was 98%. The pure crystals were obtained from ethanol, m.p. 164–165°.

Anal. Calcd. for $C_{15}H_{16}O_2SSi$: Si, 9.73. Found: Si, 9.60.

Cleavage by Hydrogen Chloride.[1,8]—Hydrogen chloride was allowed to pass for 15 hours through a refluxing solution of 0.01 to 0.02 mole of organosilicon compound in glacial acetic acid (50 to 100 ml.) and successively through a small ground glass trap immersed in a Dry Ice–acetone-bath. After cooling, the solution was poured into water and the solid which separated removed by filtration. When cleavage took place, the liquid in the trap was purified by two distillations and was shown to be trimethylsilyl chloride. The reagent used for characterizing the trimethylsilyl chloride was 9-fluorenyllithium. The product[9] formed in this manner was shown to be 9-trimethylsilylfluorene (m.p. and mixed m.p. 97–99°). The yields of dibenzothiophene from the cleavage of (II) and (III) were 99 and 97%, respectively. The percentage recoveries of dioxide from the attempted cleavages of (V) and (VI) were 94 and 97%, respectively.

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[8] See H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949), for earlier cleavage studies by this procedure.

[9] Unpublished studies by R. A. Benkeser.

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The Mechanism of Cellulose Nitration[1]

BY RALPH KLEIN AND MORRIS MENTSER

The mechanism of nitration of aromatic molecules by mixed acid has been established by rate studies[2,3,4] which show that nitration is effected by the NO_2^+ ion. Physical and chemical evidence has established the presence of this ion in the concentrated mixed acid used in nitration reactions.[5] Since cellulose is nitrated most effectively in the acid concentration region in which the NO_2^+ ion is found to exist, by analogy it might be expected that nitration of cellulose occurs *via* an electrophilic attack on the hydroxyl oxygen by the NO_2^+ ion with proton elimination. Indeed, such a mechanism has been postulated for nitration of starches.[6] It is evident that, if this mechanism is operative, cellulose nitrate prepared from ordinary cellulose and O^{18}-enriched mixed acid should have nitrate groups in which only two of the three nitrate oxygens are O^{18}-enriched. This is confirmed by the present experiments. It may be concluded that the oxygen of the alcohol groups of the cellulose is not eliminated in the nitration reaction and thus remains unenriched. An analogous result has been obtained from studies of the esterification of methyl alcohol with benzoic acid.[7]

Experimental

Samples of O^{18}-enriched cellulose nitrate were prepared by nitration of cotton linters with an O^{18}-enriched sulfuric acid–nitric acid–water mixture. Since both nitric acid and sulfuric acid exchange oxygen with water,[8,9] the admixture of heavy water to ordinary acids provides a convenient method for preparing the enriched acids. The O^{18}-enrichment factor was determined by mass spectrometer analysis of the NO resulting from a nitrometer reaction with the mixed nitrating acid.

The cellulose nitrate was analyzed for O^{18} by the method of von Grosse, *et al.*[10] The samples were heated at 750° for 1.5 hours in a quartz bulb. Under such conditions, oxygen randomization occurs among the decomposition products, and the enrichment factor could be determined by an O^{18} analysis of the CO_2 formed. The results are shown in Table I. Experiment 1(b) shows that, at the temperatures and times involved in these experiments, oxygen exchange with the quartz is negligible.

TABLE I

ENRICHMENT FACTORS FOR EQUILIBRATED DECOMPOSITION PRODUCTS OF O^{18}-ENRICHED CELLULOSE NITRATE

Expt.	Heating time, hours	Nitrogen content, %	O^{18}-Enrichment factor of nitrating acid	O^{18}-Enrichment factors of equilibrated decomposition products Calcd. 3 Enriched O-atoms in NO_3 group	2 Enriched O-atoms in NO_3 group	Exptl.
1(a)	1.5	11.1	4.9	3.6	2.7	2.2
1(b)[a]	3.0	..	...	...	...	2.2
2	1.5	11.1	4.9	3.6	2.7	2.6
3	1.5	11.1	4.9	3.6	2.7	2.7
4	1.5	8.7	5.7	3.5	2.7	2.6

[a] Same gas sample as (a) but heated 1.5 hours longer.

The number of nitrate groups per glucose unit was determined from nitrogen analysis. It was thus possible to calculate the enrichment factor resulting from oxygen randomization of the total oxygen of the cellulose nitrate molecule, assuming that either three or two of the three nitrate oxygens were enriched. These values are given in columns 4 and 5 of Table I. Except for the slightly low result of experiment 1, which may be attributed to incomplete preliminary outgassing of the quartz bulb, the experimental results of column 6 agree with column 5. This shows that the oxygen of the hydroxyl groups is not eliminated in the nitration reaction.

The authors express their appreciation to Dr. R. A. Friedel for the mass spectrometer isotope analyses.

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[1] Publication approved by the Office of Public Information, U. S. Department of Defense. Not copyrighted.

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EXPLOSIVES AND PHYSICAL SCIENCES DIVISION
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A New Preparation of 2,4-Dinitrophenylhydrazones

BY G. DANA JOHNSON

A phosphoric acid–ethanol solution of 2,4-dinitrophenylhydrazine has been found to be indefinitely stable and avoids the use of the more reactive sulfuric acid.

Reagent.—To make one liter of approximately 0.25 *M* reagent, 50 g. of 2,4-dinitrophenylhydrazine was dissolved in 600 ml. of 85% phosphoric acid in a one-liter beaker on a steam-bath. The solution was diluted with 395 ml. of 95% alcohol and clarified by suction filtration through a thin layer of Filter-Cel.

Use.—To a solution of the carbonyl compound in alcohol was added the calculated volume of reagent. Amino car-