The diethyl acetal (II), does not reduce Fehling's solution. It is very soluble in water and in most organic solvents. If the diethyl acetal is dissolved in 0.1 *N* hydrochloric acid, hydrolysis takes place very rapidly and the resulting dihydroxyacetone reduces Fehling's solution at room temperature.

Diethyl acetal of dibenzoxyacetone (III). The diethyl acetal (II) (8 g.) was dissolved in 50 ml. of pyridine and 14 g. of benzoyl chloride was added slowly, maintaining the temperature below 30°. The mixture then was heated on the steam-bath for 80 minutes and poured onto powdered ice. After standing for 2 hours the oil was extracted with ether and the ethereal extract was washed with dilute hydrochloric acid, sodium carbonate solution, and water. The ether solution was dried with sodium sulfate and the solvent was evaporated. The oily residue was crystallized from methanol furnishing 15.5 g. of thick prisms, m.p. 79–80° (85% yield).

Anal. Calc'd for $C_{21}H_{24}O_6$: C, 67.63; H, 6.50. Found: C, 67.25; H, 6.61.

Dibenzoxyacetone (IV). A solution of 10 g. of the diethyl acetal of dibenzoxyacetone (III) and 8 g. of *p*-toluenesulfonic acid in 500 ml. of methanol and 30 ml. water was refluxed 4 hours and then was concentrated to one-third its volume, diluted with water, and extracted with ether. The ethereal extract was washed with a sodium carbonate solution and water, dried over sodium sulfate, and concentrated. By addition of hexane there crystallized 7.2 g. of long needles m.p. 118–119° (90% yield). This product gave no depression in a mixture m.p. with a sample of dibenzoxyacetone obtained by benzoylation of dihydroxyacetone.[3]

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Studies in *cis*- and *trans*-Stilbazoles[1]

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This study was initiated to see if the methods previously used to form *cis*- and *trans*-2-styrylquinolinium salts[2] would be successful in the stilbazole series. Only *cis*- and *trans*-*o*-nitrostilbazole, obtained by fractional crystallization, has so far been reported.[3]

With one exception, identical stilbazolium salts were formed, either by way of a piperidine-catalyzed condensation of the picolinium salt with an aromatic aldehyde (Method A) or by quaternation of stilbazoles, obtained by the condensation of 2 (and 4)-picolines with aromatic aldehydes in acetic anhydride (Method B). These are all presumably the stable *trans* structures.

When *o*-hydroxybenzaldehyde and 2(and 4)-picoline were refluxed with acetic anhydride, *o*-acetoxy-2(and 4)-stilbazoles, were formed (XXI, XXIV). Heating to 95° with methyl iodide in a sealed vessel gave 1-methyl-*o*-hydroxy-2(and 4)-stilbazolium iodides (VIII B, XII B), deacetylation having occurred during quaternation. The piperidine-catalyzed condensation of *o*-hydroxybenzaldehyde with 2(and 4)-picoline methiodides gave different 1-methyl-*o*-hydroxy-2(and 4)-stilbazolium iodides (VIII A, XII A). A *trans* structure is assigned to these latter salts based on their longer wavelength absorption in the ultraviolet. Heating either *cis*- or *trans*-1-methyl-*o*-hydroxy-2(and 4)-stilbazolium iodides with acetic anhydride gave the identical 1-methyl-*o*-acetoxy-2(and 4)-stilbazolium iodides (IX A, IX B, XIII A, XIII B), isomerization accompanying acetylation. It may be inferred that it is only an *o*-hydroxy group which assists in stabilizing the *cis* configuration since no *cis* compounds were isolable with *p*-hydroxy groups (VII A, VII B).

That a Chugaev-type acetate decomposition probably gives rise to the *cis* configuration is evidenced by the fact that six-hour refluxing of *o*-hydroxybenzaldehyde with 4-picoline in acetic anhydride gave *cis*-*o*-acetoxy-4-stilbazole (XXIV A), whereas 72-hour refluxing gave the *trans* compound (XXIV B), which absorbs some 45 mμ longer in the ultraviolet.

Heating *p*-hydroxybenzaldehyde with 4-picoline in acetic anhydride for six hours gave *p*-acetoxy-4-stilbazole (XXV), while, after 72 hours, the deacetylated *p*-hydroxy-4-stilbazole (XXVI) was obtained.

EXPERIMENTAL[4,5]

Piperidine-catalyzed condensation of picolinium salts with aromatic aldehydes. Method A. To a solution of 5 g. (0.02 mole) of the 2(or 4)-picoline methiodide and 5 g. (0.03–0.04 mole) of aromatic aldehyde in 25 cc. of methanol was added 10 drops of piperidine. After refluxing for four hours, the reaction mixture was cooled, and the product was collected and purified.

Condensation of picolines with aromatic aldehydes in acetic anhydride. Method B. All the 2(and 4)-stilbazoles were prepared in this manner by refluxing a mixture of 0.1 mole of 2(or 4)-picoline, 0.1 mole of aromatic aldehyde, and 0.2 mole of acetic anhydride for six hours. At the end of the reflux period the major portion of the acetic acid and

(1) Presented in part before Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., September 1956.
(2) Horwitz, *J. Am. Chem. Soc.*, **77**, 1687 (1955).
(3) Räth and Lehmann, *Ber.*, **55**, 342 (1925).

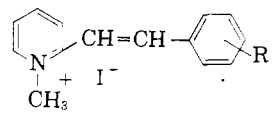
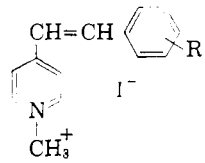
(4) All melting points are corrected. For the salts, the samples were rapidly heated to within 30° of melting and then proceeding at a rate of 3° per minute to melting. Boiling points are uncorrected.
(5) Ultraviolet spectra are on 10^{-5} *M* solutions in methanol.

TABLE I[a]

2(AND 4)-STILBAZOLE METHIODIDES

A compounds are from the piperidine-catalyzed condensation of 1,2-dimethylpyridinium iodide with aromatic aldehydes (Method A).

B compounds are from the quaternation of 2(or 4)-stilbazoles obtained by acetic anhydride condensation (Method B).

Compound	R	Yield, (%)	M.P. (°C.)	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	Nitrogen Calc'd	Nitrogen Found	λ, mμ	ε
				 2-Stilbazole methiodides								
IA	H	72	230–231[b]	$C_{14}H_{14}IN$	52.01	51.98	4.37	4.41	4.33	4.27	338	30,650
B					52.01	51.43	4.37	4.23	4.33	4.27		
IIA	*3,4*-CH_2O_2	69	274–275[c]	$C_{15}H_{14}INO_2$	49.08	49.01	3.84	3.78	3.81	3.69	282	16,650
B					49.08	48.88	3.84	3.89	3.81	3.82		
IIIA	*o*-NO_2	40	229–230	$C_{14}H_{13}IN_2O_2$	45.66	45.60	3.56	3.48	7.61	7.44	322	18,150
B					45.66	45.79	3.56	3.51	7.61	7.66		
IVA	*m*-NO_2	53	251–253[d]	$C_{14}H_{13}IN_2O_2$	45.66	45.83	3.56	3.44	7.61	7.64	265	8,790
B					45.66	45.75	3.56	3.35	7.61	7.71	326	29,870
VA	*p*-NO_2	59	253–254	$C_{14}H_{13}IN_2O_2$	45.66	46.05	3.56	3.43	7.61	7.54	335	29,300
B					45.66	45.80	3.56	3.38	7.61	7.61		
VIA	*o*-Cl	52	230–231	$C_{14}H_{13}ClIN$	47.01	46.94	3.67	3.57	3.92	3.98	331	24,140
B					47.01	46.95	3.67	3.63	3.92	3.91		
VIIA[e]	*p*-CH_3COO		230–231	$C_{16}H_{16}INO_2$	50.42	50.43	4.23	4.25	3.67	3.61	372	17,200
B					50.42	50.45	4.23	4.29	3.67	3.84		
VIIIA	*o*-OH	75	253–254[f]	$C_{14}H_{14}INO$	49.56	49.42	4.16	4.17	4.13	3.92	375	17,800
B[g]			184–185		49.56	49.63	4.16	4.33	4.13	4.03	333	13,570
IXA[h]	*o*-CH_3COO		201–202	$C_{16}H_{16}INO_2$	50.42	50.45	4.23	4.27	3.67	3.70	329[j]	9,930
B[i]					50.42	50.25	4.23	4.30	3.67	3.75		
				 4-Stilbazole methiodides								
XA	H	64	209–210[k]	$C_{14}H_{14}IN$	52.01	51.88	4.37	4.40	4.33	4.33	342	13,000
B					52.01	51.99	4.37	4.22	4.33	4.52		
XIA	*m*-NO_2	62	299–300[l]	$C_{14}H_{13}IN_2O_2$	45.66	45.70	3.56	3.36	7.61	7.56	330	25,770
B					45.66	45.85	3.56	3.38	7.61	7.50		
XIIA	*o*-OH	61	235–236	$C_{14}H_{14}INO$	49.56	49.49	4.16	4.12	4.13	4.13	383[m]	18,570
B[n]			224–225		49.56	49.57	4.16	4.22	4.13	3.89	325[j]	7,450
XIIIA[o]	*o*-CH_3COO		228–229	$C_{16}H_{16}INO_2$	50.42	50.15	4.23	4.35	3.67	3.71	334[j]	17,200
B					50.42	50.39	4.23	4.24	3.67	3.70		

[a] Solvent of recrystallization was methanol in all cases. [b] Phillips [*J. Org. Chem.*, 12, 333 (1947)] records m.p. 230–231°. [c] Above reference *b* reports m.p. 295°. [d] Above reference *b* reports m.p. 258–260°. [e] Prepared by refluxing 1-methyl-2-*p*-hydroxystilbazolium iodide in acetic anhydride for two hours. The hydroxy salt was prepared by Method A, yield 68%; m.p. 279–280° (reference *b* reports m.p. 269–270°). *Anal.* Calc'd for $C_{14}H_{14}INO$: C, 49.56; H, 4.16; N, 4.13. Found: C, 49.40; H, 4.26. [f] Above reference *b* reports m.p. 253–254°. [g] Obtained by heating 2-*o*-acetoxystilbazole (XXI) with methyl iodide at 95° for three hours in a sealed container. [h] Prepared by refluxing 1-methyl-2-*o*-hydroxystilbazolium iodide in acetic anhydride for two hours. The hydroxy salt was prepared by Method A; 82% yield; m.p. 257–258° (reference *b* reports m.p. 253–254°). *Anal.* Calc'd for $C_{14}H_{14}INO$: C, 49.56; H, 4.16; N, 4.13. Found: C, 49.49; H, 4.42; N, 4.13. [i] From VIIIB by refluxing in acetic anhydride for two hours. [j] Estimated from broad band. [k] Phillips [*J. Org. Chem.*, 14, 302 (1949)] reports m.p. 220–221°. [l] Reference *j* records no melting up to 290°. [m] Inflection point at 322 mμ, 11,730. [n] Obtained when 4-*o*-acetoxystilbazole (XXIVA) was quaternated with methyl iodide by heating in a sealed vessel for three hours on the steam-bath. [o] A compound from XIIA and B compound from XIIB, by refluxing in acetic anhydride for two hours.

acetic anhydride was removed by distillation and the residue was drowned in water (200 cc.). The mixture was made basic and, if the product crystallized out, it was collected and purified by recrystallization. If the product oiled out it was recovered by extraction with ether and purified by distillation.

Quaternation of the stilbazoles was accomplished by heating with methyl iodide in a closed vessel for three hours on the steam-bath.

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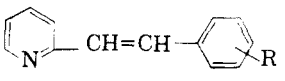
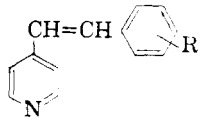
TABLE II[a]

2(AND 4)-STILBAZOLES OBTAINED BY THE CONDENSATION OF AROMATIC ALDEHYDES WITH 2(AND 4)-PICOLINE IN ACETIC ANHYDRIDE (METHOD B)

Compound	R	Yield, %	M.p. or B.p., °C.	Mm.	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	Nitrogen Calc'd	Nitrogen Found
					2-Stilbazoles						
XIV	H	52	91–92[b]		$C_{13}H_{11}N$	86.17	86.17	6.12	6.07	7.73	7.78
			140–142	2.5							
XV	3,4-CH_2O_2	61	111–112		$C_{14}H_{11}NO_2$	74.66	74.51	4.92	4.82	6.22	6.20
			180–181	2							
XVI	o-NO_2	57	102–103[c]		$C_{13}H_{10}N_2O_2$	69.17	69.10	4.45	4.42	12.39	12.34
XVII	m-NO_2	94	131–132[d]		$C_{13}H_{10}N_2O_2$	69.17	69.01	4.45	4.39	12.39	12.24
XVIII	p-NO_2	91	140–141[e]		$C_{13}H_{10}N_2O_2$	69.17	69.05	4.45	4.36	12.39	12.74
XIX	o-Cl	57	76–77		$C_{13}H_{10}ClN$	72.38	72.29	4.67	4.57	6.49	6.28
			108–110	2							
XX	p-CH_3COO	76	114–115		$C_{15}H_{13}NO_2$	75.28	75.27	5.47	5.60	5.85	5.69
XXI	o-CH_3COO	58	180–181	3.5	$C_{15}H_{13}NO_2$	75.28	75.45	5.47	5.48	5.85	5.98
					4-Stilbazoles						
XXII	H	92	129–130[f]		$C_{13}H_{11}N$	86.17	86.00	6.12	5.99	7.73	7.57
XXIII	m-NO_2	97	144–145[g]		$C_{13}H_{10}N_2O_2$	69.17	69.05	4.45	4.49	12.39	12.61
XXIVA[h]	o-CH_3COO	74	118–119		$C_{15}H_{13}NO_2$	75.28	75.44	5.47	5.51	5.85	5.76
B	o-CH_3COO	67	197–198		$C_{15}H_{13}NO_2$	75.28	75.35	5.47	5.81	5.85	6.10
XXV	p-CH_3COO	68	167–168		$C_{15}H_{13}NO_2$	75.28	75.19	5.47	5.37	5.85	5.67
XXVI[i]	p-OH	90	264–265[j]		$C_{13}H_{11}NO$	78.77	78.47	5.60	5.79	7.07	6.87

[a] Solvent of recrystallization was methanol for XVII, XVIII, XXIII, and XXVI; isopropyl alcohol for XXII; low-boiling petroleum ether for XVI, XX, XXIVA; 1,4-dioxane for XXIVB; and acetonitrile for XXV. [b] Blout *et al.* [*J. Am. Chem. Soc.*, **67**, 1315 (1945)] reports m.p. 89°. [c] Reference 2 reports m.p. 101° for the *trans* isomer. [d] Feist [*Ber.*, **34**, 465 (1901)] reports m.p. 127°. [e] Reference *d* reports m.p. 125–126°. [f] Reference *b* reports m.p. 130°. [g] Friedländer [*Ber.*, **38**, 2838 (1905)] reports m.p. 138°. [h] Ultraviolet spectra: XXIVA, λ 298 mμ; ε 26,580; XXIVB, λ 287, 332 mμ; ε 21,140, 19,220. [i] Obtained by 72-hour refluxing. [j] Chiang and Hartung [*J. Org. Chem.*, **10**, 21 (1945)] reports m.p. 215–217°.

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The Acetylation of Organic Hydroxy Compounds with Ketene

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The use of ketene in acetylating glycols, Cellosolves, carbohydrates, and other polyhydroxy organic compounds appears to be rather limited. Van Alphen[2] reports an unsuccessful attempt to acetylate glucose with ketene, while Hurd[3] and his associates, using acetone, dioxane, and pyridine as solvents and a trace of sulfuric acid as catalyst, obtained syrups which defied purification. Gwynn and Degering[4] report that ketene reacts with acetone and pyridine and this fact may have been a serious complication in the final purification. In addition Rice and Greenburg[5] have studied the rate of polymerization of ketene in various solvents and found this tendency to be a serious complication in many instances. Acetone was a rather serious offender in this regard. However, the rate of polymerization of ketene in carbon tetrachloride was the lowest of the twenty different solvents tested. The reaction constant calculated according to the bimolecular law was 0.0000465 for carbon tetrachloride and 0.0146 for acetone, both at 0°. This means that at 0° ketene polymerizes approximately 300 times faster in acetone than in carbon tetrachloride. This may offer a plausible explanation for the greater difficulty encountered in purifying the acetylation product when acetone was used as solvent.

Significant contributions to carbohydrate and other hydroxy compound acetylations with ketene

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(2) J. Van Alphen, *Rec. trav. chim*, **43**, 823 (1924).

(3) C. D. Hurd, S. M. Cantor, and A. S. Roe, *J. Am. Chem. Soc.*, **61**, 426 (1939).

(4) B. H. Gwynn and E. F. Degering, *J. Am. Chem. Soc.*, **64**, 2216 (1942).

(5) F. O. Rice and J. Greenburg, *J. Am. Chem. Soc.*, **56**, 2132 (1934).