

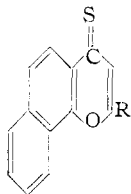
(1) A. Schönberg, A. Mustafa and G. Aziz, *THIS JOURNAL*, **76**, 4576 (1954).

III ($R = C_6H_5$). Succinic anhydride, however, does not add to 2-styryl-1,4- α -naphthopyrone.

When IIg was allowed to react with maleic anhydride, the expected addition product III ($R = \text{anisyl}$), insoluble in cold alkali, was obtained but not in an analytically pure state, probably due to a small amount of the corresponding dicarboxylic acid. The anhydride III ($R = \text{anisyl}$) was transformed to the corresponding dimethyl ester IIIb, which was obtained in a pure state.

When 2-styryl-1,4- α -naphthopyrone (IIf) was hydrolyzed with aqueous alkali, 1-hydroxy-2-acetonaphthalene and cinnamic acid were obtained on acidification.

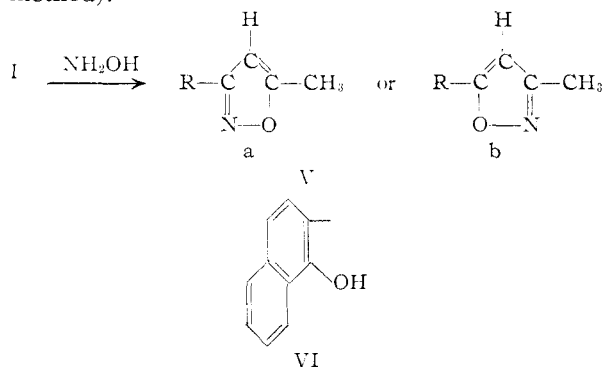
4-Thiochromones.—When I was treated with phosphorus pentasulfide IVa was obtained.



- IVa, $R = CH_3$
 b, $R = CH:CH \cdot C_6H_5$
 c, $R = CH:CHC_6H_4OCH_3-p$

IVa Condensed in the presence of piperidine³ with benzaldehyde or anisaldehyde giving IVb or IVc which are violet in color.

Action of Hydroxylamine Hydrochloride, Hydrazine Hydrate and Phenylhydrazine Hydrochloride on 2-Methyl-1,4- α -naphthopyrone.—Recently Schönberg and Sidky⁴ have shown that the 2-methylchromone derivative visnagin reacts with hydroxylamine hydrochloride in pyridine at the boiling point of the mixture to give an isoxazole derivative, we have found that the 2-methyl-1,4- α -naphthopyrone (I) reacts similarly leading to the isoxazole derivative Va or b ($R = VI$). The product gives a color reaction with ferric chloride (violet) indicating a free phenolic hydroxyl. It yields a monobenzoyl derivative (Schotten-Baumann method).

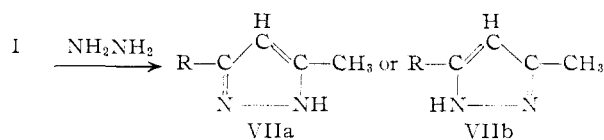


The action of hydrazine hydrate on 2-methyl-1,4- α -naphthopyrone (I) in alcohol leads to a pyrazole derivative⁵ VIIa or VIIb ($R = VI$). The product is soluble in aqueous alkali and gives a color reaction with ferric chloride (deep-green). The substance yielded a dibenzoyl derivative (Schotten-Baumann method).

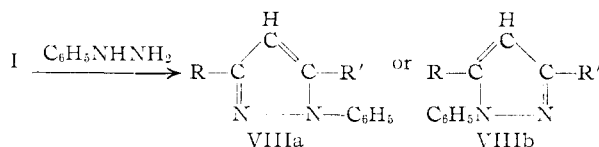
(3) For similar reactions of 2-methyl-4-thiochromones see A. Schönberg, M. M. Sidky and Aziz, *THIS JOURNAL*, **76**, 5115 (1954).

(4) A. Schönberg and M. Sidky, *ibid.*, **76**, 5128 (1953).

(5) A pyrazole derivative was also obtained when hydrazine hydrate was allowed to react with visnagin, A. Schönberg and M. Sidky, ref. 4.



The action of phenylhydrazine hydrochloride in pyridine on I leads to the pyrazole derivative VIIa or VIIb ($R = VI$, $R' = CH_3$), giving a color reaction with ferric chloride (violet).



The product obtained from phenylhydrazine hydrochloride and 2-styryl-1,4- α -naphthopyrone (IIf) (in the presence of pyridine) has the constitution VIIIa or VIIIb ($R = VI$, $R' = C_6H_5-CH=CH-$); it also gives a color reaction with ferric chloride (violet). The fact that these compounds give a ferric chloride reaction is indicative that they contain a free phenolic hydroxyl group. If the reactions between phenylhydrazine hydrochloride and I or IIf had led to their respective phenylhydrazones, the ferric chloride reaction would have been negative.

Experimental

Condensation of 2-Methyl-1,4- α -naphthopyrone (I) with Aromatic Aldehydes.—The 2-styrylchromone derivatives were obtained by the following general method. 2-Methyl-1,4- α -naphthopyrone (I)⁶ (one mole) was dissolved in a small quantity of absolute ethyl alcohol and treated at room temperature with an alcoholic solution of sodium ethoxide (one mole). The necessary aldehyde (one mole) was then added to the solution which was kept for 24 hr. at ordinary temperature. The yellow condensation product which usually separated out (compare IIa, IIb and IIc of Table I) was filtered off and purified by crystallization; in most cases a further amount of the condensation product was precipitated on dilution of the mother liquor with water. In some cases (IIc and IId) the condensation product was only precipitated on dilution of the reaction mixture with water.

Hydrolysis of 2-Styryl-1,4- α -naphthopyrone (IIf) (a).—IIf (2 g.) in aqueous sodium hydroxide (20%, 40 ml.) was refluxed for 20 hr. and allowed to cool; the filtrate was acidified (H_2SO_4) and the precipitate filtered off, washed with water and shaken with sodium carbonate solution. The residue (0.6 g.) was filtered off (giving filtrate A), crystallized from ethyl alcohol and proved by melting point and mixed melting point (103°) and the green color reaction with aqueous ferric chloride solution to be 1-hydroxy-2-acetonaphthalene. Filtrate A was acidified (H_2SO_4) and the deposit (0.4 g.), crystallized from ethyl alcohol, was proved (m.p. and mixed m.p. 133°) to be cinnamic acid.

(b).—Cinnamic acid (0.6 g.) and 1-hydroxy-2-acetonaphthalene (0.8 g.) were also obtained by refluxing IIIf (2 g.) with sodium ethoxide solution (obtained by dissolving 5 g. of sodium in 30 ml. of absolute ethyl alcohol) for 30 hr. After acidification the deposit formed was worked up as described previously.

Maleic Anhydride and (a) 2-Styryl-1,4- α -naphthopyrone (IIIf).—IIIf (1 g., 1 mole) and maleic anhydride (10 moles) in 30 ml. of dry xylene were refluxed for 15 hr. After concentration and cooling III ($R = C_6H_5$) separated out; it was washed with hot ethyl alcohol and crystallized from xylene as almost colorless crystals, m.p. 279° ; it dissolved in concentrated sulfuric acid with a pale yellow color and was insoluble in cold alkali; yield 70%.

Anal. Calcd. for $C_{25}H_{16}O_5$: C, 75.8; H, 4.0. Found: C, 76.1; H, 4.0.

(6) G. Wittig, Fr. Bangert and H. E. Richter, *Ann.*, **446**, 155 (1926).

TABLE I
 CONDENSATION OF 2-METHYL-1,4-NAPHTHOPYRONE WITH AROMATIC ALDEHYDES

Con- densation product ^a	Wt. of chro- mone, ^b g.	Wt. of alde- hyde, ^b g.	Solvent of crystalln.	M.p., °C. and color.	Yield, g., color react. with H ₂ SO ₄	Solubilities at room temp.	Formula	Analyses, %
IIa	1(A)	0.7(B)	Ethyl alc. or xylene	228 light yellow	0.7 yellow	Difficulty sol. in benzene or ben- zine (b.p. 100–120°)	C ₂₁ H ₁₃ ClO ₂	Calcd.: C, 75.8; H, 3.9 Found: C, 75.4; H, 3.9
IIb	1(A)	.6(C)	Dioxane or xylene	274–275 deep yellow	0.9 orange	Difficulty sol. in benzene, benzine (b.p. 100–120°) or ethyl alc.	C ₂₁ H ₁₃ NO ₄	Calcd.: N, 4.1 Found: N, 4.0
IIc	1(A)	.9(D)	Benzine (b.p. 100–120°)	168 yellow	0.5 orange	Easily sol. in ethyl alc. or benzene	C ₂₃ H ₂₂ O ₄	Calcd.: C, 77.7; H, 5.7 Found: C, 77.8; H, 6.0
IIId	1(A)	.6(E)	Dil. ethyl alc.	169 yellow	0.4 deep	Easily sol. in ben- zine or ethyl alc.	C ₂₃ H ₁₆ O ₂	Calcd.: C, 85.2; H, 4.9 Found: C, 85.0; H, 5.2
IIe	1(A)	.7(F)	Benzine (b.p. 100–120°) or ethyl alc.	232 yellow	0.6 orange	difficultly sol. in benzine (b.p. 100–120°) Sol. in benzene	C ₂₂ H ₁₄ O ₄	Calcd.: C, 77.2; H, 4.1 Found: C, 77.1; H, 4.2

^a IIa, 2-(1'-chloro-styryl)-1,4- α -naphthopyrone; IIb, 2-(4'-nitro-styryl)-1,4- α -naphthopyrone; IIc, 2-(3',4'-diethoxy-styryl)-1,4- α -naphthopyrone; IIId, 2-cinnamylidenemethylene-1,4- α -naphthopyrone; IIe, 2-(3',4'-methylenedioxystyryl)-1,4- α -naphthopyrone. ^b A, 2-Methyl-1,4- α -naphthopyrone; B, *o*-chlorobenzaldehyde; C, *p*-nitrobenzaldehyde; D, 3,4-diethoxybenzaldehyde; E, cinnamaldehyde; F, piperonal.

(b) 2-(*p*'-Methoxystyryl)-1,4- α -naphthopyrone (IIg).—IIg (1 g., 1 mole) and maleic anhydride (10 moles) in 30 ml. of dry xylene were refluxed for 15 hr. After concentration and cooling, the yellow reaction product was filtered off, washed with hot ethyl alcohol and crystallized from xylene; m.p. 286°, yield 70%. The addition product dissolved in concentrated sulfuric acid giving a yellow solution and was insoluble in cold alkali. III, R = *p*-C₆H₄OCH₃, (0.5 g.) was refluxed (50 minutes) with methanolic sodium hydroxide solution (1.5 g. in 18 ml. of methyl alcohol), filtered and the residue decomposed with hydrochloric acid. IIIa was soluble in sodium bicarbonate solution and was transformed into (IIIf) by dissolving in absolute methyl alcohol and passing a stream of dry hydrogen chloride through the solution for 2 hr. The mixture was then allowed to stand overnight. After concentration IIIf was obtained, by crystallization from methyl alcohol, as colorless crystals, m.p. 199°, insoluble in aqueous alkali and soluble in concentrated sulfuric acid with a yellow color.

Anal. Calcd. for C₂₈H₂₄O₇: C, 71.2; H, 5.1. Found: C, 71.1; H, 5.2.

Succinic Anhydride and 2-Styryl-1,4- α -naphthopyrone.—2-Styryl-1,4- α -naphthopyrone (1 g.) and succinic anhydride (4 g.) in 30 ml. of dry xylene were refluxed for 15 hr. After concentration and cooling the colorless crystals which separated were filtered (3.5 g.) and proved to be succinic anhydride by m.p. and mixed m.p.; on concentrating the mother liquor, the yellow solid which separated (0.8 g.) was proved to be 2-styryl-1,4- α -naphthopyrone by m.p. and mixed m.p.

2-Methyl-4-thio- α -naphthopyrone (IVa).—2-Methyl-4- α -naphthopyrone (1 g.) was refluxed with 1 g. of purified phosphorus pentasulfide⁷ in 30 ml. of dry benzene on a steam-bath for 2 hours. The hot deep red solution was filtered and the residue repeatedly extracted with boiling benzene. The combined extracts were evaporated to dryness. 2-Methyl-4-thio- α -naphthopyrone was crystallized from ethyl alcohol as violet red needles, m.p. 162°, which dissolved in concentrated sulfuric acid giving a yellow solution with green fluorescence; yield 80%.

Anal. Calcd. for C₁₄H₁₀O₂S: C, 74.3; H, 4.4; S, 14.1. Found: C, 74.5; H, 4.4; S, 14.3.

2-Styryl-4-thio- α -naphthopyrone (IVb).—2-Methyl-4-thio- α -naphthopyrone (1 g.) and benzaldehyde (0.5 g.) in 20 ml. of absolute ethyl alcohol containing 4 drops of piperidine were refluxed for 6 hr. The violet crystals that separated while refluxing were filtered and crystallized from benzene; m.p. 197°. They dissolved in concentrated sulfuric acid with an orange color; yield 0.8 g.

Anal. Calcd. for C₂₁H₁₄OS: C, 80.3; H, 4.4; S, 10.2. Found: C, 80.7; H, 4.5; S, 9.7.

(7) W. Baker, J. B. Harborne and W. D. Ollis, *J. Chem. Soc.*, 130 (1952).

2-(4'-Methoxystyryl)-4-thio- α -naphthopyrone (IVc).—From 2-methyl-4-thio- α -naphthopyrone (1 g.) and anisaldehyde (0.6 g.), as above, the violet solid that separated while refluxing was filtered and crystallized from benzene; m.p. 208°. It dissolved in concentrated sulfuric acid giving an orange solution; yield 0.9 g.

Anal. Calcd. for C₂₂H₁₆O₂S: C, 76.8; H, 4.6; S, 9.3. Found: C, 77.3; H, 4.7; S, 9.0.

2-Methyl-1,4- α -naphthopyrone and Hydroxylamine Hydrochloride.—A mixture of 0.12 g. of hydroxylamine hydrochloride in 0.5 ml. of water and 0.1 g. of 2-methyl-1,4- α -naphthopyrone in 1 ml. of pyridine was refluxed for 4 hr. The cooled mixture was acidified with dilute acetic acid, the deposit formed was filtered and crystallized from benzene as yellowish crystals, m.p. 181°. 2-[5(or 3)-Methyl-3(or 5)-isoxazolyl]-1-naphthol (Va or b, R = VI) is insoluble in water. The alcoholic solution gives a violet color with alcoholic ferric chloride solution and no color with concentrated sulfuric acid; yield 85%. It was recovered unchanged when its solution in aqueous 10% sodium hydroxide was refluxed for 1 hr. followed by cooling and acidification with dilute hydrochloric acid.

Anal. Calcd. for C₁₄H₁₁NO₂: C, 74.7; H, 4.9; N, 6.3. Found: C, 74.7; H, 5.1; N, 6.2.

Benzoylation.—To a solution of 0.5 g. of Va or b (R = VI) in 10 ml. of 10% sodium hydroxide (0.5 g.) of benzoyl chloride was added. The mixture was vigorously shaken for 15 minutes; the colorless solid (0.6 g.) that separated was filtered and crystallized from dilute ethyl alcohol; m.p. 126°. It is insoluble in aqueous sodium hydroxide (10%), gives no color with concentrated sulfuric acid, and its alcoholic solution gives no color with alcoholic ferric chloride solution.

Anal. Calcd. for C₂₁H₁₅NO₂: C, 76.6; H, 4.6; N, 4.2. Found: C, 76.4; H, 4.8; N, 4.3.

2-Methyl-1,4- α -naphthopyrone and Hydrazine Hydrate.—Hydrazine hydrate (50%) (5 g.) in 10 ml. of warm ethyl alcohol was added to a solution of 1 g. of 2-methyl-1,4- α -naphthopyrone in 10 ml. of ethyl alcohol and the mixture warmed for 15 minutes. The cooled mixture was diluted with water and the deposit formed was filtered and crystallized from benzene as colorless leaflets, m.p. 171°, yield 85%. 2-[5(or 3)-Methyl-3(or 5)-pyrazolyl]-1-naphthol (VIIa or VIIb, R = VI) gives a deep green color with alcoholic ferric chloride solution and no color with concentrated sulfuric acid. It dissolved in aqueous 10% sodium hydroxide solution.

Anal. Calcd. for C₁₄H₁₂ON₂: C, 75.0; H, 5.4; N, 12.5. Found: C, 75.3; H, 5.3; N, 12.5.

Benzoylation.—The general procedure for carrying out a Schotten-Baumann reaction was followed. The dibenzoyl derivative crystallized slowly from dilute alcohol as colorless crystals, m.p. 144–145°. It was insoluble in aqueous 10%

sodium hydroxide, dissolved in concentrated sulfuric acid giving a yellow solution and gave no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{25}H_{20}N_2O_3$: C, 77.8; H, 4.6; N, 6.5. Found: C, 77.6; H, 4.9; N, 6.5.

2-Methyl-1,4- α -naphthopyrone and Phenylhydrazine Hydrochloride.—A mixture of 0.7 g. of phenylhydrazine hydrochloride in 3 ml. of water and 1 g. of 2-methyl-1,4- α -naphthopyrone in 10 ml. of pyridine was refluxed for 4 hr. The cooled mixture was acidified with dilute acetic acid. The deposit was filtered and crystallized from benzene (b.p. 100–120°) as almost colorless crystals, m.p. 143°. 2-[1-Phenyl-5(or 3)-methyl-3(or 5)-pyrazolyl]-1-naphthol (VIIIa or VIIIb, R = VI, R' = $CH=CHC_6H_5$) was insoluble in water and its alcoholic solution gave a violet color with alcoholic ferric chloride solution; yield 85%.

Anal. Calcd. for $C_{26}H_{18}N_2O$: C, 80.0; H, 5.3; N, 9.3. Found: C, 80.3; H, 5.5; N, 9.1.

2-Styryl-1,4- α -naphthopyrone and Phenylhydrazine Hydrochloride.—The same procedure was followed with 2-styryl-1,4- α -naphthopyrone and the obtained 2-[1-phenyl-5(or 3)-styryl-3(or 5)-pyrazolyl]-1-naphthol (VIIIa or VIIIb, R = VI, R' = $CH=CHC_6H_5$) was crystallized from benzene (b.p. 100–120°), as almost colorless needles, m.p. 223° with decomposition. Its alcoholic solution gave a violet color with alcoholic ferric chloride solution; yield 80%.

Anal. Calcd. for $C_{27}H_{20}N_2O$: C, 83.5; H, 5.2; N, 7.2. Found: C, 83.1; H, 5.2; N, 7.4.

CAIRO, GIZA, EGYPT

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

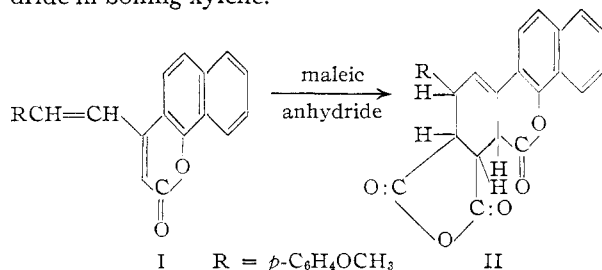
4-Styrylcoumarins in Diene Syntheses. II¹

BY AHMED MUSTAFA, MOHAMED KAMEL AND MOHAMED ALY ALLAM

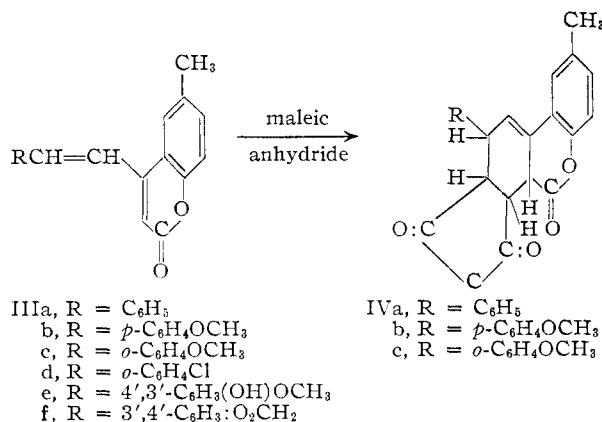
RECEIVED MARCH 19, 1956

Derivatives of 6H-dibenzo[b,d]pyran (IV, VI, IX and X), 5(6H)-oxachrysene (VIII and XI) may be obtained from 4-styrylcoumarins (III, V and VII) in the Diels-Alder reactions. An improved method for the preparation of 6-methylcoumarin-4-acetic acid, in satisfactory yield, is described. The new styryl derivatives of 4-coumarinacetic acid, used in this investigation, now have been prepared by condensation of the appropriate acid and aldehyde in the presence of pyridine and piperidine.

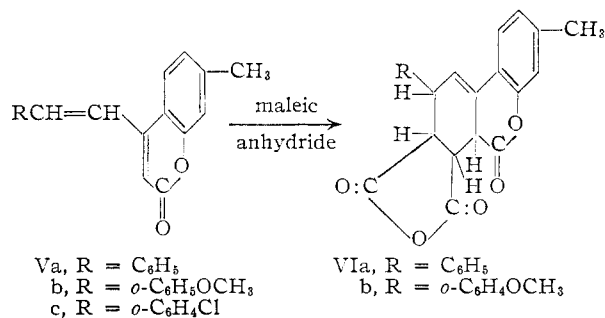
In Part I,¹ it has been shown that 4-styrylcoumarins can function as diene components in the Diels-Alder reaction, leading to easy formation of the 6H-dibenzo[b,d]pyran derivatives, *e.g.*, 6a,7,8,9-tetrahydro-6-oxo-9-(4'-methoxyphenyl)-5(6H)-oxachrysene-7,8-dicarboxylic anhydride (II) is obtained when *p*-methoxybenzylidene-4-(7,8-benzo)-coumarin (I) is allowed to react with maleic anhydride in boiling xylene.



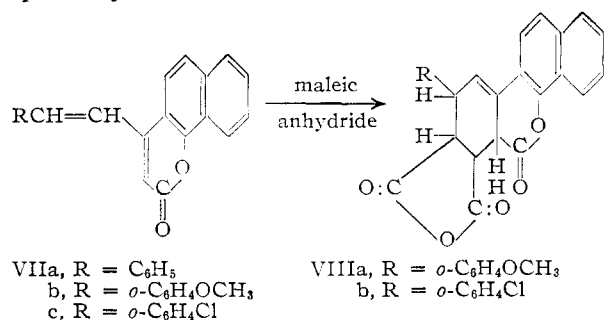
We now have extended our study and have found that similar reactions can be effected when 6-



methyl-4-styrylcoumarins (IIIa-c) and 7-methyl-4-styrylcoumarins (Va-b) are allowed to react with maleic anhydride in boiling xylene, leading by analogy to derivatives of 6H-dibenzo[b,d]pyran, IV and VI, respectively.



Similarly, the action of maleic anhydride on 4-styryl-(7,8-benzo)-coumarin derivatives (VIIb-c) leads to the formation of the adducts VIIIa-b, respectively.



The dienophilic reactivity of N-arylmaleimides now has been investigated.¹ Thus, when IIIa-c, and/or Va-b are allowed to react with the N-arylmaleimides used in this investigation, the adducts

(1) A. Mustafa and M. Kamel, *THIS JOURNAL*, **77**, 1828 (1955).