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.	Benzocyclanone 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

RECEIVED JANUARY 5, 1955

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.

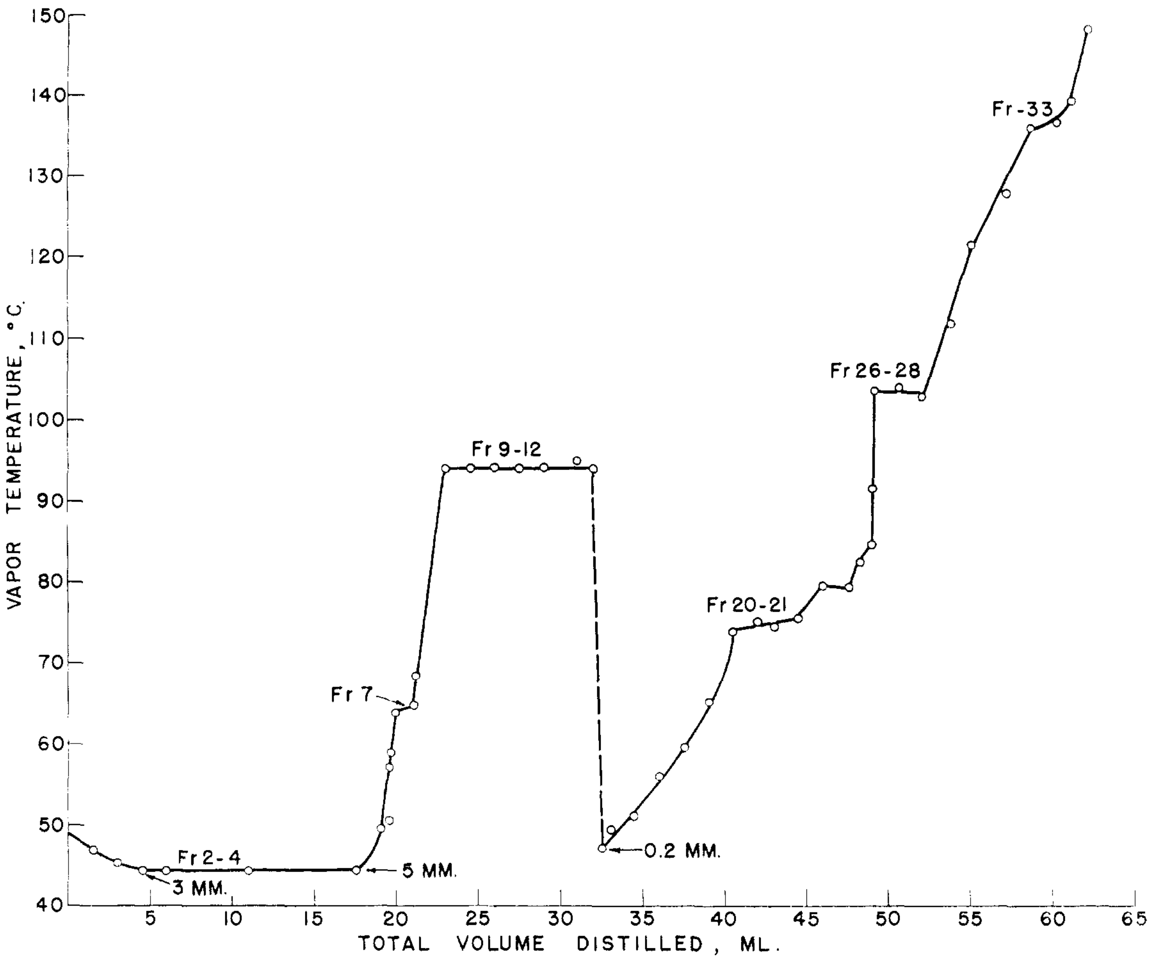
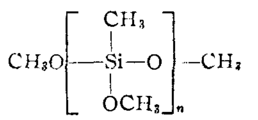
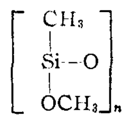


Fig. 1.—Distillation curve for hydrolysis products; $CH_3Si(OCH_3)_3:H_2O = 1.0:0.75$

compounds were isolated: three members of the linear series (general formula I), and the trimeric, pentameric and hexameric monocyclic products (general formula II).[4]


$CH_3O\left[-\overset{CH_3}{\underset{OCH_3}{Si}}-O-\right]_n CH_3$

I, n = 2, 3, 4


$\left[\overset{CH_3}{\underset{OCH_3}{Si}}-O\right]_n$

II, n = 3, 5, 6

The absence of the tetrameric product (II, n = 4) is somewhat puzzling, since it normally would be expected in higher yield than either the trimer or pentamer. It is possible that a minor portion of the cyclic tetramer is present as a contaminant in the linear tetramer (fraction 20 and 21, Fig. 1), and possibly also may be present in intermediate fractions 13–19.

Tamborski and Post[5] previously have prepared the linear, dimer, trimer and tetramer. The cyclic products have not been reported.

Experimental

Hydrolysis in Benzene with Three Molar Equivalents of Water.—Methyltrimethoxysilane was prepared from methyltrichlorosilane and anhydrous methanol in the presence of dimethylaniline, according to the method of Simpson.[6] One-half mole (88.0 g.) of methyltrimethoxysilane (b.p. 101.5–104°, $n^{20}D$ 1.3710–1.3720) was dissolved in 500 ml. of reagent-grade benzene in a three-necked flask which held a thermometer, water-cooled condenser, and Tru-Bore glass stirring assembly. The solution was brought to boiling (80.1°), and 27 g. of distilled water was added through a dropping funnel in 12 minutes. The equilibrium liquid temperature dropped rapidly to 62.8°, then dropped further to 60.8° in 13 minutes more. The mixture was cooled and filtered from 1.3 g. of solid. The two layers were separated and distilled, the upper layer consisting solely of benzene and methanol. The aqueous layer gelled during attempted vacuum distillation, giving 28 g. of a solid methylsilicone gel. In a second attempt, the aqueous layer was evaporated under rough vacuum at room temperature. The only product was again a solid gel, weighing 26.8 g. after drying briefly at 80–85°. *Anal.* Found: C, 17.7; H, 5.0; Si, 37.8; $-OCH_3$, 1.1. Calcd. for $(22CH_3SiO_{1.5}\cdot 6H_2O\cdot CH_3OH)_n$: C, 17.1; H, 5.1; Si, 38.2; $-OCH_3$, 1.9.

Hydrolysis with 1.5 Molar Equivalents of Water.—To 68.1 g. (0.5 mole) of methyltrimethoxysilane (b.p. 103°, $n^{20}D$ 1.3710) dissolved in 500 ml. of boiling reagent-grade benzene, 13.5 g. of water was added in 0.1 hr. The equilibrium liquid temperature dropped from 78 to 58° after a half-hour. The mixture was filtered to remove gel (10.5 g.). Solvents were removed under vacuum at 25–45°, leaving 32.0 g. of a liquid reaction product. Distillation at <1 mm. gave 4.9 g., b.p. 79–100°, 21.6% $-OCH_3$, and 4.3 g., b.p.

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[4] Possibilities of structural isomerism appear in either of these relatively simple series, beyond the trimeric members. There is one additional isomeric form of the linear tetramer or pentamer, and also of the cyclic tetramer. There are three possible isomers of the linear hexamer and the cyclic pentamer, and eight of the cyclic hexamer. Therefore, it is quite possible that the higher members of the series reported above are not isomerically unique.

[5] C. Tamborski and H. W. Post, *J. Org. Chem.*, **17**, 1400 (1952).

[6] W. Simpson, British Patent 635,726, April 12, 1950.

TABLE I

HYDROLYSIS PRODUCTS OF METHYLTRIMETHOXYSILANE

$CH_3Si(OCH_3)_3:H_2O = 1:0.75$

Fraction	Total vol. of flat, ml.	B.p., °C. °C.	B.p., °C. Mm.	$n^{20}D$	d^{20}_4 [a]	Analyses, % Found C	Found H	Found Si	Found Mol. wt.	Calcd. C	Calcd. H	Calcd. Si	Calcd. Mol. wt.	Molar refr. Found	Molar refr. Calcd.[b]	Formula
3	22.4	44.5	3	1.3834	1.024	32.5	8.2	24.8	226	31.8	8.0	24.8	226	51.5	52.0	$C_6H_{18}Si_2O_5$[d]
7	1.5	64	5	1.3909	1.100	27.3	7.2	31.4	260	26.6	6.8	31.2	270	58.3	58.2	$C_6H_{18}Si_3O_6$[e]
11	12.6	94	5	1.3894	1.062	30.6	7.9	27.4[c]	301	30.4	7.6	26.6	316	70.5	71.4	$C_8H_{24}Si_3O_7$[f]
21	5.9	74	0.2	1.3940	1.084	28.8	7.3	28.6	382	29.5	7.4	27.6	407	89.9	90.8	$C_{10}H_{30}Si_4O_7$[g]
28	3.0	103.5	0.2	1.3998	1.127	26.8	6.6	31.5	473	26.6	6.8	31.2	451	97.0	97.0	$C_{10}H_{30}Si_5O_{10}$[h]
33	1.5	137–141	0.2	1.4013	1.152	25.9	6.8		542	26.6	6.8		541	114.2	116.4	$C_{12}H_{36}Si_6O_{12}$[i]

[a] Determined with a Fisher–Davidson gravitometer. [b] R. O. Sauer, THIS JOURNAL, **68**, 954 (1946); E. L. Warrick, *ibid.*, **68**, 2455 (1946). [c] There is no obvious explanation for the poor correlation between calculated and found values for silicon in this case. Since the sample was taken from the middle of a good distillation "flat" and since other analytical data are in excellent agreement with "theory," there is little reason to doubt that an authentic sample of the linear trimer was obtained. The physical constants are in good agreement with those reported by Tamborski and Post.[5] [d] 1,3-Dimethyl-1,1,3,3-tetramethoxydisiloxane. [e] 1,3,5-Trimethoxy-1,3,5-trimethylcyclotrisiloxane. [f] 1,1,3,5,5-Pentamethoxy-1,3,5-trimethyltrisiloxane. [g] 1,1,3,5,7,7-Hexamethoxy-1,3,5,7-tetramethyltetrasiloxane. [h] 1,3,5,7,9-Pentamethoxy-1,3,5,7,9-pentamethylcyclopentasiloxane. [i] 1,3,5,7,9,11-Hexamethoxy-1,3,5,7,9,11-hexamethylcyclohexasiloxane.

100–118°, 18.9% OCH_3. The residue (16.7 g.) was a soft, weak gel, with 12.1% residual $-OCH_3$.

Hydrolysis with 0.75 Molar Equivalent of Water.—The initial reaction was carried out as described above, using 13.5 g. of water and 136.2 g. (1.0 mole) of methyltrimethoxysilane in 1000 ml. of benzene. After 0.9 hour, the equilibrium liquid temperature was 63.0° and the vapor temperature was 59.1°. Filtration removed 5.4 g. of gel. Solvents were removed rapidly under rough vacuum, leaving 68.3 g. of a liquid product. A rapid vacuum distillation yielded 54.9 g., boiling range 50° at 5 mm. to 208° at 1 mm. This product was redistilled in a spinning-band column. The distillation curve is shown in Fig. 1. The mid-cuts of the six distillation "flats" were analyzed, and these results are summarized in Table I.

Acknowledgment.—We are indebted to M. E. Hadsell for the spinning-band distillations, and to Mrs. Joyce Northrop and Mrs. Joan Martin for analyses.

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The Preparation of 3-Bromoquinoline Derivatives

BY SAMUEL W. TINSLEY[1]

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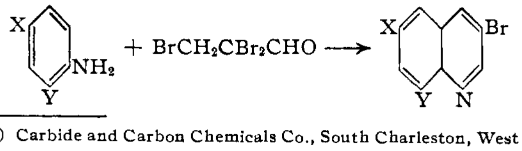
The preparation of substituted 3-bromoquinolines by the reaction of substituted anilines with 2,2,3-tribromopropanal[2] has been extended and the scope and limitations of the reaction have been investigated.

The preparation of 3-bromoquinolines by reaction of substituted anilines with 2,2,3-tribromopropanal was first undertaken to obtain nuclei from which potential antimalarial drugs might be prepared. Other 3-bromoquinolines have now been prepared in order to determine the general applicability of the reaction.

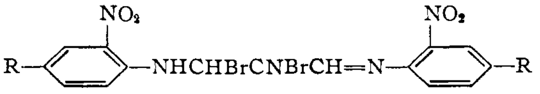
It has been confirmed that the reaction is most efficient with amines having substituents in one *ortho* and the *para* position. Thus 2,4-disubstituted anilines react to give the corresponding quinolines in yields of 30–80%, 65–80% usually being obtained.



It was reported previously[2] that *o*-nitroaniline yielded only 1% of the expected 3-bromo-8-nitroquinoline along with much larger amounts of 6-bromo-8-nitroquinoline and 3,6-dibromo-8-nitroquinoline. Bromination of the benzenoid ring also occurred with *p*-nitroaniline and anthranilic acid, although in these cases only the relatively insoluble dibromo compounds were isolated. However, with 2-methyl-5-nitroaniline, which also has an open *para* position, no bromination of the benzenoid ring occurred.

No identifiable products could be isolated by the action of the tribromoaldehyde on aniline, the three bromoanilines, 2-aminopyridine, 2-amino-4-nitrophenol or 2,5-dimethylaniline although definite, sometimes highly exothermic, reactions occurred in each case. In every instance black insoluble tars resulted. The tribromoaldehyde could not be induced to react with sulfanilic acid or 2-aminotoluene-5-sulfonic acid either under the usual conditions or by heating in the absence of solvent.

The reaction does not occur in such solvents as alcohol, ether or benzene. In the absence of solvent the tribromoaldehyde did react with 2-nitro-4-methylaniline to produce a light orange crystalline compound. This compound was converted readily to 6-methyl-8-nitroquinoline by warming in acetic acid. This intermediate was not characterized; however, analysis indicated I as a possible structure. This structure is quite similar to that postulated as an intermediate in the Skraup reaction.



I, R = CH_3
II, R = H

o-Nitroaniline also reacted in the absence of solvent to produce a small amount of crystalline intermediate whose analysis indicates a similar structure (II). It is interesting to note that cyclization of II in acetic acid yielded 3-bromo-8-nitroquinoline and no 3,6-dibromo-8-nitroquinoline or 6-bromo-8-nitroquinoline. One may speculate that such intermediates as I and II are formed by dehydrohalo-

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(1) Carbide and Carbon Chemicals Co., South Charleston, West Virginia.

(2) R. H. Baker, S. W. Tinsley, D. Butler and B. Riegel, THIS JOURNAL, **72**, 393 (1950).