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

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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

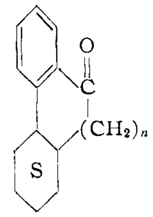
A COMPARISON OF THE CARBONYL VIBRATIONAL FREQUENCY OF SOME ALKYL ACETOPHENONES WITH THAT OF METHYL ETHYL KETONE[a]

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)

and has been found to extend to α-benzocycloöctanone (see Table II). As shown in Table II, the ring-size effect on the carbonyl frequency of the benzocyclanones closely parallels that for the cyclanones, *if* it can be assumed that the "benzene-ring effect" is approximately the same for each of the benzocyclanones (*i.e.*, 33 cm.$^{-1}$).[9]

TABLE II

CARBONYL VIBRATIONAL FREQUENCIES OF SOME CYCLANONES AND BENZOCYCLANONES[a]

Ring size	Cyclanone	Benzocyclanone Obsd.	Calcd.[b]
5	1751[c]	1723[c]	1718
6	1715	1681	1682
7	1704	1676	1671
8	1702[12]	1667	1669

[a] Measured as pure liquid, except as noted. [b] Obtained by subtracting the "benzene-ring effect," 33 cm.$^{-1}$, from the observed value for the cyclanones. [c] Measured in solution in carbon tetrachloride.

The increased carbonyl frequency found for the small ring ketones has been attributed to increased *s*-character of the carbon to oxygen valency resulting from the constraining of the angle θ ($\theta >$ C=O) to a value less than 120°.[13] It is possible that hydrogen crowding in the medium rings constrains the angle θ to a value slightly greater than 120°. This would result in a slight increase in *p*-character (over the normal bond hybridization) to the carbon to oxygen valency. Consequently, the carbon to oxygen bond would be "looser," and the vibrational frequency slightly lower than the "normal" value, that of cyclohexanone.[14]

Experimental

Materials.—All the compounds used are known and were prepared by known methods. In the following list, the reference given after the compound is to the source or method of preparation, and the reference given after the physical properties is to reported properties: acetophenone,[15] b.p. 92° (21 mm.), n^{25}_{D} 1.5320[16]; *o*-methylacetophenone,[17] b.p. 84–85° (10.5 mm.), n^{23}_{D} 1.5300[17]; 2,4-dimethylacetophenone,[18] b.p. 118–120° (32 mm.), n^{24}_{D} 1.5330[18]; 2,6-dimethylacetophenone,[4b] b.p. 118–119° (32 mm.), n^{24}_{D} 1.5146[4b]; acetomesitylene,[4b] b.p. 100–102° (7 mm.), n^{25}_{D} 1.5155[4b]; indanone-1,[19] m.p. 39–40°; tetralone-1,[19] b.p. 135° (20 mm.), n^{25}_{D} 1.5663[20]; benzosuberone,[19] b.p. 111–112° (2.4 mm.), n^{25}_{D} 1.5628[10]; 1,2-benzocycloöctene-1-one-3[11] (benzocycloöctanone), b.p. 110–112° (2–2.5 mm.), n^{25}_{D} 1.5572[10,11]; cyclopentanone,[21] b.p. 128–130°; cyclohexanone,[15] b.p. 152–153°; cycloheptanone,[21] b.p. 62–64° (14 mm.), n^{25}_{D} 1.4595.

Infrared Absorption Measurements.—A Perkin–Elmer recording infrared spectrophotometer model 21 was used. To obtain an accurate value for the carbonyl frequency, a thin sample of the pure liquid or dilute solution was used so that the intensity of the carbonyl band was about 60 to 80%. The curve was calibrated for each sample by tracing a water vapor spectrum on the same paper, both curves being traced at a very slow speed.

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[9] In α-benzocycloöctanone, the least conjugated of these benzocyclanones, the degree of resonance inhibition according to ultraviolet spectral data appears to be comparable to that in *o*-methylacetophenone.[10,11]

(10) G. D. Hedden and W. G. Brown, THIS JOURNAL, **75**, 3744 (1953).

(11) W. M. Schubert, W. A. Sweeney and H. K. Latourette, *ibid.*, **76**, 5462 (1954).

(12) Measured by S. L. Friess and P. E. Frankenberg, *ibid.*, **74**, 2679 (1952).

(13) *Cf.* L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y. 1954, p. 128.

(14) According to Fisher-Taylor-Hirschfelder models an "O-out" conformation for the benzocyclanones is highly favored over an "O-in" conformation. This would appear to rule out the explanation for the ring-size effect once advanced by Prelog,[6a] namely, that there is hydrogen bonding between the carbonyl oxygen and hydrogen atoms across the ring.

(15) Commercial.

(16) J. W. Bruhl, *J. prakt. Chem.*, [2] **50**, 131 (1894).

(17) K. von Auwers, *Ann.*, **408**, 242 (1915).

(18) C. S. Marvel, J. H. Saunders and C. G. Overberger, THIS JOURNAL, **68**, 1085 (1946).

(19) Kindly furnished by Dr. A. G. Anderson, Jr.

(20) Elsevier's "Encyclopedia of Organic Chemistry," Vol. 12B, Edited by F. Radt, Elsevier Publishing Co., Inc., New York, N. Y., 1950.

(21) Kindly furnished by Dr. H. J. Dauben, Jr.

The Partial Hydrolysis of Methyltrimethoxysilane

BY M. M. SPRUNG AND F. O. GUENTHER

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Previous papers in this series[1] described partial hydrolysis products of methyltriethoxysilane and ethyltriethoxysilane. The former hydrolyzes much more readily than the latter, and a catalyst need not necessarily be employed.

Methyltrimethoxysilane is hydrolyzed even more easily, as was shown recently by Kantor.[2] When a benzene solution is stirred rapidly at the boiling point in contact with three molar equivalents of water, *with no added catalyst*, virtually complete reaction occurs within 15 to 20 minutes. The hydrolysis products are entirely held in the lower, aqueous layer. Attempts to isolate crystalline or liquid intermediates of low molecular weight from this water solution were unsuccessful. The product, a highly hydrated, high molecular weight "methyl T-gel" with only a very small proportion of the original methoxy groups, can be represented empirically as $[6(CH_3)_2Si_2O_3 \cdot 10CH_3Si(OH)O \cdot H_2O \cdot CH_3OH]_n$. This gel must have about 13 hydroxyls and 1 methoxyl for each 22 silicons. The large number of hydroxyl groups that this implies is in agreement with the high water solubility of the initial hydrolysis product.[3]

Low molecular weight partial hydrolysis products can be isolated if half, or less than half, of the stoichiometric proportion of water is used. Under these circumstances, the initial reaction products are found in the organic solvent, rather than in the water layer, and can be isolated by distillation under vacuum. From a half-mole of methyltrimethoxysilane and 1.5 molar equivalents (0.75 mole) of water, there was obtained 9.2 g. of distillable liquid. The predominant components of this mixture are probably polycyclic, in the molecular weight range of 400 to 600, and have 3 to 4 residual methoxy groups per molecule.[1b] The residue was a weak gel.

The molar ratio of methyltrimethoxysilane to water then was reduced to 1:0.75. The crude reaction product was refractionated carefully, and six

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(1) (a) M. M. Sprung and F. O. Guenther, THIS JOURNAL, **77**, 3990 (1955); (b) **77**, 3996 (1955).

(2) S. W. Kantor, *ibid.*, **75**, 2712 (1953).

(3) This product gives off water freely on heating to higher temperatures. Ultimately, a composition near to that of "methyl T-gel," $[(CH_3)_2Si_2O_3]_n$, is attained.