precipitates dissolve, but after some minutes reprecipitation occurs. The composition of the silver salt corresponds to $(CH_3P(O)NH_2OAg)_2 \cdot AgNO_3$. The diamide hydrolyzes readily on exposure to the atmosphere; the crystals liquefy forming diammonium methyl phosphonate, but after some time the liquid resolidifies as ammonium hydrogen methyl phosphonate. Aromatic phosphonic acid diamides, such as $C_6H_5P(O)(NH_2)_2$ and tetra-alkyl-substituted aliphatic phosphonic acid diamides, such as $CH_3P(O)[N(C_2H_5)_2]_2$, are reported to be much more stable to hydrolysis.[4]

Experimental

To absolute chloroform (800 ml.), which had been saturated at −10° with dry ammonia gas, was added 38 g. of freshly distilled methylphosphonic dichloride (b.p. 63°, 14 mm.) dropwise over a period of two hours with stirring at −10 to 0°; the passage of ammonia was continued during the addition. The precipitated mixture of methylphosphonic diamide and ammonium chloride (48 g.) was collected rapidly on a Büchner funnel with a sintered-glass plate and immediately stored in a vacuum desiccator over phosphorus pentoxide. The finely powdered material, suspended in a mixture of 200 g. of anhydrous chloroform and 50 g. of anhydrous diethylamine, was refluxed gently until solution was effected and the hot solution was filtered to remove a small amount of impurities. When the filtrate was cooled to −15°, methylphosphonic diamide crystallized as large plates, which were collected on a sintered-glass plate (yield 21 g., 73.5%) and recrystallized from methanol containing 3% ether; m.p. 128–129° (sealed capillary, dec.).

Anal. Calcd. for CH_7N_2OP: C, 12.78; H, 7.45; N, 29.80; P, 32.98. Found: C, 12.86; H, 7.57; N, 29.49; P, 32.76.

Methylphosphonic diamide (0.7 g.) was dissolved in a small amount of methanol. Upon the addition of a solution of silver nitrate in 80% aqueous methanol, a white amorphous precipitate was formed. After decanting and thorough washing with methanol, the compound was dried *in vacuo* over phosphorus pentoxide prior to analysis.

Anal. Calcd. for $Ag_3C_2H_{10}N_3O_7P_2$: Ag, 56.14; N, 7.33; P, 10.80. Found: Ag, 55.35; N, 7.25; P. 10.94.

Methylphosphonic diamide (1.3563 g.), exposed to air, increased in weight as follows:

Hours	48	60	72	96	108	120
Increase, %	36.7	38.0	35.0	24.2	20.5	20.4

Calcd. increase for $CH_3P(O)(ONH_4)_2$ 38.4%, for $CH_3P(O)(OH)ONH_4$ 20.2%.

The end product ammonium hydrogen methylphosphonate was recrystallized from 80% ethanol as rhombic pyramids.

Anal. Calcd. for CH_8NO_3P: C, 10.81; H, 7.21: N, 12.61; P, 27.90. Found: C, 10.41; H, 7.19; N, 12.69; P, 27.43.

An aqueous solution of ammonium hydrogen methylphosphonate was neutralized with dilute ammonium hydroxide and silver nitrate added. The white precipitate, disilver methylphosphonate, which was dried over P_4O_{10} *in vacuo* gave almost the same silver value as the product prepared by Michaelis and Kraehne[5] from methylphosphonic acid and silver nitrate. The analytical data of both silver salts agree better with the calculated values for disilver methylphosphonate monohydrate than with those for the anhydrous salt.

Anal. Calcd. for $CH_3PO_3Ag_2 \cdot H_2O$: Ag, 67.89; P, 9.75. Found: Ag, 68.19; P, 9.75. Found by Michaelis and Kraehne: Ag, 68.91.

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[4] A. Michaelis, *Ann.*, **293**, 215 (1896); **326**, 164 (1903).

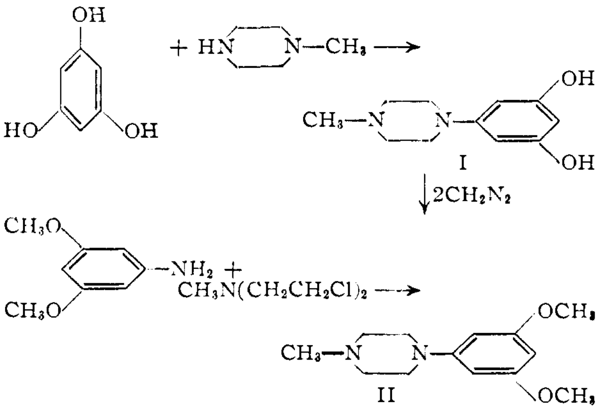
[5] A. Michaelis and B. Kraehne, *Ber.*, **31**, 1054 (1898), give the calculated silver value for $CH_3PO_3Ag_2$ as 69.72%; it should be 71.99%, and the phosphorus value 10.33%.

The Reaction of Phloroglucinol with 1-Methylpiperazine

BY ARMIGER H. SOMMERS AND JAMES D. BARNES

RECEIVED MARCH 21, 1955

Phloroglucinol has been reported to react with such cyclic amines as piperidine and piperazine to form either tertiary amines with loss of water[1] or molecular compounds corresponding to a 1:1 ratio of the reagents.[2] We have found that the reaction of phloroglucinol with 1-methylpiperazine results in the formation of 1-methyl-4-(3′,5′-dihydroxyphenyl)-piperazine (I). This material was converted by diazomethane to the corresponding dimethyl ether, 1-methyl-4-(3′,5′-dimethoxyphenyl)-piperazine (II), which was also prepared by the reaction of 3,5-dimethoxyaniline with N,N-bis-(β-chloroethyl)-methylamine. The structural identity of the products was established by their conversion to the same maleate and methiodide salts. Attempts to demethylate II using hydrobromic acid yielded only tars from which no phenolic amine could be isolated.



Acknowledgment.—We thank Mr. E. F. Shelberg and members of the Microchemical Laboratory for the analyses reported here.

Experimental

1-Methyl-4-(3′,5′-dihydroxyphenyl)-piperazine (I).—A mixture of 16.2 g. (0.1 mole) of phloroglucinol dihydrate, 10 g. (0.1 mole) of 1-methylpiperazine and 50 ml. of anhydrous toluene was boiled under a reflux condenser and water trap for 17 hours, when 4 cc. of water had been collected. The solid which was collected and dried weighed 18 g. and melted at 228–235°. It was stirred in dilute hydrochloric acid and the mixture was filtered. The filtrate was made just basic with 5% sodium hydroxide solution, and the resulting solid was recrystallized from methanol. This gave 13.5 g. of powdery solid, m.p. 236–241°. A sample of this material which was sublimed twice melted at 248–249° after preliminary darkening.

Anal. Calcd. for $C_{11}H_{16}N_2O_2$: C, 63.44: H, 7.75; N, 13.45. Found: C, 63.67; H, 7.58; N, 13.26.

The **dihydrochloride** salt obtained by evaporation of a solution of the base in dilute hydrochloric acid was recrystallized from methanol to give fine needles, m.p. 257–258°.

Anal. Calcd. for $C_{11}H_{18}Cl_2N_2O_2$: C, 46.98; H, 6.45; N, 9.96. Found: C, 46.66; H, 6.25; N, 10.03.

When this salt was sublimed at 0.2 mm., a crystalline

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[1] M. P. Schmidt and O. Süs, German Patent 639,125, *C. A.*, **31**, 1632 (1937).

[2] G. Sanna and A. Sorarù, *Rend. seminar facoltà sci. univ. Cagliari*, **12**, 34 (1942); *C. A.*, **38**, 5501 (1944).

solid, m.p. 257–261°, was obtained which analytical data indicated to be the **monohydrochloride** salt.

Anal. Calcd. for $C_{11}H_{17}ClN_2O_2$: C, 53.99; H, 7.01. Found: C, 54.12; H, 6.92.

An attempt to replace two phenolic hydroxy groups by using a ratio of two moles of 1-methylpiperazine to one mole of phloroglucinol dihydrate yielded the same monosubstitution product as described above.

1-Methyl-4-(3′,5′-dimethoxyphenyl)-piperazine (II). A. From **3,5-Dimethoxyaniline.**—A mixture of 2.8 g. of 3,5-dimethoxyaniline, 3.5 g. of N,N-bis-(β-chloroethyl)-methylamine hydrochloride, and 20 ml. of methanol was refluxed for 17 hours; 1.1 g. of sodium carbonate was added, and heating was continued for 20 hours more. The mixture was filtered, concentrated and made basic with aqueous sodium hydroxide. An organic layer which formed was extracted into benzene and distilled. After a forerun of 3,5-dimethoxyaniline there was obtained 0.7 g. of colorless oil, b.p. 125–130° at 0.1 mm.

The **maleate** salt, m.p. 145–146°, was prepared in isopropyl alcohol, and recrystallized from isopropyl alcohol-ether mixture.

Anal. Calcd. for $C_{17}H_{24}N_2O_6$: C, 57.94; H, 6.87. Found: C, 58.19; H, 6.72.

A solution of the oil in absolute alcohol was treated with methyl iodide. After three days the white crystals of **1,1-dimethyl-4-(3′,5′-dimethoxyphenyl)-piperazinium iodide,** m.p. 229–230°, were collected and dried.

Anal. Calcd. for $C_{14}H_{23}IN_2O_2$: C, 44.45; H, 6.13. Found: C, 44.52; H, 6.09.

B. From **1-Methyl-4-(3′,5′-dihydroxyphenyl)-piperazine.**—A solution of 0.5 g. of 1-methyl-4-(3′,5′-dihydroxyphenyl)-piperazine in 25 ml. of methanol was treated with a solution of about 1 g. of diazomethane in ether. The red solution was allowed to stand overnight, and was then concentrated. The residual oil was distilled to obtain 0.2 g. of yellow oil boiling at about 125° at 0.1 mm.

The **maleate** salt was prepared in isopropyl alcohol and ether. The melting point was 144–145°, not depressed by material from method A.

Anal. Calcd. for $C_{17}H_{24}N_2O_6$: C, 57.94; H, 6.87; N, 7.95; O, 27.24. Found: C, 58.00; H, 6.88; N, 8.14; O, 27.22.

The **methiodide** was prepared in ethanol and recrystallized twice from this solvent. The shiny platelets had a melting point of 230–231°, not depressed by mixture with material from method A.

Anal. Calcd. for $C_{14}H_{23}IN_2O_2$: C, 44.45; H, 6.13; N, 7.41. Found: C, 44.45; H, 6.38; N, 7.27.

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Ring-size and Conjugation Effects on the Carbonyl Vibrational Frequency of Some Benzocyclanones and Methylacetophenones

BY W. M. SCHUBERT AND W. A. SWEENEY

RECEIVED FEBRUARY 14, 1955

The carbonyl absorption frequency in the infrared of aromatic ketones is known to be lower than that of corresponding aliphatic ketones.[1] The frequency is not noticeably influenced by a change of the alkyl group attached to the carbonyl from say methyl to ethyl.[2] However, the carbonyl frequency of an aromatic ketone is shifted toward the aliphatic frequency by steric inhibition of phenyl–carbonyl conjugation.[3]

In Table I are given comparisons between the carbonyl frequency of methyl ethyl ketone and some alkyl acetophenones. It is evident that not all the shift in frequency from aliphatic to aromatic carbonyl can be attributed to conjugation with the benzene ring. Thus, 2,6-dimethylacetophenone and acetomesitylene, which according to their ultraviolet spectra are practically completely inhibited from conjugation,[4a,b] still show a carbonyl vibration shift of 18 cm.$^{-1}$ from methyl ethyl ketone. The shift in carbonyl frequency from methyl ethyl ketone is approximately the same for *o*-methylacetophenone and 2,4-dimethylacetophenone as for acetophenone, although ultraviolet spectra indicate a partial inhibition of resonance in the former two compounds.[5] The average value for this "benzene-ring effect" for the completely or partially conjugated ketones is 33 cm.$^{-1}$.

TABLE I

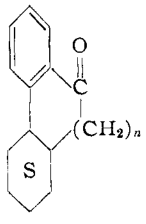
A COMPARISON OF THE CARBONYL VIBRATIONAL FREQUENCY OF SOME ALKYL ACETOPHENONES WITH THAT OF METHYL ETHYL KETONE[a]

Compound	Cm.$^{-1}$	Shift from CH_3COEt[b,c]
Methyl ethyl ketone	1718	0
Acetophenone	1686	32
o-Methylacetophenone	1688	30
2,4-Dimethylacetophenone	1683	35
3,4-Dimethylacetophenone	1681	37
2,6-Dimethylacetophenone	1700	18
Acetomesitylene	1701	17

[a] All compounds measured as pure liquids. [b] Average shift for conjugated and partially conjugated ketones, 33 cm.$^{-1}$. [c] Average shift for unconjugated ketones, 18 cm.$^{-1}$.

Benzocyclanones; Ring-Size Effect.—It is well known that the carbonyl stretching absorption band for cyclic ketones varies with ring size.[6a,b,c] The frequency decreases as the ring size is changed from cyclobutanone up to cyclohexanone, continues to decrease more slowly in the medium ring ketones and then increases again to that of cyclohexanone in the large rings.[6a]

In the benzocyclanone series, a decrease in the carbonyl frequency in passing from α-indanone to α-tetralone to α-suberone was observed by Lecomte.[7] On the other hand, Gutsche, while reporting a similar trend between the indanone I and the tetralone II, detected no difference in the carbonyl frequency between II and the suberone III.[8]



I, $n = 0$
II, $n = 1$
III, $n = 2$

The trend found by Lecomte has been confirmed

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[1] See, *e.g.*, F. A. Miller, "Organic Chemistry," Vol. III, H. Gilman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 122 ff.

[2] D. Biquard, *Bull. soc. chim.*, [5] **8**, 55 (1941).

[3] R. H. Saunders, M. J. Murray and F. F. Cleveland, This Journal **63**, 3121 (1941).

[4] (a) M. T. O'Shaughnessy and W. H. Rodebush, *ibid.*, **62**, 2906 (1940); (b) W. M. Schubert and H. K. Latourette, *ibid.*, **74**, 1829 (1952).

[5] R. B. Turner and D. M. Voitle, *ibid.*, **73**, 1403 (1951).

[6] (a) V. Prelog, *J. Chem. Soc.*, 420 (1950); (b) A. J. Birch, *Ann. Reports*, 194 (1951); (c) D. Biquard, *Bull. soc. chim.*, [5] **7**, 894 (1940).

[7] J. Lecomte, *J. Phys. Radium*, **6**, 257 (1945).

[8] C. D. Gutsche, This Journal, **73**, 787 (1951).