N-Trimethylsilyl-N,N'-diphenylurea was found to be a particularly useful silyl donor because the accompanying product of the silylation, diphenylurea, is fairly insoluble in most solvents and thus is readily separated from the silylation product. Precipitation and removal of diphenylurea allows silylations which are not favored by the position of equilibrium.

Silyl derivatives which could not be obtained by "conventional" silvlation with hexamethyldisilazane⁵ were prepared by stirring mixtures of N-trimethylsilvldiphenvlurea with the silvl acceptor in small amounts of acetonitrile at $30-35^{\circ}$ for several minutes (several hours in cases of low solubility of the acceptor), filtration of the precipitated diphenylurea, and purification of the product by distillation or sublimation. The conversion was quantitative in all cases without significant formation of by-products as determined by vapor phase chromatography or proton magnetic resonance spectra of the reaction mixtures. The yields stated refer to isolated pure product: N,N'bis(trimethylsilyl)thiourea,¹⁰ m.p. 155-158° (yield 82%). Anal. Calcd. for C7H20N2SSi2: C, 38.1; H, 9.1; N, 17.7; Si, 25.5. Found: C, 38.1; H, 9.2; N, 17.9; Si, 25.6. N,N-Dimethyl-N'-trimethylsilylurea11 had m.p. $125-129^{\circ}$ (yield 79%). Anal. Calcd. for $C_6H_{16}N_2OSi$: C, 45.0; H, 10.0; N, 17.5. Found: C, 45.3; H, 10.2; N, 17.1. N,N',N''-Tris(trimethylsilyl)guanidine (not previously reported) had b.p. 40° (0.5 mm.), n²⁰D 1.4450 (yield 72%). Anal. Calcd. for C₁₀- $H_{29}N_{3}Si_{2}$: C, 43.5; H, 10.6; N, 15.3. Found: C, 43.6; H, 10.6; N, 15.7.

Experiments with several compounds of widely differing structure containing reactive hydrogen on carbon have shown that trimethylsilyl proton exchange is readily achieved using trimethylsilyldiphenylurea as silyl donor. (1) Mixing of equimolar amounts of the silylurea and acetylacetone in benzene resulted in immediate precipitation of diphenylurea; distillation of the filtrate afforded trimethylsilylacetylacetone,¹² b.p. 102–103° (35 mm.), n^{20} D 1.4551 (yield 65%). *Anal.* Calcd. for C₈H₁₆O₂Si: C, 55.8; H, 9.3; Si, 16.3. Found: C, 55.9; H, 9.2; Si, 16.4. This compound, according to its proton magnetic resonance spectrum, is an equilibrium mixture of two isomers. Hydrolysis at room temperature is rapid and leads back to acetylacetone.

(2) The silylation of nitromethane, achieved by stirring with trimethylsilyldiphenylurea at 35° for several hours, resulted in the quantitative formation of a mixture of syn- and anti-bis(trimethylsilyl)methazonic acid,¹³ b.p. 49–51° (0.5 mm.), n^{20} D 1.4685 (isolated yield 76%). Anal. Calcd. for C₈H₂₀N₂O₃Si₂: C, 38.7; H, 8.1; N, 11.3. Found: C, 39.0; H, 8.0; N, 11.3. This may be rationalized in analogy to the formation of methazonic acid from CH₃NO₂ and base by condensation of initially formed O-trimethylsilyl-acinitromethane with excess nitromethane and silylation of the condensation product. The O-silyl ether of nitroacetaldoxime can be isolated. Bis(trimethylsilyl)methazonic acid was also obtained by silylation of methazonic acid.

(10) L. Birkofer, A. Ritter, and P. Richter, Tetrahedron Letters, 5, 195 (1962).

(11) J. Goubeau and E. Heubach, Chem. Ber., 93, 1117 (1960).



(3) Another example of a silvlation followed by further reaction of the silvl-substituted intermediate was obtained when a mixture of malononitrile and trimethylsilyldiphenylurea in benzene was stirred for 15 hr. at 5°. A trimethylsilyl-substituted trimer of malononitrile was obtained in 30% yield (along with noncrystalline by-products), colorless crystals, m.p. 170-171°. Anal. Calcd. for C₁₈H₃₀N₆Si₃: C, 52.1; H, 7.5; N, 20.2; mol. wt., 417. Found: C, 52.0; H, 7.3; N, 20.2; mol. wt., 421. Hydrolysis in ethanol yielded the parent compound, a colorless solid which could be sublimed in vacuo and recrystallized from dimethyl sulfoxide, m.p. 400° dec. Anal. Calcd. for C₉H₆N₆: C, 54.5; H, 3.2; N, 42.3. Found: C, 54.5; H, 3.0; N, 42.5. Characteristic bands in the infrared spectrum of the hydrolysis product include a single strong band at 2205 cm.⁻¹ and three strong peaks at 3240, 3350, and 3440 cm.⁻¹; no absorption is shown in the CH stretching region. The proton magnetic resonance spectrum shows a single relatively broad signal at a position varying with temperature. The evidence suggests a symmetrical triaminotricyanobenzene derivative, presumably formed by trimerization of an intermediate silvlketenimine. The fate of the



postulated intermediate is strongly influenced by reaction conditions and environment: higher temperature favors formation of unidentified noncrystalline products; adducts of malononitrile and silyl donor were observed when the silylation was carried out with bis(trimethylsilyl)acetamide.

Further evaluation of the new method of silylation is in progress.

Acknowledgment.—The author is indebted to Dr. John B. Bush, Jr., for interpretation of n.m.r. spectra and helpful discussion.

General Electric Research Johann F. Klebe Laboratory

SCHENECTADY, NEW YORK

Received June 22, 1964

Electron Spin Resonance Spectra of Organic Oxy Radicals¹



Recent interest in the e.s.r. spectra of alkoxy and peroxy radicals has prompted this report on the photolytic production of radicals in peroxides and hydroperoxides.

Di-t-butyl peroxide (BOOB) was photolyzed in the cavity of a Varian V-4502 e.s.r. spectrometer in an attempt to obtain absolute rate constants for hydrogen atom abstraction by t-butoxy radicals (BO·). The samples, 50 μ l. in volume, were deaerated and sealed (1) Issued as National Research Council Contribution No. 8108.

⁽¹²⁾ R. West, J. Am. Chem. Soc., 80, 3246 (1958).

⁽¹³⁾ H. L. Finkbeiner, J. B. Bush, Jr., and J. F. Klebe, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964.

TABLE I

g-Values of Various Oxy and Peroxy Radicals						
Radicals	P	Principal g-values		Average	Ref.	Method of radical preparation
HO	2.0127	2.0077	2.0077	2.0094	a	γ -Irradiation of ice
HO				2.0119	Ь	$Ti^{3+} + H_2O_2$
CH ₃ O· C ₂ H ₅ O· ^c	2.034	2,007	2.002	2.014	d	Ultraviolet $+$ the alcohol glass
HOO	2.026	2.011	2.011	2.016	e	Tritiated ice
HOO				2.0132	Ь	$Ti^{3+} + H_2O_2$
$C_6H_3(CH_3)_2COO\cdot$				2.0144 - 2.0155	b, f, g	Oxidation of $C_6H_5C(CH_3)_2H$ and $Ce^{4+} + C_6H_5C(CH_3)_2OOH$
Alkyl OO				2.0148 - 2.0155	h	Electron irradiation of $RH + O_2$
$\rm NH_2CO(CF_3)CFOO\cdot$	2.0267	2.0193	2.0102	2.0187	i	γ -Irradiation of CF ₃ CF ₂ CONH ₂ + O ₂
(CH ₃) ₃ COO·				2.0137	This work	Ultraviolet on $(CH_3)_3COOH$ glass
$C_{10}H_{11}\left(\begin{array}{c}O\\OO\end{array}\right)$	2.0306	2.0085	2.0073	2.0155	This work	Ultraviolet on C10H11OOH crystal

^a J. A. McMillan, M. S. Matheson, and B. Smaller, J. Chem. Phys., **33**, 609 (1960). ^b L. H. Piette, G. Bulow, and K. Loeffler, preprint of paper presented to the Division of Petroleum Chemistry, 147th National Meeting of the American Chemical Society. Philadelphia, Pa., April, 1964. ^c This assignment is only tentative since the authors point out that these radicals may possibly be the corresponding peroxy radicals. ^d P. J. Sullivan and W. S. Koski, J. Am. Chem. Soc., **85**, 384 (1963); **86**, 159 (1964). ^e Estimated from J. Kroh, B. C. Green, and J. W. T. Spinks, Can. J. Chem., **40**, 413 (1962). ^f Ya. S. Lebedev, V. F. Tsepalov, and V. Ya. Shlyapintokh, Dokl. Akad. Nauk SSSR, **139**, 1409 (1961). ^e See ref. 6. ^h R. W. Fessenden and R. N. Schuler, J. Chem. Phys., **39**, 2147 (1963). ⁱ R. Lontz, Bull. Am. Phys. Soc., **8**, 328 (1963).

under vacuum into 2-mm. i.d. Pyrex tubes. No radicals were detected in BOOB which had been carefully distilled and then passed through alumina prior to photolysis. However, radicals were readily detected in commercial BOOB. Their spectra consisted of a rather broad single line ($\Delta H_{\text{max. slope}} \approx 5$ gauss) having a g-value of 2.014 but varying as much as \pm 0.001 in different solvents. The radicals decayed with first-order kinetics in a variety of solvents when the light was switched off (see Fig. 1). Under continuous irradiation the radicals disappeared in a few minutes. The radicals probably arise from the traces of t-butyl hydroperoxide (BOOH) which are present as an impurity in commercial BOOB since an apparently identical radical can be generated in purified BOOB by the addition of small quantities of BOOH. The radical, which is believed to be the peroxy radical BOO, could also be detected by the photolysis of pure BOOH in which it had a g-value of $2.0137 \pm$ 0.0002. In pure BOOH in the glassy state the radical decayed with first-order kinetics having a half-life of 50 sec. at -4° and 60 sec. at -21° . Radicals with a g-value of 2.014 were also detected by the photolysis of liquid cumene hydroperoxide ($\Delta H_{\text{max. slope}} \approx 2$ gauss), liquid isopropyl hydroperoxide, and glassy ethyl hydroperoxide. These radicals, which did not exhibit any resolvable hyperfine interaction, are also believed to be peroxy radicals.

These results differ markedly from those of Piette and Landgraf, who report² that the photolyses of BOOH and two other butyl hydroperoxides all give alkoxy radicals which undergo a second-order decay and which all have a g-value of 2.003. In the present work no radicals with g = 2.003 could be detected by the photolysis of BOOH, BOOB, or dicumyl peroxide in Pyrex or quartz tubes even at 77°K. The present results are consistent with the suggestion^{3,4} that the spectrum detected by the photolysis of hydroperoxides at g = 2.014 is due to peroxy radicals formed in the rapid reaction

$RO + ROOH \longrightarrow ROH + ROO$

the peroxy radical being much less reactive than the corresponding alkoxy radical.



Fig. 1.—Half-lives for the first-order decay of the radical produced from commercial di-t-butyl peroxide in different solvents: 12% BOOB in *n*-pentane, O; toluene, Δ ; chlorobenzene, \Box ; CCl₁F, $\mathbf{\nabla}$; 25% BOOB in CCl₃F, $\mathbf{\blacksquare}$; undiluted BOOB, $\mathbf{\bullet}$.

Table I lists g-values for various oxy and peroxy radicals. There is no completely authenticated gvalue for an alkoxy radical (see footnote c in Table I) unless the \cdot OH radical is regarded as a reasonable model. Therefore, although it may be true that a g-value in the range 2.014 to 2.019 can be used to distinguish peroxy radicals from alkyl radicals (and R₂NO· radicals), as suggested by Thomas,⁵ it does not follow that the same criterion can be applied to distinguish between peroxy and alkoxy radicals. That (5) J. R. Thomas, J. Am. Chem. Soc., **85**, 591 (1963); **86**, 959 (1964).

⁽²⁾ L. H. Piette and W. C. Landgraf, J. Chem. Phys., 32, 1107 (1960).

⁽³⁾ G. A. Russell in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 108.

 ⁽⁴⁾ M. C. R. Symons in "Advances in Physical Organic Chemistry,"
 V. Gold, Ed., Academic Press, New York, N. Y., 1963, p. 283.

K. U. INGOLD

J. R. MORTON

is, e.s.r. spectra do not at present provide an unequivocal means for distinguishing between RO· and RO₂ radicals. The difficulty is illustrated by our measurement of the principal g-values of the radical produced by the photolysis of a single crystal of α -tetralin hydroperoxide (Table I). The spectrum of this radical (average g = 2.0155) consists of a doublet with an isotropic splitting of about 9 gauss from which it would be tempting to conclude that it is the α -tetralyloxy radical (C₁₀H₁₁O·). However, the possibility that it is the corresponding peroxy radical (C₁₀H₁₁O₂·) with an appreciable spin density on both oxygen atoms³ cannot be entirely ruled out.

Division of Applied Chemistry National Research Council Ottawa, Canada

RECEIVED MAY 25, 1964

S-Vinyl-O-t-butyl Thiolcarbonate. A New Route to Polymercaptans¹

Sir:

We wish to report the synthesis of S-vinyl-O-tbutyl thiolcarbonate (I), a new monomeric precursor to polymercaptans containing a thermally removable or acid-labile sulfhydryl blocking group. This monomer can be utilized in the preparation of copolymers of polyvinyl mercaptan which contain acid- or basesensitive substituents. These copolymers are being investigated as possible radiation prophylactics and as polymeric systems for enzymatic processes.

S-vinyl-O-t-butyl thiolcarbonate² was synthesized by the following sequence of reactions: S-(β -chloroethyl) chlorothiolformate (II) was prepared from ethylene sulfide and phosgene according to the procedure of Ringsdorf and Overberger.^{2b} Addition of an ether solution of II (0.5 mole) to a solution of potassium t-butoxide (1.0 mole) in a 1:1 t-butyl alcoholether mixture at 20° resulted in concurrent esterification and dehydrohalogenation to produce I. Purification by fractional distillation afforded a 51.5% yield of S-vinyl-O-t-butyl thiolcarbonate, b.p. 60.5-61° (15 mm.), n^{25} D 1.4642 (lit.¹ n^{25} D 1.4642), plus a 6% yield of S-(β -chloroethyl)-O-t-butyl thiolcarbonate (III), b.p. 48-49° (0.5 mm.), n^{25} D 1.4722 (lit.¹ n^{25} D 1.4722).

$$ClCH_{2}CH_{2}S - C - Cl + 2K^{+-}O - C(CH_{3})_{3} \longrightarrow$$

$$II \quad O$$

$$CH_{2} = CH - S - C - O - C(CH_{3})_{3} + I$$

$$I \quad O$$

$$ClCH_{2}CH_{2}S - C - O - C(CH_{3})_{3}$$

$$G \quad III$$

S-Vinyl-O-*t*-butyl thiolcarbonate polymerized readily in bulk or solution in the presence of free-radical initiators. The polymer was soluble in aromatic hydrocarbons and halogenated solvents and could be precipitated by addition to aliphatic hydrocarbons or methanol. A range of molecular weights could be prepared by varying catalyst concentrations but the following discussion of hydrolysis procedures pertains specifically to a polymer with an intrinsic viscosity of 0.45. In copolymerization experiments the monomer has been shown to be similar in reactivity to the Svinyl carbamates.⁸

The acid lability of the *t*-butyloxocarbonyl group has been utilized in peptide synthesis for the protection of amino substituents.⁴ Analogous reactivity was observed for the thiolcarbonates. Treatment of a 1% solution of poly(S-vinyl-O-*t*-butyl thiolcarbonate) in 6:1 chloroform-tetrachloroethane with anhydrous hydrogen bromide for 4 hr. resulted in an evolution of carbon dioxide and isobutylene and yielded a solution of polyvinyl mercaptan. The polymercaptan was isolated by precipitation using methanol as the nonsolvent and purified by dissolution in dimethyl sulfoxide and reprecipitation. Mercaptan assay⁵ indicated that 84% removal of the *t*-butyloxocarbonyl group had occurred.

Recently the thermal removal of the t-butyloxocarbonyl group from glycidic esters,6 carbonic anhydrides,7 carbamates,8 and 1-N-carbo-t-butoxy-5-phenylpyrazolidone-3⁹ has been reported. Since the reaction appeared general and the thermal decomposition of S-methyl thiolcarbonates was known,10 poly(S-vinyl-O-t-butyl thiolcarbonate) was investigated. It was found that heating a 15% solution of polymer in N-methylpyrrolidone under nitrogen to 150° induced a vigorous evolution of carbon dioxide and isobutylene. The isobutylene was identified by the formation of N-t-butylbenzamide from benzonitrile via the Ritter reaction.¹¹ Quantitative determination of carbon dioxide by absorption on Ascarite indicated that 89% reaction had occurred after 2 hr. This was in good agreement with a mercaptan assay of 82% for the polyvinyl mercaptan solution. The polyvinyl mercaptan was soluble in dimethyl sulfoxide, N,N-dimethylformamide, dioxane, and 5% sodium hydroxide.

The relative mildness of the conditions required for hydrolysis and the freedom from side reactions makes this a very versatile procedure for the preparation of mercaptans. The remarkably low decomposition temperature and the formation of isobutylene suggests an intramolecular mechanism similar to that proposed for the Chugaev reaction.¹² A mechanism of this type should be quite general making the *t*-butyloxocarbonyl group a thermally removable protective group for a variety of substituents containing active hydrogens. Studies are now in progress to elucidate this mechanism and to extend the scope of the reaction.

Details of the copolymerization experiments and the oxidation of the polyvinyl mercaptan with molecular oxygen will be reported in the near future.

(3) H. Ringsdorf, N. Weinshenker, and C. G. Overberger, *ibid.*, **64**, 126 (1963).

(4) (a) F. C. McKay and N. F. Albertson, J. Am. Chem. Soc., **79**, 4686 (1957); (b) G. W. Anderson and A. C. McGregor, *ibid.*, **79**, 6180 (1957).

(5) A modification of the procedure described by C. G. Overberger, J. J. Ferraro, and F. W. Orttung, J. Org. Chem., ${\bf 26},\ 3458\ (1961),\ was used.$

(6) E. D. Blanchard, Jr., and G. Büchi, J. Am. Chem. Soc., 85, 955 (1963).
(7) C. J. Michejda and D. S. Tarbell, J. Org. Chem., 29, 1168 (1964).

(8) W. J. Bailey and J. R. Griffith, Polymer Preprints, 5, 279 (1964).

(9) N. M. Weinshenker, B.S. Thesis, Polytechnic Institute of Brooklyn, 1964.

(10) E. Salomaa, Ann. Acad. Sci. Fennicae Ser. II, 94, 1 (1959).

(11) J. J. Ritter and P. D. Minieri, J. Am. Chem. Soc., 70, 4045 (1948)

(12) (a) G. L. O'Connor and H. R. Nace, *ibid.*, **75**, 2118 (1953); (b) R. F. W. Bader and A. N. Bourns, *Can. J. Chem.*, **39**, 348 (1961).

⁽¹⁾ This is the 27th in a series of papers concerned with new monomers and polymers; for the previous paper in this series see C. G. Overberger and W. H. Daly, J. Org. Chem., **29**, 757 (1964).

^{(2) (}a) Previously reported as a by-product from the dehydrohalogenation of S,S-(β -chloroethyl) dithiolcarbonate [C. G. Overberger and W. H. Daly, ref. 1]; (b) H. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **44**, 418 (1961).