Anal. Calcd. for C₃₁H₅₀O₄: C, 76.50; H, 10.36. Found: C, 76.21; H, 10.10.

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

Anal. Caled. for C₃₈H₈₄O₆: 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 cathylates¹⁶ were unsuccessful.

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

DETROIT, MICHIGAN

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

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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 compo-



nents in the Diels–Alder reaction seems not to have been investigated.² We have now found that, in the heterocyclic series, the oxygen-containing 4styryl-7-methylcoumarins (II) and 4-styryl-7,8benzocoumarins (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).

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.



(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-tolylmaleimide³ 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 Nphenyl- and N-p-tolylmaleimide, yielding the adducts VIIIa-h, respectively.



2,3-Dimethylquinoxaline (IX) rearranges to a diene X which now reacts with maleic anhydride⁴ 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-Nphenyl-2,3-phenazinedicarboximide (XIa) or 1,2,3,-4,4a,10a-hexahydro-N-phenyl-2,3-phenazinedicarboximide (XIb).



Methods of Preparation.—Dey and Row⁵ have shown that 7-methylcoumarin-4-acetic acid and

(3) Cf. the dienophilic reactivity of N-phenylmaleimide and its psubstituted 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).

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-Styrvlcoumarins (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 tem-perature 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 petro-leum (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-4acetic 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. Gen-eral Procedure.—A solution of 0.5 g. of the styryl deriva-tive 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-

		SH I STIC	Deo oninitarito					
M.p., b °C.	Color with H2SO4	Yield, %	Formula	Carbo Calcd.	on, % Found	Hydro Caled.	en, % Found	
130-131°	Yellgreen	33	$C_{18}H_{14}O_2$	82.4	82.0	5.3	5.1	
186 - 187	Orred	45	$C_{19}H_{16}O_2$	82.6	82.2	5.8	5.7	
208	Brown	45	$C_{19}H_{14}O_{4}$	74.5	74.0	4.6	4.5	
176	Orred	62	$C_{21}H_{14}O_2$	84.6	84.2	4.7	4.7	
212 - 213	Orred	65	$C_{22}H_{16}O_2$	84.6	84.4	5.1	5.0	
212	Brown	65	$C_{22}H_{16}O_{4}$	76.8	76.6	4.6	4.6	
196	Brown	45	$C_{22}H_{14}O_4$	77.2	76.7	4.1	4.1	
	M.p., b °C. 130–131 ^c 186–187 208 176 212–213 212 196	M.p.,b Color with H ₂ SO ₄ 130-131° Yellgreen 186-187 Orred 208 Brown 176 Orred 212-213 Orred 212 Brown 196 Brown	M.p.,b Color with H ₁ SO ₄ Yield, % 130-131° Yellgreen 33 186-187 Orred 45 208 Brown 45 176 Orred 62 212-213 Orred 65 212 Brown 65 196 Brown 45	$\begin{array}{c ccccc} M.p.,b & Color with \\ H_2SO_4 & Yield, \\ H_2SO_4 & \% & Formula \\ 130-131^c & Yellgreen & 33 & C_{18}H_{14}O_2 \\ 186-187 & Orred & 45 & C_{19}H_{16}O_2 \\ 208 & Brown & 45 & C_{19}H_{14}O_4 \\ 176 & Orred & 62 & C_{21}H_{14}O_2 \\ 212-213 & Orred & 65 & C_{22}H_{16}O_2 \\ 212 & Brown & 65 & C_{22}H_{16}O_4 \\ 196 & Brown & 45 & C_{22}H_{10}O_4 \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	

TABLE I

^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.

I ABLE II

Adducts from Maleic Anhydride

4-Styryl- coumarins	Adducts	Heat- ing time, hr.	Sol- vent for crystn.°	Color with H2SO4	M.p., ª °C.	Yield, %	Formula	Carb Caled.	on, % Found	Hydro Caled.	gen, % Found
IId	IIIa	3	Α	None	248	92	$C_{23}H_{18}O_{6}$	70.8	70.8	4.6	4.6
IIc	IIIb	3	в	None	322	81	$C_{22}H_{16}O_6$	70.2	69.8	4.2	4.1
IVa	Va	5	в	Yellow	268	90	$C_{25}H_{1\ell}O_5$	75.7	75.6	4.0	4.1
IVc	Vb	2	C	Yellgreen	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

• 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	ing time, in hr.	vent for crystn. ^a	M.p., ^b °C.	Color with H2SO4	Vield, %	Formula	Carb Caled.	on, % Found	Hydro Calcd.	gen, % Found	Nitro Caled.	gen, % Found
IIa	VIIa	3	Α	305	None	80	$C_{29}H_{23}NO_5$	74.8	74.4	4.9	4.9	3.0	3.1
IIb	VIIb ^e	3	в	322	None	62	$C_{28}H_{21}NO_5$	74.5	74.4	4.7	4.6	3.1	3.1
IIc	VIIc ^{cd}	4	С	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	в	308	Yellow	92	$C_{31}H_{21}NO_4$	79.0	79.1	4.5	4.2	3.0	3.0
IVb	VIIIb	5	в	312	Yellow	89	$C_{32}H_{23}NO_4$	79.2	79.3	4.7	4.4	2.9	3.0
IVe	VIIIc	3	С	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	в	296	Gryellow	62	$C_{32}H_{23}\mathrm{NO}_6$	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

						- 1							
4-Styryl- coumarins	Adduct	Heat- ing time, in hr.	Sol- vent for crystn. ^a	M.p., ^b °C.	Color with H ₂ SO ₄	Yield, %	Formula	Carb Caled.	on, % Found	Hydro Caled.	gen, % Found	Nitro Caled.	ogen, % Found
IId	VIId	3	Α	270 - 271	Yellow	81	$C_{\rm 30}H_{\rm 25}NO_5$	75.2	74.8	5.2	5.0	2.9	3.0
IVa	VIIIe	4	в	286	Yellgreen	84	$C_{32}H_{23}NO_4$	79.2	79.1	4.7	4.7	2.9	2.6
IVb	VIIIf	3	в	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	Α	308	Yellow	87	$C_{33}H_{25}NO_5$	76.9	76.9	4.9	5.0	2.7	2.7
IVd	VIIIh	3	в	290	Yellow	63	$C_{33}H_{25}\mathrm{NO}_6$	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.

Heat. Sol.

The adducts with N-phenyl- and N-p-tolylmaleimide are listed in Tables III and IV, respectively. Action of N-Phenylmaleimide on 2,3-Dimethylquinoxa-

Action of N-Phenylmaleimide on 2,3-Dimethylquinoxaine (IX).—Five-tenths gram of IX⁶ and 0.5 g. of N-phenylmaleimide in 15 ml. of dry xylene were refluxed for six hours.

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

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 $C_{20}H_{17}N_8O_2$: 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.

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