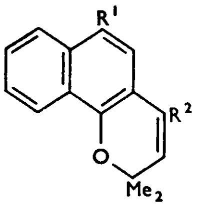
289. *The Reaction between Lapachenole and* 2 : 4-*Dinitrophenylhydrazine.*

By R. Livingstone and R. B. Watson.

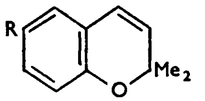
This reaction has been shown to result in the formation of the 2 : 4-dinitrophenylhydrazone of the corresponding 2 : 2-dimethylchromanone and has been extended to related naphthopyrans and chromens.

Lapachenole [1] (I*a*) with 2 : 4-dinitrophenylhydrazine in ethanolic or butanolic sulphuric acid yielded a product formed by the addition of 1 mol. of lapachenole and 1 mol. of 2 : 4-dinitrophenylhydrazine.[2] Lapachenole dimer [1] under similar conditions did not afford a derivative, but 6 : 6-dimethylnaphtho(1′ : 2′-2 : 3)pyran (I*b*) slowly formed a derivative in ethanolic solution. 4′-Chloro-6 : 6-dimethylnaphtho(1′ : 2′-2 : 3)pyran (I*c*) and 2 : 2-dimethylchromen [3] (II*a*) failed to react in ethanol but formed derivatives in refluxing butanol. Dimerisation of lapachenole results in the disappearance of the non-aromatic double bond, indicating that it is probably involved in this " abnormal " reaction with 2 : 4-dinitrophenylhydrazine.

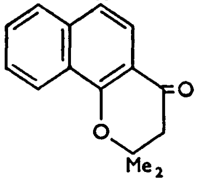
The derivative from 6 : 6-dimethylnaphtho(1′ : 2′-2 : 3)pyran was resistant to hydrolysis with dilute acid and to decomposition by pyruvic acid. It was insoluble in sodium hydroxide or sodium hydrogen carbonate solution, but soluble in chloroform or pyridine. These solubilities, coupled with the fact that the derivative could be eluted from alumina with organic solvents, suggested a cyclic structure.



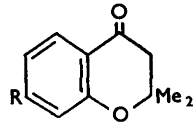
(I) (*a*) $R^1 = OCH_3$, $R^2 = H$.
(*b*) $R^1 = H$, $R^2 = H$.
(*c*) $R^1 = Cl$, $R^2 = H$.
(*d*) $R^1 = H$, $R^2 = CH_3$.



(II) (*a*) $R^1 = H$.
(*b*) $R^1 = OCH_3$.



(III) (*a*) $R = H$.
(*b*) $R = OCH_3$.



(IV) (*a*) $R = OCH_3$.
(*b*) $R = H$.

The product was not the 2 : 4-dinitrophenylhydrazone of 1-hydroxy-2-*iso*valerylnaphthalene, obtained by an extension of the method involving Fries re-arrangement of α-naphthol esters.[4] The absence of the hydroxyl group in the " abnormal " compound was confirmed by infrared spectroscopy. The cyclic structure was shown to be of the chromanone type by extending the reaction to 7-methoxy-2 : 2-dimethylchromen in

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[1] Livingstone and Whiting, *J.*, 1955, **3631**.

[2] D. H. R. Barton, personal communication.

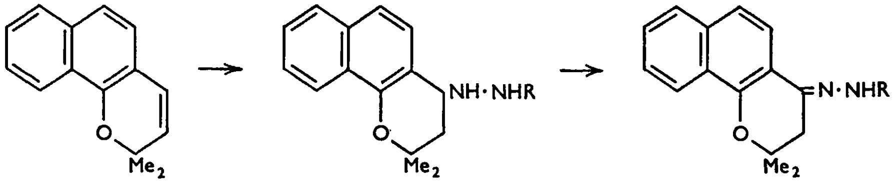
[3] Shriner and Sharp, *J. Org. Chem.*, 1939, **4**, 575; Smith and Ruoff, *J. Amer. Chem. Soc.*, 1940, **62**, 145.

[4] Stroughton, *ibid.*, 1935, **57**, 202.

butanol, which afforded the 2 : 4-dinitrophenylhydrazone of 7-methoxy-2 : 2-dimethylchroman-4-one [5] (IV*a*).

The 2 : 4-dinitrophenylhydrazones of 2 : 2-dimethyl-7 : 8-benzochroman-4-one (III*a*), its 6-methoxy-derivative [6] (III*b*), and 2 : 2-dimethylchroman-4-one [7] (IV*b*) were also shown to be identical with the products obtained as above from (I*b*), lapachenole, and (II*a*). The authentic specimens were prepared by the Fries re-arrangement of ββ-dimethylacryloyl esters.[8]

The reaction could be regarded as involving dehydrogenation of the addition product (see scheme), a reaction comparable with the dehydrogenation of alcohol by excess of 2 : 4-dinitrophenylhydrazine.[9] Such a mechanism would explain the fact that 7-methoxy-2 : 2-dimethylchromen and phenylhydrazine in butanolic sulphuric acid failed to yield any derivative. 4 : 6 : 6-Trimethylnaphtho(1′ : 2′-2 : 3)pyran (I*d*) with 2 : 4-dinitrophenylhydrazine in butanol also failed to yield a derivative, the elimination of the methyl group being difficult to envisage under the conditions of the reaction. Presumably the addition step is reversible and unless dehydrogenation supervenes the adduct reverts to its precursors.



6-Methoxy-2 : 2-dimethylchromen (II*b*) showed a lower reactivity than its 7-methoxy-analogue, and 2 : 2-diphenyl-1 : 2-benzopyran [10] failed to yield any derivative when heated under reflux with 2 : 4-dinitrophenylhydrazine in butanolic sulphuric acid.

EXPERIMENTAL

Ultraviolet absorption spectra were determined in $CHCl_3$ with a Unicam S.P.500 spectrophotometer.

Lapachenole 2 : 4-*Dinitrophenylhydrazine Derivative.*—Lapachenole (0·5 g.), 2 : 4-dinitrophenylhydrazine (1 g.), ethanol (100 c.c.), and sulphuric acid (2 c.c.) were refluxed for 1 hr. and the precipitate purified by chromatography on alumina from benzene. The *product* (see below) separated from acetic acid in red-brown needles, m. p. 293—296° (Found : C, 59·95; H, 4·45; N, 12·45; OMe, 7·1. $C_{22}H_{20}O_6N_4$ requires C, 60·5; H, 4·6; N, 12·8; OMe, 7·1%), $\lambda_{max.}$ 2460, 3320, 4250 Å (log ε 4·39, 4·12, 4·43).

6 : 6-*Dimethylnaphtho*(1′ : 2′-2 : 3)*pyran* 2 : 4-*Dinitrophenylhydrazine Derivative.*—6 : 6-Dimethylnaphtho(1′ : 2′-2 : 3)pyran (I*b*) (0·9 g.), 2 : 4-dinitrophenylhydrazine (1 g.), ethanol (100 c.c.), and sulphuric acid (2 c.c.) was refluxed for 3½ hr., then set aside overnight. The precipitated *product* was purified by chromatography on alumina from benzene. Crystallisation from acetic acid afforded needles, m. p. 279—280° (0·12 g., 7%) (Found : C, 62·4; H, 4·25; N, 13·75. $C_{21}H_{18}O_5N_4$ requires C, 62·1; H, 4·5; N, 13·8%), $\lambda_{max.}$ 3100 and 4050 Å (log ε 3·96, 4·44).

Reaction of 2 : 4-*Dinitrophenylhydrazine and* 2 : 2-*Dimethylchromens in Butanol.*—Dimethylchromen (1 mole), 2 : 4-dinitrophenylhydrazine (2·2 moles), butan-1-ol (3·5 l./mole), and sulphuric acid (0·38 l./mole) were refluxed for 3 hr. The residue afforded by the removal of solvent and excess of hydrazine was purified by chromatography on alumina from benzene. The derivative was recrystallised from a suitable solvent.

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[5] Bridge, Crocker, Cubin, and Robertson, *J.*, 1937, 1530.
[6] Livingstone and Watson, *ibid.*, *J.*, 1956, 3701.
[7] Baker, Floyd, McOmie, Pope, Weaving, and Wild, *J.*, 1956, 2015.
[8] Cavill, Dean, McGookin, Marshall, and Robertson, *J.*, 1954, 4173.
[9] Braude and Forbes, *J.*, 1951, 1762.
[10] Löwenbein, *Ber.*, 1924, **75**, 779.

(a) 2 : 2-*Dimethylchromen* (II*a*). The product, obtained as reddish needles from benzene and then from ethyl acetate, had m. p. 215—216° alone or mixed with 2 : 2-dimethylchroman-4-one 2 : 4-dinitrophenylhydrazone.[7]

(b) 6-*Methoxy*-2 : 2-*dimethylchromen* (II*b*). The *derivative* obtained as orange-red needles from benzene had m. p. 199—207° (5%) (Found : C, 56·1; H, 4·8; N, 14·1. $C_{18}H_{18}O_6N_4$ requires C, 56·0; H, 4·7; N, 14·5%).

(c) 7-*Methoxy*-2 : 2-*dimethylchromen*. A derivative obtained as blood-red needles from benzene and then from ethyl acetate had m. p. 219—220° (10%) alone or mixed with 7-methoxy-2 : 2-dimethylchroman-4-one 2 : 4-dinitrophenylhydrazone [5] (Found : C, 55·6; H, 4·7; N, 14·4. Calc. for $C_{18}H_{18}O_6N_4$: C, 56·0; H, 4·8; N, 14·4%).

(d) 4′-*Chloro*-6 : 6-*dimethylnaphtho*(1′ : 2′-2 : 3)*pyran* (I*c*). A solid, which separated from the solution during the heating, was purified separately from the residue. The *product* was obtained as orange-red plates (from benzene), m. p. 281—282° (Found: C, 56·8; H, 4·0; N, 12·6; Cl, 7·4. $C_{21}H_{17}O_5N_4Cl$ requires C, 57·2; H, 4·0; N, 12·7; Cl, 8·0%).

6-*Methoxy*-2 : 2-*dimethyl*-7 : 8-*benzochroman*-4-*one* 2 : 4-*Dinitrophenylhydrazone*.—The crude derivative, obtained by treating a warm ethanolic solution of 6-methoxy-2 : 2-dimethyl-7 : 8-benzochroman-4-one [6] with an excess of Brady's reagent, was purified by chromatography on alumina from benzene. Crystallisation from benzene afforded carmine plates, m. p. 292—293° (decomp.) alone or mixed with the 2 : 4-dinitrophenylhydrazone product from lapachenole (Found : C, 59·95; Cl, 4·45; N, 13·05%).

1-*Naphthyl* ββ-*Dimethylacrylate*.—α-Naphthol (5·25 g.), 3-methylbut-2-enoyl chloride (3·5 c.c.), and magnesium were refluxed in benzene (30 c.c.) for 1 hr., yielding the *ester*, b. p. 191—194°/13 mm., yellow prisms, m. p. 46—47° (4·33 g.) (Found : C, 79·5; H, 5·9. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%).

2 : 2-*Dimethyl*-7 : 8-*benzochroman*-4-*one*.—Naphthyl ββ-dimethylacrylate (4·3 g.) and aluminium chloride (4·5 g.) were heated together at 140—150° for 2½ hr. and after acidic decomposition and ether-extraction furnished a yellow oil, b. p. 172—184°/2 mm. (1·25 g.). The distillate was refluxed in ethanol (25 c.c.) and 3% hydrochloric acid (15 c.c.) for 24 hr. After evaporation of solvent, the residue was saturated with ammonium sulphate. The product was isolated with ether and chromatographed on alumina from benzene, affording the *chromanone* as a viscous oil (0·77 g.) (Found : C, 79·5; H, 5·9. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%). Its 2 : 4-dinitrophenylhydrazone formed red needles (from benzene), m. p. 279—280°, alone or mixed with the 6 : 6-dimethylnaphtho(1′ : 2′-2 : 3)pyran 2 : 4-dinitrophenylhydrazine derivative (Found : N, 13·75%).

1-*Hydroxy*-2-iso*valerylnaphthalene*.—α-Naphthol (14·4 g.) and *iso*valeryl chloride (13 c.c.), when refluxed for 1 hr., afforded 1-*naphthyl* iso*valerate*, b. p. 178°/12 mm. (10 g.) (Found : C, 79·1; H, 7·3. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%), which (10 g.) was heated with aluminium chloride (10 g.) for 2 hr. at 100° and then for 1 hr. at 120°. After decomposition with dilute acid and steam-distillation, the product was extracted with ether from the distillate. Evaporation and crystallisation from aqueous ethanol yielded 1-hydroxy-2-*iso*valerylnaphthalene as pale yellow needles, m. p. 63—64° (lit.,[11] m. p. 64—65°) (Found : C, 79·1; H, 7·3. Calc. for $C_{15}H_{16}O_2$: C, 78·9; H, 7·1%). The 2 : 4-*dinitrophenylhydrazone* crystallised from nitrobenzene as red needles, m. p. 242—244° (decomp.) (Found : N, 13·3. $C_{21}H_{20}O_5N_4$ requires N, 13·7%).

Preparation of Dimethylchromens and Dimethylnaphthopyrans.—The coumarin (0·05 mole) in dry benzene (200 c.c.) was added slowly (1½ hr.) to a stirred Grignard solution from methyl iodide (0·17 mole), magnesium (0·17 g.-atom), and ether (50 c.c.). The solution was refluxed for 1 hr. and set aside overnight. Decomposition with 22% ammonium chloride solution (150 c.c.) and extraction with ether gave an ethereal solution, which was washed with water and dried ($CaCl_2$). Removal of solvent and distillation gave the chromens and naphthopyrans. Picrates were prepared from methanolic solutions of the components.

6 : 6-*Dimethylnaphtho*(1′ : 2′-2 : 3)*pyran* (I*b*) (from 7 : 8-benzocoumarin [12]), b. p. 172—176°/15 mm. (55%) (Found : C, 85·5; H, 7·0. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%), gave a *picrate*, red needles, m. p. 123—125° (Found : N, 9·6. $C_{21}H_{17}O_8N_3$ requires N, 9·6%).

4 : 6 : 6-*Trimethylnaphtho*(1′ : 2′-2 : 3)*pyran* (I*d*) (from 4-methyl-7 : 8-benzocoumarin [13]), b. p. 182—184°/15 mm. (75%) (Found: C, 85·95; H, 7·4. $C_{16}H_{16}O$ requires C, 85·7;

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[11] Yuoh-Fong Chi and Cherng-Tsum Jung, *J. Amer. Chem. Soc.*, 1941, **63**, 3155.

[12] Dey, Rao, and Sankaranarayanan, *J. Indian Chem. Soc.*, 1932, **9**, 71.

H, 7·2%), gave a *picrate*, dark-red needles, m. p. 124—125° (Found: N, 9·2. $C_{22}H_{19}O_8N_3$ requires N, 9·3%).

4′-*Chloro*-6 : 6-*dimethylnaphtho*(1′ : 2′ : 2 : 3)*pyran* (I*c*) (from 6-chloro-7 : 8-benzocoumarin [14]) had b. p. 168—170°/15 mm., m. p. 52—54° (33%) (Found: C, 73·2; H, 5·9; Cl, 13·7. $C_{15}H_{13}OCl$ requires C, 73·6; H, 5·4; Cl, 14·5%).

7-*Methoxy*-2 : 2-*dimethylchromen* (from 7-methoxycoumarin [5]) had b. p. 140—141°/16 mm., n_D^{21} 1·5548 (44%) (Found: C, 75·4; H, 7·2. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

6-*Methoxy*-2 : 2-*dimethylchromen* (II*b*) (from 6-methoxycoumarin [15]) had b. p. 132—136°/15 mm., n_D^{19} 1·5558 (47%) (Found: C, 75·3; H, 7·1%).

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MUNICIPAL COLLEGE, BURNLEY.

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[13] Henry, Sandrock, and Robertson, *J.*, 1931, 2426.

[14] Chakravarti and Bagchi, *J. Indian Chem. Soc.*, 1936, **13**, 649.

[15] Ferd, Tiemann, and Muller, *Ber.*, 1881, **14**, 1996.