Anal. Calcd. for $C_{31}H_{50}O_4$: C, 76.50; H, 10.36. Found: C, 76.21; H, 10.10.

Acetylation of 88 mg. of the diol with acetic anhydride–pyridine at room temperature furnished 79 mg. of the corresponding **diacetate**, m.p. 252–259°, $[\alpha]^{26}D$ +31°.

Anal. Calcd. for $C_{35}H_{54}O_6$: C, 73.64; H, 9.54. Found: C, 73.32; H, 9.51.

The combined ether eluates weighed 256 mg. and after recrystallization from methanol gave 175 mg. of methyl machaerinate (VIa) (infrared comparison and undepressed mixture melting point) m.p. 231–234°, $[\alpha]^{27}D$ +78°. Acetylation (room temperature) of 70 mg. of this material led, after one recrystallization from ether, to 66 mg. of methyl diacetylmachaerinate (VIc), m.p. 278–280°; identity was established in the usual manner by mixture melting point and infrared comparison.

Attempts to establish a difference in the reactivity of the isomeric diols through the corresponding cathylates[16] were unsuccessful.

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[16] L. F. Fieser, J. E. Herz, M. W. Klohs, M. A. Romero and T. Utne, THIS JOURNAL, **74**, 3309 (1952).

DETROIT, MICHIGAN

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

4-Styrylcoumarins and 2,3-Dimethylquinoxaline in Diene Syntheses

BY AHMED MUSTAFA AND MOHAMED KAMEL

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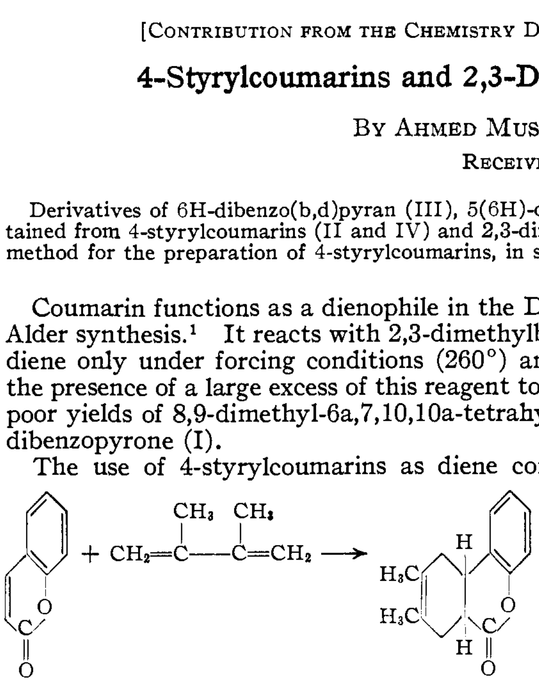
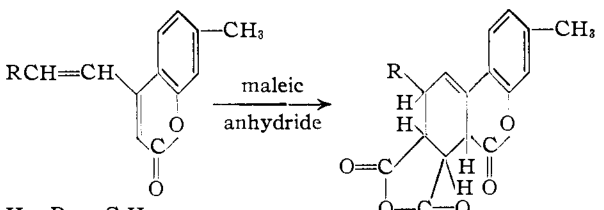
Derivatives of 6H-dibenzo(b,d)pyran (III), 5(6H)-oxachrysene (V) and hexahydrophenazine (XIa or XIb) may be obtained from 4-styrylcoumarins (II and IV) and 2,3-dimethylquinoxaline (IX) in the Diels–Alder reactions. An improved method for the preparation of 4-styrylcoumarins, in satisfactory yields, is described.

Coumarin functions as a dienophile in the Diels–Alder synthesis.[1] It reacts with 2,3-dimethylbutadiene only under forcing conditions (260°) and in the presence of a large excess of this reagent to give poor yields of 8,9-dimethyl-6a,7,10,10a-tetrahydrodibenzopyrone (I).

The use of 4-styrylcoumarins as diene components in the Diels–Alder reaction seems not to have been investigated.[2] We have now found that, in the heterocyclic series, the oxygen-containing 4-styryl-7-methylcoumarins (II) and 4-styryl-7,8-benzocoumarins (IV), having conjugated double bonds, one of which is part of the heterocyclic ring, show the diene behavior. They add dienophile components such as maleic anhydride. Thus, an easy formation of the 6H-dibenzo(b,d)pyran derivatives (III) is available, *e.g.*, IIIa is obtained when 4′-methoxy-4-styryl-7-methylcoumarin (IId) is allowed to react with maleic anhydride in boiling xylene. Similar results, leading to IIIb, were observed in the case of 4′-hydroxy-4-styryl-7-methylcoumarin (IIc).



I

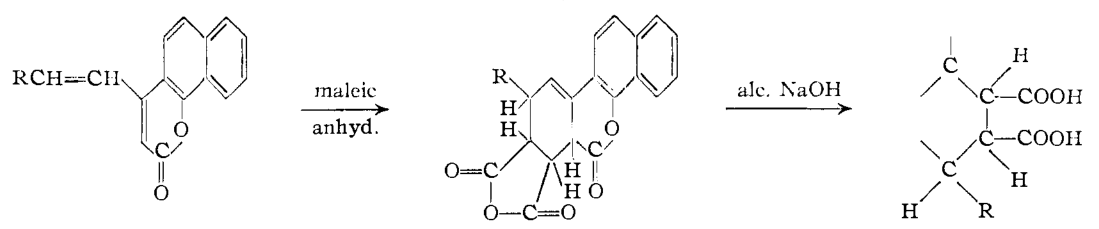


IIa, R = C_6H_5
b, R = p-$C_6H_4CH_3$
c, R = p-C_6H_4OH
d, R = p-$C_6H_4OCH_3$
e, R = 4′,3′-$C_6H_3(OH)OCH_3$
f, R = 3′,4′-C_6H_3:O_2CH_2

IIIa, R = p-$C_6H_4OCH_3$
b, R = p-C_6H_4OH

Similar reactions were carried out with 4-styryl-7,8-benzocoumarins (IVa, IVc and IVe), leading to derivatives of 5(6H)-oxachrysene (V), namely, Va–Vc, respectively.

The adducts obtained by these Diels–Alder syntheses are practically colorless and are insoluble in alkali. Treatment of adduct Vb with alcoholic sodium hydroxide and subsequent acidification yielded the corresponding alkali-soluble acid which was proved to be identical with the product obtained by the action of maleic acid on IVc. Treatment of the adduct acid with acetic anhydride regenerated Vb.



IVa, R = C_6H_5
b, R = p-$C_6H_4CH_3$
c, R = p-$C_6H_4OCH_3$
d, R = 4′,3′-$C_6H_3(OH)OCH_3$
e, R = 3′,4′-C_6H_3:O_2CH_2

Va, R = C_6H_5
b, R = p-$C_6H_4OCH_3$
c, R = 3′,4′-C_6H_3:O_2CH_2

VI
(abbreviated formula)

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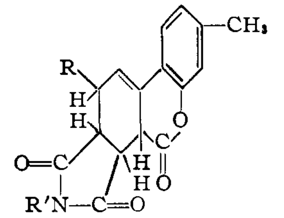
[1] R. Adams, W. D. McPhee, R. B. Carlin and Z. W. Wicks, THIS JOURNAL, **65**, 356 (1943); R. Adams and R. B. Carlin, *ibid.*, **65**, 360 (1943).

[2] *Cf.* The diene behavior of 2-styrylchromones toward dienophiles, *e.g.*, maleic anhydride (A. Schönberg, A. Mustafa and G. Aziz, *ibid.*, **76**, 4576 (1954).

We also have investigated the dienophilic reactivity of N-phenyl- and N-*p*-tolylmaleimide[3] toward II and IV. Thus, when IId was allowed to react with N-phenylmaleimide in boiling xylene VIIa was obtained. Similar results also were obtained by the action of N-phenylmaleimide on 4-styrylcoumarins (IIc and IId) and of N-*p*-tolylmaleimide on IId, leading to the adducts VIIb, VIIc and VIId, respectively.

4-Styryl-7,8-benzocoumarins (IVa-d) and N-phenyl- and N-*p*-tolylmaleimide, yielding the adducts VIIIa–h, respectively.

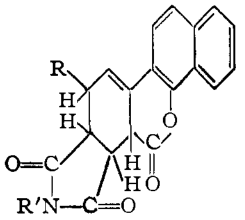


VIIa, R = *p*-$C_6H_4OCH_3$, R′ = C_6H_5

b, R = *p*-C_6H_4OH, R′ = C_6H_5

c, R = 4′,3′-$C_6H_3(OH)$-OCH_3, R′ = C_6H_5

d, R = *p*-$C_6H_4OCH_3$, R′ = *p*-$C_6H_4CH_3$



VIIIa, R = R′ = C_6H_5

b, R = *p*-$C_6H_4CH_3$, R′ = C_6H_5

c, R = *p*-$C_6H_4OCH_3$, R′ = C_6H_5

d, R = 4′,3′-$C_6H_3(OH)$-OCH_3, R′ = C_6H_5

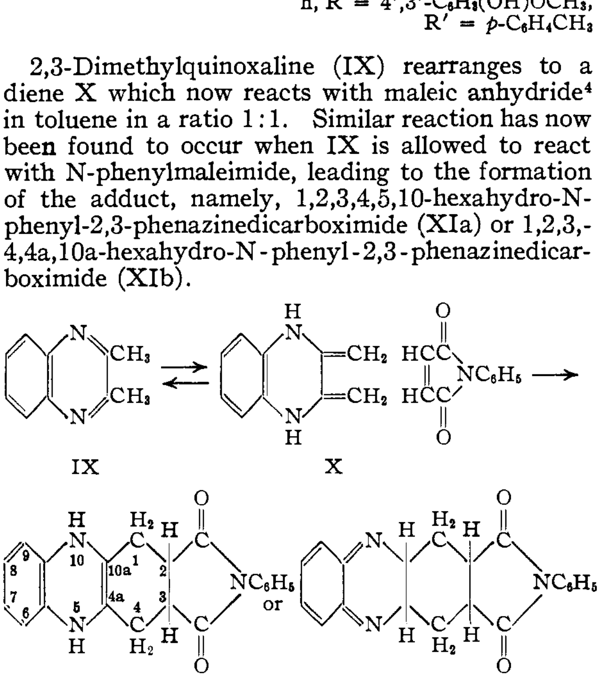
e, R = C_6H_5, R′ = *p*-$C_6H_4CH_3$

f, R = R′ = *p*-$C_6H_4CH_3$

g, R = *p*-$C_6H_4OCH_3$, R′ = *p*-$C_6H_4CH_3$

h, R = 4′,3′-$C_6H_3(OH)OCH_3$, R′ = *p*-$C_6H_4CH_3$

2,3-Dimethylquinoxaline (IX) rearranges to a diene X which now reacts with maleic anhydride[4] in toluene in a ratio 1:1. Similar reaction has now been found to occur when IX is allowed to react with N-phenylmaleimide, leading to the formation of the adduct, namely, 1,2,3,4,5,10-hexahydro-N-phenyl-2,3-phenazinedicarboximide (XIa) or 1,2,3,-4,4a,10a-hexahydro-N-phenyl-2,3-phenazinedicarboximide (XIb).



IX X

XIa XIb

Methods of Preparation.—Dey and Row[5] have shown that 7-methylcoumarin-4-acetic acid and 7,8-benzocoumarin-4-acetic acid condense with aromatic aldehydes in the presence of piperidine to give the corresponding 4-styrylcoumarins (II and IV), respectively, without reporting the yields. We now have found that when the condensation is carried out in the presence of pyridine and few drops of piperidine the new styryl derivatives (IIa, IIb, IIf and IVa, IVb and IVe), as well as the styryl derivatives formerly prepared by Dey and Row and used in this investigation, are obtained in satisfactory yields.

Experimental

Preparation of 4-Styrylcoumarins (II and IV). General Procedure.—To a mixture of the corresponding coumarin-4-acetic acid (0.02 mole) and the appropriate aldehyde (0.03 mole) in 30 ml. of dry pyridine was added 10 drops of freshly distilled piperidine. The reaction mixture was heated gradually at 125–130° (bath temp.) and kept to that temperature for six hours. After it was cooled, water was added dropwise until the formation of a slight turbidity. The reaction mixture was then kept aside (ice-chest) for a half-hour and the yellow styryl derivative was filtered off, washed with cold ethyl alcohol (*ca.* 30 ml.) and crystallized from a suitable solvent.

The 4-styryl-7-methyl- (IIa, IIb and IIf) and 4-styryl-7,8-benzocoumarins (IVa, IVb, IVd and IVe) are listed in Table I. In general, they are soluble in chloroform, hot benzene and xylene, but are sparingly soluble in light petroleum (b.p. 50–60°). Their yellow solutions in carbon tetrachloride decolorize readily the color of bromine solution in the same solvent.

IIc was obtained in 40% yield when 7-methylcoumarin-4-acetic acid was allowed to react with *p*-hydroxybenzaldehyde as described above, maintaining the temperature of the bath at 140°.

IId, IIe and IVc were obtained according to the above general procedure in 52, 42 and 63% yield, respectively.

Action of Maleic Anhydride on 4-Styrylcoumarins. General Procedure.—A solution of 0.5 g. of the styryl derivative and 1 g. of maleic anhydride in 20 ml. of dry xylene was refluxed for the number of hours indicated in Table II. The crystalline colorless solid, so obtained, was filtered off, washed with cold dry benzene (*ca.* 20 ml.) and crystallized from a suitable solvent.

The adducts of 4-styrylcoumarins and maleic anhydride are listed in Table II. In general, they are sparingly soluble in benzene and petroleum ether (b.p. 60–80°).

Opening of the Anhydride.—Sixty-six hundredths gram of Vb was dissolved in 24 ml. of methyl alcohol containing 1 g. of sodium hydroxide and the reaction mixture was refluxed for 15 minutes, during which time a red color was developed. It was filtered while hot and decomposed with ice-cold dilute hydrochloric acid, followed by filtration. After one hour standing 6a,7,8,9-tetrahydro-6-oxo-9-(4′-methoxyphenyl)-5(6H)-oxachrysene-7,8-dicarboxylic acid (VI) was crystallized from ethyl alcohol, m.p. 266° dec.; it is soluble in sodium bicarbonate solution, and is identical with the product obtained by the action of maleic acid on IVc (see below); yield *ca.* 0.45 g.

Reconversion to the Anhydride.—A solution of 0.5 g. of VI in 10 ml. of acetic anhydride was refluxed for four hours (calcium chloride tube). The crystals that separated on cooling and which were insoluble in sodium carbonate solution proved to be Vb (m.p. and mixed m.p.).

Action of Maleic Acid on IVc.—A mixture of 0.5 g. of IVc, 1 g. of maleic acid and 30 ml. of dry xylene was refluxed for six hours. The colorless crystals that separated after cooling were recrystallized from ethyl alcohol, m.p. 266° dec., yield *ca.* 90%. *Anal.* Calcd. for $C_{26}H_{20}O_7$: C, 70.3; H, 4.5. Found: C, 69.8; H, 4.4. The acid VI dissolves in sodium bicarbonate solution and gives a yellowish-green color with concentrated sulfuric acid.

Action of N-Phenyl- and N-*p*-Tolylmaleimide on 4-Styrylcoumarins.—The same procedure described in the case of maleic anhydride has been followed. A solution of 0.5 g. of the styryl derivative and 0.8 g. of the N-arylmaleimide in 20 ml. of dry xylene was refluxed for the time period (*cf.* Table III and IV), during which the yellow color of the solu-

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[3] *Cf.* the dienophilic reactivity of N-phenylmaleimide and its *p*-substituted derivatives toward 6,6-diphenylfulvene (H. D. Barnstorff and J. S. Meek, Division of Organic Chemistry of the American Chemical Society, abstracts of papers presented at Kansas City, Mo., March 23 to April 1, 1954, p. 29N).

[4] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 654 (1943).

[5] B. B. Dey and K. K. Row, *J. Indian Chem. Soc.*, **1**, 107, 277 (1924).

TABLE I

NEW 4-STYRYLCOUMARINS

4-Styryl-coumarins[a]	M.p.,[b] °C.	Color with H_2SO_4	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
IIa	130–131[c]	Yell.-green	33	$C_{16}H_{14}O_2$	82.4	82.0	5.3	5.1
IIb	186–187	Or.-red	45	$C_{19}H_{16}O_2$	82.6	82.2	5.8	5.7
IIf	208	Brown	45	$C_{19}H_{14}O_4$	74.5	74.0	4.6	4.5
IVa	176	Or.-red	62	$C_{21}H_{14}O_2$	84.6	84.2	4.7	4.7
IVb	212–213	Or.-red	65	$C_{22}H_{16}O_2$	84.6	84.4	5.1	5.0
IVd	212	Brown	65	$C_{22}H_{16}O_4$	76.8	76.6	4.6	4.6
IVe	196	Brown	45	$C_{22}H_{14}O_4$	77.2	76.7	4.1	4.1

[a] Unless otherwise mentioned, the styrylcoumarins were crystallized from glacial acetic acid. [b] All melting points are uncorrected. [c] The product was crystallized from ethyl alcohol.

TABLE II

ADDUCTS FROM MALEIC ANHYDRIDE

4-Styryl-coumarins	Adducts	Heating time, hr.	Solvent for crystn.[c]	Color with H_2SO_4	M.p.,[a] °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
IId	IIIa	3	A	None	248	92	$C_{23}H_{16}O_6$	70.8	70.8	4.6	4.6
IIc	IIIb[b]	3	B	None	322	81	$C_{22}H_{16}O_6$	70.2	69.8	4.2	4.1
IVa	Va	5	B	Yellow	268	90	$C_{25}H_{16}O_5$	75.7	75.6	4.0	4.1
IVc	Vb	2	C	Yell.-green	274	94	$C_{26}H_{18}O_6$	73.3	73.0	4.2	4.3
IVe	Vc	3	D	Yellow	260	71	$C_{26}H_{16}O_7$	70.9	70.4	3.6	3.6

[a] All melting points are uncorrected; and the products melt with decomposition. [b] The product is soluble in aqueous sodium hydroxide solution. [c] A, xylene; B, nitrobenzene; C, acetic anhydride; D, glacial acetic acid.

TABLE III

ADDUCTS FROM N-PHENYLMALEIMIDE

4-Styryl-coumarins	Adduct	Heating time, in hr.	Solvent for crystn.[a]	M.p.,[b] °C.	Color with H_2SO_4	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
IIa	VIIa	3	A	305	None	80	$C_{29}H_{23}NO_5$	74.8	74.4	4.9	4.9	3.0	3.1
IIb	VIIb[c]	3	B	322	None	62	$C_{26}H_{21}NO_5$	74.5	74.4	4.7	4.6	3.1	3.1
IIc	VIIc[cd]	4	C	272	Pale yell.	60	$C_{29}H_{23}NO_6$	72.3	72.0	4.8	4.6	2.9	2.8
IVa	VIIIa	5	B	308	Yellow	92	$C_{31}H_{21}NO_4$	79.0	79.1	4.5	4.2	3.0	3.0
IVb	VIIIb	5	B	312	Yellow	89	$C_{32}H_{23}NO_4$	79.2	79.3	4.7	4.4	2.9	3.0
IVc	VIIIc	3	C	318–319	Yellow	95	$C_{32}H_{23}NO_5$	76.6	76.4	4.6	4.6	2.8	2.9
IVd	VIIId	4	B	296	Gr.-yellow	62	$C_{32}H_{23}NO_6$	74.3	74.2	4.4	4.4	2.7	2.7

[a] A, chloroform; B, xylene; C, nitrobenzene. [b] All melting points are uncorrected; the adducts melt with decomposition. [c] The adduct is soluble in aqueous sodium hydroxide. [d] Alcoholic solution of the adduct gives light-green color with alcoholic ferric chloride solution.

TABLE IV

ADDUCTS FROM N-*p*-TOLYLMALEIMIDE

4-Styryl-coumarins	Adduct	Heating time, in hr.	Solvent for crystn.[a]	M.p.,[b] °C.	Color with H_2SO_4	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
IId	VIId	3	A	270–271	Yellow	81	$C_{30}H_{25}NO_5$	75.2	74.8	5.2	5.0	2.9	3.0
IVa	VIIIe	4	B	286	Yell.-green	84	$C_{32}H_{23}NO_4$	79.2	79.1	4.7	4.7	2.9	2.6
IVb	VIIIf	3	B	304	Pale yell.	90	$C_{33}H_{25}NO_4$	79.4	79.0	5.0	4.8	2.8	2.8
IVc	VIIIg	3	A	308	Yellow	87	$C_{33}H_{25}NO_5$	76.9	76.9	4.9	5.0	2.7	2.7
IVd	VIIIh	3	B	290	Yellow	63	$C_{33}H_{25}NO_6$	74.6	74.3	4.7	4.5	2.6	2.7

[a] A, Dioxane; B, xylene. [b] All melting points are uncorrected.

tion was almost discharged and the separation of the adduct took place.

The adducts with N-phenyl- and N-*p*-tolylmaleimide are listed in Tables III and IV, respectively.

Action of N-Phenylmaleimide on 2,3-Dimethylquinoxaline (IX).—Five-tenths gram of IX[6] and 0.5 g. of N-phenylmaleimide in 15 ml. of dry xylene were refluxed for six hours. The mixture was left overnight and on concentration almost colorless crystals were separated, which upon recrystallization from a mixture of benzene and light petroleum gave colorless crystals (0.12 g.), m.p. 184°. *Anal.* Calcd. for $C_{20}H_{17}N_3O_2$: C, 72.5; H, 5.1; N, 12.7. Found: C, 72.5; H, 5.0; N, 12.7. XIa or XIb is easily soluble in benzene and xylene, difficultly soluble in light petroleum, and gives a yellow color with concentrated sulfuric acid.

GIZA, CAIRO, EGYPT

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(6) S. Gabriel and A. Sonn, *Ber.*, **40**, 4852 (1907).