, 4·9%; equiv., 130).

Meconin-α-acetic Acid.—(*a*) 2-Carboxy-3 : 4-dimethoxycinnamic acid was melted and then crystallised once from water, to give meconinacetic acid as needles, m. p. 167° (Found : C, 57·3; H, 5·0%; equiv., 265. Calc. for $C_{12}H_{12}O_6$: C, 57·1; H, 4·8%; equiv., 252). Light absorption in ethanol : Max. at 2130 (ε = 25,000) and 3060 Å (ε = 4200).

(*b*) 2-Carboxy-3 : 4-dimethoxycinnamic acid (100 mg.) was crystallised once from hydrochloric acid (6 c.c.; 3N.), to give meconinacetic acid as needles, m. p. 167° (Found : C, 57·35; H, 4·85%; equiv., 248).

β-(2-Carbomethoxy-3 : 4-dimethoxyphenyl)propionic Acid.—2-Carbomethoxy-3 : 4-dimethoxycinnamic acid (1·33 g.) in water (100 c.c.) containing sodium hydrogen carbonate (0·42 g.) was shaken with platinum (from 100 mg. of Adams's platinum oxide) in an atmosphere of hydrogen at 18°/1 atm. When hydrogen absorption ceased (observed, 136 c.c.; calc., 132 c.c.) the catalyst was removed by filtration and the solution acidified (Congo-red) with hydrochloric acid (2N.). The solution was extracted with ether (3 × 40 c.c.), and the dried (Na_2SO_4) extract evaporated to give an oil which rapidly solidified. Crystallisation from light petroleum (b. p. 40—60°) gave *β-(2-carbomethoxy-3 : 4-dimethoxyphenyl)propionic acid* (0·71 g.) as needles, m. p. 88—89° (Found : C, 58·5; H, 6·2. $C_{13}H_{16}O_6$ requires C, 58·3; H, 6·0%). The acid-ester (300 mg.) in potassium hydroxide (5 c.c.; 2N.) was heated on the steam-bath for 1 hour. The solution was acidified (Congo-red) with hydrochloric acid (2N.) and extracted with ether (3 × 10 c.c.), the combined extracts being dried (Na_2SO_4) and evaporated. The residual oil was dissolved in benzene (5 c.c.), and the solvent removed. Crystallisation of the residue from benzene–light petroleum (b. p. 40—60°) gave β-(2-carboxy-3 : 4-dimethoxyphenyl)propionic acid (260 mg.) as small prismatic needles, m. p. 125—126° (Schöpf *et al.*, *loc. cit.*, give m. p. 125—127° for the anhydrous acid prepared by catalytic hydrogenation of 2-carboxy-3 : 4-dimethoxycinnamic acid) (Found : C, 56·5; H, 5·7%; equiv., 125. Calc. for $C_{12}H_{14}O_6$: C, 56·7; H, 5·6%; equiv., 127).

3-Methylindan-1-one.—1 : 2-Dihydro-1-keto-4-methyl-2-thianaphthalene-3-carboxylic acid (Dijksman and Newbold, *loc. cit.*) (0·5 g.) was heated under reflux for 5 hours with a suspension of Raney nickel (5 g.; W.6. prepared according to *Org. Synth.*, **29**, 25) in ethanol (50 c.c.). After removal of the nickel the filtrate and ethanol washings were concentrated to 5 c.c., water (50 c.c.) was added, and the mixture was extracted with ether (4 × 20 c.c.). The ethereal

solution was washed with sodium hydroxide (20 c.c.; N.) and then water (2 × 20 c.c.), and dried (Na_2SO_4). Removal of the ether gave a colourless oil (0·28 g.); treatment of a portion of this oil (0·14 g.) with semicarbazide acetate gave 3-methylindan-1-one semicarbazone (0·16 g.) as needles (from ethanol), m. p. 231° (decomp.) (Found: C, 65·4; H, 6·1. Calc. for $C_{11}H_{13}ON_3$: C, 65·0; H, 6·4%). Light absorption in ethanol: Max. at 2100 (ε = 16,500), 2590 (ε = 17,700), 2790 (ε = 18,400), 2980 (ε = 15,300), and 3080 Å (ε = 13,950); the substance was undepressed in m. p. when mixed with a specimen, m. p. 231° (decomp.) (von Braun and Kirschbaum, *Ber.*, 1913, **46**, 3041, give m. p. 230—231°), prepared from 3-methylindan-1-one obtained by the method of Koelsch, Hochmann, and Le Claire [*J. Amer. Chem. Soc.*, 1943, **65**, 59; absorption max., in ethanol, at 2130 (ε = 15,100), 2690 (ε = 18,100), 2790 (ε = 18,600), 2980 (ε = 15,900), and 3080 Å (ε = 14,600)]. The crude 3-methylindan-1-one (0·14 g.) on treatment with Brady's reagent gave a 2 : 4-dinitrophenylhydrazone (0·26 g.) as red prismatic needles, m. p. 239—240° (decomp.), from ethyl acetate (Found: C, 59·3; H, 3·9. Calc. for $C_{16}H_{14}O_4N_4$: C, 59·3; H, 4·3%). Light absorption in chloroform: Max. at 2500 (ε = 12,000) and 3890 Å (ε = 31,200). It showed no m. p. depression when mixed with an authentic specimen, m. p. 239—240° (decomp.) (Marvel, Dec, and Cooke, *ibid.*, 1940, **62**, 3499, give m. p. 239—241°), which showed absorption max., in chloroform, at 2500 (ε = 11,000) and 3900 Å (ε = 31,000).

6 : 7-*Dimethoxyindan-1-one.*—This was obtained as an oil (1·7 g.) by treatment of 1 : 2-dihydro-1-keto-7 : 8-dimethoxy-2-thianaphthalene-3-carboxylic acid (4·0 g.) with Raney nickel as described above. The oil (0·5 g.) on treatment with aqueous-ethanolic semicarbazide acetate gave 6 : 7-dimethoxyindan-1-one semicarbazone (0·32 g.) as small needles, m. p. 217—219° (decomp.), from aqueous ethanol (Found: C, 57·5; H, 6·0. Calc. for $C_{12}H_{15}O_3N_3$: C, 57·8; H, 6·0%). Light absorption in ethanol: Max. at 2210 (ε = 25,600), 2810 (ε = 19,800), inflection at 3100 Å (ε = 9300). It was undepressed in m. p. when mixed with a specimen of the authentic semicarbazone, m. p. 217—219° (decomp.) [(Schöpf *et al.*, *loc. cit.*, give m. p. 217—219° (decomp.) for the monohydrate (from ethanol)], which had absorption max., in ethanol, at 2200 (ε = 25,000), 2800 (ε = 19,000), inflection at 3100 Å (ε = 9000). The crude 6 : 7-dimethoxyindan-1-one (0·5 g.) gave with Brady's reagent the 2 : 4-*dinitrophenylhydrazone* (0·71 g.) which separated from chloroform–light petroleum (b. p. 60—80°) as bright red needles, m. p. 246—248° (decomp.) (Found: C, 55·3; H, 4·2. $C_{17}H_{16}O_6N_4$ requires C, 54·9; H, 4·3%). Light absorption in chloroform: Max. at 2490 (ε = 13,900) and 3900 Å (ε = 29,100). The compound gave no m. p. depression on mixture with a specimen [m. p. 246—248° (decomp.)] prepared from 6 : 7-dimethoxyindan-1-one prepared as described by Schöpf *et al.* (*loc. cit.*), which separated as bright red needles from chloroform–light petroleum (b. p. 60—80°) (Found: C, 55·1; H, 4·5%) and showed light absorption max., in chloroform, at 2470 (ε = 14,600) and 3910 Å (ε = 29,000).

Indan-1-one.—(*a*) 1 : 2-Dihydro-1-keto-2-thianaphthalene (1·4 g.) was heated under reflux for 5 hours with a suspension of Raney nickel (14 g.) in ethanol (100 c.c.). The filtered solution and ethanol washings were evaporated under reduced pressure, water (50 c.c.) was added to the residue, and the mixture steam-distilled until the distillate was free from oil. The oil solidified when the distillate was cooled in ice. The solid A (0·11 g.), m. p. 36—38°, was separated and the filtrate extracted with ether (3 × 25 c.c.), the combined extracts being dried (Na_2SO_4) and evaporated to give a further 0·42 g. of indan-1-one. Sublimation of the solid A at 60°/10^{-3} mm. gave a sublimate, m. p. 38—40° alone or mixed with an authentic specimen (m. p. 39—41°) (*Org. Synth.*, Coll. Vol. II, 336). The crude indan-1-one (0·20 g.) was converted into the semicarbazone (0·27 g.) which separated from ethanol as small prisms, m. p. 237° (decomp.) (Found: C, 63·8; H, 5·4. Calc. for $C_{10}H_{11}ON_3$: C, 63·5; H, 5·8%). Light absorption in ethanol: Max. at 2080 (ε = 17,000), 2690 (ε = 16,300), 2780 (ε = 16,200), 2990 (ε = 14,600), and 3090 (ε = 12,900), inflection at 2200 Å (ε = 12,000). The semicarbazone was not depressed in m. p. on mixture with an authentic specimen, m. p. 237° (decomp.), of indan-1-one semicarbazone [Revis and Kipping, *J.*, 1897, **71**, 238, give m. p. 239° (decomp.); von Auwers and Auffenberg, *Ber.*, 1919, **52**, 92, give m. p. 233° (decomp.)], which gave absorption max., in ethanol, at 2070 (ε = 16,100), 2700 (ε = 16,500), 2800 (ε = 16,600), 2970 (ε = 14,200), and 3080 (ε = 12,900), inflection at 2200 Å (ε = 12,700). A specimen of the crude indan-1-one (0·20 g.) with Brady's reagent gave indan-1-one 2 : 4-dinitrophenylhydrazone (0·41 g.) which separated from ethyl acetate as red rods, m. p. 258—260° (decomp.) (Found: C, 58·0; H, 3·6. Calc. for $C_{15}H_{12}O_4N_4$: C, 57·8; H, 3·85%). Light absorption in chloroform: Max. at 2500 (ε = 13,500) and 3900 Å (ε = 31,000). The derivative showed no m. p. depression when mixed with authentic indan-1-one 2 : 4-dinitrophenylhydrazone, m. p. 258—260° (decomp.) (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955, gives m. p. 258°; Seka and Kellermann, *Ber.*, 1942,

75, 1730, give m. p. 265°) [absorption max., in chloroform, at 2500 (ε = 15,000) and 3890 Å (ε = 30,800)].

(*b*) 1 : 2-Dihydro-1-keto-2-thianaphthalene-3-carboxylic acid (3·0 g.) was treated as above, to give crude indan-1-one (1·2 g.). This was not purified but was converted into the semicarbazone (0·61 g. from 0·5 g.) and the 2 : 4-dinitrophenylhydrazone (0·87 g. from 0·5 g.). The semicarbazone separated from ethanol as small prisms, m. p. 237° (decomp.) alone or mixed with authentic indan-1-one semicarbazone (Found : C, 63·4; H, 5·8%). Light absorption in ethanol : very similar to that recorded above. The 2 : 4-dinitrophenylhydrazone formed small red needles (from ethyl acetate), m. p. 258—260° (decomp.) undepressed on mixture with indan-1-one 2 : 4-dinitrophenylhydrazone (Found : C, 58·3; H, 3·7%). Light absorption in chloroform : Max. at 2500 (ε = 14,400) and 3880 Å (ε = 31,900).

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