this way, 90% of the reaction product was isolated. An additional 8% was recovered by vacuum evaporation of the mother liquor. Formamidine hydrochloride was identified by analysis and by the mixture melting point of its picrate with an authentic sample of formamidine picrate.

Anal. Calc'd for CH_5ClN_2: N, 34.80; Cl, 44.10. Found: N, 34.43, 34.24; Cl, 43.63, 43.48.

Anal. Calc'd for *formamidine picrate* $C_7H_7N_5O_8$: C, 30.75; H, 2.56; N, 25.61. Found: C, 30.76, 30.90; H, 2.56, 2.66; N, 25.53, 25.57.

1,2,4-Triazole (V). To a solution of 16.2 g. (0.2 mole) of 1,3,5-triazine in 600 ml. of absolute alcohol (previously distilled from metallic sodium), there was added 20.55 g. (0.3 mole) of well-powdered hydrazine monohydrochloride. The mixture then was refluxed for eight hours. After cooling, 9 g. of ammonium chloride was filtered off. An additional amount (7 g.) was precipitated upon addition of ether to the filtrate, thus resulting in an almost quantitative yield (Calc'd 16.35 g.). The red-colored alcohol-ether filtrate was evaporated *in vacuo* to dryness. The remainder, 21 g., was recrystallized from chloroform yielding pure 1,2,4-triazole (95%). A mixture melting point with an authentic sample was without depression.

Anal. Calc'd for $C_2H_3N_3$: N, 60.87. Found: N, 60.80, 60.70.

1-Methyl-1,2,4-triazole. To a solution of 3.24 g. of *s*-triazine in 30 ml. of absolute ethanol 4.95 g. of methyl hydrazine hydrochloride was added. The reaction started immediately with evolution of heat and was completed by refluxing for eight hours. The precipitated ammonium chloride (2.2 g.) then was filtered off and the alcohol was removed through an efficient column. The oily residue was extracted with ether and an additional 0.9 g. of ammonium chloride which remained undissolved was removed by filtration. From the ethereal filtrate the ether was distilled leaving behind 4.0 g. of a yellowish oil which was almost pure 1-methyl-1,2,4-triazole. By distillation under atmospheric pressure the base was obtained colorless; b.p. 175–176°; m.p. 20°; yield: 81%.

Anal. Calc'd for $C_3H_5N_3$: N, 50.57. Found: N, 50.12, 50.10.

1-Phenyl-1,2,4-triazole (VI). A mixture of 16.2 g. of *s*-triazine and 43.4 g. of phenylhydrazine hydrochloride in 200 ml. of absolute alcohol was refluxed for 12 hours. After cooling, 12.5 g. of ammonium chloride was filtered off and the filtrate was distilled to remove the alcohol. There remained 36 g. of a light colored oil which crystallized upon storage in an icebox and consisted of almost pure 1-phenyl-1,2,4-triazole. By distillation under atmospheric pressure the base was obtained pure; b.p. 268–270°; m.p. 47°; yield: 83%.

Anal. Calc'd for $C_8H_7N_3$: N, 28.95. Found: N, 28.63, 28.68.

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Some Derivatives of Dihydroxyacetone

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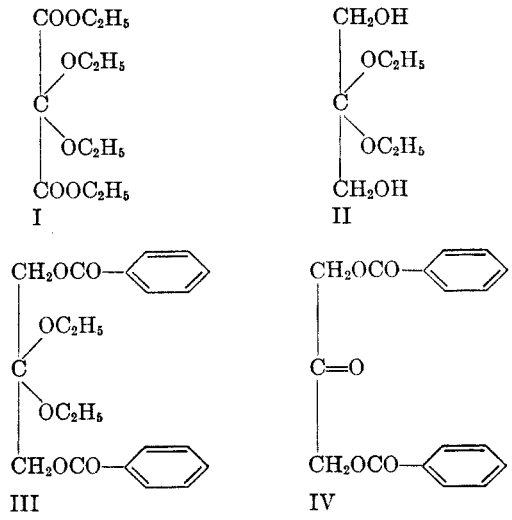
In connection with a study on carbohydrates it was necessary to prepare the diethyl acetal of dihydroxyacetone. Various methods of ketalation of dihydroxyacetone were investigated without success. However it was found that reduction of diethoxy diethyl malonate (I) with lithium aluminum hydride, afforded the desired acetal (II) in very good yield.



This acetal is a crystalline substance which can be stored for long periods without decomposition. It does not reduce Fehling's solution. Mineral acids immediately cause hydrolysis and the resulting solution reduces Fehling's solution, even at room temperature.

The diethyl acetal can be benzoylated very easily to the corresponding dibenzoate (III) and the hydrolysis of the acetal grouping in III gave dibenzoxyacetone (IV) in almost quantitative yield.

EXPERIMENTAL[1]

We would like to thank Mrs. A. González from Syntex, S. A., for the microanalyses and Mr. F. Casas for technical assistance.

Diethoxy diethyl malonate was prepared from dibromo diethyl malonate according to Bischoff.[2]

Diethyl acetal of dihydroxyacetone (II). Diethoxy diethyl malonate (I) (50 g.) was dissolved in 400 ml. of anhydrous ether. The solution was added at room temperature during 2 hours with mechanical stirring to a slurry of 10 g. of lithium aluminum hydride in 300 ml. of ether, the mixture was refluxed 15 minutes, and the excess of hydride was destroyed with ethyl acetate; 20 ml. of a saturated solution of sodium sulfate was added with stirring and then enough anhydrous sodium sulfate until a clear solution was formed. The inorganic solids were filtered and thoroughly washed with ethyl acetate. The combined liquors were evaporated and the oily residue was crystallized by addition of hexane giving 27 g. of diethyl acetal (II) (81% yield) m.p. 79–80°. The analytical sample was obtained by repeated crystallization from ether-hexane. The product appears as long needles, m.p. 87–89°.

Anal. Calc'd for $C_7H_{16}O_4$: C, 51.20; H, 9.81. Found: C, 51.40; H, 9.83.

(1) The melting points are uncorrected.
(2) Bischoff, *Ber.*, **30**, 487 (1897).

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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(3) Fischer, Taube, and Baer, *Ber.*, **60**, 479 (1927).

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.