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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(7) Z. Maceriewicz, *Roczniki Chem.*, **24**, 144 (1950).

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(11) Compare, for example, the infrared spectra of *cis*- and *trans*-cinnamaldehyde; G. Gamboni, V. Theus, and H. Schinz, *Helv. Chim. Acta*, **38**, 255 (1955).

(12) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959, p. 89.

(13) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," Benjamin, New York, 1961, Chap. 2.

(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.

(15) E. O. Bishop and R. E. Richards, *Mol. Phys.*, **3**, 114 (1960).

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

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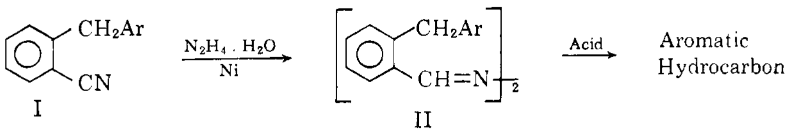
(2) This investigation was carried out during the tenure of a Predoctoral Fellowship from the National Cancer Institute, U.S. Public Health Service.

(3) S. Pietra and C. Trinchera, *Gazz. ital. chim.*, **85**, 1705 (1955).



	Nitrile		Azine	% Yield	Hydrocarbon	% Yield
Ia.	Ar = C_6H_5[a]	IIa.	Ar = C_6H_5	90	Anthracene	95
Ib.	Ar = 2,3-$(CH_3)_2C_6H_3$[b]	IIb.	Ar = 2,3-$(CH_3)_2C_6H_3$	88	1,2-Dimethylanthracene	90
Ic.	Ar = 1-$C_{10}H_7$[c]	IIc.	Ar = 1-$C_{10}H_7$	92	Benz[*a*]anthracene	98
Id.	Ar = 2-$C_{10}H_7$[c]	IId.	Ar = 2-$C_{10}H_7$	91	Benz[*a*]anthracene	95

[a] See C. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940). [b] See S. G. Quo, Ph.D. thesis, Virginia Polytechnic Institute, Blacksburg, Virginia. [c] See F. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, **77**, 3413 (1953).

unrelated investigation on the mechanism of the acid-catalyzed aromatic cyclodehydration reaction, Bradsher and Vingiello[4] have shown that the rate of formation of anthracene from 2-benzylbenzaldehyde is extremely rapid. These observations made it seem likely that properly substituted aromatic nitriles could be converted to the corresponding polynuclear aromatic hydrocarbons. When applied to 2-(arylmethyl)benzonitriles, this should lead to a general synthesis of anthracenes and the benzo derivatives of anthracene. The validity of this assumption was established by the synthesis of anthracene by the partial reduction of 2-benzylbenzonitrile (Ia. Ar = phenyl) with hydrazine hydrate and Raney nickel followed by the acid cyclization of the resulting 2-benzylbenzaldazine (IIa. Ar = phenyl). The synthesis of 1,2-dimethylanthracene was also effected. Benz[*a*]anthracene was prepared by the acid hydrolysis of 2-(1-naphthylmethyl)benzaldazine (IIc. Ar = 1-naphthyl) and also by the acid hydrolysis of 2-(2-naphthylmethyl)benzaldazine (IId. Ar = 2-naphthyl). The azines IIb, IIc, and IId were also prepared in very good yields from the corresponding nitriles Ib, Ic, and Id by the reaction with hydrazine hydrate and Raney nickel. From this preliminary investigation it appears that the preceding method of synthesis of polynuclear aromatic hydrocarbons has general application.

Experimental

General Procedure.—One gram of nitrile, 0.5 g. of Raney nickel,[5] 10 ml. of 85% hydrazine hydrate, and 50 ml. of 95% ethanol were heated at 50–55° until the evolution of ammonia ceased. The nickel catalyst was removed by filtration and the ethanolic solution was concentrated until the azine precipitated. The collected azine (see Table I) was heated under reflux with 50% sulfuric acid (or 10 ml. of 48% hydrobromic acid and 20 ml. of glacial acetic acid). The hydrocarbon was isolated by extraction with benzene and concentration of the benzene extracts.

TABLE I

2-(ARYLMETHYL)BENZALDAZINES (II)[a]

	M.p.[b]	Formula	Calcd. C	Calcd. H	Calcd. N	Found[c] C	Found[c] H	Found[c] N	(C = N)[d]
IIa	142–143	$C_{28}H_{24}N_2$	86.56	6.23	7.21	86.74	6.20	7.19	6.20 μ
IIb	196–197	$C_{32}H_{32}N_2$	86.44	7.26	6.30	86.74	7.08	6.20	6.20 μ
IIc	171–172	$C_{36}H_{28}N_2$	88.49	5.78	5.73	87.80	6.40	6.02	6.19 μ
IId	169–170	$C_{36}H_{28}N_2$	88.49	5.78	5.73	87.84	6.20	6.00	6.19 μ

[a] Recrystallized from benzene–ethanol as yellow needles. [b] Uncorrected; determined on Thomas–Hoover melting point apparatus. [c] Geller Laboratories, Bardonia, New York. [d] Infrared spectra obtained on a Perkin-Elmer Model 21, 0.5% in KBr.

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[4] C. Bradsher and F. Vingiello, *J. Am. Chem. Soc.*, **71**, 1434 (1949).

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Hydrolysis of Simple Aromatic Esters and Carbonates

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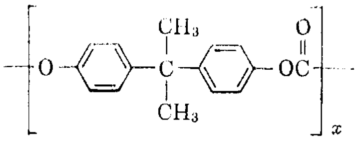
It has been reported[2] that aromatic polycarbonates derived from 2,2-bis(4-hydroxyphenyl)propane,



are much more resistant to hydrolytic degradation than aromatic polyesters obtained from condensation of *m*-hydroxybenzoic acid,

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[2] R. Gilkey and J. R. Caldwell, *J. Appl. Polymer Sci.*, **2**, 198 (1959).