

When quinacetophenone was condensed with an equimolar amount of benzaldehyde in the presence of aqueous alkali, 6-hydroxyflavanone (II) was again found to be the chief product.<sup>13</sup> But a paper chromatographic study of the reaction (which was complete in three to four days at room temperature) revealed the presence of 2',5'-dihydroxychalcone (III) and the new by-product, 6-hydroxy-3-benzylidene flavanone (IV). With the 1:1 gram ratio of aldehyde to acetophenone suggested by Vyas and Shah<sup>14</sup> IV was often the chief crystallizable product. In fact, we propose that the yellow material, m.p. 215°, designated by them as the chalcone III was the by-product IV.<sup>15</sup> We obtained red-orange crystals, m.p. 173°, in less than a 10% yield which was shown to be the chalcone by the absorption spectrum and by conversion to II.<sup>16</sup> The structure of the by-product IV was confirmed by its synthesis from II and benzaldehyde in both acidic and basic media.

The ultraviolet and infrared absorption spectra of IV reveals its hybrid character, since they resemble both those of chalcones and flavanones. A Fisher-Hirschfelder model shows that the  $\alpha,\beta$ -unsaturated ketonic group is held rigidly in IV (unlike the situation of free rotation in chalcones) by the superimposed  $\gamma$ -pyrone ring and that steric hindrance between the two "B" phenyl rings prevents planarity of the carbonyl and ethylenic linkages. As a result, IV is lighter in color than III and has the carbonyl band at 1670  $\text{cm}^{-1}$  in the infrared, resembling that of II not of III.

#### Experimental<sup>17</sup>

**General Conditions of Reaction.**—Quinacetophenone (1–3-g. samples) and benzaldehyde were dissolved in 95% alcohol (7–60 ml.) and cooled. Simultaneously the mixture was flushed with nitrogen and 40% aqueous potassium hydroxide (7–30 ml.) was added slowly. The flask was tightly stoppered and allowed to stand 3–4 days at room temperature or in the refrigerator; paper chromatography was used to determine the disappearance of quinacetophenone. The ruby-red reaction mixture was then acidified and the resulting precipitate washed free of benzoic acid with saturated bicarbonate.

**6-Hydroxyflavanone (II)** was obtained as the main product (32.5%) when a mole to mole ratio of benzaldehyde to quinacetophenone was employed and concentrated hydrochloric acid was used to precipitate the yellow product. After repeated recrystallizations from 95% alcohol, the last traces of yellow color (due to III) were removed from this material by passing it through a column packed with a washed<sup>18</sup>

mixture of nylon<sup>19</sup> powder and Celite<sup>20,21</sup> (2:1). When the 30% methanolic eluate<sup>22</sup> was allowed to stand several days in the refrigerator, pure white crystals of II separated.

**2',5'-Dihydroxychalcone (III)** could be isolated in 4–9% yields from a similar reaction mixture if the acidification was done with 6 *N* hydrochloric acid and the yellow-orange precipitate was extracted with methanol. On evaporation of the methanol crude chalcone was deposited; this was obtained as orange-red crystals after repeated recrystallization from benzene. When III was refluxed with dilute alcoholic hydrochloric acid for 10 hr., it was converted into II.

**6-Hydroxy-3-benzylidene flavanone (IV)** was obtained as the main product (28–37%) when equal weights of quinacetophenone and benzaldehyde were used (a 1:1.3 molar ratio). A larger excess of benzaldehyde (up to 7 moles) increased the yields, a 50% yield being isolated after recrystallization from methanol. The same compound was obtained in a 70% yield by substituting 6-hydroxyflavanone (II) for quinacetophenone in the standard procedure with excess benzaldehyde and running the reaction for 1 day. The same compound was also isolated in 29% yield when an alcoholic solution of 0.184 g. of 6-hydroxyflavanone and 0.6 g. of benzaldehyde was saturated with hydrogen chloride and allowed to stand for 4 days at room temperature. Mixed melting points proved the identity of the three samples of IV. The yellow methyl ether of this compound was prepared by means of dimethyl sulfate and anhydrous potassium carbonate in anhydrous acetone. When IV was refluxed for 10 days with dilute alcoholic hydrochloric acid, no color change occurred and the melting point of the product was little changed. Paper chromatography showed a second spot appearing.

(19) Polypenco Nylon Powder, The Polymer Corp., Reading, Pa.

(20) Johns Manville.

(21) R. Neu, *Nature*, **182**, 660 (1958).

(22) III eluates only with 75% methanol.

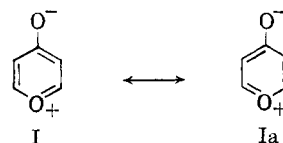
#### Diels-Alder Reaction. Experiments with 2,6-Distyryl- $\gamma$ -pyrone and 2-Styrylchromones

GAMIL AZIZ

Department of Chemistry, Faculty of Science,  
University of Cairo, Giza, Egypt, U.A.R.

Received November 21, 1961

$\gamma$ -Pyrone derivatives differ from *p*-quinones to which they bear structural resemblance as the former do not function as dienophiles in the Diels-Alder reaction. This may be attributed to the important contribution of structures I and Ia to the actual state of the molecule.<sup>1,2</sup>



The use of 2,6-distyryl- $\gamma$ -pyrone as a diene component in the Diels-Alder reaction seems not to have been investigated so far. In the present in-

(13) A. Robertson, V. Venkateswarlu, and W. B. Whalley, *J. Chem. Soc.*, 3137 (1954).

(14) G. N. Vyas and N. M. Shah, *J. Indian Chem. Soc.*, **26**, 273 (1949).

(15) The methyl ether of IV melts relatively close to that reported by Vyas and Shah<sup>14</sup> for their chalcone.

(16) Vyas and Shah<sup>14</sup> report no such reaction for their supposed chalcone although the reaction was reported for all other chalcones in their paper.

(17) Melting points are uncorrected.

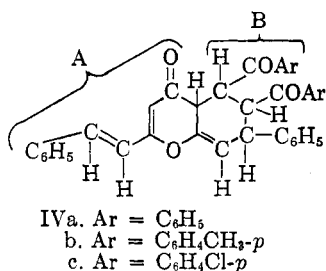
(18) Washed with benzene, ether, ethyl acetate, acetone, methanol, and hot water (R. Birzgalis, M.A. thesis, Wellesley College, 1960, p. 43).

(1) K. Alder in "Newer Methods of Preparative Organic Chemistry," New York, 1948, p. 501.

(2) B. Eistert, "Tautomerie und Mesomerie," F. Enke, Stuttgart, 1938, p. 56 ff.

vestigation it is found that the adducts (IVa, IVb, IVc) have been formed by the interaction of 2,6-distyryl- $\gamma$ -pyrone (II) as diene component and *trans*-diaroylethylenes (IIIa, IIIb, IIIc) as dienophiles in boiling anisole. The reaction has been extended to 2-styrylchromone (IX), 2-styrylkhellin (XIa), and 2-styrylvisnagin (XIb).

(A). **Experiments with 2,6-Distyryl- $\gamma$ -pyrone.**—Chromone derivatives (IVa, IVb, IVc) are easily formed when 2,6-distyryl- $\gamma$ -pyrone (II) is allowed to react with *trans*-diaroyl-ethylenes (IIIa, IIIb, IIIc) in boiling anisole. The analyses of the adducts obtained by the action of dibenzoyl ethylene and di-*p*-toluylethylene on 2,6-distyryl- $\gamma$ -pyrones are in fair agreement with both structures in which one or two molecules of the dienophile may be added to the distyryl compound. However, molecular weight determinations (cryoscopic method) indicated that only one molecule of the dienophile has been added to the distyryl compound, and hence the adducts are probably 2-styrylchromone derivatives. The structure assigned to these adducts is supported by a study of their absorption spectra.



The maxima at 315 m $\mu$  (Table I) appear to be due to the chromophore C<sub>6</sub>H<sub>5</sub>CH=CHCH=CHC=O (A), since the same band was observed in the absorption spectrum of cinnamylidene acetone (VI). The maxima at 248, 258 and 258 m $\mu$ , respectively (see Fig. 1), appear to be due to the aryl group (B) since acetophenone absorbs at  $\lambda_{\max}$  244 m $\mu$  ( $\epsilon_{\max}$  15,850).<sup>3</sup> The fact that the molecular extinction coefficient of these adducts at the short wave length region is double that for acetophenone is good evidence for the presence of two such groups in the molecule.

TABLE I<sup>a</sup>

Formula of the compound	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\min}$	$\epsilon_{\min}$	Figure
IVa	315	34,953	275	16,020	I, IVa
	248	32,040			
IVb	315	35,904	280	22,032	I, IVb
	258	29,884	240	18,768	
IVc	315	34,480	280	21,346	I, IVc
	258	32,429	240	23,809	
VI	315	35,787	250	1,812	I, VI

<sup>a</sup> The measurements were carried out with a Perkin-Elmer Spectrocord Model 4000A, in absolute ethanol.

It is of interest to note that only one molecule of the *trans*-diaroylethylene is added to the 2,6-di-

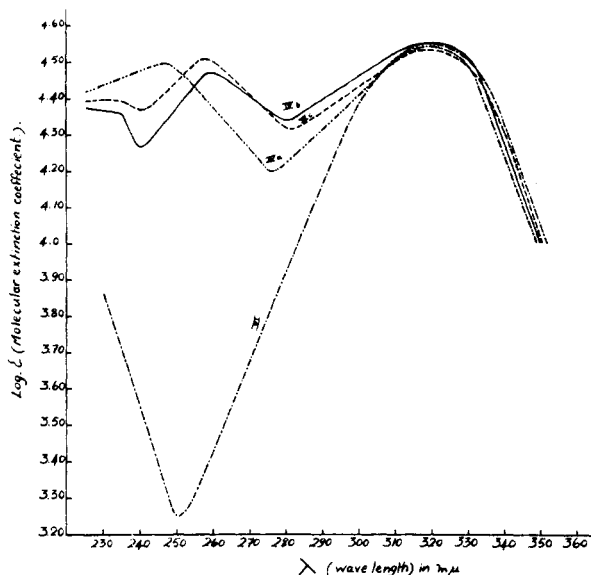
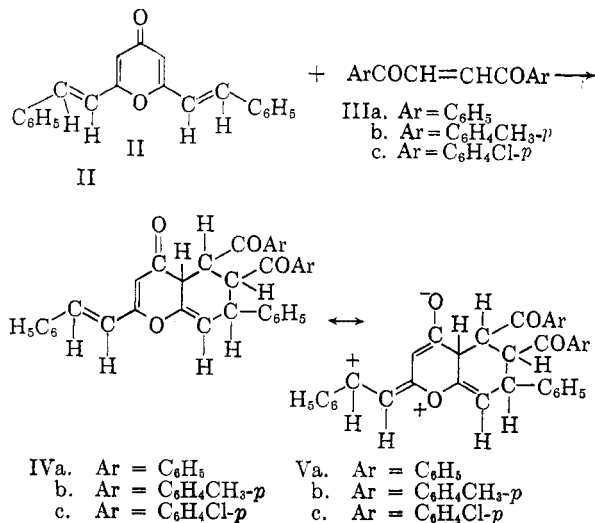
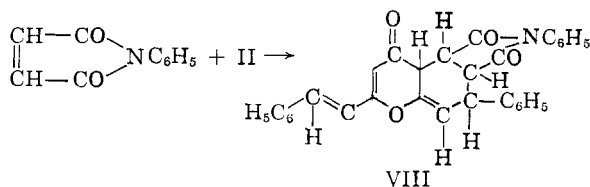


Figure 1

styryl- $\gamma$ -pyrone, even when excess of the former is used and the duration of heating is prolonged. This may be due to a weakening of the diene character of the 1:1 adduct by the cross conjugation as shown in V.



When *N*-phenylmaleimide (VII) is allowed to react with 2,6-distyryl- $\gamma$ -pyrone (II) in boiling xylene, one molecule of the former is added to give VIII (cf., A. Mustafa and M. A. Ibrahim).<sup>4</sup>



(3) Gillman and Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold, Ltd., London, 1955, p. 126.

(4) A. Mustafa and M. A. Ibrahim, *J. Org. Chem.*, **21**, 849 (1956).

TABLE II

Ad-duct compound	Styryl compound	Dienophile	Solvent	Time of heating, hr.	M.p., °C.	Yield, g.	Calcd.				Found				
							C	H	N	Cl	Mol. wt.	C	H	N	Cl
IV <sup>b</sup> <sup>a</sup>	1 g.	111b, 1.76 g.	Anisole, 50 ml.	25	266	0.25	C <sub>35</sub> H <sub>32</sub> O <sub>4</sub>	82.97	5.6	...	564	82.7	5.9	...	571
IV <sup>c</sup> <sup>b</sup>	1 g.	IIIc, 2.34 g.	Anisole, 40 ml.	30	248	0.24	C <sub>37</sub> H <sub>30</sub> O <sub>4</sub> Cl <sub>2</sub>	73.4	4.4	...	11.7	73.8	4.4	...	11.8
VIII <sup>c</sup>	0.5 g.	VII, 1.1 g.	Xylene, 30 ml.	10	292	0.26	C <sub>31</sub> H <sub>28</sub> O <sub>4</sub> N	78.62	4.86	2.99	...	77.9	4.8	3.36	...

<sup>a</sup> IV<sup>b</sup>—4a,5,6,7-Tetrahydro-5,6-di-*p*-tolyl-7-phenyl-2-styrylchromone. <sup>b</sup> IV<sup>c</sup>—4a,5,6,7-Tetrahydro-5,6-dichlorodibenzoyl-7-phenyl-2-styrylchromone. <sup>c</sup> VIII—7-Phenyl-2-styryl-4a,5,6,7-tetrahydrochromone (N-phenyl)-5,6-dicarboximide.

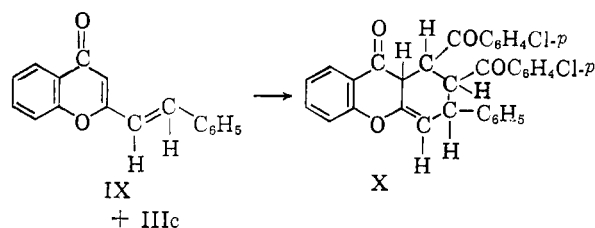
TABLE III

Ad-duct	Styryl compound	Dienophile	Solvent	Time of heating, hr.	Volume of anisole	M.p.	Yield, g.	Calcd.			Found			
								C	H	Cl	C	H	Cl	
XIIa <sup>a</sup>	XIa, 0.7 g.	IIIc, 0.6 g.	Benzene + pet. ether (b.p. 60–80°)	30	25 ml.	230°	0.21	C <sub>37</sub> H <sub>28</sub> O <sub>7</sub> Cl <sub>2</sub>	68	4.0	10.86	67.8	4.0	10.39
XIIb <sup>b</sup>	XIb, 1 g.	IIIa, 0.42 g.	Alcohol + benzene	30	35 ml.	246°	0.26	C <sub>38</sub> H <sub>26</sub> O <sub>6</sub>	77.97	4.7	...	77.7	4.8	...
XIIc <sup>c</sup>	XIb, 0.58 g.	IIIc, 0.5 g.	Benzene + pet. ether (b.p. 60–80°)	35	25 ml.	258°	0.25	C <sub>38</sub> H <sub>24</sub> O <sub>6</sub> Cl <sub>2</sub>	69.34	3.85	11.39	68.9	3.65	11.0

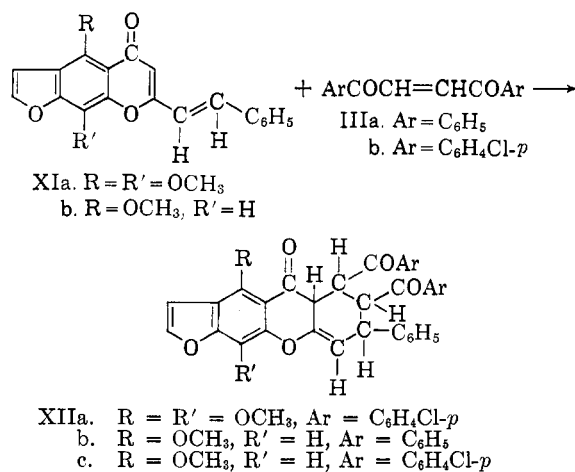
<sup>a</sup> XIIa—5a,6,7,8-Tetrahydro-6,7-*p,p'*-dichlorodibenzoyl-4,11-dimethoxy-5-oxo-5*H*-8-phenylfuro(3,2-*b*)xanthene. <sup>b</sup> XIIb—5a,6,7,8-Tetrahydro-6,7-dibenzoyl-4-methoxy-5-oxo-5*H*-8-phenylfuro(3,2-*b*)xanthene. <sup>c</sup> XIIc—5a,6,7,8-Tetrahydro-6,7-*p,p'*-dichlorodibenzoyl-4-methoxy-5-oxo-5*H*-8-phenylfuro(3,2-*b*)xanthene.

Although the adducts contain ketonic groups, they fail to condense with ketonic reagents, *e.g.* hydroxylamine, phenylhydrazine, and 2,4-dinitrophenylhydrazine. Compounds having ketonic groups and behaving similarly have been reported in the literature.<sup>5,6</sup>

(B). Experiments with 2-Styrylchromones.—The use of 2-styrylchromones as diene components has already been investigated.<sup>4,7</sup> In the present work 2-styrylchromone (IX) is allowed to react with *p,p*-dichlorodibenzoyl-ethylene (IIIc) in boiling anisole leading to the formation of xanthene derivative (X).



Similarly, 2-styrylkhellin (XIa) reacts with *p,p*-dichlorodibenzoyl-ethylene (IIIc) to give the adduct (XIIa), while 2-styrylvisnagin (XIb) reacts with both dibenzoyl-ethylene and *p,p*-dichlorodibenzoyl-ethylene to give the adducts XIIb and XIIc, respectively.



### Experimental

The method of Boon, *et al.*,<sup>8</sup> for the preparation of 2,6-distyryl- $\gamma$ -pyrone has been modified and a better yield was obtained.

**Preparation of 2,6-Distyryl- $\gamma$ -pyrone.**—To the cooled solution of 2,6-dimethylpyrone<sup>9</sup> [purified by recrystallization from benzene-petroleum ether (b.p. 60–80°)] 1 g. (0.008 mole) in 15 ml. of absolute ethyl alcohol, and benzaldehyde (freshly distilled in a stream of dry carbon dioxide) 1.7 g.

(5) O. M. Aly, W. I. Awad, and A. M. Islam, *J. Org. Chem.*, **23**, 1623 (1958).

(6) M. Cesaris, *Gazz. Chim. Ital.*, **42**, II, 453.

(7) A. Schönberg, A. Mustafa, and G. Aziz, *J. Am. Chem. Soc.*, **76**, 4576 (1954).

(8) A. A. Boon, K. J. McKenzie, and J. Trotter, *J. Proc. Chem. Soc.*, **30**, 2058 (1914).

(9) Arndt, *et al.*, *Ber.*, **69**, 2373 (1936).

