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.

Acknowledgment. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, through a Type G grant, and by the National Science Foundation, Grant GP 3537.

(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.

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[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-

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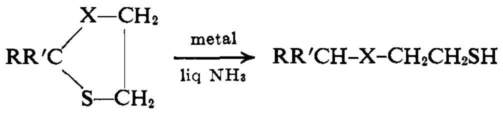
[1] F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, **53**, 352 (1931); R. H. Sifferd and V. du Vigneaud, *J. Biol. Chem.*, **108**, 753 (1935); D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1 (1951).

[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-

pounds were to affect the disubstituted carbon atom and were to stop after the first reductive cleavage of a C–S bond had occurred, a convenient method for the synthesis of β-alkoxy and β-thioalkoxy mercaptans would be at hand.



I II

X = O or S

In actual fact, the above reaction proved generally valuable in the synthesis of β-alkoxy mercaptans from monothioketals using calcium as the metal. Examples are shown in Table I. In a few instances, yields were low due to the occurrence of a simultaneous cleavage reaction to give RR′C=O (further reduced to RR′-CHOH), $CH_2{=}CH_2$, and H_2S. The reduction of dithioketals (Table II) gave excellent yields in three out of the four cases in which it has been studied.

Table I

Thioacetal or -ketal I, X = O R	R′	Mercaptan II, X = O Bp, °C (mm)	$n^{20}D$	% yield[a] Anal.	Isol.
$(CH_3)_2CH$	H	51–53 (11)	1.4482[b]	19–22	7
$C_6H_5CH_2$	H	100–101 (1.3)	1.5363	76	73
CH_3	CH_3	66–67 (43)	1.4460[c]	24	16
$(CH_3)_2CH$	CH_3	63.5–64 (11)	1.4470	73–78	72
$(CH_3)_2CHCH_2$	CH_3	79 (15)	1.4465	62–63	54
$(CH_3)_3C$	CH_3	70–71.5 (11)	1.4472	88–90	82
n-C_6H_{13}	CH_3	62 (0.3)	1.4534	55–63	41
$(CH_3)_2CH$	$(CH_3)_2CH$	58 (2.2)	1.4532	76–83	69
$C_6H_5CH_2$	CH_3	104 (1.3)	1.5264	91–94	88
$C_6H_5CH_2CH_2$	CH_3	90–91 (0.2)	1.5230	53–59	47
Cyclopentylidene		54 (2.2)	1.4856[e]	37	25
Cyclohexylidene		96 (14)	1.4860[d]	66–72	49

[a] First column gives analytical yields determined by iodine titration. Second column gives yield of compound isolated. All compounds, except those previously reported in the literature, were analyzed for C and H; analyses found are within accepted limits. [b] M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 245 (1954)] report: bp 45.2–45.5° (9 mm), $n^{20}D$ 1.4444. [c] Bp 56.1–56.4° (44 mm), $n^{20}D$ 1.4424. [d] Bp 73–73.5° (4.5 mm), $n^{20}D$ 1.4864. [e] At 22°.

Table II

Thioacetal or -ketal I, X = S R	R′	Mercaptan II, X = S Bp, °C (mm)	$n^{20}D$	% yield[a] Anal.	Isol.
$(CH_3)_2CH$	H	92 (15)	1.5084	95–96	85
Cyclohexylidene		85 (0.6)	1.5420	92–93	85
Cyclohexylidene[b]		100.5 (0.7)	1.5347	90–93	84

[a] See footnote *a*, Table I. [b] Homologous trimethylene dithioketal derived from cyclohexanone and $HSCH_2CH_2CH_2SH$.

The only limitation found in the reduction of monothioketals and -acetals is that, if R or R′ = phenyl, hydrogenolysis to an alkylbenzene occurs[3] (R = C_6H_5, R′ = H: toluene formed in 75%; R = C_6H_5, R′ = CH_3: ethylbenzene formed in 75%). The exact limitations of the dithioketal and -acetal reaction are, at the moment, insufficiently defined; an attempt to reduce the phenylacetaldehyde derivative, R = $C_6H_5CH_2$, R′ = H, led to cleavage to ethylbenzene (71%) and ethanedithiol (97% analytical yield).

The starting materials for this investigation are readily available from aldehydes or ketones and β-mercaptoethanol, ethanedithiol, or propane-1,3-dithiol, as the case may be.[4] A typical reduction is carried out as follows.

To 600 ml of liquid ammonia contained in a 1-l. round-bottom, three-necked flask fitted with a pressure-equalized addition funnel, mechanical stirrer, and an outlet tube was added 2.5 g (0.061 g-atom) of calcium turnings. When the metal had dissolved (after *ca.* 5 min), a solution of 9.70 g (0.05 mole) of the monothioketal of phenylacetone (2-benzyl-2-methyl-1,3-oxathiolane) in 100 ml of ether was added dropwise to the blue solution over a period of 5–10 min. The excess calcium was then destroyed by the addition of small amounts of solid ammonium chloride, the ammonia was allowed to evaporate, and the residual gray slurry was treated with 100 ml of 10% hydrochloric acid. The layers were separated and the acidic aqueous layer was extracted three times with 50-ml portions of ether. The combined ether solutions were dried over magnesium sulfate and concentrated to give 9.50 g of a clear yellow oil. A small aliquot of this oil was removed and titrated for mercaptan content with iodine;[5] the yield of mercaptan was 91%. The remainder of the oil was distilled, bp 97° (1.3 mm), yield 8.60 g (88%) (see Table I). The infrared and nmr spectra were compatible with the assigned structure.

In a number of reductions studied, calcium gave better yields than did sodium, lithium, or potassium, and ammonia was found to be superior to methylamine and ethylamine (with lithium).

The present method makes β-alkoxy mercaptans and β- and γ-thioalkoxy mercaptans readily available. It assumes added significance in the light of the availability of a great variety of 2-substituted and 2,2-disubstituted 1,3-dithianes through the recently developed ingenious synthetic schemes of Corey and Seebach involving alkylation and acylation of anions of dithioketals.[6]

Previous methods of preparing alkoxy mercaptans were either lengthy, involving conversion of β-hydroxy ethers,[7] $ROCH_2CH_2OH$, to halides or tosylates, followed by displacement with acid sulfide, thiocyanate, or thiolacetate, followed, if need be, by reduction or saponification;[8] or inconvenient, involving addition of hydrogen sulfide to vinyl ethers under pressure,[9] or reaction of

schmitt, *Ber.*, **66B**, 233 (1933). For other failures of similar reactions, see ref 3.

(2a) NOTE ADDED IN PROOF. After this communication had been submitted a few additional examples of dithioketal reduction and an example of monothioketal reduction were published by E. D. Brown, S. M. Igbal, and L. N. Owen, *J. Chem. Soc.*, 415 (1964).

(3) *Cf.* L. A. Stocken, *ibid.*, 592 (1947); A. R. Pinder and H. Smith, *ibid.*, 113 (1954).

(4) E. J. Salmi, *Ber.*, **71B**, 1803 (1938); *cf.* E. L. Eliel, L. A. Pilato, and V. G. Badding, *J. Am. Chem. Soc.*, **84**, 2377 (1962).

(5) D. P. Harnish and D. S. Tarbell, *Anal. Chem.*, **21**, 968 (1949).

(6) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1965).

(7) E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Am. Chem. Soc.*, **84**, 2371 (1962).

(8) *E.g.*, L. J. Goldsworthy, G. F. Harding, W. L. Norris, S. G. P. Plant, and B. Selton, *J. Chem. Soc.*, 2177 (1948); J. H. Chapman and L. N. Owen, *ibid.*, 579 (1950).

(9) (a) M. F. Shostakovsky, E. N. Prilezhaeva, and E. S. Shapiro, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 235, 245 (1954); (b) *ibid.*, 325 (1953); this might be a convenient method by addition of thiolacetic acid followed by saponification.

alcohols with ethylene sulfide.[10,11a] Thioalkoxy mercaptans have been prepared by the last method from mercaptans and ethylene sulfides.[11] An authentic sample of cyclohexyl β-mercaptoethyl ether was, in fact, obtained in 36% yield from cyclohexyl β-hydroxyethyl ether[7] *via* the chloride and thiocyanate; it corresponded in boiling point (89–91° (10 mm)), refractive index ($n^{18}D$ 1.4868), and infrared spectrum to the sample listed in Table I.

(10) R. Oda, *Mem. Fac. Eng. Kyoto Univ.*, 14, 195 (1952); *Chem. Abstr.*, **48**, 1935*c* (1954).

(11) *E.g.*, (a) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2675 (1947); (b) E. M. Meade and F. N. Woodward, *J. Chem. Soc.*, 1894 (1948); C. C. J. Culvenor, W. Davies, and N. S. Heath, *ibid.*, 282 (1949); E. P. Adams, *et al.*, *ibid.*, 2649 (1960).

(12) We acknowledge support by Air Force Office of Scientific Research Grant AF-AFOSR-772-65.

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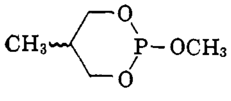
Geometric Isomerism in Six-Membered Ring Phosphites[1]

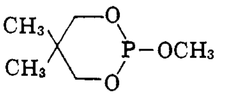
Sir:

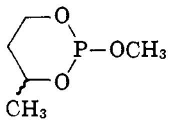
Several groups have shown that unsymmetrically substituted phosphines can be isolated in their enantiomorphic forms.[2] These substances have been of considerable value in studying the mechanisms of many reactions of phosphines. The situation with respect to other trisubstituted phosphorus compounds is much different in that no optical or geometric isomers have been available. There is a report that five-membered ring cyclic phosphites are configurationally stable about the phosphorus atom. This conclusion is based on nmr evidence alone, and no separation of these substances has been achieved.[3] It is the purpose of this report to describe the preparation of several six-membered ring phosphites. The data indicate that these materials exist as *cis* and *trans* isomers, and it has been found that these isomers can be prepared, in some cases, relatively free of each other.

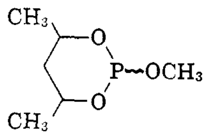
Condensation of 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-butanediol, *meso*-2,4-pentanediol, and a mixture of *meso*- and *dl*-2,4-pentanediol with trimethyl phosphite yielded the cyclic phosphites I–V.[4]

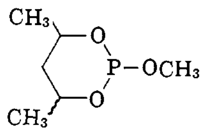
The phosphite I showed two doublets for $C-CH_3$ absorption at 0.69 ($J = 6$ cps) and 1.28 ($J = 6$ cps) ppm; their relative areas were 4:1. These absorptions are very similar indeed to those of II which occur at 0.70 and 1.18 ppm. Glpc analysis of I under several conditions has only given one major peak. Oxidation of I by *t*-butyl hydroperoxide gave a mixture of two phosphates which could be separated by glpc. The ratio of the two phosphates was essentially the same as that of the two phosphites. These phosphates had $C-CH_3$ absorptions at 0.84 ($J = 7$ cps) and 1.17 ($J = 7$ cps) ppm. The phosphate from II has $C-CH_3$ at 0.89 and 1.23 ppm.


Ia,b


II


IIIa,b


IVa,b


V

The phosphite, III, showed $C-CH_3$ absorption at 1.15 ($J = 6$ cps) ppm. Oxidation by *t*-butyl hydroperoxide gave two phosphates, 95:5; oxidation by mercuric oxide gave the same phosphates but in different relative amounts, *ca.* 7:3. These two phosphates can be separated by distillation and glpc. They show $C-CH_3$ absorptions at 1.34 ($J = 7$ cps) and 1.39 ($J = 7$ cps) ppm; each doublet is further split by coupling to phosphorus ($J = 2$ cps). Reaction of 1,3-butanediol with phosphorus trichloride yielded the cyclic phosphorochloridite, $C-CH_3$, at 1.30 ($J = 6$ cps) ppm. Treatment of this material with sodium methoxide in ether gave IIIa and a new material, IIIb, $C-CH_3$ 1.36 ($J = 6$ cps) ppm. Glpc analysis gave two peaks which were incompletely separated. Treatment of this mixture with a trace of methanol caused rapid isomerization of IIIb to IIIa as evidenced by nmr and glpc. The relative amounts of IIIa and b obtained by this method varies rather considerably from experiment to experiment. The highest percentage of IIIb obtained to date is 72, as determined by nmr. Oxidation of this mixture with cumene hydroperoxide gave the two phosphates obtained by mercuric oxide oxidation of IIIa. The ratio of isomers in this case was 3:7, which is in agreement with that predicted by the nmr analysis of the phosphite mixture.[5]

The phosphite IVa, prepared from *meso*-2,4-pentanediol by transesterification, has $C-CH_3$ absorption at 1.15 ($J = 6$ cps) ppm. The phosphite V, from the *dl*-glycol, has $C-CH_3$ at 1.19 ($J = 6$ cps) and 1.42 ($J = 6$ cps) ppm. Treatment of a mixture of *meso*- and *dl*-glycols, *ca.* 4:1, with phosphorus trichloride gave a mixture of cyclic phosphorochloridites. This mixture was treated with sodium methoxide in ether. The product had $C-CH_3$ absorption for IVa and V. There was also $C-CH_3$ absorption at 1.25 ($J = 6$ cps) ppm. The integrated nmr spectrum indicated that the original mixture consisted of 25% IVa, 19% V, and 56% of the new material, IVb. Treatment of this mixture with a trace of methanol led to the loss of the 1.25 ppm absorption and an increase in the absorptions due to IVa.

Glpc analysis of the mixture showed that IVa and V were present. A third material was also present, as evidenced by a broadening of the IVa peak. This

(1) Research supported by the National Institutes of Health under GM 12625.

(2) (a) W. E. McEwen, "Topics in Phosphorus Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1965, pp 1–41; (b) L. Horner, *Pure Appl. Chem.*, 9, 225 (1964).

(3) H. Goldwhite, *Chem. Ind.* (London), 494 (1964).

(4) Satisfactory analyses were obtained for all compounds described here. Their integrated nmr spectra were in accord with the assigned structures. The nmr spectra were recorded on solutions in carbon tetrachloride except for those of IVa and b which were taken on benzene solutions. Tetramethylsilane was used as an internal standard throughout.

(5) See D. B. Denney and J. W. Hanifin, *Tetrahedron Letters*, No. 30, 2177 (1963), for arguments concerning the stereospecificity of hydroperoxide oxidations of trisubstituted phosphorus compounds.