[Contribution from the Chemical Laboratory of McGill University and from the Kodak Research Laboratories]

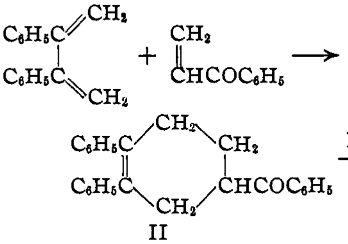
Addition Reactions of Vinyl Phenyl Ketone. VI. The Diene Synthesis

By C. F. H. Allen, A. C. Bell, Alan Bell and James Van Allan

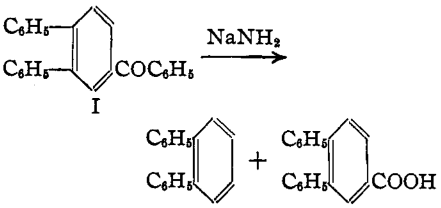
In a paper describing the reactions used in determining the structure of a dimeric diphenylcyclopentadienone,[1] one of the intermediate degradation products was the previously unknown 3,4-diphenylbenzophenone I, which was degraded stepwise to *o*-diphenylbenzene. This series of reactions demonstrated the presence of a benzene ring and two phenyl groups in the *ortho* position, but did not locate the benzoyl group. The original purpose of this work was to synthesize 3,4-diphenylbenzophenone by an unambiguous method, and show its identity with the ketone secured as mentioned. Not only has this been successfully accomplished, but its 6-carboxylic acid XXIV also has been synthetically prepared, proving conclusively the place of attachment of the indene ring in the bimolecular product. In addition, other products resulting from the use of vinyl phenyl ketone in the diene synthesis are described.

Vinyl phenyl ketone adds readily to many substances containing a conjugated system of double bonds, and, in general, the addition products have the expected properties. The reaction is most useful with unsaturated ketones; it is less satisfactory with hydrocarbons, and fails with furans.

2,3-Diphenylbutadiene-1,3[2] added vinyl phenyl ketone on long refluxing in xylene solution. The tetrahydroketone II was dehydrogenated by bromine to 3,4-diphenylbenzophenone I. As prepared in this way the latter proved to be identical with a specimen secured from the original degradation[1]; further, each gave the same oxime and 2,4-dinitrophenylhydrazone. In all instances, mixed melting points were not depressed. Finally, the ketone was cleaved by a sodium amide fusion to yield *o*-diphenylbenzene and 3,4-diphenylbenzoic acid.

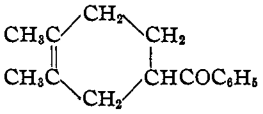


II

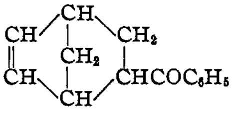


1,4-Diphenylbutadiene did not add vinyl phenyl ketone nearly as readily as the 2,3-isomer, and a crystalline addition product was not obtained. On treatment of the sirupy mixture with sulfur, 2,5-diphenylbenzophenone resulted. This was cleaved with sodium amide to terphenyl, thus showing that a six-membered ring had been formed in the addition.

The addition product from 2,3-dimethylbutadiene resembled the one from 2,3-diphenylbutadiene, except that it formed a dibromide instead of being dehydrogenated by bromine. The dimethyl tetrahydroketone III was dehydrogenated by sulfur to the known 3,4-dimethylbenzophenone.

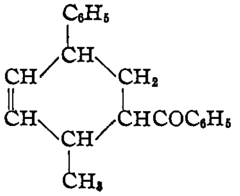


III

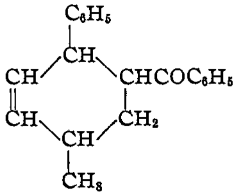


IV

Cyclopentadiene gave a homogeneous liquid that undoubtedly is represented by the structure IV. 1-Phenyl-4-methylbutadiene-1,3 gave a solid addition product that readily added bromine. The mode of addition was not determined; the tetrahydrobenzophenone may be either Va or Vb.



Va



Vb

The liquid product from isoprene decomposed on distillation, but a ketonic derivative having the correct analysis was prepared from one fraction. Phellandrene gave a hopeless mixture, while with cyclohexadiene no product was obtained except β-ethoxypropiophenone, $C_2H_5OCH_2CH_2COC_6H_5$, VI, when alcohol was used as a solvent.

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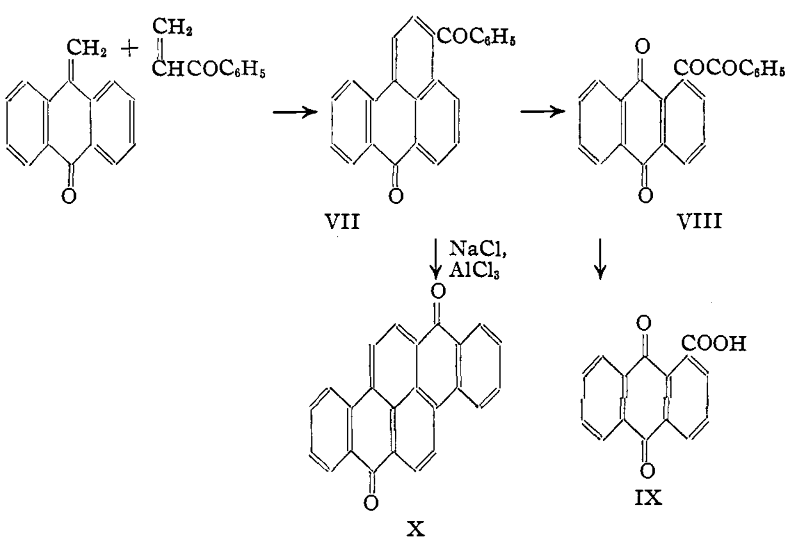
[1] Allen and Spanagel, This Journal, 55, 3773 (1933).

[2] Allen, Eliot and Bell, *Can. J. Research, B*, **17**, 75 (1939).

The use of methyleneanthrone furnished Bz-1-benzoylbenzanthrone VII directly. Although the product was identical with a specimen prepared as described in the patent literature,[3] its structure was independently shown by oxidation with chromic acid to α-benzoylformylanthraquinone VIII, which was then cleaved by sodium peroxide to anthraquinone-α-carboxylic acid IX.

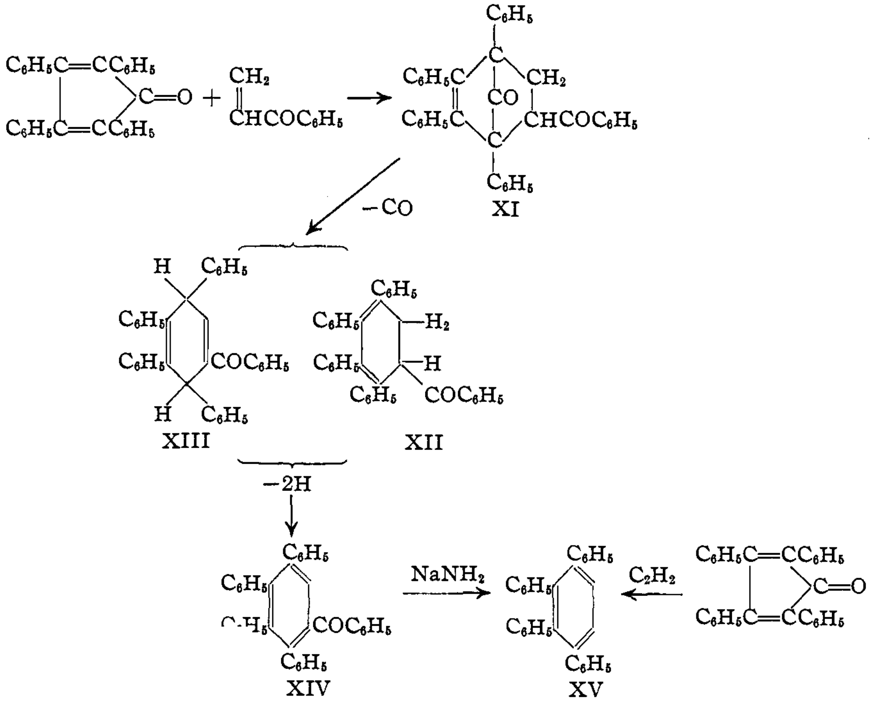


The formation of the benzanthrone VII shows that the direction of addition is that indicated by the formulas to the extent of at least 85%.

The Bz-1-benzoylbenzanthrone VII was also dehydrogenated in a sodium–aluminum chloride melt to 4,5,9,10-dibenzpyrene-3,8-quinone X identical in all respects with a specimen secured by the patent directions.[4]

Vinyl phenyl ketone added very easily to highly arylated cyclopentadienones; the primary addition products containing the carbonyl bridge could usually be isolated as would be expected.[1,5] Thus, tetraphenylcyclopentadienone gave the substance represented by formula XI. On moderate heating the bridge was lost as carbon monoxide, and two isomeric dihydrobenzophenones were formed. These may be geometrical isomers or some of the numerous possible forms differing only in the location of the double bonds, XII, XIII. When the addition reaction was carried out in a high-boiling solvent, these products resulted directly, the lower-melting form being the main product. The latter was also secured by heating the higher-melting modification at elevated temperatures for a short time.

Both the tetraphenyldihydrobenzophenones were easily dehydrogenated to yield tetraphenylbenzophenone XIV, and the latter was cleaved by sodium amide with the consequent formation of the known 1,2,3,4-tetraphenylbenzene XV.[6]



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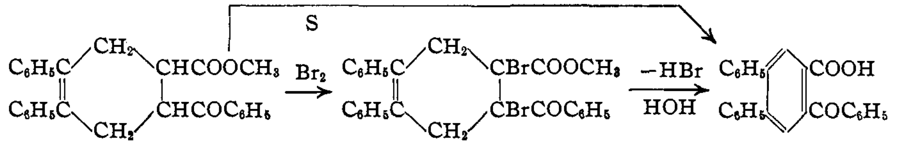
[3] German Patent 420,412; *Frdl.*, **15**, 736 (1928).

[4] German Patent 412,053; *Frdl.*, **15**, 731 (1928). In the patent the color with concd. sulfuric acid is said to be a blue-violet. A specimen of the quinone prepared exactly by the patent directions, as well as the one obtained in this work, gave a red-violet color with concd. sulfuric acid.

[5] Allen and Sheps, *Can. J. Research*, **11**, 171 (1934).

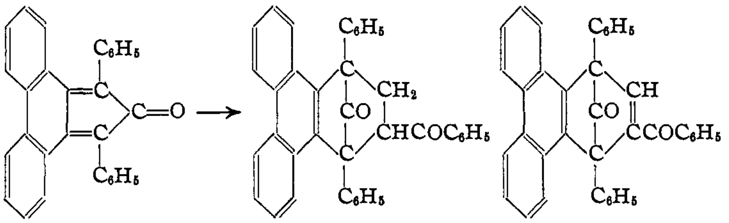
[6] Dilthey, U. S. Patent 2,097,854; *C. A.*, **32**, 367 (1938).



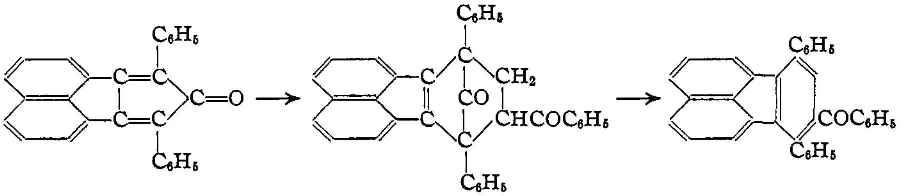
XXII XXIII XXIV

This sequence of reactions clearly demonstrates the presence of a benzene ring in the addition product.

The cyclic ketones XVI and XVII also were used; the former gave an addition product XVIII only, but with the latter the tendency to lose the bridge and yield the aromatic form XXI was so great that the addition product XX was obtained analytically pure only with difficulty. When β-dimethylaminopropiophenone was substituted for β-chloropropiophenone, dimethylamine was eliminated; the resulting compound appeared to be the dihydro bridged ketone XIX or a reduction product.



XVI XVIII XIX

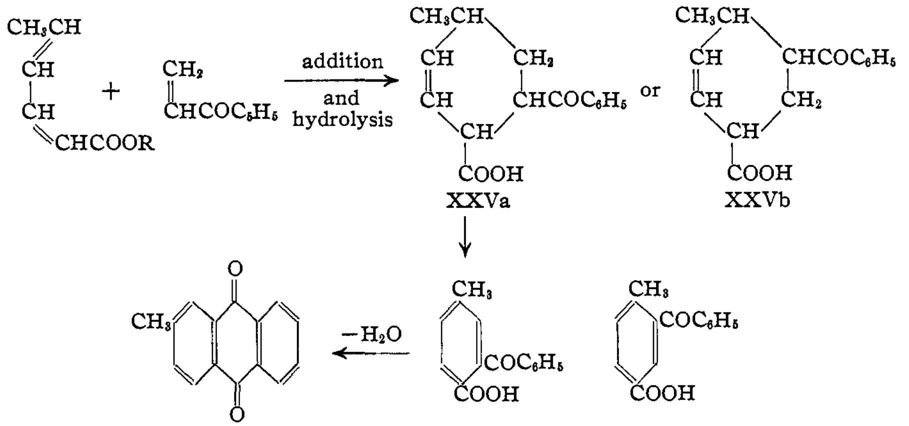


XVII XX XXI

Methyl β-benzoylacrylate and 2,3-diphenylbutadiene easily formed an addition product XXII. This did not decolorize bromine in a cold chloroform solution, but when the solution was heated, the halogen was completely used, hydrogen bromide was evolved, and a crystalline product resulted. Analysis showed the presence of two atoms of bromine. While the substance may be a dibromide, formed by addition of a molecule of bromine, it seems more probable that it is a substitution product XXIII, because (1) tetrahydrodiphenylbenzophenone II is dehydrogenated by bromine with no evidence of formation of a dibromide, and (2) this substance loses hydrogen bromide on heating, to give an oil that with alcoholic potash yields 6-carboxy-3,4-diphenylbenzophenone.

The ester XXII did not give a tractable product on sulfur dehydrogenation, but on treatment of the melt with alcoholic potash, followed by acidification, the aromatic acid XXIV precipitated. This was identical with the specimen secured previously.[1]

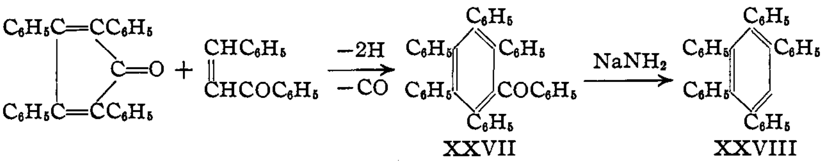
Vinyl phenyl ketone added readily to ethyl sorbate. Since there is a possibility of the formation of eight isomers, no attempt was made to separate the oily ester, but a part was hydrolyzed directly to the solid acids. Addition could have taken place so as to form either XXVa or XXVb. In order to distinguish, the remainder of the ester was dehydrogenated and hydrolyzed to the aromatic keto acids XXVIa or XXVIb, thus reducing the number of isomers to two. Treatment of these by concd. sulfuric acid would be expected to dehydrate XXVIa to β-methylanthraquinone but would have no effect on XXVIb. When this was done,



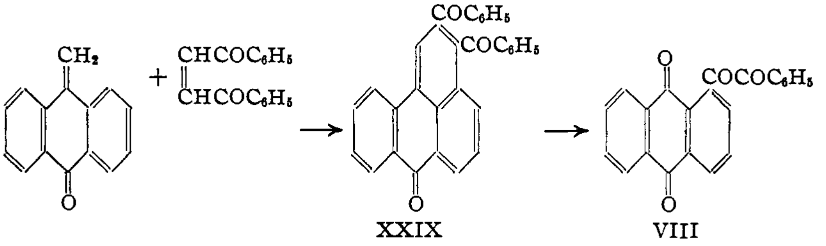
XXVa XXVb XXVIa XXVIb

β-methylanthraquinone only was obtained, there being no acidic fraction recovered. Hence, the keto acid must have been almost exclusively XXVIa; the addition product acid must have been XXVa, and addition must have taken place nearly quantitatively in the direction indicated. No attempt was made to secure all the possible stereoisomeric forms of XXVa.

In an earlier paper[7] it was noted that the substituted vinyl phenyl ketone, benzalacetophenone, failed to react with tetraphenylcyclopentadienone. In the meantime, by operating in boiling trichlorobenzene, it has been found possible to force the addition, but the bridge and two hydrogen atoms are lost, so that the product is the aromatic pentaphenylbenzophenone XXVII. The latter was cleaved by the use of sodium amide, to give the known pentaphenylbenzene XXVIII.



trans-Dibenzoylethylene has been added to methyleneanthrone; the product is Bz-1-Bz-2-dibenzoylbenzanthrone XXIX. Its structure is evident from the production of α-benzoylformylanthraquinone VIII upon oxidation with chromium trioxide.



Furan, sylvan, and 2,5-dimethylfuran did not add to the pure ketone. In alcohol, β-ethoxypropiophenone VI was obtained.

Experimental

A. Reactions with Dienes. (a) 2,3-Diphenylbutadiene-1,3; 3,4-Diphenyltetrahydrobenzophenone.—The addition reactions were carried on in the same general manner as has been described in the earlier papers in this series, the main feature being the use of vinyl phenyl ketone in solution, as obtained from the interaction of potassium acetate and β-chloropropiophenone. This enables one to avoid the losses involved in its isolation. It also has been found that the β-dialkylaminoacetophenone hydrochloride can be substituted for the β-chloroketone, though the yields are not as good.[8]

A mixture of 11 g. of the hydrocarbon, 9.2 g. of β-chloropropiophenone, 5.4 g. of sodium acetate, and 75 cc. of xylene was refluxed for sixty hours and the solvent removed *in vacuo*. Most of the residual sirup dissolved in hot methanol, from which 8.5 g. of the ketone separated in fine prisms on cooling; recrystallization from ligroin (90–120°) gave a white product, m. p. 83°.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.8; H, 6.6. Found: C, 89.1; H, 6.6.

The 2,4-dinitrophenylhydrazone was obtained in the usual manner; it crystallized in orange rods from methanol–dioxane, m. p. 203°.

Anal. Calcd. for $C_{31}H_{26}O_4N_4$: N, 10.8. Found: N, 10.5.

For dehydrogenation 8 g. of bromine in 20 cc. of chloroform was added slowly to 7.8 g. of the addition product in 15 cc. of the same solvent; large amounts of hydrogen bromide were evolved. The sirup left on evaporation of the solvent solidified when treated with methanol; the yield of white solid was 7.5 g. (97%). On recrystallization from ethanol it separated in white prisms, m. p. 133°. A mixed melting point with a sample of the ketone[1] resulting from the degradation was not depressed. The oxime and 2,4-dinitrophenylhydrazone were prepared, compared, and found to be identical. The second derivative is new; it was secured by the usual procedure. It separated from dioxane–methanol in microscopic orange prisms, m. p. 248°.

Anal. Calcd. for $C_{31}H_{22}O_4N_4$: N, 10.9. Found: N, 10.6.

Sodium Amide Fusion.[9]—A mixture of 4 g. of 3,4-diphenylbenzophenone, 10 cc. of cymene, and 0.7 g. of powdered sodium amide was refluxed for six hours. The cooled solution was extracted with water and the alkaline layer separated. The cymene was then removed and the residue distilled with steam; 1.9 g. (70%) of *o*-diphenylbenzene was secured (mixed melting point not depressed). Acidification of the alkaline solution gave 0.2 g. (7%) of 3,4-diphenylbenzoic acid.[2]

(b) **1,4-Diphenylbutadiene; 2,5-Diphenylbenzophenone.**—Exactly as described under the 2,3-isomer, a mixture of the same quantities of the components was refluxed for forty-eight hours and the solvent removed under reduced pressure. Upon extraction of the residue with methanol, 3.5 g. of diene remained undissolved. The methanol

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[7] Allen and Sheps, *Can. J. Research*, **11**, 173 (1934).

[8] Mannich and Fourneau, *Ber.*, **71**, 2090 (1938).

[9] Haller and Bauer, *Ann. phys. chim.*, [8] **16**, 145 (1909); Lucas, *ibid.*, **17**, 127 (1909).

in the extract was replaced by chloroform and treated with bromine in the usual manner; 8 g. of a halogen-containing solid was obtained. This melted at 215° and analyzed for a dibromide of diphenylbutadiene. This and the unreacted hydrocarbon accounted for 70% of the diene, thus indicating not over 30% of addition.

In a later run, the methanol-soluble fraction was distilled *in vacuo*, and a sirupy distillate, b. p. 250–255° at 4–5 mm., secured; the analysis was about 1% low. It was not further purified, but at once dehydrogenated by heating 2.5 g. with 0.5 g. of sulfur at 200° for two hours; the residue was extracted with hot alcohol, from which 1.3 g. of the ketone separated. 2,5-Diphenylbenzophenone crystallizes in rods, m. p. 130°.

Anal. Calcd. for $C_{25}H_{18}O$: C, 89.8; H, 5.4. Found: C, 89.6; H, 5.4.

Sodium Amide Fusion.—In a similar manner, 0.20 g. of 2,5-diphenylbenzophenone gave 0.11 g. (80%) of *p*-diphenylbenzene; the melting point and mixed melting point with an authentic specimen were 211–212°.

(c) **2,3-Dimethylbutadiene; 3,4-Dimethyltetrahydrobenzophenone III.**—After refluxing a mixture of 8.4 g. of β-chloropropiophenone, 8 g. of potassium acetate and 30 cc. of 2,3-dimethylbutadiene for twenty-four hours, adding ether and filtering the inorganic salts, fractionation *in vacuo* gave the addition product, b. p. 184–188° at 12 mm. On redistillation it boiled from 163–165° at 6 mm.; the yield was 4 g.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.4. Found: C, 84.1; H, 8.5.

The 2,4-dinitrophenylhydrazone, secured by the usual procedure, separated from methanol in orange-yellow leaflets, m. p. 152°.

Anal. Calcd. for $C_{21}H_{22}O_4N_4$: N, 14.2. Found: N, 14.1.

On treatment of the addition product with bromine there was no apparent action in the cold; on warming, hydrogen bromide was given off. The only substance isolated was a dibromide; this crystallized from ethanol in long white needles, m. p. 132°.

Anal. Calcd. for $C_{15}H_{18}OBr_2$: C, 48.1; H, 4.8; Br, 42.8. Found: C, 47.7; H, 4.8; Br, 42.8.

Dehydrogenation to the known 3,4-dimethylbenzophenone[10] was readily accomplished by heating 2.1 g. of the substance III with 0.8 g. of sulfur in a metal bath at 190–230°. When gas evolution had become negligible, the cooled melt was extracted with ethanol; 1 g. of ketone was obtained. The melting point (45°) was not depressed on admixture with a specimen secured by Elbs' method.

The 2,4-dinitrophenylhydrazone of this ketone was secured by the usual procedure. It separated from chloroform–methanol in microscopic prisms, m. p. 252°.

Anal. Calcd. for $C_{21}H_{18}O_4N_4$: N, 14.4. Found: N, 13.9.

(d) **Benzoylmethylphenylcyclohexene Va or Vb.**—A mixture of 7.2 g. of 1-phenyl-4-methylbutadiene-1,3,[11] 9.5 g. of β-chloropropiophenone, 6.3 g. of potassium acetate and 20 cc. of trichlorobenzene was refluxed for eight hours and distilled *in vacuo*. The portion of b. p. 150–167° at 1 mm. on redistillation boiled at 157–159° at 1 mm. On standing it crystallized, 5 g. of pure ketone being obtained; this separated from methanol in prisms, m. p. 61°.

Anal. Calcd. for $C_{20}H_{20}O$: C, 87.0; H, 7.1. Found: C, 86.4, 86.4; H, 7.3, 7.2.

The dibromide was obtained readily by treatment with bromine in chloroform, although there was some evolution of hydrogen bromide. It crystallized from methanol in plates or prisms, m. p. 125°.

Anal. Calcd. for $C_{20}H_{20}OBr_2$: Br, 36.7. Found: Br, 36.3.

(e) **1-Benzoyl-1,2,3,6-tetrahydro-3,6-methanobenzene IV.**—A mixture of 13 g. of cyclopentadiene, 25 g. of β-chloropropiophenone, 23 g. of potassium acetate and 50 cc. of toluene was heated in a sealed bottle at 95–100° for thirty hours. Inorganic salts were filtered after adding ether to facilitate manipulation and the solution fractionated *in vacuo*. The portion, b. p. 122–124° at 3 mm., was collected in a yield of 16 g.; n^{26}_{D} 1.5648.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.7; H, 7.1. Found: C, 84.3; H, 7.1.

The semicarbazone, obtained in the usual manner, separated from alcohol in shiny prisms, m. p. 178–180°.

Anal. Calcd. for $C_{15}H_{17}ON_3$: N, 16.4. Found: N, 16.1.

The addition product decolorizes permanganate and bromine in chloroform instantly.

(f) **Miscellaneous.**—A mixture of 10 g. of isoprene, 16.8 g. of β-chloropropiophenone, 15 g. of potassium acetate, and 15 cc. of toluene was heated in a steam-bath in a pressure bottle for twenty-four hours. After removal of the inorganic salt by precipitation with ether, the liquid was distilled *in vacuo*. The fraction, b. p. 120–122° at 2 mm., gave a 2,4-dinitrophenylhydrazone, m. p. 137°.

Anal. Calcd. for $C_{20}H_{20}O_4N_4$: N, 14.7. Found: N, 14.5.

From commercial phellandrene and the alcoholic solution of vinyl phenyl ketone an oil, b. p. 183–185° at 2 mm., was obtained in a 37% yield. It decolorized bromine instantly, with evolution of hydrogen bromide. The 2,4-dinitrophenylhydrazone was an oil, and a semicarbazone was not secured. The analysis was not satisfactory.

Anal. Calcd. for $C_{19}H_{24}O$: C, 85.1; H, 8.9. Found: C, 84.1; H, 8.6.

β-Ethoxypropiophenone VI was obtained when cyclohexadiene and an alcoholic solution of the unsaturated ketone were allowed to react (described under furan).

B. **Reactions with Ketones.** (a) **Bz-1-Benzoylbenzanthrone VII.**—A mixture of 5.2 g. of methyleneanthrone,[12] 6 g. of β-chloropropiophenone, 6 g. of potassium acetate, and 35 cc. of nitrobenzene was stirred and refluxed for two and a half hours at 180–190°; it became very dark and set to a mass of crystals on cooling. The solid was filtered after triturating with 125 cc. of methanol, washing with the same solvent until bright yellow, and then with water to remove soluble salts. It dissolved readily in hot acetic acid or chloroform. The analytical

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(10) Elbs, *J. prakt. Chem.*, **33**, 180 (1886); **35**, 467 (1887).

(11) Klages, *Ber.*, **40**, 1769 (1907).

(12) Barnett and Matthews, *Ber.*, **59**, 767 (1926).

sample was recrystallized from chloroform–methanol, from which it separated in brownish-yellow needles, m. p. 192°. The yield was 6.5 g., 84%.

Anal. Calcd. for $C_{24}H_{14}O_2$: C, 86.2; H, 4.2. Found: C, 86.0; H, 4.2.

It was also synthesized from Bz-1-carboxybenzanthrone,[3] the requisite acid being secured through the diazo reaction from Bz-1-aminobenzanthrone, and also by the interaction of methyleneanthrone and β-chloropropionic acid.[13]

A mixture of 2 g. of the Bz-1-acid, 4 g. of phosphorus pentachloride, and 20 cc. of benzene was warmed on the steam-bath as long as hydrogen chloride was evolved, then cooled, and, after addition of 4 g. of anhydrous aluminum chloride, warmed for an hour at 70°. It was then poured upon ice, the benzene steam-distilled, and the residue boiled with hydrochloric acid, filtered, and washed. On recrystallization from 4 cc. of nitrobenzene, the Bz-1-benzoylbenzanthrone separated in brownish-yellow needles, m. p. 190–192°. A mixed melting point with the substance secured by the first procedure was 191–192°.

Oxidation by Chromium Trioxide.—To a solution of 1.9 g. of the ketone in 20 cc. of acetic acid, 5 g. of chromic acid in 36 cc. of 50% acetic acid was added slowly, the mixture was refluxed for five minutes, cooled, and 50 cc. of water added to precipitate the diketone VIII. The crystals so obtained were bright yellow, but the surface rapidly became greenish-colored, until after several recrystallizations from chloroform–methanol, from which it separated in rods, m. p. 174°.

Anal. Calcd. for $C_{22}H_{12}O_4$: C, 77.6; H, 3.6. Found: C, 77.6; H, 3.5.

This diketone gave a brown color with concd. sulfuric acid and a clear blue vat with alkaline hydrosulfite.

Cleavage.—To a suspension of 1.5 g. of the diketone in 30 cc. of cold water, 4 g. of sodium peroxide was added; after five hours' standing, the mixture was warmed to 70° and the unreacted solid filtered. Acidification of the filtrate precipitated anthraquinone-α-carboxylic acid. For identification this was converted into the methyl ester through the silver salt; a mixed melting point with an authentic sample was not depressed.

4,5,9,10-Dibenzpyrene-3,8-quinone X.—The sodium–aluminum chloride from 20 g. of anhydrous aluminum chloride and 4 g. of salt was mixed with 2 g. of Bz-1-benzoylbenzanthrone and the temperature raised to 180–200°, where it was held for eight hours. The melt was decomposed by iced hydrochloric acid and the dye filtered. It was then converted to a red vat by alkaline hydrosulfite, the solution was filtered and aerated. The orange-yellow dye was collected on a filter. After recrystallization from nitrobenzene it formed rods that melted at 385–388°. A mixed melting point with an authentic sample[4] (m. p. 386–388°) was 384–386°. Both samples gave the same red-violet color with concd. sulfuric acid.

(b) **Tetraphenylbenzophenone and Related Compounds.** (1) **3,4,5,6-Tetraphenyl-7-keto-1-benzoyl-1,2,3,6-tetrahydro-3,6-methanobenzene XI.**—A mixture of 134 g. of tetraphenylcyclopentadienone, 230 g. of β-chloropropiophenone, 200 g. of potassium acetate, and 520 cc. of toluene was refluxed for three hours, or until the red color had disappeared. After cooling, the pulverized solid was filtered, digested with warm (50°) water for one hour, filtered, and washed first with water and then with 400 cc. of acetone. Final purification was accomplished by recrystallization from toluene or mixtures of chloroform–methanol and ethyl acetate–methanol. The addition product XI forms prisms which melt at 210° to a red liquid with gas evolution. The yield was practically quantitative.

Anal. Calcd. for $C_{38}H_{28}O_2$: C, 88.4; H, 5.4. Found: C, 88.5; H, 5.4.

This addition product is insoluble in the alcohols and ether, slightly soluble in carbon tetrachloride, but dissolves easily in hot chloroform, ethyl acetate, benzene, toluene, and acetic acid. It was recovered unchanged after boiling with permanganate in acetone, glacial acetic acid, and selenium dioxide or hydrogen peroxide. Bromine in chloroform, and chromic acid in acetic acid slowly attacked it, but gave ill-defined products from which no individual substance could be isolated.

The addition product also resulted, less conveniently, when a benzene solution of vinyl phenyl ketone and tetraphenylcyclopentadienone was refluxed for two hours, or when the components were heated in the absence of a solvent at 130°. It was also obtained when one replaced the β-chloropropiophenone by an equivalent amount of β-dimethylaminopropiophenone hydrochloride; after twenty-four hours the yield was but 25%.

(2) **Dihydro-3,4,5,6-tetraphenylbenzophenones XII or XIII.**—The dihydroketone was easily secured by pyrolysis of the addition product or by carrying out the addition reactions in boiling trichlorobenzene or nitrobenzene, substituting β-dimethylaminopropiophenone for β-chloropropiophenone.

(i) **Pyrolysis: High-Melting Form.**—Ten grams of the addition product was heated for ten minutes in a metal bath at 215°; it formed a reddish liquid which evolved carbon monoxide; a few oily drops collected in the upper part of the flask, and the pungent odor of vinyl methyl ketone was evident. The cooled melt was taken up in chloroform and diluted with methanol. The dihydroketone crystallizes in pale yellow rods, m. p. 177°. It is sparingly soluble in the alcohols, acetone, and ether, but dissolves easily in ethyl acetate, chloroform, carbon tetrachloride, acetic acid, and benzene.

Anal. Calcd. for $C_{37}H_{28}O$: C, 91.0; H, 5.7. Found: C, 90.8; H, 5.7.

(ii) **Low-Melting Form.**—A mixture of 7.6 g. of tetraphenylcyclopentadienone, 6 g. of β-dimethylaminopropiophenone hydrochloride (or an equivalent amount of β-chloropropiophenone), 6 g. of potassium acetate, and 35 cc. of trichlorobenzene was heated at 180–190° for three hours with stirring; dimethylamine was evolved and the mixture became colorless after two hours. The potassium salts were precipitated by the addition of 50 cc. of methanol, and, after filtering, the solvent was removed *in vacuo*. The hard residue was taken up in chloroform and recrystallized in the usual manner. It forms pale yellow very fine rods, m. p. 158–159°.

Anal. Calcd. for $C_{37}H_{28}O$: C, 91.0; H, 5.7. Found: C, 91.2, 91.2; H, 5.5, 5.6.

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(13) German Patent 597,325; *Frdl.*, **21**, 1121 (1936).

When nitrobenzene was substituted for trichlorobenzene, the high-melting isomer was isolated; the reaction product was rather sticky and not easy to manipulate.

The high-melting isomer (1 g., m. p. 177°) was heated at 250–270° for fifteen minutes, cooled, taken up in chloroform, and methanol added to incipient crystallization. After filtration, the solid melted at 156–158°; when it was mixed with the analytical sample, the melting point was 157–158°.

Mixtures of the low and high-melting forms may soften as low as 138°, but usually do not form a clear liquid until about 173°. They are often obtained in the pyrolysis of large quantities of the addition product.

(3) **2,3,4,5-Tetraphenylbenzophenone XIV.**—This ketone was obtained from both forms of the dihydro compound by the dehydrogenating action of bromine, permanganate, and sulfur. The yields were good by all procedures. In each instance the melting points of the products were the same, and there was no depression on admixture.

(i) **Action of Bromine.**—To a solution of 1.0 g. of the dihydroketone in 8 cc. of chloroform was added 0.4 g. of bromine in 2 cc. of the same solvent. Hydrogen bromide was evolved; after three minutes on the steam-bath, methanol was added to incipient crystallization. After standing several hours, 0.8 g. of the aromatic ketone had separated. It forms long rods, m. p. 190°. The solubilities are the same as those of the dihydro compound.

Anal. Calcd. for $C_{37}H_{26}O$: C, 91.1; H, 5.4. Found: C, 91.3; H, 5.4.

(ii) **Action of Permanganate.**—A solution of 2 g. of the dihydroketone in 30 cc. of acetone was warmed, and potassium permanganate in acetone added as long as it was decolorized. The oxides of manganese were filtered and the solvent evaporated; the residue was crystallized from chloroform–methanol; 1.3 g. of product was secured.

(iii) **Sulfur Fusion.**—A mixture of 2 g. of the dihydroketone and 0.4 g. of sulfur was heated in a metal bath at 240–250° for fifteen to twenty minutes, when the evolution of gas became negligible. The cooled melt was dissolved, filtered, and recrystallized; the yield was 1 g.

(4) **1,2,3,4-Tetraphenylbenzene, XV.**—One gram each of the tetraphenylbenzophenone and pulverized sodium amide in 50 cc. of *p*-cymene was refluxed for eight hours. The cooled mixture was washed with water, and the hydrocarbon slowly crystallized in a yield of 50%. Recrystallization from acetic acid gave a product, m. p. 193°. The melting point was not depressed on admixture with a specimen secured by Dilthey's procedure.[6]

(c) **Polynuclear Series.**—A mixture of 2 g. of the green unsaturated ketone XVII, 2.5 g. of β-chloropropiophenone, 2 g. of potassium acetate, and 25 cc. of toluene was heated until the green color disappeared (two hours), cooled, the inorganic salts filtered, and the solution concentrated to about 15 cc. Methanol was added to precipitate the yellow reaction product, which was recrystallized from chloroform–methanol. The addition product XX separated in prisms, m. p. 189–190°.

Anal. Calcd. for $C_{35}H_{24}O_2$: C, 88.5; H, 4.9. Found: C, 88.1, 88.3; H, 5.1, 5.1.

It dissolved readily in hot acetic acid but the melting point of the crystalline product was lowered; subsequent purification from chloroform–methanol gave a yellow substance, m. p. 194–195°, with analytical figures approaching the bridgeless formula XXI.

Anal. Calcd. for $C_{35}H_{24}O$: C, 91.3; H, 5.2. Found: C, 90.2, 90.5; H, 5.1, 5.2.

In a similar manner from β-chloropropiophenone and 3.8 g. of diphenylenediphenylcyclopentadienone XVI there was obtained an addition product XVIII, which separated from chloroform–methanol in white needles, m. p. 273°. Above the melting point it dissociated appreciably into its components.

Anal. Calcd. for $C_{38}H_{26}O_2$: C, 88.7; H, 5.4. Found: C, 88.4; H, 5.1.

When β-dimethylaminovinyl phenyl ketone was substituted for the β-chloropropiophenone, the resulting substance appeared to be the dihydro-bridged ketone XIX or its reduction product; the latter, however, is not identical with XVIII, nor are the two interconvertible. This reaction is being studied further. The ketone XIX separated from chloroform in very fine white needles, m. p. 312–315°.

Anal. Calcd. for $C_{38}H_{24}O_2$: C, 89.1; H, 4.7; for $C_{35}H_{26}O_2$: C, 88.7; H, 5.4. Found: C, 88.8; H, 5.3.

C. Miscellaneous. (a) **Methyl Benzoylacrylate; Methyl 2-Benzoyl-4,5-diphenyltetrahydrobenzoate XXII.**—A solution of 0.6 g. of 2,3-diphenylbutadiene and 0.6 g. of methyl β-benzoylacrylate was heated for fifteen hours at 165°. The cooled residue was taken up in boiling methanol and treated with Norite; on cooling, the addition product separated in fine white prisms. The yield was 0.6 g., 52% of the theoretical amount. It could also be secured in a yield of 20% by refluxing a xylene solution of the components for sixty hours. The analytical sample was recrystallized from methanol; m. p. 147°.

Anal. Calcd. for $C_{27}H_{24}O_3$: C, 81.8; H, 6.1. Found: C, 82.0; H, 6.0.

The addition product did not react appreciably with bromine in a cold chloroform solution, but, on warming, hydrogen bromide was evolved in considerable amount. On evaporation of the solvent, followed by crystallization from methanol, a substance containing two bromine atoms was secured. It separates in rods, m. p. 183°, with decomposition.

Anal. Calcd. for $C_{27}H_{22}O_3Br_2$: C, 58.5; H, 4.0; Br, 28.9. Found: C, 58.7; H, 4.0; Br, 28.6.

Dehydrogenation was accomplished by heating 0.8 g. of the ester and 0.2 g. of sulfur for several hours at 230°. The untractable melt was warmed with alcoholic potash, evaporated to dryness and extracted with water. Acidification of the filtered solution precipitated the 6-carboxy-3,4-diphenylbenzophenone XXIV, which was recrystallized from dilute methanol. The melting point was 240–241° and was not depressed when mixed with a specimen of the original ketoacid.[1]

(b) From a mixture of 16.8 g. of β-chloropropiophenone, 12.8 g. of ethyl sorbate, 9.8 g. of potassium acetate and 50 cc. of xylene, refluxed eighteen hours and treated in the usual manner, was obtained 13.4 g. of the addition product (mixed esters), m. p. 165–170° at 3 mm. It was hydrolyzed by refluxing with 3 g. of potassium hydroxide in 50 cc. of ethanol for two and a half hours; the solution was then poured into water, filtered and the oily acid that separated on acidification allowed to crystallize slowly from methanol. In this way, 8 g. of mixed stereoisomers XXVa, m. p. 128–133°, was secured on recrystallization from ethanol; one form was easily isolated in a yield of 75%; it separates in tiny rods, m. p. 162–163°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.6. Found: C, 73.7; H, 6.5.

The crude ester (5.2 g.) was also dehydrogenated by heating with 0.7 g. of sulfur at 200–240° for ten minutes; the cooled melt was extracted with alcohol, and the filtered solution refluxed for two hours after the addition of 1.4 g. of potassium hydroxide. After dilution it was treated with Norite, filtered, and acidified, the oily acid being dehydrated directly, as follows: a mixture of 1 g. of this and 4.6 cc. of 20% fuming sulfuric acid was warmed on the steam-bath for two hours, and, after cooling, poured into water. The precipitate was insoluble in sodium hydroxide. After two crystallizations from alcohol it melted at 166° and did not depress the melting point of an authentic sample of β-methylanthraquinone.

(c) **2,3,4,5,6-Pentaphenylbenzophenone XXII.**—A mixture of 9.5 g. of tetraphenylcyclopentadienone, 6 g. of benzalacetophenone, and 30 cc. of trichlorobenzene was refluxed for twenty-four hours (210–213°); the red color gradually diminished but never entirely disappeared. On cooling, the product separated; it was filtered and recrystallized from chloroform–methanol. The melting point and mixed melting point with an authentic sample[7] were 338° (341° cor.). The ketone sublimes in long needles.

Anal. Calcd. for $C_{43}H_{30}O$: C, 91.8; H, 5.4. Found: C, 91.8; H, 5.5.

Pentaphenylbenzene XXIII.—The sodium amide cleavage was carried out as described under the tetraphenyl homolog, using 5 g. of ketone and 8 g. of amide; the yield of hydrocarbon was 1.8 g., m. p. 245–246°. A mixed melting point with a specimen secured by Dilthey's procedure[6] was not depressed.

(d) **Bz-1-Bz-2-Dibenzoylbenzanthrone, XXIX.**—This ketone appears to exist in polymorphic forms, one, melting at 208°, being formed when the components are refluxed in trichlorobenzene, and the other, m. p. 286°, when nitrobenzene is used as a solvent. Both forms separate from solutions as yellow rods, give the same scarlet color in concd. sulfuric acid, and show comparable solubilities in the same solvents, but the lower-melting form is changed into the higher by sulfuric acid.

A mixture of 2 g. of methyleneanthrone, 3 g. of *trans*-dibenzoylethylene, and 10 cc. of trichlorobenzene was refluxed for five hours, cooled, and 15 cc. of methanol added with stirring; the reddish crystals that separated were filtered and washed. This product was a mixture of uncertain composition that required repeated recrystallization before a substance having a constant melting point was obtained. The red color only slowly disappeared, although bromine removed it at once without greatly improving the melting point. The most suitable solvent was chloroform–methanol. When nitrobenzene was used, the high-melting form separated at once. Both forms are insoluble in the alcohols and ether, but dissolve readily in hot chloroform, acetic acid, and dioxane.

Anal. Calcd. for $C_{31}H_{18}O_3$: C, 84.9; H, 4.1. Found: (208°) C, 85.3; H, 4.0; (286°) C, 85.2; H, 4.1.

Oxidation.—A mixture of 2.5 g. of the ketone, 5 g. of chromium trioxide, and 86 cc. of acetic acid was refluxed for ten minutes, cooled, and diluted with 300 cc. of water. After two hours the precipitate was filtered and washed. The solid was extracted with dilute sodium carbonate solution, filtered, and acidified, the benzoic acid being extracted with ether and identified in the usual manner. The solid, insoluble in sodium carbonate, was crystallized from methanol and found to be identical with the α-benzoylformylanthraquinone VIII secured in another way as described above. The dibenzoylbenzanthrone XXIX was unaffected by melting with sodium–aluminum chloride at 170°.

(e) **Mixtures of vinyl phenyl ketone with furan, sylvan, and 2,5-dimethylfuran** did not react when allowed to stand at room temperature. When an alcoholic solution, prepared by the usual treatment of β-chloropropiophenone with potassium acetate, was heated with furan in a sealed tube, β-ethoxypropiophenone VI resulted. The latter was isolated, the 2,4-dinitrophenylhydrazone prepared, and both analyzed. The derivative separates from alcohol in orange prisms, m. p. 158°.

Anal. Calcd. for $C_{11}H_{14}O_2$ (VI): C, 74.2; H, 7.9; for the derivative, $C_{17}H_{18}O_5N_4$: N, 15.6. Found: (VI) C, 74.3; H, 7.8; (2,4-dinitrophenylhydrazone): N, 15.5.

(f) **Isolation of Vinyl Phenyl Ketone.**—In all the papers in this series, an alcoholic solution of β-chloropropiophenone containing an equivalent of potassium acetate has been used just as though it were vinyl phenyl ketone. That it actually does contain the unsaturated ketone, and is not β-acetoxypropiophenone, was shown by isolation of the free ketone. It was only necessary to extract the solution with chloroform (ether was avoided, as traces of peroxide caused polymerization to a tough, horn-like mass), wash out alcohol with water, and distil *in vacuo*. The yield of pale yellow oil was 71–78%, the lower quantity being obtained when 100 g. of chloroketone was employed; there was more loss by polymerization during the time of heating.

The distilled ketone keeps fairly well for several days at a low temperature (−9°), but at room temperature soon becomes solid. The effect of *p*-benzylaminophenol, hydroquinone, phenyl-β-naphthylamine, and copper acetate as stabilizers was examined; the last two were useless, but the others seemed to decrease the rate of polymerization. A specimen containing hydroquinone became quite viscous in six weeks but was not further changed after five years. This specimen was a dimeric form.

Calcd. Mol. wt., $(132)_x$. Found, in benzene: mol. wt., 257, 266, 259, whence $x = 2$.

The formation of the unsaturated ketone by the action of potassium acetate on β-chloropropiophenone would not of necessity be anticipated, for sodium cyanide gives β-cyanopropiophenone.[14]

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[14] Allen and Young, *J. Org. Chem.*, **2**, 231 (1937).

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]

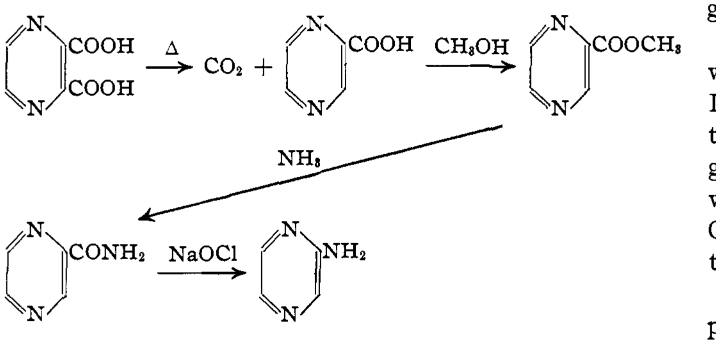
Syntheses in the Pyrazine Series. II. Preparation and Properties of Aminopyrazine

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.

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%.

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(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).

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