melting point with an authentic sample of *p*-toluenesulfonamide was 131–134°. The literature melting point for this compound is 137.4°.[8]

The above acidic aqueous layer was neutralized, cooled, and extracted with benzene. Evaporation of the benzene solution yielded 0.11 g. (12%) of IV, m.p. 180–183°. The mixture melting point with an authentic sample (see below) was not depressed.

Identification of the product of m.p. 133–136° as III was substantiated by its behavior with hydrazine under conditions described by Leonard, Ruyle, and Bannister.[9] A product of m.p. 208–210° was obtained in 85% yield. These authors report m.p. 209–210° for 3-amino-4-quinazolinone prepared in this fashion.

Hydrolysis of II.—A solution of 3.10 g. of II in 200 cc. of 90% ethanol: 10% water was heated 10 hr. at reflux. Hot water was slowly added to the hot solution until a faint turbidity appeared. Cooling with ice caused white leaflets to separate, and a small second crop was gained by extracting the mother liquor with ether. The total yield of IV was 2.96 g. (98%), and the m.p. 182–185°.

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$: C, 57.91; H, 4.86; N, 9.65; neut. equiv., 290. Found[7]: C, 57.91; H, 4.68; N, 9.64 (micro Kjeldahl); neut. equiv. 291, 292 (potentiometric titration *vs.* NaOH solution).

To a solution of 3.0 g. of II in 50 cc. of dioxane, 40 cc. of 5% aqueous sodium hydroxide was added. The mixture was kept 24 hr. at room temperature, poured into 50 cc. of water, and extracted with three 40-cc. portions of benzene There was no residue on evaporation of the benzene. Neutralization and cooling of the aqueous layer caused 0.80 g. (28%) of IV, m.p. 179–183° to separate. The aqueous mother liquor was acidified and 0.28 g. (16%) of *p*-toluenesulfonamide, m.p. 128–132°, was thereby obtained.

Preparation of IV from Isatoic Anhydride.—*p*-Toluenesulfonamide (20.5 g., 0.12 mole) was allowed to react with 5.0 g. (0.09 mole) of potassium hydroxide in 10 cc. of water. The resulting salt was dried, though not purified. All of it was combined with 4.9 g. (0.03 mole) of isatoic anhydride (generously furnished by the Maumee Chemical Co.) and 50 cc. of dimethylformamide. The potassium salt dissolved as the mixture was slowly heated to 160°, at which temperature it was held for 7 hr. It was cooled and poured into 250 cc. of cold water. The resulting solution was cloudy, and a solid separated on acidification. Water (400 cc.) was added, and the mixture was heated to boiling and filtered hot. The white solid collected on the filter was extracted by 300 cc. of boiling water and dried. The IV so obtained, m.p 180–183°, weighed 3.7 g. (44%). The mixture melting point with IV from hydrolysis of II was 183–185°, and the infrared spectra were identical.

4-Thiophenoxyquinazoline.—Solutions of 1.7 g. of 4-chloroquinazoline[10] in 30 cc. of dioxane and of 5.2 g. of thiophenol in 25 cc. of 5% aqueous sodium hydroxide were combined and allowed to stand 2 hr. at room temperature. The product was isolated by standard procedures and finally crystallized from aqueous ethanol. 4-Thiophenoxyquinazoline (1.07 g.; 45%) was obtained as white crystals of m.p. 115–116°.

Anal. Calcd. for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23. Found[7]: C, 70.86; H, 4.78.

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The Determination of the Styryl[1] Geometry of the 6-Styryl-4-methoxy-2-pyrones by Proton Magnetic Resonance Spectroscopy

PETER BEAK AND HERBERT ABELSON

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

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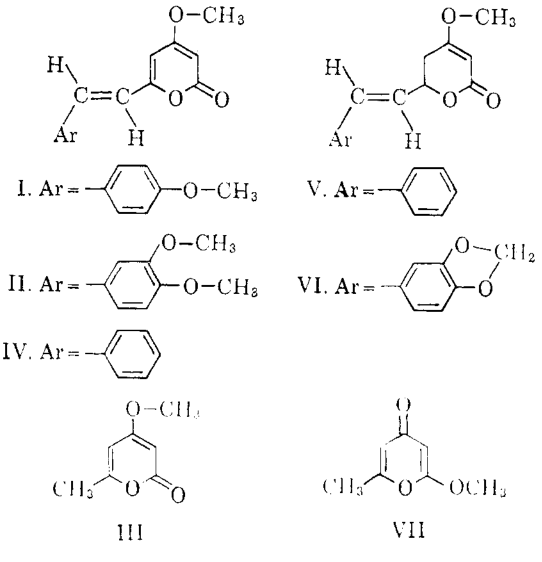
The proton magnetic resonance spectra of a 6-styryl-4-methoxy-2-pyrone derived from a pyrone isolated from a fungus[2] and of the 6-styryl-4-methoxy-2-pyrones and the 5,6-dihydro-6-styryl-4-methoxy-2-pyrones realized from the higher plants[3] confirm a *trans* geometry for the styryl groups in these compounds.

Actually, the syntheses of the 6-styryl-4-methoxy-2-pyrones indicate that the styryl system is *trans* substituted. Yangonin[4] (I) and tri-O-methylhispidin[2] (II) have been synthesized by the base-catalyzed condensation of 6-methyl-4-methoxy-2-pyrone (III) with the appropriate aldehyde; a method which has produced *trans* styryl groups in similar cases.[5,6] The syntheses 5,6-dehydrokawain[7] (IV), kawain[8,9] (V), and methysticin[10] (VI) proceeded from *trans* cinnamyl compounds



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[1] The term styryl is used herein, as in the previous literature, to denote an Ar—CH=CH— group.

[2] R. L. Edwards, D. G. Lewis, and D. V. Wilson, *J. Chem. Soc.*, 4995 (1961); J. D. Bu'lock and H. G. Smith, *Experientia*, **17**, 553 (1961).

[3] See R. Hänsel, P. Bähr, and J. Elich, *Arch. Pharm.*, **294**, 739 (1961), footnotes 4 and 5 for leading references to the chemistry and pharmacology of these compounds. A reasonable biosynthesis for these compounds has recently been proposed by A. J. Birch, "XVIIth International Congress of Pure and Applied Chemistry," Butterworths, London, 1960, p. 73.

[4] J. D. Bu'lock and H. G. Smith, *J. Chem. Soc.*, 502 (1960).

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in a manner such that a change in this geometry would not be expected. The other syntheses reported for these compounds[3] are consistent with this interpretation.

Neither ultraviolet nor infrared[11] spectroscopy provides a definitive assignment of geometry to these systems. Information on this point is furnished by the p.m.r. spectra of compounds I, II, IV, V, and VI.

The important features of these spectra are summarized in the following table:

TABLE I

CHEMICAL SHIFTS[a] (IN τ, P.P.M.) AND SPIN-SPIN COUPLING CONSTANTS (IN C.P.S.)

	H_3	H_5	H_6	H_7	H_8	J_{35}	J_{78}	J_{67}	J_{57}
I	4.50	4.07		3.51	2.53	2.0	16.0		
II	4.52	4.06		3.49	2.59	2.0	16.0		
IV	4.50	4.04		3.50	2.58[b]	2.0	16.3		
V	4.76	7.48 7.39	4.87	3.72	3.25		16.0	5.9	
VI	4.77	7.49 7.40	5.02	3.90	3.55[b]		16.0	6.3	
III	4.56	4.16		7.79		2.4			0.9
VII	4.51	3.99		7.75		2.0			0.8

[a] The chemical shifts refer to the position of the origin of the multiplet. The resonances of the unrecorded protons are unexceptional. [b] One peak of the H_8 doublet is presumed to be hidden by the resonances of the aromatic protons.

The styryl protons comprise an AB[12,13] system in the spectra of I, II, and IV and a modified[14] AB system in the spectra of V and VI. The magnitude of the coupling constant between the styryl protons is in accord with only a *trans* arrangement of the styryl system.[15,16]

Ultraviolet and infrared correlations[4,17,18] have been used, sometimes in conjunction with chemical data, to assign structures to 6-methyl-4-methoxy-2-pyrone (III) and 6-methyl-2-methoxy-4-pyrone (VII). These assignments proved to be critical in deciding the structures of the naturally occurring 2-pyrones. Conceivably p.m.r. spectroscopy might also provide a distinction between these isomers. That this is not the case is demonstrated by the values recorded in the table for compounds III and VII.

Experimental

Compounds I, II, III, IV, and VII were prepared by the methods of Bu'lock and Smith.[2,4] III had the same melting point, ultraviolet and infrared spectra as those recorded in the literature.[19]

The proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer with *ca.* 35% deuterochloroform solutions containing tetramethylsilane as an internal standard.

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(14) The resonance of the 7 proton is split further by interaction with the 6 proton. The pattern observed for the five protons in these compounds exemplifies a deceptive AB portion of an ABX system of the type discussed by R. J. Abraham and W. G. Schneider, *Can. J. Chem.*, **39**, 216 (1961). A theoretical fit to the observed spectra is provided by assigning $J_{AB} = 13.5$ c.p.s., $J_{AX} = 8.5$ c.p.s., $J_{BX} = 0$ and $\nu_A - \nu_B = 4.2$ c.p.s. Unfortunately, J_{AB} is an assumed value and the X portion of the spectrum, which could confirm these values, was not well resolved.

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Reaction of Nitriles with Hydrazine Hydrate and Raney Nickel. The Synthesis of Polynuclear Aromatic Hydrocarbons[1]

WALTER W. ZAJAC, JR., AND RONALD H. DENK[2]

Department of Chemistry, Villanova University, Villanova, Pennsylvania

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Pietra and Trinchera[3] reported the use of hydrazine hydrate and Raney nickel as an effective combination for the partial reduction of six aromatic nitriles to the hydrazones or azines, which can be hydrolyzed to the corresponding aldehydes in good yield. We are currently investigating the scope and limitations of this reaction. In a completely

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(2) This investigation was carried out during the tenure of a Predoctoral Fellowship from the National Cancer Institute, U.S. Public Health Service.

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