

a methyl group is readily eliminated on the basis of the complexity of this pattern, while a complex absorption pattern would be expected in this region if the dimer contained a cyclopropane group containing three methine protons as in structure III. No absorption appears in this region of the n.m.r. spectrum of the known dimer, IV. Confirmation of the presence of two double bonds and a cyclopropane ring in III is obtained from the n.m.r. spectrum of the reduced dimer (after three moles of hydrogen have been consumed). The n.m.r. spectrum of this compound shows no absorption in the vinyl proton region or in the cyclopropane region.

Lord and Walker⁶ found that the ratio of compound III to IV produced in the dimerization of cyclooctatetraene depended upon the temperature at which the dimerization was run. If the dimerization was carried out above 200° or if III was heated for some time at such temperatures, IV was obtained. These observations were confirmed. The ease of this conversion of III to IV, which does not appear to be reversible, implies that the two dimers are not greatly dissimilar, and that the structure proposed for the unknown dimer, III, should enable one to understand the change to the other. These requirements are met by structure III. The double bond b and the cyclopropane ring comprise a vinylcyclopropane moiety. Vinylcyclopropane is known to rearrange to cyclopentene at high temperatures.¹³ Thermal rearrangement of the vinylcyclopropane moiety in III to a cyclopentene moiety would give the known dimer IV.¹⁴

The possibility of the dimer, II, being a precursor to III seems reasonable on the basis of an intramolecular Diels–Alder reaction. There are two possible stereochemical configurations for compound II, the *cis* isomer (*cis*-cyclobutane protons) and the *trans* isomer (*trans*-cyclobutane protons). Only in the *cis* compound would the geometry be favorable for an intramolecular Diels–Alder cyclization. Attempts to cyclize an authentic sample of II¹⁵ under a variety of conditions has given only polymers. This inability of intramolecular Diels–Alder cyclization is a good indication that the dimer, II (obtained at low temperatures), has the *trans* configuration. Further studies on the stereochemistry of II, as well as the sequence of reactions leading to the dimers of cyclooctatetraene, are currently being investigated.

Acknowledgment.—The author wishes to express his appreciation to Dr. Karl Folkers for helpful suggestions throughout the course of this work.

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(14) The vinylcyclopropane moiety is within a bicyclo[5.1.0]octene-2 ring system which is known to rearrange thermally to 1,4-cyclooctadiene [W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963)]. However, this type of rearrangement is impossible in III since it would give a compound with a bridgehead double bond.

(15) Kindly supplied by Dr. G. Schröder, European Research Associates, Union Carbide, Bruxelles, Belgium.

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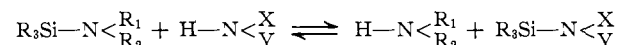
New Silyl Donors

Sir:

Silylation of amine, amide, and hydroxyl functions has become a valuable tool for separation and analysis

of compounds with a high degree of hydrogen bonding. Replacement of protons by silyl groups can lead to derivatives of considerably higher vapor pressure which after distillation or vapor phase chromatographic separation can readily be reconverted into the starting materials.

The silylamine–amine exchange reaction introduced by Larsson and Smith¹ has found extensive use in the preparation of silyl-substituted amines,² amides, lactams, carbamates, and ureas.³ Hexamethyldisilazane and other disilazanes also undergo this silyl-transfer reaction which has been used in preparing silyl derivatives of peptides,⁴ ureas,⁵ tetrazoles,⁶ and flavonoid compounds.⁷ Silylations with silylamines, silanedi- amines and -triamines, as well as disilazanes are based on a relatively slow exchange reaction between silyl donor and acceptor. The success of the procedure



depends on the removal of the lower boiling amine HNR_1R_2 , a process which usually requires several hours of heating at the reflux temperature of the mixture.

We have now found that N-silyl-substituted aromatic ureas and amides represent very powerful silyl donors. The equilibrium in solutions of these donors in mixtures with amines, amides, or hydroxyl compounds is established *within a few minutes at room temperature*, a time that is several orders of magnitude shorter than that required by "conventional" silyl donors. Furthermore, the position of equilibrium is such that nearly quantitative silylation of aliphatic or aromatic acceptors occurs within this period of time if disilyl-substituted amides like $CH_3C(OSiMe_3)=NSiMe_3$ ⁸ are applied. Use of monosilyl-substituted donors like $C_6H_5N(SiMe_3)-CO-NHC_6H_5$ leads to complete silylation of aliphatic acceptors while aromatic amines or amides require removal of one of the products from the equilibrium for complete silylation.

The difference in rate of silylation between "amine-type" and "amide-type" silyl donors is demonstrated by the following experiments.

Equimolar mixtures of N,N'-dimethylurea as silyl acceptor and (a) hexamethyldisilazane, (b) N-trimethylsilylpiperidine, (c) N-trimethylsilylaniline, and (d) N-trimethylsilyl-N,N'-diphenylurea⁵ in acetonitrile were prepared and the progress of the reaction was followed by vapor phase chromatography. The extent of N-trimethylsilyl-N,N'-dimethylurea formation after 75 hr. at room temperature was: (a) 0%; (b) 10%; (c) 3%. Mixture d, containing trimethylsilyl-diphenylurea as silyl donor, showed complete conversion to N-trimethylsilyldimethylurea after 1 min. at room temperature. Silylations with other amide-type donors were followed by proton magnetic resonance spectroscopy of the mixtures which confirmed the rapid rates of silylation.⁹

(1) E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949).

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(3) P. L. DeBenneville and M. J. Hurwitz, U. S. Patent 2,876,209 (1959).

(4) L. Birkofer, A. Ritter, and P. Neuhausen, *Ann.*, **659**, 190 (1962).

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(6) L. Birkofer, A. Ritter, and P. Richter, *Chem. Ber.*, **96**, 2750 (1963).

(7) A. C. Weiss, Jr., R. E. Lundin, and D. J. Stern, *Tetrahedron Letters*, **10**, 513 (1964).

(8) L. Birkofer, A. Ritter, and W. Giessler, *Angew. Chem.*, **75**, 93 (1963).

(9) J. F. Klebe, J. B. Bush, Jr., and J. E. Lyons, *J. Am. Chem. Soc.*, in press.

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 hexamethyldisilazane⁵ 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,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° (yield 79%). *Anal.* Calcd. for C₈H₁₆N₂O₂Si: 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*_D²⁰ 1.4450 (yield 72%). *Anal.* Calcd. for C₁₀H₂₉N₃Si₂: 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*_D²⁰ 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.

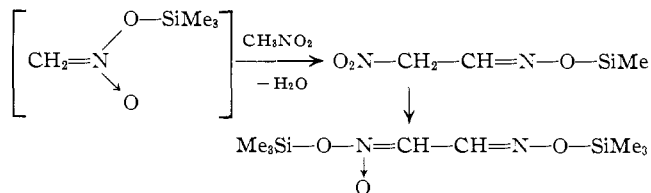
(2) The silylation of nitromethane, achieved by stirring with trimethylsilyldiphenylurea at 35° for several hours, resulted in the quantitative formation of a mixture of *syn*- and *anti*-bis(trimethylsilyl)methazonic acid,¹³ b.p. 49–51° (0.5 mm.), *n*_D²⁰ 1.4685 (isolated yield 76%). *Anal.* Calcd. 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-*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.

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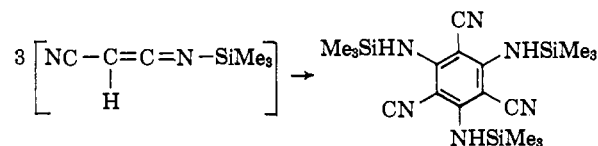
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(3) Another example of a silylation followed by further reaction of the silyl-substituted intermediate was obtained when a mixture of malononitrile and trimethylsilyldiphenylurea in benzene was stirred for 15 hr. at 5°. A trimethylsilyl-substituted trimer of malononitrile was obtained in 30% yield (along with noncrystalline by-products), colorless crystals, m.p. 170–171°. *Anal.* Calcd. for 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 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 Radicals¹

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

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