Table II. Terminal Nucleosides

RNA, 50 mg.	Method of hydrolysis	Moles of nucleosides/mole of nucleic acid[a]			
		A	G	C	U
f2	KOH, VI	0.91	<0.05	0.18	<0.05
..	Pancreatic ribonuclease	0.78	<0.05	<0.05	<0.05
MS2	KOH, VI	0.94	<0.05	0.15	<0.05
..	.. ..	0.93	<0.05	0.16	<0.05
WG	.. ..	0.21	0.25	0.33	0.27
..	Pancreatic ribonuclease	<0.05	<0.05	<0.05	<0.05
..	Ribonuclease T₁	<0.05	0.27	<0.05	0.25

[a] Calculations were based on a chain length of 3000 nucleotides for the f2- and MS2-RNA and 1500 nucleotides for the WG-RNA.

Figure 1. Correlation of $4 + \log k_2$ and σ^+ for the reaction of phenylpentamethyldisilanes with perbenzoic acid in benzene at 45.0°.

as adenosine (recently determined by Sugiyama[3] using the isotope dilution method). The ribosomal RNA from wheat germ (WG) produced all four nucleosides on alkaline hydrolysis. On digestion with pancreatic ribonuclease, however, none of the nucleosides was liberated, showing that none of the nucleic acid molecules contains pyrimidines as their penultimate bases. Ribonuclease T₁ which splits RNA specifically at the guanosine-3' phosphoryl positions gave quantities of guanosine and uridine equal to those obtained in the alkaline hydrolysis. Thus the majority of the chains in this ribosomal nucleic acid must possess the terminal sequences: –GpU, –GpG, –ApA, and –ApC.

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(3) T. Sugiyama, *J. Mol. Biol.*, **11**, 856 (1965).

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A Novel Oxidation Reaction of Organodisilanes with Perbenzoic Acid

Sir:

During the course of an investigation of the properties of silicon–silicon bonding, we have found a novel oxidation reaction of organodisilanes with perbenzoic acid involving direct insertion of an oxygen atom into the silicon–silicon bonding.

R(CH₃)₂Si–Si(CH₃)₃ + PhCO₃H ⟶

I   R(CH₃)₂Si–O–Si(CH₃)₃ + PhCO₂H
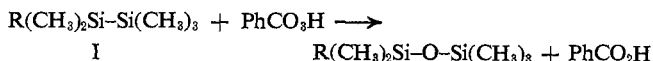
In a typical experiment 9.9 g. (0.048 mole) of phenylpentamethyldisilane (I, R = C₆H₅) was treated with 0.096 mole of perbenzoic acid in dichloromethane at room temperature. After standing overnight to ensure complete reaction, the reaction mixture was washed with water, sodium carbonate solution, and water, dried over anhydrous magnesium sulfate, and distilled, to yield, after removal of the solvent, 9.2 g. (86%) of phenylpentamethyldisiloxane. Careful examination of the reaction mixture by v.p.c. revealed that there was no other product such as hexamethyldisiloxane or diphenyltetramethyldisiloxane. In a similar manner, hexamethyldisilane gave hexamethyldisiloxane
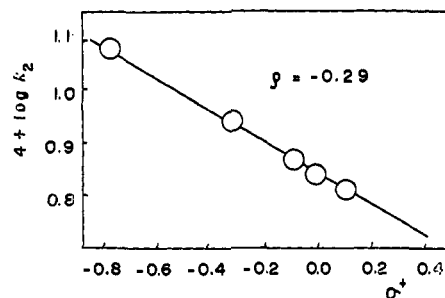
almost quantitatively. In the case of vinyldisilane, both the vinyl and disilanyl groups were oxidized; thus, vinylpentamethyldisilane gave pentamethyldisiloxanylepoxyethane (II) in quantitative yield, b.p. 49.0° (23 mm.), n^{20}D 1.4125, d^{20}_4 0.8887, MR (calcd. 53.52) 53.38. *Anal.* Calcd. for C₇H₁₈O₂Si₂: C, 44.16; H, 9.53. Found: C, 44.38; H, 9.38.

$$CH_2{=}CHSi(CH_3)_2Si(CH_3)_3 \xrightarrow{2PhCO_3H} $$

CH₂—CH—SiMe₂—O—SiMe₃ \ O /   II
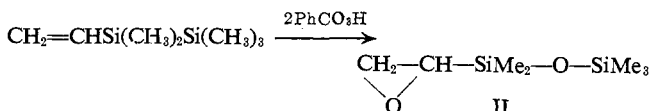
The n.m.r. spectrum[1] of II in carbon tetrachloride (cyclohexane internal standard) showed a singlet at τ 9.92 for protons of five methyl groups and a typical epoxide pattern[2] consisting of a quartet centered at τ 8.00 and double quartet centered at 7.53 and 7.18 ($J_{\alpha\beta} = 5$ c.p.s., $J_{\alpha\beta'} = 4$ c.p.s., $J_{\beta\beta'} = 7.5$ c.p.s.). Again there was no other siloxane.

It is advantageous in this oxidation reaction that the reaction could be carried out without cleavage of the phenyl–silicon bond, unlike other electrophilic reactions with silicon compounds such as halogenation of disilanes.[3]

The kinetics of the reaction have been studied in benzene. The extent of reaction was followed by the standard iodometric titration of perbenzoic acid.[4] The second-order law was found to be obeyed accurately in this reaction, and the results are listed in Table I. The qualitative effects of substituents are in accord with the characters of disilanes and perbenzoic acid as nucleophilic and electrophilic reagents, respectively. Figure 1 shows an excellent linear plot of $\log k_2$ vs. σ^+ of Brown and Okamoto[5] for substituted phenylpentamethyldisilanes (shown in Table I). These results may indicate that certain substituents on the phenyl ring of the disilanes are capable of resonance interaction with the silicon atom, possibly through p_π–d_π conjugation,[6] to make the silicon–silicon bond more nucleophilic. Substitution of a phenyl group for

(1) We are grateful to Dr. K. Tori, Shionogi Research Laboratory, for the determination of the spectrum.
(2) R. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 81.
(3) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 354.
(4) Y. Nagai, *J. Soc. Org. Syn. Chem. Japan*, **19**, 527, 533, 537 (1961).
(5) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
(6) For spectral evidence, see H. Sakurai and M. Kumada, *Bull. Chem. Soc. Japan*, **37**, 1894 (1964); H. Gilman, W. H. Schwebke *Chem. Ind.* (London), 1063 (1964); *J. Organometal. Chem.*, **2**, 369 (1964).

a methyl decreases the reactivity of disilanes toward perbenzoic acid, and qualitatively this is the same tendency as was observed with the series of phenyl substituted ethylenes.[7]

Disilanes	$k_2 \times 10^4$, 1. mole^{-1} sec.$^{-1}$
Me$_3$SiSiMe$_3$	11.7, 11.9
p-MeOC$_6$H$_4$SiMe$_2$SiMe$_3$	11.9, 11.9
p-MeC$_6$H$_4$SiMe$_2$SiMe$_3$	8.79, 8.77
m-MeC$_6$H$_4$SiMe$_2$SiMe$_3$	7.44, 7.32
C$_6$H$_5$SiMe$_2$SiMe$_3$	6.93, 7.00
p-ClC$_6$H$_4$SiMe$_2$SiMe$_3$	6.46, 6.50
C$_6$H$_5$SiMe$_2$SiMe$_2$C$_6$H$_5$	3.89, 3.87

These results suggest that a possible mechanism for this reaction is direct insertion of an oxygen atom,
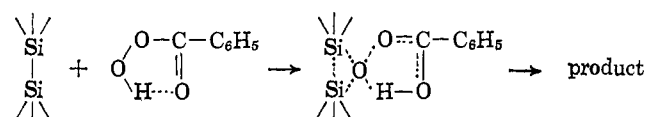
involving electrophilic attack of disilane by a cyclic hydrogen-bonded form of the peracid.[8]

We are investigating the mechanism of the reaction in detail and are extending our studies to the 1,2-diphenyl-tetramethyldisilane system, solvent effect, and stereochemistry.

(7) B. M. Lynch and K. H. Pausacker, J. Chem. Soc., 1525 (1955).
(8) An analogous molecular mechanism was first suggested by Bartlett [P. D. Bartlett, Record Chem. Progr., 11, 47 (1950)] for epoxidation and proposed for the mode of action of perbenzoic acid on 4,4'-dichlorodibenzyl sulfide [C. G. Overberger and R. W. Cummins, J. Am. Chem. Soc., 75, 4250 (1953)], trans-stilbenes,[7] methyl phenyl sulfoxides, and diphenyl sulfoxides [A. Cerniani and G. Modena, Gazz. chim. ital., 89, 843 (1959)], and α,α'-dimethylstilbenes.[4]

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Benzocyclobutene Derivatives from the Reactions of Benzyne with Vinyl Ethers and Esters

Sir:

Cycloaddition reactions of benzyne with olefins to give benzocyclobutene derivatives are relatively rare.[1] More generally, reactions with simple olefins yield mixtures of products resulting from hydrogen abstraction.[1a,2]

We wish to report on the synthetically useful reactions of benzyne with the electron-rich systems ethyl vinyl ether and vinyl acetate to form derivatives of benzocyclobutenol. In the case of 1-ethoxyvinyl acetate, benzocyclobutenone is a minor product, the main

(1) (a) H. E. Simmons, J. Am. Chem. Soc., 83, 1657 (1961), observed the first examples of cycloaddition with the strained olefins bicyclo-[2.2.1]heptadiene and bicyclo[2.2.1]heptene; (b) G. Wittig and H. Durr, Ann., 672, 55 (1964), reported the formation of 4–6% of cycloaddition product from the reaction of benzyne with 2,3-dimethylbutadiene; see also (c) M. Kuehne, J. Am. Chem. Soc., 84, 837 (1962), and M. Kuehne and T. Kitagawa, J. Org. Chem., 29, 1270 (1964), for examples of cycloaddition among reaction products of benzyne with enamines.
(2) E. M. Arnett, ibid., 25, 324 (1960).

reaction involving a novel *ortho* disubstitution of the benzene ring.[3]

Benzenediazonium-2-carboxylate was refluxed with a sixfold excess of ethyl vinyl ether in methylene chloride solution for 45 min. After concentration of the solution, chromatography on neutral alumina, and distillation of the product (35° at 225 μ), ethyl benzocyclobutenyl ether (I) was obtained in ca. 40% yield. Anal. Calcd. for C$_{10}$H$_{12}$O: C, 81.04; H, 8.16. Found: C, 80.84; H, 8.06. The structure of the ether follows from its ultraviolet absorption spectrum (λ_{max}^{EtOH} 260 mμ (log ε 3.09), 266 (3.27), and 272 (3.25)) and from the n.m.r. spectrum: τ 2.8 (singlet, 4 H), 5.03 (quartet, 1 H), 6.2–7.15 (multiplet, 4 H), and 8.9 (triplet, 3 H).[4] Conversion of the ether to the corresponding acetate (II) using acetic anhydride, boron trifluoride etherate, and lithium bromide[5] confirmed the structure (Chart I).

Chart I
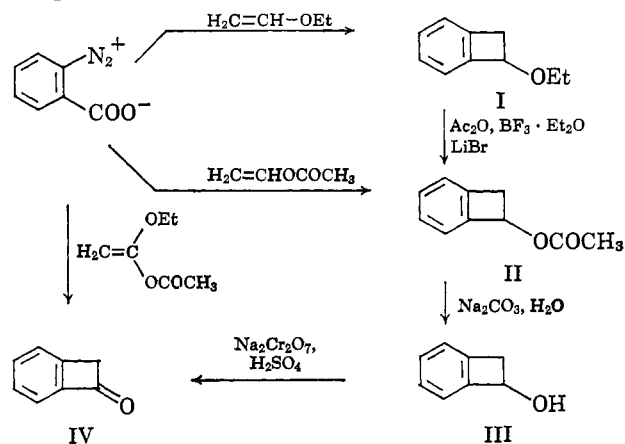
By heating benzenediazonium-2-carboxylate with excess vinyl acetate in methylene chloride and working up the reaction mixture as described above (using silica gel instead of alumina), benzocyclobutenyl acetate (II) could be prepared directly (ca. 45%). Anal. Calcd. for C$_{10}$H$_{10}$O$_2$: C, 74.06; H, 6.21. Found: C, 73.85; H, 6.36. The n.m.r. spectrum shows peaks at τ 2.78 (singlet, 4 H), 4.16 (quartet, 1 H), 6.25–7.05 (octet, 2 H), and 8.02 (singlet, 3 H). Hydrolysis of the acetate with 5% aqueous sodium carbonate[6] in ethanol yielded benzocyclobutenol (III), m.p. 58.5–59.5° (lit. 58°).

The reaction of benzyne with 1-ethoxyvinyl acetate[7] in refluxing methylene chloride followed by distillation and then chromatography on silica gel yielded two products. The minor component (4%) was a liquid showing a split carbonyl absorption in the infrared at $\lambda_{max}^{CCl_4}$ 1782 and 1762 cm.$^{-1}$.[6] The ultraviolet spectrum corresponds exactly to the values reported for benzo-

(3) The benzyne used in this work was generated in methylene chloride solution containing an excess of vinyl ether or ester, according to the procedure of Stiles and co-workers: M. Stiles, R. G. Miller, and U. Burckhardt, J. Am. Chem. Soc., 85, 1792 (1963). We thank Prof. Stiles for a personal communication describing revised details of this procedure.
(4) For related ultraviolet and n.m.r. data on benzocyclobutene derivatives see: (a) M. P. Cava and D. R. Napier, ibid., 80, 2255 (1958); (b) W. Baker, J. F. W. McOmie, and D. R. Preston, J. Chem. Soc., 2971 (1961); (c) H. Nozaki, R. Noyori, and N. Kozaki, Tetrahedron, 20, 641 (1964); (d) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, ibid., 20, 1179 (1964).
(5) R. D. Youssefyeh and Y. Mazur, Tetrahedron Letters, No. 26, 1287 (1962).
(6) M. P. Cava and K. Muth, J. Am. Chem. Soc., 82, 652 (1960), report a similar hydrolysis of benzocyclobutenyl trifluoroacetate to the alcohol.
(7) H. H. Wasserman and P. S. Wharton, ibid., 82, 661 (1960).