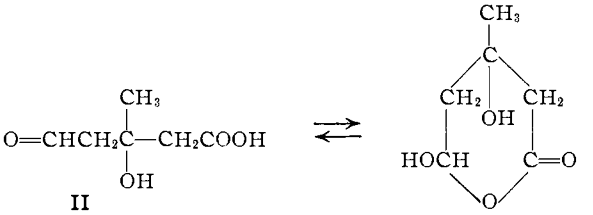
yielded ethyl DL-3-hydroxy-3-methyl-5,5-dimethoxypentanoate (III), b.p. 61–63° (0.1 mm.), $n^{25}D$ 1.4353. (*Anal.* Calcd. for $C_{10}H_{20}O_5$: C, 54.53; H, 9.15. Found: C, 54.79; H, 8.95.) Hydrolysis of III with sodium hydroxide yielded DL-3-hydroxy-3-methyl-5,5-dimethoxypentanoic acid (IV) which was isolated as the crystalline N,N'-dibenzylethylenediammonium salt, m.p. 107–107.5°. (*Anal.* Calcd. for $C_{32}H_{52}N_2O_{10}$: C, 61.52; H, 8.39; N, 4.48. Found: C, 61.32; H, 8.73; N, 4.60.) Hydrolysis of IV at 25° with 0.1*N* hydrochloric acid yielded DL-3-hydroxy-3-methylglutaraldehydic acid (II) in solution. The presence of the unstable and reactive aldehyde II was proven by reduction of it with either hydrogen over a platinum catalyst or with sodium borohydride in alkaline solution to give DL-mevalonic acid (I) in apparently quantitative yield as based on microbiological assay. Varying the time of acid hydrolysis of IV from 15 minutes to 5 hours did not appreciably reduce the high yield of DL-mevalonic acid, although dehydration and decarboxylation of II to 3-methylcrotonaldehyde was observed when more vigorous hydrolysis conditions were employed. After either reduction step, the DL-mevalonic acid was isolated as its crystalline N,N'-dibenzylethylenediammonium salt in *ca.* 30% yield. This product was shown to be identical with an authentic sample of N,N'-dibenzylethylenediammonium bis-(DL-mevalonate) by comparison of the infrared spectra, by a mixed melting point determination and by microbiological assay with *Lactobacillus acidophilus*, ATCC 4963.



II

Solutions of the aldehyde were prepared from the acetal immediately before biological testing. The microbiological activity of DL-3-hydroxy-3-methylglutaraldehydic acid for *Lactobacillus acidophilus* was found to be about 1/200 that of DL-mevalonic acid. The corresponding dimethylacetal (IV) was essentially inactive in this test. The effect of the aldehyde II on the incorporation of acetate into cholesterol was studied. Experiments (Table I) show that DL-3-hydroxy-3-methylglutaraldehydic acid suppresses the incorporation of 1-C^{14}-labelled acetate into cholesterol by rat liver homogenate to about the same degree as mevalonic acid. The corresponding acetal was inactive in this system. Work is in progress to prepare the labelled aldehyde so that it can be studied in this and other biosynthetic systems.

TABLE I

INHIBITION OF THE INCORPORATION OF 1-C^{14}-LABELLED ACETATE INTO CHOLESTEROL

Each flask contained 5 ml. of rat liver homogenate, 1 mg. each of ATP and DPN, and 0.2 mg. 1-C^{14}-acetate (2.44 μcurie). Compounds were added as indicated. Final volume was 10 ml. Gas phase was 95% O_2–5% CO_2. Incubation with agitation was carried out at 37° for 4.5 hr. Cholesterol was isolated and counted as the digitonide.

Compound added	Level, mg.	Experiment 1 Recovered cholesterol c.p.m./mg. C	Experiment 1 % Inhibition	Experiment 2 Recovered cholesterol c.p.m./mg. C	Experiment 2 % Inhibition
None	. . .	5,294	. .	16,519	. .
DL-Mevalonic	1.0	. . .	. .	9,288	44
acid	1.5	1,808	66	6,340	62
	3.0	212	96	305	96
DL-Mevaldic	1.0	4,294	19	11,919	28
acid	1.5	1,349	75	11,007	33
	3.0	184	97	2,221	87
DL-3-Hydroxy-	1.5	5,574	0	17,030	0
3-methyl-	3.0	. . .	. .	16,828	0
5,5-dimethoxypentanoic acid					

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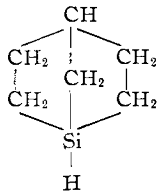
RECEIVED MAY 13, 1957

STEREOCHEMISTRY OF HYDRIDE ION DISPLACEMENT FROM SILICON. ENHANCED RATES AT BRIDGEHEAD AND 4-RING SILICON ATOMS[1]

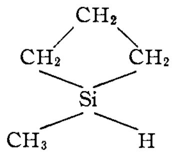
Sir:

The reactions of triorganosilanes, R_3SiH, with hydroxide ion in 95% ethanol have received much study and proceed $R_3SiH + OH^- + SH \rightarrow R_3SiOH + H_2 + S^-$, where SH represents solvent. Hydroxide is not consumed and hydrogen formation (which is quantitative) follows a pseudo first order rate law. These reactions are first order with respect to both silane and hydroxide, $-d[\text{silane}]/dt = k_2 [\text{silane}][OH^-]$,[2] and are thus formally similar to S_N2 displacements on carbon from the standpoint of kinetics.

In this communication we wish to record data on the reactivities of bridgehead (I) and 4-ring (II) silicon hydrides relative to the reactivities of acyclic and other previously known cyclic silicon hydrides.[3,4]



I



II

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[1] Paper 53 in a series on organosilicon chemistry; for 52 see L. H. Sommer, O. W. Steward and P. G. Campbell, THIS JOURNAL, **79**, in press (1957).

[2] For a recent paper on hydrogen isotope effects and pertinent references to earlier work on these reactions see L. Kaplan and K. E. Wilzbach, *ibid.*, **77**, 1297 (1955).

[3] The bridgehead silane, I, has been reported, L. H. Sommer and O. F. Bennett, *ibid.*, **79**, 1008 (1957).

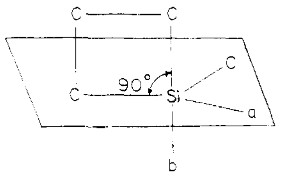
[4] The 4-ring silane, II, 1-methyl-1-silacyclobutane, b.p. 63° (733 mm.), $n^{20}D$ 1.4313 was prepared by a conventional 3-step procedure from allyl chloride and methyldichlorosilane as starting materials. *Anal.* Calcd. for $C_4H_{10}Si$: Si, 32.6; H (attached to Si), 1.16. Found: Si, 32.2; H (attached to Si), 1.11. The infrared spectrum of II had the sharp maximum at 8.9 μ characteristic of four other silacyclobutane compounds prepared in This Laboratory.

For reactions of R_3SiH with OH^- in 95% ethanol at 35° relative rates (k_2) are, for $(C_2H_5)_3SiH$ = 1; I, 10^3; II, 10^4–10^5; $(CH_2)_4Si(CH_3)H$, 10; $(CH_2)_5Si(CH_3)H$, 10^{-1}. For $(C_2H_5)_3SiH$ at 35°, k_2 = 0.1 min.$^{-1}$, mole^{-1} l.[5,6]

The corresponding disiloxane, bis-(1-silabicyclo-[2.2.1]heptyl) oxide,[3] m.p. 76°, was isolated in 40% yield (62 mg.) from the kinetics runs with I and perfectly linear pseudo first order plots were obtained. The 4-ring silane, II, gives 60% of the theoretical hydrogen at an extremely fast rate and 40% at a different rate which is smaller than the first by a factor of about three powers of ten. The latter rate has been shown to comprise hydrogen evolution from *sym*-di-*n*-propyldimethyldisiloxane which is formed by ring-opening of II (C-Si cleavage by OH^-) in competition with the evolution of hydrogen from the 4-ring silane.[7]

Thus, it is clear that displacement of hydride ion by hydroxide ion proceeds *far more rapidly* at bridgehead[8] and 4-ring silicon atoms than at silicon in ordinary a-cyclic and 5- as well as 6-ring silicon hydrides. These results comprise a complete reversal of the structure-reactivity relationships observed for displacements at carbon when the same comparisons are made.[9]

The above facts are in accord with the hypothesis outlined in our earlier communication.[3] Thus, in the reaction of II with hydroxide the geometry of the Si(5) addition compound would approximate one of two (idealized) structures: (1) a = H, b = OH; (2) a = OH, b = H.



On the above model of Si(5) complex for II with hydroxide ion[10] and similar models for I and other cyclic and acyclic hydrides, structure-reactivity relations resulting from steric factors are readily explained in terms of three factors: (1) ease of formation of Si(5) resulting from groups on silicon being "pulled back" in Si(4), away from the path of reagent attack. (2) I-Strain in Si(5) relative to Si(4).[11] (3) Steric strain in Si(5) relative to Si(4) due to increased "crowding" of groups in the former.[12]

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[5] Relative rates for the 5- and 6-ring silanes are based on data in R. West, THIS JOURNAL, **76**, 6015 (1954).

[6] Salt effects on k_2 resulting from change in KOH concentration should not appreciably affect the above relative rates tabulation which covers the range 0.003 *N* to 0.2 *N* KOH; see J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 813 (1955).

[7] In 95% ethanol at 35° the 4-ring silane gives 60% of the theoretical hydrogen with an ammonia–ammonium iodide buffer (0.5 *N* NH_3, 0.05 *N* NH_4I) at a rate which corresponds to a half-life of 7.5 minutes. The same reagent gives *no hydrogen* in a reasonable time with the highly reactive triphenylsilane.

[8] Energies of activation, E_a, for $(C_2H_5)_3SiH$ and I are 16 kcal./mole and 7 kcal./mole, respectively. The latter value was calculated from rate data at 0 and −24° using 0.0579 *N* KOH. Relative rate for I at 35° is a calculated value based on the E_a.

[9] For a recent excellent summary of data on effects of ring size on reactivity, see A. Streitwieser, Jr., *Chem. Rev.*, **56**, 666–670 (1956).

[10] There are, of course, four possible structures of Si(5) for II which would have the H-Si-OH angle near 90°, but two of these would be energetically unfavorable since the C-Si-C angle would be constrained from an ideal angle of 120° to *W*90° by the silacyclobutane system.

[11] H. C. Brown and M. Borkowski, THIS JOURNAL, **74**, 1894 (1952), and other earlier papers on the elegant I-Strain hypothesis.

[12] Relative rate (k_2) for t-$C_4H_9Si(CH_3)_2H$ is 10^{-2}. Unpublished work of L. H. Sommer and W. P. Barie, Jr.

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RECEIVED MAY 23, 1957

THE PREMIXED OZONE-HYDROGEN FLAME[1]

Sir:

Mixing of pure ozone with combustible substances usually leads to self-ignition, explosion or detonation and *premixed* pure ozone–fuel flames have not been reported. They are interesting not only because of the higher enthalpy content of the O_3–fuel *vs.* the O_2–fuel system, but primarily because the combustion kinetics in the flame front of the O_3-systems can be expected to be substantially faster than for the corresponding O_2–systems.

We have described recently the combustion flame of ozone to oxygen.[2] We also found that pure ozone can be mixed with pure hydrogen at −78° and even at 20° and 1 atm. without explosion and with no, or practically no, reaction for several hours.

Pure ozone–hydrogen mixtures of any desired composition were prepared by mixing known volumes of the two gases. The mixtures were burned at −78° initial temperature using the same technique as before.[2] (The Reynolds numbers of all flames were below 2000.) The burning velocities were determined by the standard schlieren method. The same apparatus was used to measure the burning velocity of the H_2–O_2 system. The results are presented in Fig. 1. The experimental burning velocities at 195°K. initial temperature and 1.0 atm., were for 6.0, 12.0, 18.2, 18.5, 25.0 and 100.0 mole % O_3, respectively, 207 ± 5, 664 ± 57, 1290 ± 20, 1330 ± 30, 1680 ± 80 and 270 ± 7 cm./sec.

Mixtures of 94.0 to 75.0% H_2 (rest pure ozone) could be burned readily. These O_3–H_2 flames are brighter than the corresponding O_2 flames but like the latter their luminosity is low. The stoichiometric mixture, *i.e.*, 3.0 vol. H_2 + 1.0 vol. O_3, which could be appropriately called "super-knall gas," burns very rapidly at a velocity of 1680 ± 80 cm./sec., whereas "knall gas," classically considered the fastest burning gas mixture, burns at 610 cm./sec. or 1/2.75 as rapidly. In mixtures on the ozone-rich side of the stoichiometric point the flame front degenerates very rapidly to a detona-

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600) 1475. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] A. G. Streng and A. V. Grosse, THIS JOURNAL, **79**, 1517 (1957); see also *Proc. VIth International Symposium on Combustion*, Aug. 19–24, 1956; *Proc. International Ozone Conference*, Chicago, Ill., Nov. 28–30, 1956.