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

Diels–Alder Reaction. II. Experiments with 2-Styrylchromones. On the Nature of the Dimer of 1,3-Diphenylisobenzofuran

BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND GAMIL AZIZ

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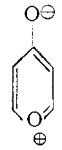
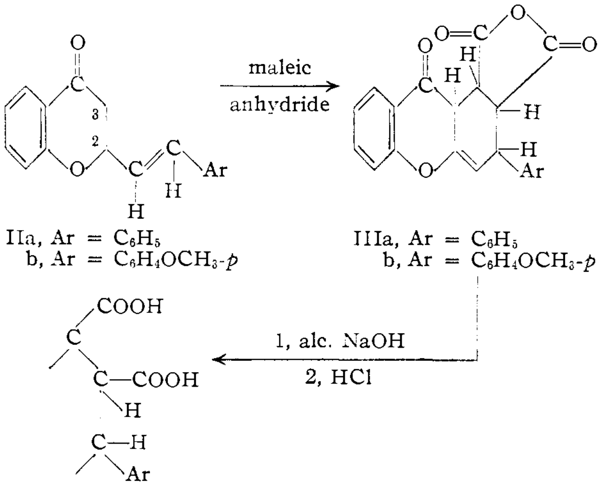
Xanthone derivatives may be obtained from 2-styrylchromones by Diels–Alder reactions. It seems possible that the dimer of 1,3-diphenylisobenzofuran is a Diels–Alder adduct having formula X.

The non-conjugated position of the double bonds in γ-pyrones should permit them to function as dienophiles in the Diels–Alder synthesis. However, it seems that no condensation of this type has been carried out. In this respect, γ-pyrones differ fundamentally from *p*-quinones to which they bear structural resemblance. The inactivity of γ-pyrones may be related to an electromeric displacement of their bonds to zwitterion forms[1,2] (*cf.* I). The use of 2-styrylchromones as diene components in the Diels–Alder reaction seems not to have been investigated so far. Here possible electromeric displacement in analogy to I seems not to interfere, because we have observed an easy formation of the xanthone derivatives IIIa when 2-styrylchromones IIa are allowed to react with maleic anhydride in boiling xylene. Similar results leading to IIb were observed in the case of 4′-methoxy-2-styrylchromone (IIb).



I

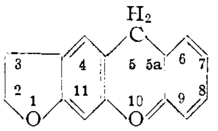


IIa, Ar = C_6H_5
b, Ar = $C_6H_4OCH_3$-*p*

IIIa, Ar = C_6H_5
b, Ar = $C_6H_4OCH_3$-*p*

IIIc (abbreviated formula)

Similar reactions were carried out with the styryl derivatives (Va and b) obtainable from khellin (IVa) and visnagin (IVb) leading to derivatives of 5H-furo(3,2-b)xanthene (VII), namely, VIa and VIb, respectively. Attention is drawn to the fact that 2-styrylkhellin Va forms deep-yellow crystals, whereas the crystals of 2-styrylvisnagin (Vb) are almost colorless. It seems possible that this difference in color is due to the fact that these two substances are not analogs from the stereochemical point of view (the double bond in the styryl groups allows for *cis–trans* isomerism). A difference in color is reported in the case of 1,2-dibenzoylethylene, one stereoisomeric form being yellow, the other being colorless.[3]

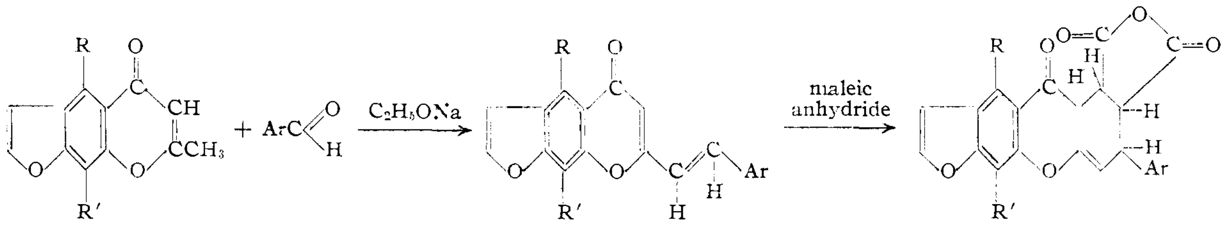


VII

The substances obtained by these Diels–Alder syntheses are practically colorless and are insoluble in alkali. IIIa was treated with alcoholic sodium hydroxide; on acidification an acid (IIIc) was obtained, soluble in alkali; on treatment with acetic anhydride IIIa was regenerated.

In contrast to the easy addition of maleic anhydride to 2-styrylchromone, we find that 2-styryl-3-methylchromone (see IIa) does not add maleic anhydride under conditions which proved successful in the case of IIa and even under more drastic conditions (boiling phenetole was used as a solvent and the duration of heating was prolonged). The negative result may be due to steric hindrance.

On the Nature of the Dimer of 1,3-Diphenylisobenzofuran.—The dimer was first obtained from 1,3-diphenylisobenzofuran (VIII) by the action of light, its constitution as IX[4] has, as far as we are



IVa, R = R′ = OCH_3
b, R = OCH_3, R′ = H

Va, R = R′ = OCH_3; Ar = C_6H_5
b, R = OCH_3, R′ = H, Ar = C_6H_5

VIa, R = R′ = OCH_3, Ar = C_6H_5
b, R = OCH_3, R′ = H, Ar = C_6H_5

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(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.

(3) J. B. Conant and R. E. Lutz, THIS JOURNAL, **45**, 1303 (1923).

(4) A. Guyot and J. Catel, *Bull. soc. chim.*, **35**, 1127 (1906).

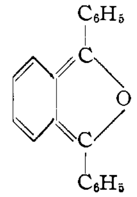
TABLE I

Formula and m.p. of the adduct, °C.	Formula and wt. in f. of the styryl cmpd.	Time of heating in hr.	Vol. xylene, ml.	Solvent of cryst.	Yield, g.	Formula	Carbon, %		Hydrogen, %	
							Calcd.	Found	Calcd.	Found
IIIb, 268	IIb, 0.8	30	30	Xylene	0.35	$C_{22}H_{16}O_6$	70.2	70.3	4.2	4.3
VIa, 256 d.	Va, 1.0	10	25	Dioxane	0.3	$C_{25}H_{18}O_8$	67.3	66.9	4.0	4.2
VIb, 256 d.	Vb, 1.0	10	20	Acetone	0.4	$C_{24}H_{16}O_7$	69.2	68.9	3.8	3.9

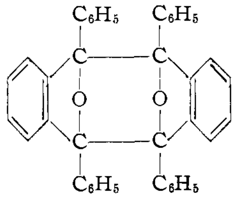
Formal names of adducts given in Table I

Number	Name
IIIb	1,2,3,9a-Tetrahydro-9-oxo-3-*p*-methoxyphenyl-1,2-xanthenedicarboxylic anhydride
VIa	5a,6,7,8-Tetrahydro-4,11-dimethoxy-5-oxo-5H-furo(3,2-b)xanthene-6,7-dicarboxylic anhydride
VIb	5a,6,7,8-Tetrahydro-4-methoxy-5-oxo-5H-furo(3,2-b)xanthene-6,7-dicarboxylic anhydride

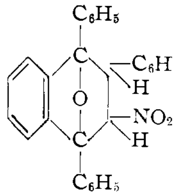
aware, never been challenged. It was also accepted by Schönberg and Mustafa[5] who obtained the dimer from VIII by heating. We wish to stress that the constitution IX has never been proved and it seems not impossible that the product is to be regarded as a Diels–Alder adduct X. It is well known that VIII undergoes Diels–Alder reactions, *e.g.*, with β-nitrostyrene forming XI.[6]



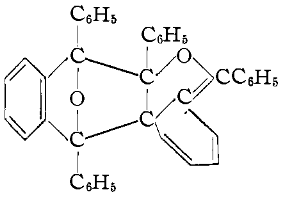
VIII



IX



XI



X

Experimental

Action of Maleic Anhydride on 2-Styrylchromones.—A solution of 1 g. of 2-styrylchromone IIa[7] (1 mole) and 4 g. of maleic anhydride (10 mols.) in 30 ml. of dry xylene was refluxed for 12 hours. After concentration and cooling 1,2,3,9a-tetrahydro-9-oxo-3-phenyl-1,2-xanthenedicarboxylic anhydride (IIIa) separated out, was filtered off, washed with hot ethyl alcohol and then crystallized from xylene, m.p. 246°, yield is about 0.65 g. *Anal.* Calcd. for $C_{21}H_{14}O_5$: C, 72.8; H, 4.0. Found: C, 73.3; H, 4.0.

Table I shows the experimental details of other Diels–Alder reactions.

2-Styrylkhellin (Va).—To the cooled solution (in ice) of 0.5 g. of khellin and 0.25 g. of benzaldehyde in 10 ml. of absolute ethyl alcohol was added a cooled solution of 0.05 g. of sodium in 5 ml. of absolute ethyl alcohol. The small amount of the solid that separated was brought into solution by slight warming and the reaction mixture was kept overnight at room temperature. The yellow deposit was filtered off, washed with a little alcohol and crystallized from the same solvent, as deep-yellow needles, m.p. 196°. Va is easily soluble in warm benzene and dissolves in concentrated sulfuric acid with a red-brown color; yield is *ca.* 0.42 g. *Anal.* Calcd. for $C_{21}H_{16}O_6$: C, 72.4; H, 4.6. Found: C, 72.3; H, 4.5.

2-Styrylvisnagin (Vb).—This substance was prepared from visnagin and benzaldehyde in a similar way and obtained in almost colorless crystals from ethyl alcohol, m.p. 176° (brownish melt). Vb dissolves in concentrated sulfuric acid with an orange color; yield is *ca.* 80%. *Anal.* Calcd. for $C_{20}H_{14}O_4$: C, 75.4; H, 4.4. Found: C, 74.8; H, 4.3.

Opening of the Anhydride by Alkali.—IIIa, 0.35 g., was refluxed with methanolic sodium hydroxide. The sodium salt, which separated out, was filtered off and decomposed by hydrochloric acid. 3,9a-Dihydro-9-oxo-3-phenyl-1,2-xanthenedicarboxylic acid (IIIc) was crystallized from dilute methyl alcohol, m.p. *ca.* 258° (dec. and evolution of gas); it is soluble in sodium bicarbonate solution; yield is *ca.* 0.21 g. IIIc crystallizes with one mole of water of crystallization. *Anal.* Calcd. for $C_{21}H_{16}O_6 \cdot H_2O$: C, 66.0; H, 4.7. Found: C, 66.0; H, 5.0.

IIIc was readily converted to the corresponding dimethyl ester by the action of absolute methyl alcohol and dry hydrogen chloride gas. It formed almost colorless crystals from light petroleum (b.p. 50–70°), m.p. 66–68°. *Anal.* Calcd. for $C_{23}H_{20}O_6$: C, 70.4; H, 5.1. Found: C, 70.2; H, 5.2.

Reconversion to the Anhydride.—Refluxing 0.25 g. of the acid with acetic anhydride reconverted it to the anhydride (m.p. and mixed m.p.). *Anal.* Calcd. for $C_{21}H_{14}O_5$: C, 72.8; H, 4.0. Found: C, 72.3; H, 4.0.

2-Styryl-3-methylchromone and Maleic Anhydride.—A solution of 0.35 g. of 2-styryl-3-methylchromone[8] and 2 g. of maleic anhydride in 20 ml. of phenetole was refluxed for 24 hours. The phenetole was distilled off in vacuum and the residue was crystallized from ethyl alcohol, yielding 0.24 g. of 2-styryl-3-methylchromone (m.p. and mixed m.p. determination).

CAIRO, EGYPT

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[5] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 2126 (1948).

[6] C. F. H. Allen, A. Bell and J. W. Gates, Jr., *J. Org. Chem.*, **8**, 373 (1943).

[7] U. S. Cheema, K. C. Gulati and K. Venkataraman, *J. Chem. Soc.*, 925 (1932).

[8] I. M. Heilbron, H. Barnes and R. A. Morton, *J. Chem. Soc.*, 2559 (1923).