Summary

1. Vinyl phenyl ketone adds readily to many substances containing a conjugated system of double bonds.

2. Addition products were obtained from this unsaturated ketone and 2,3- and 1,4-diphenylbutadienes, 1-phenyl-4-methylbutadiene, 2,3-dimethylbutadiene, cyclopentadiene, tetraphenylcyclopentadienone, and ethyl sorbate.

3. Secondary reaction products resulted from vinyl phenyl ketone and methyleneanthrone, *trans*-dibenzoylethylene and methyleneanthrone, and from benzalacetophenone and tetraphenylcyclopentadienone.

4. Methyl β-benzoylacrylate and 2,3-diphenylbutadiene also gave an addition product.

5. 3,4-Diphenylbenzophenone and its 6-carboxylic acid were synthesized and shown to be identical with specimens previously secured by degradation of a polynuclear indene derivative.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

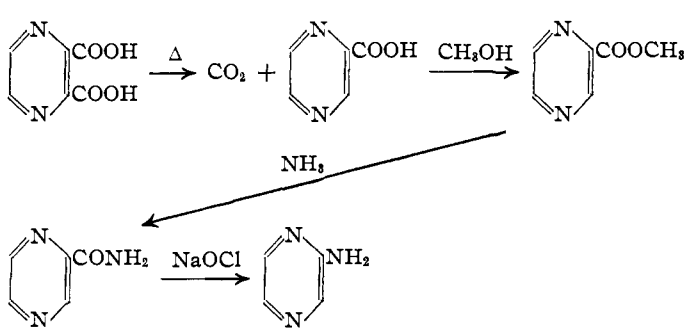
Syntheses in the Pyrazine Series. II. Preparation and Properties of Aminopyrazine

BY STANLEY A. HALL AND PAUL E. SPOERRI

Certain derivatives of diaminopyridine such as pyridium,[1] and its modifications,[2] exhibit valuable bacteriostatic properties.[3] However, little is known about the corresponding amino pyrazines.

Gabriel and Sonn[4] obtained aminopyrazine from pyrazine-2,3-dicarboxylic acid. However, their product was impure; m. p. 110–117°. Moreover, their synthesis is complicated by side reactions.

We have synthesized aminopyrazine by a modification of the method of Gabriel and Sonn



The Hofmann degradation of pyrazine-carboxylamide has not been described in the literature. An interesting intermediate compound was isolated which immediately decomposed with much effervescence in dilute acid (mineral or acetic) to give the desired aminopyrazine. This intermediate compound was identified as sodium pyrazine-carbamate.

(1) U. S. Patents 1,680,108-9-10-11 (1928).
(2) Bowie, *Brit. Med. J.*, **II**, 283–284 (1938).
(3) Ostromislensky, THIS JOURNAL, **56**, 1713–1714 (1934).
(4) Gabriel and Sonn, *Ber.*, **40**, 4851–4860 (1907).

Although Mohr,[5] in his study of the mechanism of the Hofmann reaction, isolated barium phenylcarbamate, this is the first time, as far as can be ascertained, that the Hofmann degradation of an amide has proceeded only to the stage of a stable sodium carbamate which must then be decomposed by acidification in order to obtain the amine. This adds confirmation to Mohr's theory of the mechanism of the Hofmann reaction and it also shows up the characteristic stabilizing effect of the pyrazine ring upon certain functional groups.

Aminopyrazine was obtained in pure white crystalline form, m. p. 117–118°. It is very soluble in water, giving a solution neutral to litmus. Aminopyrazine gives only a very faint isonitrile test, which differs from the observations of Gabriel and Sonn who reported a distinct isonitrile test.

Both aminopyrazine and acetaminopyrazine sublime without decomposition.

Experimental

Pyrazine-carboxylic Acid.—33.9 g. of pyrazine-2,3-dicarboxylic acid (m. p. 190°) was heated rapidly to 210° in a vacuum sublimation chamber. At 3 to 4 mm., simultaneous decarboxylation and sublimation took place. After resubliming *in vacuo* the product was recrystallized from hot water.

Fine white needles of pyrazine-carboxylic acid were obtained: m. p. 225° (decompn.); m. p. 225° (decompn.), Gabriel and Sonn; m. p. 229° (decompn.), Stoehr; yield 17.5 g. or 70.0%.

(5) Mohr, *J. prakt. Chem.*, (2) **73**, 117–191, 229 (1906).

Methyl Pyrazine-carboxylate.—10.5 g. of oven-dried pyrazine-carboxylic acid in 105 g. of absolute methyl alcohol saturated with dry hydrogen chloride was distilled at reduced pressure to remove excess hydrogen chloride. The residue was neutralized with saturated sodium carbonate solution and extracted with ethyl acetate. After evaporation of the ethyl acetate the solid reddish-yellow residue was sublimed at 4 mm. in an oil-bath at 100°. The pure white crystals melted at 59° unchanged after several recrystallizations from ether and other solvents (m. p. 62°; British Patent 451,304); yield 8.4 g. or 72%.

Pyrazine-carboxylamide.—8.4 g. of methylpyrazine-carboxylate in 8.4 g. of warm methyl alcohol was added to a saturated absolute methyl alcohol (17 g., 0°) solution of ammonia. The white crystals were filtered off the next day, washed with methanol, ether and dried: m. p. 189° (lit. m. p. 188°; British Patent 451,304); yield 6.9 g. or 92%.

Aminopyrazine.—After dissolving 4.2 g. of chlorine in 13.8 g. of sodium hydroxide and 150 g. of ice and water, 6.9 g. of finely powdered pyrazine-carboxylamide was added. The solution was warmed, with stirring for one hour.

The next day, the needle-like crystals were filtered off and dried; 3.5 g. of the product dissolved in water gave an alkaline solution which evolved carbon dioxide on acidification. The ethyl acetate extract of the neutralized solution was evaporated, leaving a solid yellowish residue which sublimed completely at 3 mm.; temp. of oil-bath 100°; yield, 1.5 g. of pure aminopyrazine.

The original filtrate was acidified and an alcoholic picric acid solution added. The picrate obtained and washed with alcohol, ether and dried had no definite m. p. but decomposed at 214 to 250°. The suspension of the picrate in cooled ether was saturated with hydrogen chloride. The hydrochloride filtered off and washed with ether was neutralized with saturated sodium carbonate solution and extracted with ethyl acetate. The residue remaining after the evaporation of the ethyl acetate was sublimed at 3 mm.; temp. of oil-bath 100°; yield of aminopyrazine, 0.9 g.; combined yields of aminopyrazine 2.9 g. or 55%: m. p. 117–118° (lit. m. p. 110–117°, Gabriel and Sonn).

Anal. Calculated for $C_4H_5N_3$: C, 50.5; H, 5.30; N, 44.2. Found: C, 50.4, 50.3; H, 5.16, 5.16; N, 44.1, 43.9.

Acetaminopyrazine.—M. p. 133°.

Anal. Calculated for $C_6H_7H_3O$: C, 52.54; H, 5.11; N, 30.66. Found: C, 52.50, 52.73; H, 6.25, 6.15; N, 28.99.

Intermediate Product in the Hofmann Reaction.—The properties of the needle-like crystals obtained were found to be as follows: no definite m. p.; began to turn brown at 257°; black at 275°; very soluble in water to give an alkaline solution; insoluble in organic solvents including absolute alcohol; contains sodium; halogen test negative; effervesces (CO_2 evolved) in dilute acid (mineral or acetic) to form aminopyrazine. The intermediate compound evidently is sodium pyrazine carbamate. *Anal.* Calculated for $C_5H_4N_3O_2Na$: N, 26.1; Na, 14.3. Found: N, 25.9; Na, 14.4.

Summary

1. The Hofmann degradation on pyrazine carboxylamide gave a 55% yield of aminopyrazine, m. p. 117–118°.

2. From the Hofmann reaction an intermediate compound was isolated and identified as sodium pyrazine-carbamate, which on acidification gave aminopyrazine and carbon dioxide.

BROOKLYN, N. Y. RECEIVED OCTOBER 25, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Conversion of Arylbismuth Halides to Triarylbismuth Compounds

BY HENRY GILMAN AND H. L. YABLUNKY

We have observed that one of the intermediate types formed in the recently described synthesis of triarylbismuth compounds by the diazonium reaction[1] is R_2BiX. This suggested an examination of procedures for the conversion of such compounds to the R_3Bi compounds. The best reagent, we now find, for this purpose is hydrazine hydrate. This reagent was first used to convert 2-furylmercuric chloride and phenylmercuric chloride to 2,2′-difurylmercury and diphenylmercury, respectively[2]; and it was shown subsequently that hydrazine is a reagent of choice for converting RHgX to R_2Hg compounds.[3]

If the equilibrium

$$3R_2BiX \rightleftharpoons 2R_3Bi + BiX_3$$

is valid, then one of the functions of the hydrazine may be to reduce the bismuth halide. The procedure was next extended successfully to the conversion of phenylbismuth dibromide to triphenylbismuth, and to the conversion of R_3BiX_2 compounds to the corresponding triarylbismuth compounds. Attention might be directed to two

(1) Gilman and Svigoon, THIS JOURNAL, **61**, 3586 (1939).

(2) Gilman and Wright, *ibid.*, **55**, 3302 (1933).

(3) Gilman and Barnett, *Rec. trav. chim.*, **55**, 563 (1936).