$C_{22}H_{24}O_4N_2$: C, 69.47; H, 6.31; N, 7.37. Found: C, 69.25; H, 6.61; N, 7.23. This was hydrolysed by heating with a mixture of hydrochloric acid (4 cc. of 20%) and glacial acetic acid (4 cc.). After the evolution of carbon dioxide had ceased, the whole was concentrated in vacuum and the residue was triturated with acetone, giving solid amine hydrochloride, which was then crystallised from alcohol, forming colorless minute crystals of m.p. 230° (decomp.), after becoming brown at about 222° . Yield, 0.4 g. The hydrochloride is readily soluble in water and stable in the air. Although the free base comes in minute sandy crystals of m.p. 261° (decomp.) from pyridine, it is fairly unstable in the air, rapidly changing from white to orange. *Anal.* Calcd. for $C_{14}H_{18}O_2N_2 \cdot 2HCl$: C, 52.67; H, 6.32; N, 8.78. Found: C, 52.75; H, 6.33; N, 9.00.

A mixture of the hydrochloride (0.1 g.), sodium formate (0.06 g.), formic acid (0.13 g. of 90%) and formalin (0.1 g. of 30%) was heated on a steam bath for about 10 hours. A small amount of hydrochloric acid was then added and the whole was evaporated in vacuum. The residue was dissolved in water, filtered and the filtrate was basified with soda and extracted with chloroform, dried and evaporated. Since the free base was found to be unstable in the air, it was turned into the hydrochloride and purified from alcohol, forming colorless crystalline powder, which browns towards 274° , but does not decompose below 300° . *Anal.* Calcd. for $C_{16}H_{22}O_2N_2 \cdot 2HCl$: C, 55.33; H, 6.97; N, 8.07. Found: C, 55.16; H, 7.16; N, 7.88.

Summary

For the purpose of biological assessment an amino-hydrobenzoquinolicine mentioned in the title and its *N*-dimethyl derivative were synthesized. β -3,4-Methylenedioxyphenylethyl bromide was heated with ethyl isonicotinate to form a quarternary bromide (I), which was then oxidized to the corresponding pyridone carboxylic acid (II) by the usual method. Its reduction product, the piperidone carboxylic acid (IV), was then cyclized and the product was treated with alcohol, giving carbethoxy-benzoquinolicinium salt (V), which was then reduced to hydrobenzoquinolicine (VI). Modified Curtius degradation was then applied to (VI), furnishing the final product (VII). Its *N*-dimethyl derivative was also prepared.

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334. Norio Sugimoto, Jun'iti Iwao and Hideo Kakemi: Synthesis of *p*-Nitrophenyl Ketones. II. Synthesis of some *p*-Nitrophenyl Alkyl Ketones.

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In the first paper²⁾ of this series, Sugasawa and the present authors made known that *p*-nitroacetophenone can advantageously be prepared from *p*-aminoacetophenone through Sandmeyer's reaction, the yield as high as 65% of the theoretical amount being obtained.

This method of preparation was now successfully applied to the synthesis of various other *p*-aminophenyl ketones of the general formula $NO_2-C_6H_4-CO-R$, where R represents hydrogen and several alkyl groups as are shown in the experimental section. *p*-Nitrobenzophenone and *p*-nitro-*p'*-methylbenzophenone were also prepared. This work will be continued.

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Experimental

p-Aminophenyl ketones were prepared from acetanilide and acid chlorides by Friedel-Crafts' reaction, followed by hydrolysis.

General procedure for the preparation of *p*-nitrophenyl ketones—*p*-Aminophenyl ketones (0.1 mole) was dissolved in dil. nitric acid (28.7 g. of 77% HNO₃ and 130 cc. water)²⁾ and diazotized below 5° (23 g. of 90% NaNO₂ and 50 cc. water), and some more sodium nitrite was added, so as to form diazonium nitrite solution. On the other hand, cupri-cuprosulfite was prepared from cupric sulfate (25 g. of crystal), water (75 cc.) and sodium nitrite (50 g. of 90%), to which another 28.5 g.-portion of sodium nitrite was added. The diazo-solution was now introduced with stirring. After the evolution of nitrogen had ceased, the crystalline substance separated was filtered with suction, dissolved in ether or benzene, washed with water, dried and evaporated, and the residue was then purified through recrystallization or distillation in vacuum. The results obtained are tabulated below:

R	m.p. of <i>p</i> -NH ₂ -C ₆ H ₄ -CO-R	m.p. of <i>p</i> -NO ₂ -C ₆ H ₄ COR	Yield % ³⁾
H	72-74°	106°	50, 21 ⁴⁾
CH ₃	107°	80°	65
C ₂ H ₅	140°	90° ⁵⁾	47
<i>n</i> -C ₃ H ₇	84°	66-67° ⁶⁾	38
<i>n</i> -C ₄ H ₉	74-75° ^{4) 7)}	31° ⁸⁾	31
<i>n</i> -C ₅ H ₁₁	86° ^{4) 9)}	44° ¹⁰⁾	29
C ₆ H ₅	124°	136°	36
<i>p</i> -CH ₃ -C ₆ H ₄	180°	120°	29

- 2) For the less soluble diazonium salts more water was used.
- 3) The diazo-salt becomes more and more stable as the number of carbon in R increases, and this is probably responsible for decrease in yield.
- 4) Sulfuric acid was used instead of nitric acid for diazotization.
- 5) m.p. 114° in the literature (Beilstein VII, 303), but 90-91° according to Hartung and Foster (C.A. 40, 2129 (1946)).
- 6) New compound. Pale yellow plates from dil. alcohol. C₁₀H₁₁O₃N requires C 62.18, H 5.70, N 7.25; Found: C 62.48, H 5.69, N 7.05.
- 7) New compound. Faint yellow scales from dil. alcohol. C₁₁H₁₅ON requires C 74.58, H 8.47, N 7.91; Found: C 74.25, H 8.36, N 8.10.
- 8) New compound. Oxime. Faint yellow needles from dil. alcohol. C₁₁H₁₄O₃N₂ requires C 59.46, H 6.31, N 12.61; Found: C 58.78, H 6.03, N 13.11.
- 9) New compound. Light yellow needles from dil. alcohol. C₁₂H₁₇ON requires C 75.39, H 8.90, N 7.33; Found C 75.40, H 9.11, N 7.38.
- 10) New compound: Oxime. Light yellow needles from dil. alcohol. C₁₂H₁₆O₃N₂ requires C 61.02, H 6.78, N 11.86; Found C 60.50, H 6.90, N 11.95.