NOTES

1,4-DIARYLPHTHALAZINES AND 1,3-DIARYLISOBENZOFURANS

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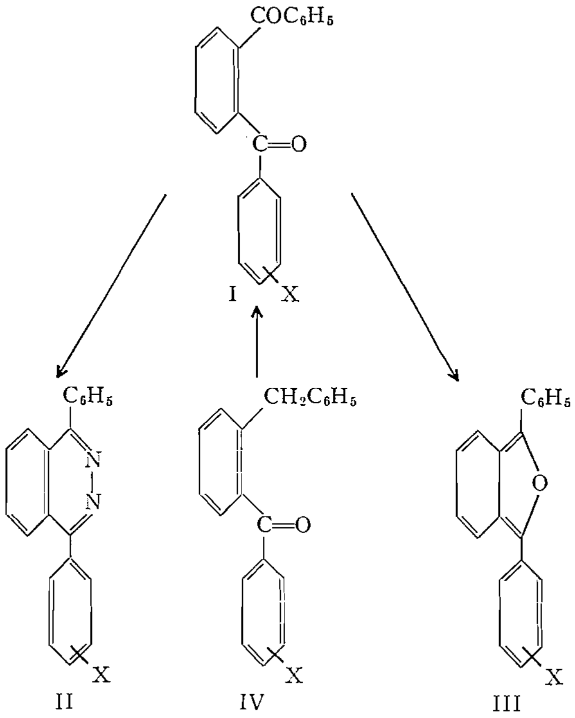
In connection with our studies on polynuclear aromatic compounds it became necessary to synthesize a series of unsymmetrically substituted 1,4-diarylphthalazines and 1,3-diarylisobenzofurans. Unsymmetrically substituted 2-benzoylbenzophenones (I) were the starting compounds for both the phthalazines and the isobenzofurans.



The most general route for the synthesis of the diketones (I) is via the oxidation of the substituted 2-benzylbenzophenones (IV) (1–4). During this investigation the chromium trioxide - acetic acid system (3) was used to effect the oxidation of the substituted 2-benzylbenzophenones (IV; X = 4′-CH_3, 4′-Cl, or 4′-Br) (see Table I). The remaining diketones (I; X = 2′-Cl, 2′-Br, 3′-CF_3, and 4′-F) used in this work had been prepared previously (3–5).

The diketones (I) were smoothly condensed with 85% hydrazine hydrate in acetic acid to the corresponding 1,4-diarylphthalazines (II) (see Table II).

The method of Cava *et al.* (6) employing potassium borohydride for the conversion of 1,2-diaroylbenzenes (I) into 1,3-diarylisobenzofurans (III) was used in this work and

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[1] *Abstracted in part from the thesis of Donald Pichler presented to Villanova University, Villanova, Pennsylvania, in partial fulfillment of the requirements for the M.S. degree (1964).*

Canadian Journal of Chemistry. Volume 44 (1966)

TABLE I
1,2-Diaroylbenzenes (I)

				Analysis (%)							
				Calcd.			Found				
X	Yield (%)	Melting point (°C)	Formula	C	H	Halogen	C	H	Halogen	λ_{max} (mμ)	$\lambda_{C=O}$ (μ)
4′-Cl	94	136–137	$C_{20}H_{13}ClO_2$	74.89	4.09	11.05	75.01	4.25	11.04	257	6.03
4′-Br	98	146–147	$C_{20}H_{13}BrO_2$	65.77	3.59	21.88	65.69	3.46	21.75	257	6.03
4′-CH$_3$	86	144–145*	$C_{21}H_{16}O_2$	83.98	5.37		84.19	5.32		258	6.03

*Guyot and Vallette (10) report m.p. 139°.

TABLE II
1,4-Diarylphthalazines (II)

				Analysis (%)								
				Calcd.				Found				
X	Yield (%)	Melting point (°C)	Formula	C	H	Halogen	N	C	H	Halogen	N	λ_{max} (mμ)
2′-Cl	95	139	$C_{20}H_{13}ClN_2$	75.83	4.14	11.19	8.84	75.78	4.10	10.78	9.46	230, 295
4′-Cl	95	185–187	$C_{20}H_{13}ClN_2$	75.83	4.14	11.19	8.84	75.75	4.25	11.27	8.76	226, 298
2′-Br	67	134–135	$C_{20}H_{13}BrN_2$	66.50	3.63	22.12	7.75	66.57	3.90	22.12	7.67	224, 294
4′-Br	88	192–193	$C_{20}H_{13}BrN_2$	66.50	3.63	22.12	7.75	66.55	3.57	22.24	7.58	234, 298
3′-CF$_3$	89	193–194	$C_{21}H_{13}F_3N_2$	71.99	3.74	16.27	8.00	71.70	3.95	15.55	8.45	225, 296
4′-F	84	191–192	$C_{20}H_{13}FN_2$	79.98	4.36	6.33	9.33	80.05	4.39		9.65	244, 297
4′-CH$_3$	95	171–172*	$C_{21}H_{16}N_2$	85.11	5.44		9.45	84.69	5.60		9.92	224, 300

*Guyot and Vallette (10) report m.p. 117°.

TABLE III

1,3-Diarylisobenzofurans (III)

X	Yield (%)	Melting point (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. Halogen	Found C	Found H	Found Halogen	λ_{max} (mμ)
2′-Cl	49	70–71	$C_{20}H_{13}ClO$	78.82	4.30	11.63	79.01	4.15	11.95	266, 413
4′-Cl	51	101–102	$C_{20}H_{13}ClO$	78.82	4.30	11.63	78.52	4.14	11.81	265, 415
2′-Br	51	59–60	$C_{20}H_{13}BrO$	68.79	3.75	22.88	69.10	3.86	23.07	266, 415
4′-Br	48	120–121	$C_{20}H_{13}BrO$	68.79	3.75	22.88	69.11	3.79	22.99	267, 416
3′-CF_3	37	103–104	$C_{21}H_{13}F_3O$	74.55	3.87	16.85	74.30	3.80	16.05	267, 410
4′-F	71	82–83	$C_{20}H_{13}FO$	83.32	4.54	6.59	83.07	4.92	7.12	260, 398
4′-CH_3	75	84–85*	$C_{21}H_{16}O$	88.70	5.67		88.89	5.48		268, 410

*Guyot and Vallette (10) report m.p. 83°.

was also found to be superior to the older methods employing zinc and acetic acid (7) or zinc and alcoholic sodium hydroxide (8). The new isobenzofurans that were prepared are listed in Table III.

EXPERIMENTAL

Melting points were determined on a Thomas–Hoover melting point apparatus and are uncorrected. Microanalyses were carried out by Alfred Bernhardt, Mülheim, Germany. Infrared spectra were obtained on a Perkin–Elmer infracord, 0.25% in KBr. Ultraviolet and visible spectra were obtained on a Perkin–Elmer model 202 spectrophotometer, 1 cm cells, 95% ethanol as solvent.

The 2-benzoylbenzophenones (I) were prepared by the method of Vingiello *et al.* (3). The 1,4-diarylphthalazines (II) were prepared by the method of Blicke and Swisher (9). The 1,3-diarylisobenzofurans (III) were prepared by the method of Cava *et al.* (6).

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Received November 25, 1965.

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THE OXIDATION OF 1,2;5,6-DI-*O*-ISOPROPYLIDENE-D-GLUCOSE BY DIMETHYL SULFOXIDE - ACETIC ANHYDRIDE

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A simple method of selective oxidation with a readily available reagent would be of great value in the field of carbohydrate chemistry. Recently Albright and Goldman reported a general method for the oxidation of alcohols to their corresponding carbonyl derivatives with dimethyl sulfoxide (DMSO) and certain acid anhydrides (1). The procedure, especially useful for the oxidation of sterically hindered hydroxyl groups, was recommended for compounds such as indole alkaloids which are sensitive to nonselective oxidizing agents. The present communication reports the use of DMSO – acetic anhydride for the oxidation of 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (I). Although it is possible to convert this compound into 1,2;5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (II) in 80% yield with ruthenium tetroxide (2), oxidation with more common reagents is difficult (3, 4). By careful control of the conditions, Theander (4) oxidized I with chromium trioxide - pyridine complex in acetic acid and obtained the 3-keto derivative (II) in 6% yield. Theander also found that sodium borohydride reduced II stereospecifically and practically quantitatively to 1,2;5,6-di-*O*-isopropylidene-α-D-allofuranose (III), which crystallized with ease. This provided a convenient route to the rare monosaccharide D-allose, as well as evidence for the presence of II.

In the present work, the oxidation of I by DMSO – acetic anhydride was found to be virtually complete after 24 h at room temperature. After removal of the solvents by distillation, the oxidized residue was dissolved in aqueous ethanol and reduced with sodium