

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

Anal. Calcd. for $C_{28}H_{20}N_2O_3$: 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=CHC₆H₅) was insoluble in water and its alcoholic solution gave a violet color with alcoholic ferric chloride solution; yield 85%.

Anal. Calcd. for $C_{20}H_{16}N_2O$: 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=CHC₆H₅) 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]

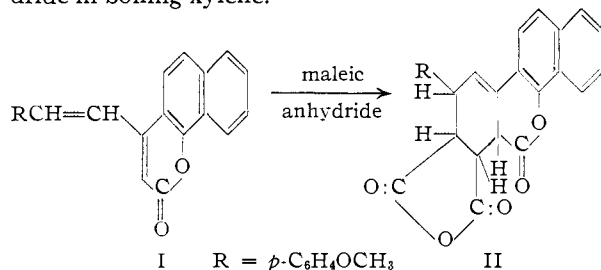
4-Styrylcoumarins in Diene Syntheses. II¹

BY AHMED MUSTAFA, MOHAMED KAMEL AND MOHAMED ALY ALLAM

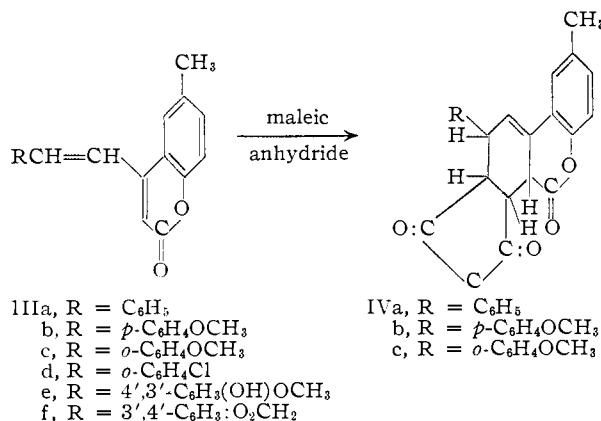
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Derivatives of 6H-dibenzo[b,d]pyran (IV, VI, IX and X), 5(6H)-oxachrysene (VIII and XI) may be obtained from 4-styrylcoumarins (III, V and VII) in the Diels-Alder reactions. An improved method for the preparation of 6-methylcoumarin-4-acetic acid, 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.

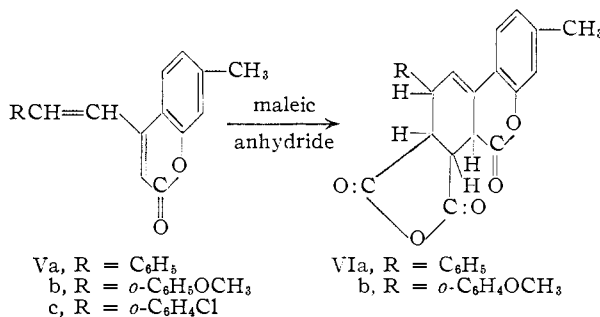
In Part I,¹ it has been shown that 4-styrylcoumarins can function as diene components in the Diels-Alder reaction, leading to easy formation of the 6H-dibenzo[b,d]pyran derivatives, *e.g.*, 6a,7,8,9-tetrahydro-6-oxo-9-(4'-methoxyphenyl)-5(6H)-oxachrysene-7,8-dicarboxylic anhydride (II) is obtained when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



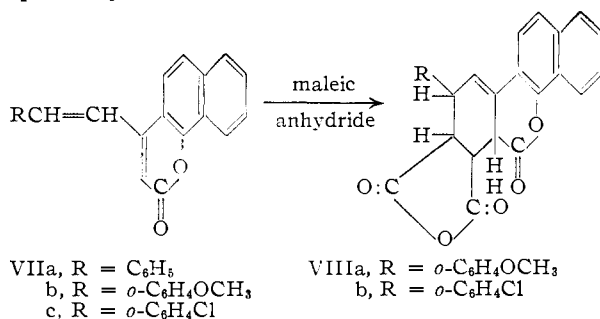
We now have extended our study and have found that similar reactions can be effected when 6-



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).

TABLE I
 NEW 4-STYRYLCOUMARINS

4-Styryl-coumarin	M.p., ^a °C.	Yield, %	Solvent for cryst. ^b	Color with H ₂ SO ₄	Formula	Carbon		Analyses, % Hydrogen		Chlorine	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	133	40	A	Yellow	C ₁₈ H ₁₄ O ₂	82.42	82.29	5.38	5.19		
IIIb	164	45	B	Or.-red	C ₁₉ H ₁₆ O ₃	78.08	77.89	5.48	5.32		
IIIc	194	60	C	Or.-red	C ₁₉ H ₁₆ O ₃	78.08	77.75	5.48	5.28		
IIId	210	50	C	Yellow	C ₁₉ H ₁₃ ClO ₂	72.85	72.76	4.38	4.11	11.97	11.58
IIIe	150	30	A	Or.-red	C ₁₉ H ₁₆ O ₄	74.04	73.94	5.19	4.95		
IIIf	218	20	D	Or.-red chang- ing to brown	C ₁₉ H ₁₄ O ₄	74.45	74.41	4.60	4.46		
Vb	145	60	E	Orange	C ₁₉ H ₁₆ O ₃	78.08	77.83	5.48	5.35		
Vc	168	35	F	Yellow	C ₁₉ H ₁₃ ClO ₂	72.85	72.42	4.38	4.16	11.97	11.46
VIIb	178	65	C	Orange	C ₂₂ H ₁₆ O ₃	80.48	80.18	4.87	4.75		
VIIc	210	50	C	Orange	C ₂₁ H ₁₃ ClO ₂	75.78	75.62	3.91	3.75	10.67	10.48

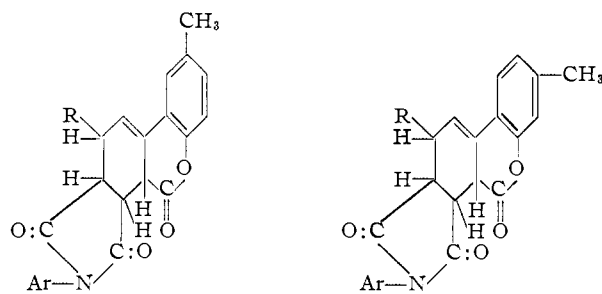
^a Melting points are uncorrected. ^b A, petroleum ether (b.p. 80–100°); B, petroleum ether (b.p. 100–120°); C, acetic acid; D, benzene; E, a mixture of benzene and light petroleum (b.p. 40–60°); F, ethyl alcohol.

 TABLE II
 ADDUCTS FROM MALEIC ANHYDRIDE

4-Styryl-coumarin	Adduct	Heating time, hr.	Solvent for cryst. ^a	M.p., ^b °C.	Yield, %	Color with H ₂ SO ₄	Formula	Analyses, % Carbon		Analyses, % Hydrogen	
								Calcd.	Found	Calcd.	Found
IIIa	IVa	5	A	194	50	None	C ₂₂ H ₁₆ O ₅	73.32	73.11	4.48	4.35
IIIb	IVb	4	A	238	78	None	C ₂₃ H ₁₈ O ₆	70.76	70.54	4.65	4.61
IIIc	IVc	6	B	249	85	Yellow	C ₂₃ H ₁₈ O ₆	70.76	70.61	4.65	4.48
Va	VIa	4	A	250	70	Pale-yell.	C ₂₂ H ₁₆ O ₅	73.32	73.18	4.48	4.39
Vb	VIb	7	A	244	90	Yell.-brown	C ₂₃ H ₁₈ O ₆	70.76	70.57	4.65	4.47
VIIb	VIIIa	6	A	321	80	Yellow ^c	C ₂₆ H ₁₈ O ₆	73.23	73.14	4.26	4.12
VIIc	VIIIb	8	C	300	75	Yellow ^c	C ₂₅ H ₁₅ ClO ₅ ^d	69.69	69.51	3.48	3.32

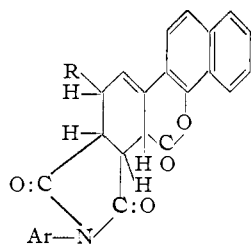
^a A, acetic anhydride; B, xylene; C, nitrobenzene. ^b All melting points are uncorrected. ^c The yellow solution in sulfuric acid acquires deep green fluorescence. ^d Calcd.: Cl, 8.24. Found: Cl, 8.10.

IX and X are obtained. Similarly, VIIa-b form the adducts XIa-c when treated with N-arylmaleimides.



IXa, Ar = R = C₆H₅
 b, R = *p*-C₆H₄OCH₃,
 Ar = C₆H₅
 c, R = *o*-C₆H₄OCH₃,
 Ar = C₆H₅
 d, R = C₆H₅,
 Ar = *p*-C₆H₄CH₃
 e, R = *p*-C₆H₄OCH₃, Ar = *p*-C₆H₄CH₃
 f, R = *o*-C₆H₄OCH₃, Ar = *p*-C₆H₄CH₃
 g, R = C₆H₅, Ar = 2',4'-C₆H₃(CH₃)₂
 h, R = *p*-C₆H₄OCH₃, Ar = 2',4'-C₆H₃(CH₃)₂

Xa, R = Ar = C₆H₅
 b, R = *o*-C₆H₄OCH₃,
 Ar = C₆H₅
 c, R = C₆H₅,
 Ar = *p*-C₆H₄CH₃
 d, R = *o*-C₆H₄OCH₃,
 Ar = *p*-C₆H₄CH₃



XIa, R = *o*-C₆H₄OCH₃,
 Ar = C₆H₅
 b, R = *o*-C₆H₄OCH₃,
 Ar = *p*-C₆H₄CH₃
 c, R = CH₃,
 Ar = 2',4'-C₆H₃(CH₃)₂

The adducts obtained by these Diels-Alder syn-

theses are practically colorless and are insoluble in alkali.

Methods of Preparation.—The 6-methylcoumarin-4-acetic acid needed in this investigation now has been prepared in 65% yield by adopting the procedure of Dey and Row² for the preparation of coumarin-4-acetic acid.

The new styryl derivatives, listed in Table I, have been prepared by allowing the 4-coumarinacetic acid derivatives to condense with the appropriate aldehyde in the presence of pyridine and a few drops of piperidine.¹

Experimental

Preparation of 4-Styrylcoumarins. 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 freshly distilled pyridine was added 10 drops of freshly distilled piperidine. The reaction mixture was heated gradually to 125–130° (bath temp.) and kept at that temperature for six hours. After it was cooled, water was added dropwise until the solution became slightly turbid. The reaction mixture was then cooled (ice-chest) for half an 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-6-methyl-(IIIa-f), 4-styryl-7-methyl-(Vb-c) and 4-styryl-7,8-benzocoumarins (VIIb-c) are listed in Table I. In general, they are soluble in chloroform, hot benzene and xylene, but are sparingly soluble in light petroleum ether (b.p. 50–60°). Their yellow solutions in carbon tetrachloride decolorize readily bromine in the same solvent.

Action of Maleic Anhydride on 4-Styrylcoumarins.—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

(2) B. B. Dey and K. K. Row, *J. Indian Chem. Soc.*, **1**, 107 (1927).

TABLE III
 ADDUCTS FROM N-PHENYLMALEIMIDE

4-Styryl-coumarin	Adduct	Heat- ing time, hr.	Sol- vent for cryst. ^a	M.p., °C. ^b	Yield, %	Color with H ₂ SO ₄	Formula	Carbon		Analyses, % Hydrogen		Nitrogen	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	IXa	4	A	274	90	Pale-yell.	C ₂₅ H ₂₁ NO ₄	77.22	76.89	4.85	4.71	3.22	3.12
IIIb	IXb	5	B	296	92	None	C ₂₉ H ₂₃ NO ₅	74.82	74.73	4.98	4.82	3.01	2.97
IIIc	IXc	6	C	215	95	Green	C ₂₉ H ₂₃ NO ₅	74.82	74.65	4.98	4.81	3.01	2.78
Va	Xa	5	D	282	85	None	C ₂₃ H ₂₁ NO ₄	77.22	77.18	4.85	4.81	3.22	3.06
Vb	Xb	10	E	186	40	Yellow	C ₂₉ H ₂₃ NO ₅	74.82	74.73	4.98	4.79	3.01	2.86
VIIb	XIa	8	F	215	70	Yellow	C ₃₂ H ₂₅ NO ₅	76.63	76.48	4.62	4.51	2.81	2.57

^a A, dioxane; B, nitrobenzene; C, phenetole; D, benzene; E, a mixture of benzene and ether; F, xylene. ^b All melting points are uncorrected. ^c The yellow solution in sulfuric acid acquires green fluorescence.

 TABLE IV
 ADDUCTS FROM N-*p*-TOLYLMALEIMIDE

4-Styryl-coumarin	Adduct	Heat- ing time, hr.	Sol- vent for cryst. ^a	M.p., ^b °C.	Yield, %	Color with H ₂ SO ₄	Formula	Carbon		Analyses, % Hydrogen		Nitrogen	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	IXd	5	A	214	80	None	C ₂₉ H ₂₅ NO ₄	77.48	77.26	5.16	5.07	3.12	2.98
IIIb	IXe	4	A	276	90	None	C ₃₀ H ₂₅ NO ₅	75.14	74.98	5.26	5.11	2.92	2.79
IIIc	IXf	12	B	198	40	None	C ₂₆ H ₂₅ NO ₅	75.14	74.79	5.26	5.09	2.92	2.81
Va	Xc	5	C	286	82	None	C ₂₉ H ₂₅ NO ₄	77.48	77.33	5.16	5.13	3.12	3.05
VIIb	XIb	6	C	234-235	60	Orange ^c	C ₃₃ H ₂₅ NO ₅	76.88	76.87	4.89	4.87	2.72	3.01

^a A, nitrobenzene; B, benzene; C, phenetole. ^b All melting points are uncorrected. ^c The orange color turns yellow with green fluorescence after some time.

 TABLE V
 ADDUCTS FROM N-2,4-DIMETHYLPHENYLMALEIMIDE^a

4-Styryl-coumarin	Adduct	Heat- ing time, hr.	Sol- vent for cryst. ^b	M.p., ^c °C.	Yield, %	Color with H ₂ SO ₄	Formula	Carbon		Analyses, % Hydrogen		Nitrogen	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	IXg	5	A	264	90	Pale-yell.	C ₃₀ H ₂₅ NO ₄	77.73	77.58	5.44	5.32	3.02	2.91
IIIb	IXh	6	B	296	95	Brown	C ₃₁ H ₂₇ NO ₅	77.97	77.68	5.70	5.56	2.93	2.76
VIIa	XIc	4	C	330	93	Yellow	C ₃₃ H ₂₅ NO ₄	79.34	79.14	5.04	4.91	2.80	2.66

^a The preparation of A. Mustafa, S. M. A. D. Zayed and S. A. Khattab, *THIS JOURNAL*, **78**, 145 (1956), was used. ^b A, a mixture of chloroform and light petroleum ether (b.p. 40-60°), B, dioxane; C, chloroform. ^c All melting points are uncorrected.

are listed in Table II. In general, they are sparingly soluble in benzene and petroleum ether (b.p. 60-80°).

Action of N-Arylmaleimides 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.* Tables III, IV

and V), during which the yellow color of the solution was almost discharged and the separation of the adduct took place.

The adducts with N-phenyl-, N-*p*-tolyl- and N-2,4-dimethylphenylmaleimide are listed in Tables III, IV and V, respectively.

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