

This conclusion may be transferred to the polymerization of α,β - d_2 and d_0 monomers.

Isopropyl acrylate- β - d_1 with $\gamma = 1/6$ was prepared by the following procedure. After the hydroxyl group of propargyl alcohol was protected by an addition reaction with 2,3-dihydropyran,⁶ a THF solution of the adduct was added to an excess amount of ethyl Grignard in THF to form the Grignard reagent of the adduct, and heavy water was added to the Grignard solution. After addition of 20% sulfuric acid to the product the deuterated adduct was extracted and purified by vacuum distillation. The deuteration was repeated twice. Deuterated propargyl alcohol liberated by acid hydrolysis of the adduct was extracted, vacuum distilled, then converted to acid by Wolf's method,⁷ and esterified. The acetylenic proton content in the deuterated ester was found to be less than 0.5% by n.m.r. inspection. The deuterated ester was hydrogenated at -20° using the Lindlar catalyst.⁸ The value of γ of isopropyl acrylate- β - d_1 thus obtained was estimated from the intensities of the β -proton signals of the acrylate shown in Figure 2.

Isopropyl acrylate- β - d_1 with $\gamma = 1$ was prepared from monomers with $\gamma = 1/6$ and $\gamma = 3/2$. The monomer with $\gamma = 3/2$ was obtained by addition of DCl to acetylene, conversion to Grignard reagent, carboxylation, and esterification.

(6) H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc.*, 3646 (1950).

(7) V. Wolf, *Chem. Ber.*, **86**, 735 (1953).

(8) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

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Ozone: A New Cleavage Reagent for Organosilanes

Sir:

Previous studies of the combustion of alkylsilanes in the vapor phase^{1,2} have yielded flame velocities for these compounds approximately two to four times greater than those for their corresponding all-carbon analogs. It was also noted that whereas such burning rates for silanes vary significantly with molecular structure, those for a wide variety of hydrocarbons all have approximately the same value independent of structure.³

(1) R. L. Schalla, G. R. McDonald, and M. Gerstein in "Fifth Symposium (International) on Combustion," Reinhold Publishing Corp., New York, N. Y., 1955, pp. 705-710.

(2) M. Gerstein in "Seventh Symposium (International) on Combustion," Butterworths Scientific Publications, London, 1959, pp. 903-905.

These results suggested that silanes may be oxidized by a mechanism not available to hydrocarbons, *e.g.*, one involving the availability of 3d orbitals in silicon. To test this hypothesis, various organosilanes were treated with the more reactive allotrope of oxygen, ozone.

We now wish to report that ozone cleaves the Si-Y bond in molecules of the general structure R_3Si-Y , where R is an organic group and Y is an alkyl, trialkylsilyloxy, hydrogen, or hydroxyl substituent. In all cases, the resulting products are hydroxysilanes and siloxanes.

Triethylsilane reacts exothermally with ozone, yielding triethylhydroxysilane as the initial major product after 2 hr. of bubbling a 4% solution of ozone in oxygen through the neat liquid at 24° . The identity of the product was checked by microanalysis and by comparison of physical properties, vapor phase chromatographic behavior, and infrared absorption spectrum with those of an authentic sample of triethylsilanol prepared by the hydrolysis of triethylchlorosilane. After continued ozonization for an additional 6 hr., the product was found by vapor phase chromatography to contain hexaethyldisiloxane, hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane.

Treatment of triethylsilanol with ozone for 12 hr. afforded about 50% yield of hexaethyldisiloxane. Extended treatment of the silanol or hexaethyldisiloxane with ozone gave, in each case, hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane.

Cleavage of a silicon-alkyl bond was observed when ozone was bubbled through tetraethylsilane for 18 hr. at room temperature. The silicon-containing products, as evidenced by vapor phase chromatography, were identical with those obtained from the reaction of triethylhydroxysilane above.

The rates of cleavage by ozone fall in the order: $Si-H \gg$ (dehydration of $SiOH$ to siloxane) $\sim Si-R$. Pure oxygen does not cause any of these cleavage reactions to occur significantly at room temperature even after three- to fivefold longer reaction times.

Work is continuing on the elucidation of the mechanistic path, occurrence of intermediates, and the influence of molecular structure in this newly found ozone reaction.

(3) M. Gerstein, O. Levine, and E. L. Wong, *J. Am. Chem. Soc.*, **73**, 418 (1951).

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