

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" silylation with hexamethyldisilazane<sup>5</sup> were prepared by stirring mixtures of N-trimethylsilyldiphenylurea with the silyl acceptor in small amounts of acetonitrile at 30–35° 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,<sup>10</sup> m.p. 155–158° (yield 82%). *Anal.* Calcd. for C<sub>7</sub>H<sub>20</sub>N<sub>2</sub>SSi<sub>2</sub>: 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'-trimethylsilylurea<sup>11</sup> had m.p. 125–129° (yield 79%). *Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Si: 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.), *n*<sub>D</sub><sup>20</sup> 1.4450 (yield 72%). *Anal.* Calcd. for C<sub>10</sub>H<sub>29</sub>N<sub>3</sub>Si<sub>2</sub>: 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,<sup>12</sup> b.p. 102–103° (35 mm.), *n*<sub>D</sub><sup>20</sup> 1.4551 (yield 65%). *Anal.* Calcd. for C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>Si: 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.

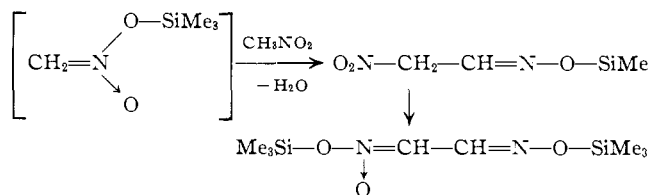
(2) The silylation of nitromethane, achieved by stirring with trimethylsilyldiphenylurea at 35° for several hours, resulted in the quantitative formation of a mixture of *syn*- and *anti*-bis(trimethylsilyl)methazonic acid,<sup>13</sup> b.p. 49–51° (0.5 mm.), *n*<sub>D</sub><sup>20</sup> 1.4685 (isolated yield 76%). *Anal.* Calcd. for C<sub>8</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub>: 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 CH<sub>3</sub>NO<sub>2</sub> and base by condensation of initially formed O-trimethylsilyl-*aci*-nitromethane 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).

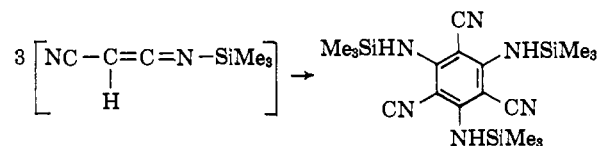
(11) J. Goubeau and E. Heubach, *Chem. Ber.*, **93**, 1117 (1960).

(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.



(3) Another example of a silylation followed by further reaction of the silyl-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 C<sub>18</sub>H<sub>30</sub>N<sub>6</sub>Si<sub>3</sub>: 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 C<sub>9</sub>H<sub>6</sub>N<sub>6</sub>: 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.<sup>-1</sup> and three strong peaks at 3240, 3350, and 3440 cm.<sup>-1</sup>; 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 silylketenimine. 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.

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### Electron Spin Resonance Spectra of Organic Oxy Radicals<sup>1</sup>

Sir:

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 μl. in volume, were deaerated and sealed

(1) Issued as National Research Council Contribution No. 8108.

TABLE I

g-VALUES OF VARIOUS OXY AND PEROXY RADICALS

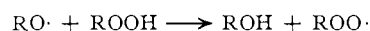
Radicals	Principal g-values			Average	Ref.	Method of radical preparation
	$g_{11}$	$g_{22}$	$g_{33}$			
HO·	2.0127	2.0077	2.0077	2.0094	<i>a</i>	$\gamma$ -Irradiation of ice
HO·				2.0119	<i>b</i>	Ti <sup>3+</sup> + H <sub>2</sub> O <sub>2</sub>
CH <sub>3</sub> O· C <sub>2</sub> H <sub>5</sub> O· <sup>c</sup>	2.034	2.007	2.002	2.014	<i>d</i>	Ultraviolet + the alcohol glass
HOO·	2.026	2.011	2.011	2.016	<i>e</i>	Tritiated ice
HOO·				2.0132	<i>b</i>	Ti <sup>3+</sup> + H <sub>2</sub> O <sub>2</sub>
C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> COO·				2.0144– 2.0155	<i>b, f, g</i>	Oxidation of C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> H and Ce <sup>4+</sup> + C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>2</sub> OOH
Alkyl OO·				2.0148– 2.0155	<i>h</i>	Electron irradiation of RH + O <sub>2</sub>
NH <sub>2</sub> CO(CF <sub>3</sub> )CFOO·	2.0267	2.0193	2.0102	2.0187	<i>i</i>	$\gamma$ -Irradiation of CF <sub>3</sub> CF <sub>2</sub> CONH <sub>2</sub> + O <sub>2</sub>
(CH <sub>3</sub> ) <sub>3</sub> COO·				2.0137	This work	Ultraviolet on (CH <sub>3</sub> ) <sub>3</sub> COOH glass
C <sub>10</sub> H <sub>11</sub> ( $\begin{smallmatrix} \text{O} \cdot \\ \text{OO} \cdot \end{smallmatrix}$ )	2.0306	2.0085	2.0073	2.0155	This work	Ultraviolet on C <sub>10</sub> H <sub>11</sub> OOH crystal

<sup>a</sup> J. A. McMillan, M. S. Matheson, and B. Smaller, *J. Chem. Phys.*, **33**, 609 (1960). <sup>b</sup> 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. <sup>c</sup> This assignment is only tentative since the authors point out that these radicals may possibly be the corresponding peroxy radicals. <sup>d</sup> P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 384 (1963); **86**, 159 (1964). <sup>e</sup> Estimated from J. Kroh, B. C. Green, and J. W. T. Spinks, *Can. J. Chem.*, **40**, 413 (1962). <sup>f</sup> Ya. S. Lebedev, V. F. Tsepalov, and V. Ya. Shlyapintokh, *Dokl. Akad. Nauk SSSR*, **139**, 1409 (1961). <sup>g</sup> See ref. 6. <sup>h</sup> R. W. Fessenden and R. N. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). <sup>i</sup> 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  $-4^\circ$  and 60 sec. at  $-21^\circ$ . 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 report<sup>2</sup> 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  $77^\circ\text{K}$ . The present results are consistent with the suggestion<sup>3,4</sup> that the spectrum detected by the photolysis of hydroper-

oxides at  $g = 2.014$  is due to peroxy radicals formed in the rapid reaction



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

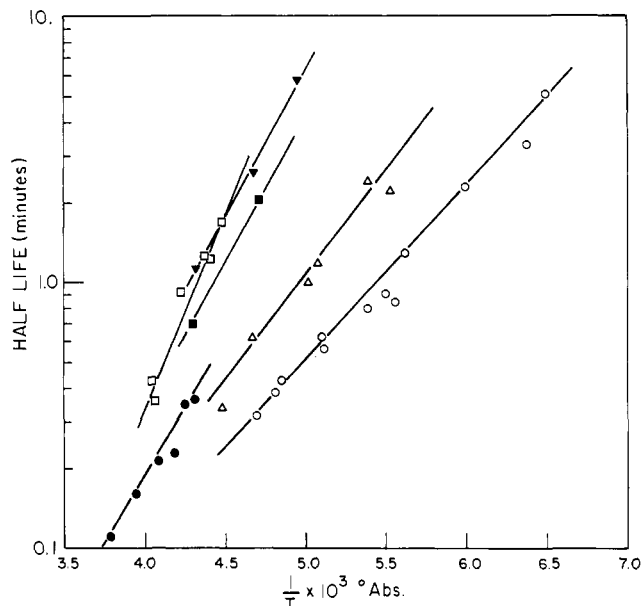


Fig. 1.—Half-lives for the first-order decay of the radical produced from commercial di-*t*-butyl peroxide in different solvents: 12% BOOB in *n*-pentane, O; toluene,  $\Delta$ ; chlorobenzene,  $\square$ ; CCl<sub>4</sub>F,  $\blacktriangledown$ ; 25% BOOB in CCl<sub>4</sub>F,  $\blacksquare$ ; undiluted BOOB,  $\bullet$ .

Table I lists  $g$ -values for various oxy and peroxy radicals. There is no completely authenticated  $g$ -value for an alkoxy radical (see footnote *c* in Table I) unless the ·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 R<sub>2</sub>NO· radicals), as suggested by Thomas,<sup>5</sup> 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.

