much slower than solvent capture, the optical yield measures the relative rates of attack on the two faces of III. Finally the optical yield might be a measure of the amounts of III and IV resulting from dissociation. More complicated mechanisms could of course be operative.

In support of the idea that a torsional barrier in cation III controls the stereochemistry of substitution other results of Wallis and Adams may be mentioned. Treatment of *l*-1,2-benzo-9-phenylxanthyl-9-thioglycolic acid according to reactions 1 and 2 gives products showing no detectable optical activity.[1,19]

Our results indicate that substitution processes involving phenylbiphenyl-α-naphthylmethyl radical and anion, as well as similar systems, might be stereospecific. Furthermore, with suitably substituted compounds, the likelihood of isolating an optically active carbonium ion, radical, and carbanion is clear. These expectations are being investigated.

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(19) G. Wittig, F. Vidal, and E. Bohnert, *Chem. Ber.*, **83**, 359 (1950).

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The Cleavage of Silanes by Oxides of Nitrogen

Sir:

As an extension of our studies on the interaction of organosilanes with ozone,[1] we wish to report the observation that the oxides of nitrogen, generally called[2] "nitrogen dioxide,"[3] "nitrogen trioxide,"[4] nitric oxide (NO), and nitrous oxide (N_2O), also individually react cleanly with Si–X bonds, where X = H, OH, OR, Si, alkyl, and aryl, to give cleavage products at room temperature.

Triethylsilane reacts exothermally with nitrogen dioxide to yield triethylsilanol and hexaethyldisiloxane. In a separate experiment, under similar conditions, triethylsilanol readily gave the dehydration product, hexaethyldisiloxane.

The silicon–silicon bond in hexamethyldisilane is also cleanly cleaved by nitrogen dioxide to hexamethyldisiloxane in 95% yield.

Rupture of the silicon–alkyl bond was observed when tetraethylsilane was allowed to react with nitrogen dioxide. The principal products obtained were hexaethyldisiloxane and acetic acid. Under similar conditions, hexaethyldisiloxane yielded hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane, based on vapor phase chromatographic analysis and comparison with authentic samples. A number of smaller unidentified peaks were observed, but the three mentioned siloxanes accounted for about 95% of the reaction product.

The silicon–aryl bond was also cleaved in trimethylphenylsilane by nitrogen dioxide to produce hexamethyldisiloxane and nitrobenzene. When all of the phenyl group had been removed from silicon, the vapor phase chromatogram of the crude reaction product did not show the presence of any polysiloxane components other than the disiloxane.

The rate of cleavage of an ethyl group from hexaethyldisiloxane by nitrogen dioxide was slow compared to that from tetraethylsilane. This indication of some stabilization effect of oxygen on silicon was observed also with ozone.[1] However, all other cleavage reactions proceeded readily and with exothermicity at room temperature to give reaction products in good (90%) yields.

Nitrogen trioxide cleaved triethylsilane to triethylsilanol at room temperature. Nitric oxide also produced the silanol with complete reaction in less than 6 hr, whereas nitrous oxide gave only 10% conversion after 6 hr.

It appears that the oxides of nitrogen behave similarly toward organosilanes, but with differing degrees of activity. In decreasing order of reactivity, we find nitrogen dioxide, nitrogen trioxide, nitric oxide, and, much slower, nitrous oxide. Which of the components in the equilibrium mixtures[3,4] is the principal reactive species is not known, although NO_2 or N_2O_4 appears to be the most powerful. Nitric acid, which can form from the nitrogen oxides and water,[5] does not appear to be responsible for the observed cleavage reaction.

(1) L. Spialter and J. D. Austin, *J. Am. Chem. Soc.*, **87**, 4406 (1965).

(2) "Matheson Gas Data Book," The Matheson Co., Inc., East Rutherford, N. J., 1961.

(3) An equilibrium mixture of about 80% N_2O_4 and 20% NO_2 at 27° (ref 2).

(4) Largely dissociated into NO and NO_2 in the vapor state at room temperature (ref 2).

(5) N. V. Sidgwick, "The Chemical Elements and Their Compounds," University Press, Oxford, 1951, p 689.

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A Facile Synthesis of β-Alkoxy Mercaptans and β-Thioalkoxy Mercaptans

Sir:

The reduction of sulfides RSR′ to mercaptans by sodium in liquid ammonia is a well-known reaction,[1] of great importance in the removal of S-protective groups, especially in peptide synthesis. The reaction is not of great value in the synthesis of mercaptans as such, however, since the needed sulfides are generally made from mercaptans in the first instance.

Among the readily accessible compounds containing an RSR′ function are mono- and dithioketals and -acetals. It occurred to us[2,2a] that, if reduction in these com-

(1) F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, **53**, 352 (1931); R. H. Sifferd and V. du Vigneaud, *J. Biol. Chem.*, **108**, 753 (1935); D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1 (1951).

(2) See L. A. Pilato, Ph.D. Dissertation, Notre Dame University, 1962, p 59. We are grateful to Professor J. P. Danehy for his encouragement of this idea. Subsequent to inception of this work we found an isolated instance of the reaction in the literature, *viz.*, the reduction of the acetone ketal of 1,2-dithioglycerol to 2-thioisopropoxy-3-hydroxypropyl mercaptan: L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 2938 (1950); other, similar reductions described in the literature lead to complete desulfurization—*e.g.*, N. S. Crossley and H. B. Henbest, *ibid.*, 4413 (1960); R. D. Stolow and M. M. Bonaventura, *Tetrahedron Letters*, 95 (1964)—or to more complicated reaction courses—*e.g.*, Q. F. Soper, W. E. Buting, J. E. Cochran, and A. Pohland, *J. Am. Chem. Soc.*, **76**, 4109 (1954); A. Schönberg, E. Petersen, and H. Kalt-