64714-70-1; **17**, 16110-80-8; **18**, 19914-84-2; **19**, 19914-85-3; **20**, 64753-30-6; **20a**, 64753-31-7; **21**, 64753-32-8; **21a**, 64753-33-9; **22**, 64714-55-2; **22a**, 64714-56-3; **23**, 64714-57-4; **24**, 64753-27-1; **25**, 64753-28-2; **26**, 61153-78-4; **26a**, 61177-56-8; **29**, 61247-14-1; **32** acetate, 61153-80-8; **30**, 1502-29-0; **31**, 64714-58-5; acetyl chloride, 75-36-5; 3-bromocyclohexene, 1521-51-3.

References and Notes

(1) Taken in part from the thesis submitted by J.H.T. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, June, 1970.
(2) E. J. Corey, *J. Am. Chem. Soc.*, **75**, 3297 (1953).
(3) R. Metze and P. Schreiber, *Chem. Ber.*, **89**, 2470 (1956); D. Q. Quan, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **267**, 1074 (1968).
(4) See B. Waegell, *Bull. Soc. Chim. Fr.*, 855 (1964), for the related reduction of *cis*-2,6-dibromo-3,3,5,5-tetramethylcyclohexanone.
(5) Epoxidation of 3-bromocyclohexene with *p*-nitroperbenzoic acid has been reported[6] to give epoxide **4** containing 10% of the isomeric epoxide **5**. The epoxide we have prepared shows a single peak on GLC employing an apiezon column at 100 °C.
(6) P. L. Barili, G. Bellucci, F. Marioni, and V. Scartoni, *J. Org. Chem.*, **40**, 3331 (1975).
(7) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 293–294, and references cited therein.
(8) J. Fajkos and J. Joska, *Collect. Czech. Chem. Commun.*, **27**, 1849 (1962).
(9) J. A. Marshall, N. Cohen, and K. R. Arenson, *J. Org. Chem.*, **30**, 762 (1965).
(10) J. K. Addy and R. E. Parker, *J. Chem. Soc.*, 915 (1963).
(11) R. A. Bannard, A. A. Casselman, E. J. Langstaff, and R. Y. Moir, *Can. J. Chem.*, **46**, 35 (1968).
(12) D. G. Needler, *Diss. Abstr.*, **24**, 1401 (1963).
(13) J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 1386 (1969), and references cited therein.
(14) E. W. Garbisch and J. Wohllebe, *Chem. Commun.*, 306 (1968).
(15) We have been unable to crystallize *trans,trans*-**21**, although Garbisch reported it melts at 49 °C. It may be more than coincidence that *trans*-bromo *cis*-epoxide **24** melts at 47–49 °C.
(16) J. D. Dunitz and H. M. M. Shearer, *Helv. Chim. Acta*, **43**, 18 (1960); J. Dehli and P. Groth, *Acta Chem. Scand.*, **23**, 587 (1969); A. Kwok-Tong Cheng, Ph.D. Thesis, University of California, Los Angeles, 1973.
(17) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 559 (1964).
(18) Only the most abundant of the isotope cluster is reported.
(19) K. Ziegler, A. Spath, E. Schaaf, W. Schumann, and E. Winkelman, *Justus Liebigs Ann. Chem.*, **551**, 80 (1942).
(20) A. C. Cope, H. R. Nace, and L. L. Estes, *J. Am. Chem. Soc.*, **72**, 1123 (1950).
(21) G. Hesse and F. Urbanek, *Chem. Ber.*, **91**, 2733 (1958).
(22) H. E. Baumgarten, Ed., "Organic Synthesis", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 283.
(23) L. I. Zakharkin and V. V. Korneva, *Izv. Akad. Nauk SSSR*, 1817 (1962).

Reaction of Lithium *N,N*-Dialkylamide Enolates with Trialkylchlorosilanes

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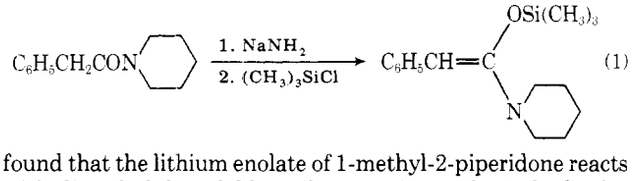
Lithium *N,N*-dialkylamide enolates were reacted in THF solution with trialkylchlorosilanes to give both C-silylated and O-silylated products. Acetamide enolates give predominantly C-silylation, while more highly substituted amide enolates give predominantly O-silylation with trimethylchlorosilane. *tert*-Butyldimethylchlorosilane gives increased amounts of O-silylation. Both C-silylated and O-silylated products hydrolyze with aqueous acid to the starting amide. O-Silylated compounds isomerize to C-silylated products on heating.

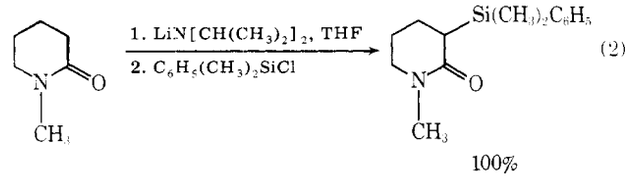
The reactions of ketone and ester enolates with trialkylhalosilanes have been studied extensively. Ketone enolates silylate exclusively at oxygen to form trialkylsilyl enol ethers.[1] Ester enolates, on the other hand, silylate at either oxygen (O-silylation) or at carbon (C-silylation) depending on the structure of the ester.[2]

In contrast, only fragmentary reports on the reaction of amide enolates with silylating reagents have appeared. Klebe reported that the sodium enolate of 1-phenylacetylpiperidide reacts with trimethylchlorosilane to give the O-silylated product, α-(1-piperidino)-β-phenyl-*O*-trimethylsilylvinyl ether, in unspecified yield (eq 1).[3] On the other hand, Trost



(1)

found that the lithium enolate of 1-methyl-2-piperidone reacts with dimethylphenylchlorosilane to give exclusively C-silylation (eq 2).[4] Most recently, Hudrlik reported that the lithium enolate of *N,N*-dimethylacetamide gave a 78% yield of the C-silylation product (eq 3), while the enolate of *N*-acetylaziridine gave a 33% yield of the O-silylation product (eq 4).[5]



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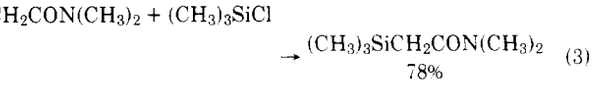

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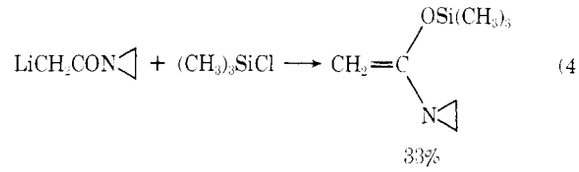

(4)

We recently reported that lithium *N,N*-dialkylamide enolates have appreciably greater stability than lithium ester enolates.[6] Considering the growing synthetic importance of the silyl derivatives of ester enolates,[7] we have undertaken a study of the reaction of *N,N*-dialkylamide enolates with trialkylhalosilanes. We report here the results of that study, together with information on the hydrolytic and thermal behavior of the products.

Results and Discussion

Silylation of Lithium Amide Enolates. Solutions of lithio *N,N*-dialkylamides were prepared by addition of the appropriate amide to tetrahydrofuran (THF) solutions of lithium diisopropylamide at 0 °C (eq 5).[6] The solutions were treated with a slight excess of silylating reagent (either trimethylchlorosilane or *tert*-butyldimethylchlorosilane) and then allowed to stir at room temperature for 30 min. The resultant

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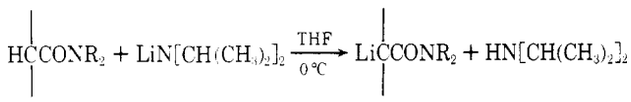

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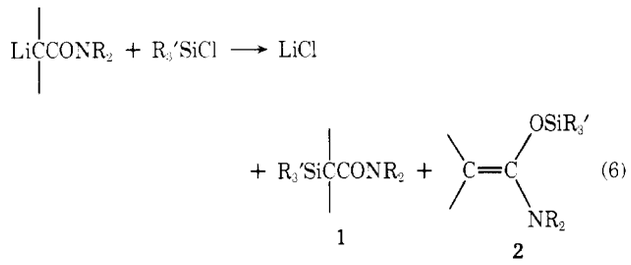
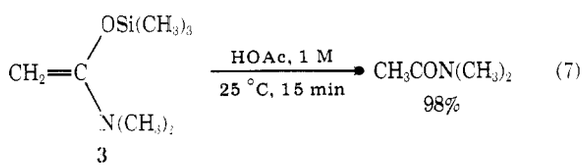
mixtures of C-silylated (**1**) and O-silylated (**2**) products (eq 6) were analyzed by GLC with the results shown in Table I.



(6)

The enolate of *N,N*-dimethylacetamide is silylated by trimethylchlorosilane almost exclusively at carbon (entry 1, Table I). Alkyl substitution at the α carbon, however, strongly favors O-silylation, presumably for steric reasons (entries 2, 3, and 6). On the other hand, substitution of bulkier groups at the nitrogen of the amide leads to slightly greater amounts of C-silylated products (entry 1 vs. entry 4 and entry 2 vs. entry 5). These results are similar to those reported for the effect of alkyl substitution on the reaction of lithium ester enolates with silylating reagents.[2b] Finally, the bulkier silylating reagent, *tert*-butyldimethylchlorosilane, tends to give increased amounts of O-silylated products (entry 7 vs. entry 1 and entry 9 vs. entry 2), especially in the presence of hexamethylphosphoric triamide (entry 8).

The identity of silylation products was based primarily on the observed ^{1}H NMR coupling patterns; however, the chemical shifts of α protons are also diagnostic. Thus, the chemical shift of α protons for **1** is similar to that of the starting amides (δ 2.0–2.5), while the chemical shift of vinyl protons for the corresponding **2** is always at lower field (δ 2.7–3.5). In addition, the O-silylated products were more readily hydrolyzed by dilute acid. For example, the *O*-trimethylsilyl derivative of *N,N*-dimethylacetamide (**3**) is hydrolyzed quantitatively by stirring a THF solution with 1 M acetic acid at room temperature (eq 7). Under similar conditions, the *C*-trimethylsilyl derivative **4** is stable to 2 M acetic acid but is hydrolyzed rapidly with 1 M hydrochloric acid



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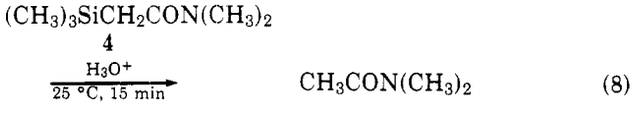
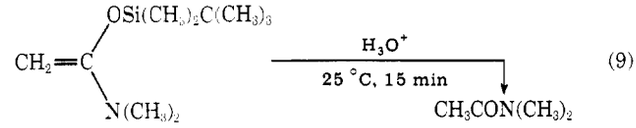


(8)

2 M HOAc, trace (99% recovered **4**)
1 M HCl, 83% (5 min); 100% (15 min)

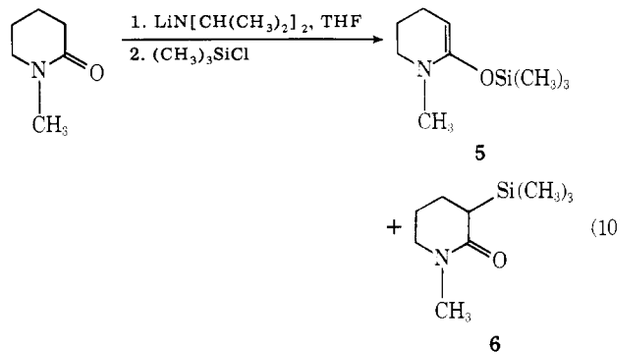
As expected, the *tert*-butyldimethylsilyl derivatives are more resistant to hydrolysis than the corresponding trimethylsilyl derivatives (eq 9), and this fact may be of use in synthetic applications. The rapid hydrolysis of the O-silylated amides is similar to the behavior reported for the O-silylated derivatives of ester enolates.[2b] However, the C-silylated derivatives of ester enolates appear to be more stable to acid-catalyzed hydrolysis. For example, ethyl 2-trimethylsilylacetate is unchanged after stirring a THF solution with 2 M hydrochloric acid for 15 min at 25 °C.[2b]



(9)

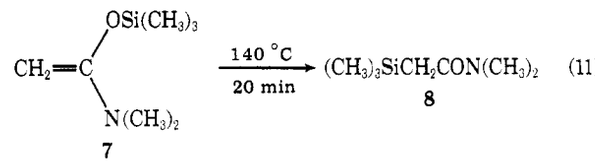
1 M HOAc, trace
1 M HCl, 100% (5 min)

Isomerization of O-Silylated and C-Silylated Products. The product ratios shown in Table I did not change when reaction mixtures were allowed to stir for up to 12 h at room temperature prior to quenching. With one exception, there was no evidence for isomerization on GLC, as indicated by close agreement of product ratios determined by both GLC and by ^{1}H NMR. Again, with one exception, the major component of each reaction could be isolated by vacuum distillation, and samples so obtained remained pure on storage for periods of several months. The exceptional compound was the O-silylated derivative of *N*-methylpiperidone (**5**). GLC analyses of reaction mixtures containing **5** showed up to 70% of the C-silylated derivative **6**, while ^{1}H NMR analysis indicated only 10% of **6** (eq 10). Furthermore, vacuum distillation



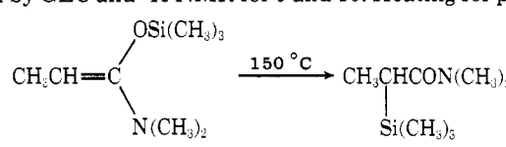
(10)

of the reaction mixtures gave only low yields of **5** (20–30%), together with 40–50% yields of **6**. Although samples of **5** obtained in this way were stable on storage at room temperature, as judged by ^{1}H NMR analysis, injection onto the GLC again showed **6** as the major component. Consequently, it appears that **5** thermally isomerizes to the more stable **6**. A similar isomerization was previously observed by Lutsenko[8] who reported that the *O*-silyl derivative of *N,N*-dimethylacetamide (**7**) is quantitatively isomerized to the *C*-silyl derivative **8** in 20 min at 140 °C (eq 11).



(11)

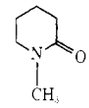
We examined the isomerization of the *O*-silyl derivative of *N,N*-dimethylpropanoamide (**9**) to the C-silylated derivative **10**. A pure sample of **9** was heated under an argon atmosphere to 150 °C, and samples were removed periodically and analyzed by GLC and ^{1}H NMR for **9** and **10**. Heating for periods



0 min, 100% **9**, 0% **10**
1 h, 68% **9**, 32% **10**
8 h, 50% **9**, 50% **10**
48 h, 18% **9**, 82% **10**

longer than 48 h gave a slightly greater ratio of **10** to **9** but the total recovery decreased and several higher boiling compo-

Table I. Reaction of Lithio *N,N*-Dialkylacetamides with Silyl Halides



Entry	Amide	Silyl halide[a]	Yields, %[b] *C*-Silyl	*O*-Silyl
1	$CH_3CON(CH_3)_2$	TMCS	93	7
2	$CH_3CH_2CON(CH_3)_2$	TMCS	10	90
3	$CH_3CH_2CH_2CON(CH_3)_2$	TMCS	<1	99
4	$CH_3CON(CH_2CH_3)_2$	TMCS	95	5
5	$CH_3CH_2CON[CH(CH_3)_2]_2$	TMCS	40	60
6		TMCS	10	90
7	$CH_3CON(CH_3)_2$	TBCS	65	35
8	$CH_3CON(CH_3)_2$	TBCS, HMPA[c]	35	75
9	$CH_3CH_2CON(CH_3)_2$	TBCS	<1	99

[a] TMCS is trimethylchlorosilane; TBCS is *tert*-butyldimethylchlorosilane. [b] Yields are relative yields obtained by GLC; absolute yields were in the range 90–100%. [c] Reaction run in the presence of hexamethylphosphoric triamide.

Scheme I

$$(CH_3)_3SiCH_2CON(CH_3)_2 \rightarrow (CH_3)_3SiN(CH_3)_2 + CH_2{=}C{=}O$$

$$CH_2C{=}O + 7 \text{ or } 8 \rightarrow 11$$

nents appeared. Although these components were not identified, we did observe that heating solutions of 4 to 150 °C for 60 min gave a single high-boiling product, identified as *N,N*-dimethyl-3-trimethylsiloxy-3-propenoamide (**11**).

$$\underset{4}{(CH_3)_3SiCH_2CON(CH_3)_2} \xrightarrow[1\text{ h}]{150\text{ °C}} \underset{11}{CH_2{=}C(OSi(CH_3)_3)CH_2CON(CH_3)_2} \quad (11)$$

11 was previously observed as a product of the reaction of ketene with the *O*-silyl derivative of *N,N*-dimethylacetamide 7.[8] A likely pathway for the formation of **11** is thus as shown in Scheme I.[9]

It appears likely that *C*-silyl derivatives of amides are generally more stable than the *O*-silyl derivatives. Presumably, this is a result of a greater resonance interaction of the nitrogen atom with the amide carbonyl in the *C*-silyl derivative. In accord with this, it is noted that the *C*-silyl derivatives show separate ^1H NMR signals for the two alkyl groups attached to nitrogen, indicative of restricted rotation around the N–CO bond while the *O*-silyl derivatives invariably show identical chemical shifts for the alkyl groups attached to nitrogen.

Experimental Section

^1H NMR spectra were recorded on a Varian T-60 with Me_4Si as the internal standard. Infrared spectra were recorded in CCl_4 solution using a Perkin-Elmer 237B grating spectrometer. GLC analyses were obtained with a Varian 920 using 6 ft × 0.25 in. stainless steel columns packed with 3% Carbowax 20M on non-acid-washed Chromosorb G support. The same column was used for preparative GLC. *n*-Butyllithium (Aldrich) was titrated before use by the procedure of Watson and Eastham.[10] Diisopropylamine was distilled from CaH_2 and stored under argon. THF was distilled from the sodium ketyl of benzophenone just prior to use.

Silylation of *N,N*-Dialkylamides with Trimethylchlorosilane. Procedures for GLC Analysis. The following procedure, illustrated for *N,N*-dimethylacetamide, is representative of procedures used to obtain the results in Table I. A 50-mL round-bottomed flask equipped with a magnetic stirring bar, septum inlet, and mercury bubbler was flushed with argon and charged with 10 mL of pentane and 6.30 mL (10 mmol) of *n*-butyllithium in hexane. The flask was immersed in an ice–water bath and 1.4 mL (10 mmol) of diisopropylamine was injected. The cooling bath was removed and the reaction mixture was stirred for 5 min at room temperature. Volatile material was removed under vacuum and the white residue of lithium diisopropylamide was dissolved in 20 mL of THF. The flask was then immersed in an ice–water bath and 0.95 mL (10 mmol) of *N,N*-dimethylacetamide was added dropwise. After 15 min, the resultant clear solution of lithio *N,N*-dimethylacetamide was treated with 1.40 mL (11 mmol) of trimethylchlorosilane, added dropwise. The reaction mixture was allowed to reach room temperature and stirred for 20 min. Pentane (20 mL) was then added to precipitate LiCl, and the filtered solution was analyzed directly by GLC using internal standard to establish the presence of 8.9 mmol (89%) of *N,N*-dimethyltrimethylsilylacetamide (**4**) and 0.67 mmol (6.7%) of 1-trimethylsiloxy-1-dimethylaminoethene (**3**). A similar procedure was used with other amides to obtain the results presented in Table I.

Silylation of *N,N*-Dialkylamides with *tert*-Butyldimethylchlorosilane. Procedure for GLC Analysis. A procedure identical with that described above was used except that 1.65 g (11 mmol) of *tert*-butyldimethylchlorosilane[11] was substituted for the trimethylchlorosilane, and the reaction mixtures were stirred at room temperature for 10 h prior to addition of pentane and GLC analysis. Reactions using HMPA as solvent additive (1.7 mL, 10 mmol, added just prior to silyl halide) were appreciably faster but were analyzed after 2 h at room temperature.

Silylation of *N,N*-Dialkylamides. Preparative Scale. Reactions were run as described above except that a 50-mmol scale of *N,N*-dialkylamide was used. Minor components comprising less than 10% of the product yield were generally isolated by preparative GLC. *C*-Silylated products were isolated by addition of 10 mL of 1 M acetic acid (a minimal amount is necessary because many of the low molecular weight products are extremely soluble in water) to the reaction mixture. The separated organic layer was dried over anhydrous K_2C0_3 and subjected to vacuum distillation. *O*-Silylated products, because of their ease of hydrolysis, were generally obtained by direct vacuum distillation of unquenched reaction mixtures. Using this procedure, the following compounds were obtained (all new products gave satisfactory C and H elemental analysis).

***N,N*-Dimethyl-2-trimethylsilylacetamide:** isolated yield, 80%; bp (0.2 Torr) 47–49 °C; ^1H NMR (CCl_4, internal Me_4Si) δ 2.87 (s, 3 H), 2.73 (s, 3 H), 1.30 (s, 2 H), 0.07 (s, 9 H).

1-Trimethylsiloxy-1-dimethylaminoethene: isolated by preparative GLC; ^1H NMR (CCl_4, internal Me_4Si) δ 2.89 (d, 1 H, J = 2 Hz), 2.86 (d, 1 H, J = 2 Hz), 2.47 (s, 6 H), 0.15 (s, 9 H).

1-Trimethylsiloxy-1-dimethylaminopropene: isolated yield, 82%; bp (0.2 Torr) 55–58 °C; ^1H NMR (CCl_4, internal Me_4Si) δ 3.5 (q, 1 H, J = 6 Hz), 2.4 (s, 6 H), 1.5 (d, 3 H, J = 6 Hz), 0.25 (s, 9 H).

***N,N*-Dimethyl-2-trimethylsilylpropanoamide:** isolated by preparative GLC; ^1H NMR (CCl_4, internal Me_4Si) δ 3.1 (s, 3 H), 2.9 (s, 3 H), 2.4 (q, 1 H, J = 6 Hz), 1.6 (d, 3 H, J = 6 Hz), 0.10 (s, 9 H).

1-Trimethylsiloxy-1-dimethylamino-1-butene: isolated yield, 85%; bp (0.1 Torr) 50–52 °C; ^1H NMR (CCl_4, internal Me_4Si) δ 3.57 (t, 1 H), 2.5 (s, 6 H), 1.42 (m, 2 H), 1.01 (t, 3 H), 0.27 (s, 9 H).

***N,N*-Diethyl-2-trimethylsilylpropanoamide:** isolated yield, 80%; bp (0.1 Torr) 50–52 °C; ^1H NMR (CCl_4, internal Me_4Si) δ 3.20 (q, 4 H), 1.8 (s, 2 H), 1.2 (m, 6 H), 0.05 (s, 9 H).

N,N-Diisopropyl-2-trimethylsilylpropanoamide: isolated yield, 34%; bp (0.05 Torr) 60–61 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.4 (m, 2 H), 2.4 (q, 1 H, J = 5 Hz), 1.6 (d, 3 H, J = 5 Hz), 1.4 (m, 12 H), 0.10 (s, 9 H).

1-Trimethylsiloxy-1-diisopropylaminopropene: isolated by preparative GLC; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.4 (q, 1 H, J = 6 Hz), 2.6 (m, 2 H), 1.5 (d, 3 H), 1.4 (m, 12 H), 0.23 (s, 9 H).

O-Silylated derivative of 1-methyl-2-piperidine (5): isolated yield, 25%; bp (3 Torr) 80–85 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.9 (t, 1 H, J = 4 Hz), 3.0 (m, 2 H), 2.7 (s, 3 H), 2.0 (m, 4 H), 0.14 (s, 9 H).

C-Silylated derivative of 1-methyl-2-piperidone (6): isolated yield, 40%; bp (4 Torr) 98–100 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.4 (m, 2 H), 3.1 (s, 3 H), 2.5 (m, 1 H), 2.0 (m, 4 H), 0.08 (s, 9 H).

1-*tert*-Butyldimethylsiloxy-1-dimethylaminoethene: isolated by preparative GLC; ^{1}H NMR (CCl_4, internal Me_4Si) δ 2.77 (m, 2 H), 2.43 (s, 6 H), 0.87 (s, 9 H), 0.13 (s, 6 H); IR (CCl_4) 1640 cm^{-1} (C=C).

N,N-Dimethyl-2-*tert*-butyldimethylsilylacetamide: isolated yield (THF solvent), 60%; bp (0.6 Torr) 88–90 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 2.93 (s, 3 H), 2.83 (s, 3 H), 1.83 (s, 2 H), 0.93 (s, 9 H), 0.07 (s, 6 H); IR (CCl_4) 1630 cm^{-1} (C=O).

1-*tert*-Butyldimethylsiloxy-1-dimethylaminopropene: isolated yield, 90%; bp (0.6 Torr) 58 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.50 (q, 1 H), 2.37 (s, 6 H), 1.43 (d, 3 H), 0.97 (s, 9 H), 0.13 (s, 6 H); IR (CCl_4) 1665 cm^{-1} (C=C).

Hydrolysis of Silylated Derivatives of Amides. *N,N*-Dimethyltrimethylsilylacetamide (**4**), 10 mmol, was dissolved in 10 mL of THF in a round-bottom flask under a nitrogen atmosphere. Acetic acid (5 mL, 2 M) was injected and the solution was stirred for 15 min in a 25 °C water bath. At the end of this time, the solution was saturated with anhydrous K_2CO_3 and analyzed by GLC. The recovery of **4** was 99% (9.9 mmol). A similar experiment using 5 mL of 2 M hydrochloric acid in place of acetic acid gave a 17% yield of **4** (1.7 mmol), together with a 83% yield of *N,N*-dimethylacetamide (8.3 mmol) after 5 min of stirring and a 100% yield (10 mmol) of *N,N*-dimethylacetamide after 15 min. Similar procedures were used with other silylated derivatives.

Thermolysis of 4. A 50-mL round-bottom flask equipped with septum inlet and reflux condenser was flushed with nitrogen and 5.4 mL (15 mmol) of **4** was injected. The compound was heated to 160 °C for 1 h. At the end of this time, GLC analysis showed traces of **4** (<1 mmol), together with a component of longer retention time. Vacuum distillation gave 1.0 g (5 mmol) of **11**: bp (0.1 Torr) 60–65 °C; ^{1}H NMR spectrum (CCl_4, internal Me_4Si) δ 4.1 (m, 2 H), 3.0 (s, 2 H), 2.9 (s, 3 H), 2.8 (s, 3 H), 0.21 (s, 9 H).

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Registry No.—**3**, 23138-90-1; **4**, 23184-28-3; **5**, 64728-08-1; **6**, 64728-09-2; 1-trimethylsiloxy-1-dimethylaminopropene, 64728-10-5; *N,N*-dimethyl-2-trimethylsilylpropanoamide, 64728-11-6; 1-trimethylsilyloxy-1-dimethylamino-1-butene, 64728-12-7; *N,N*-diethyl-2-trimethylsilylpropanoamide, 64728-13-8; *N,N*-diisopropyl-2-trimethylsilylpropanoamide, 64728-14-9; 1-trimethylsiloxy-1-diisopropylaminopropene, 64728-15-0; 1-*tert*-butyldimethylsiloxy-1-dimethylaminoethene, 64728-16-1; *N,N*-dimethyl-2-*tert*-butyldimethylsilylacetamide, 64728-17-2; 1-*tert*-butyldimethylsiloxy-1-dimethylaminopropene, 64728-18-3; *N,N*-dimethylacetamide, 127-19-5; lithio *N,N*-dimethylacetamide, 55259-70-6; *N,N*-dimethylpropanoamide, 758-96-3; lithio *N,N*-dimethylpropanoamide, 58079-54-2; *N,N*-dimethylbutyramide, 760-79-2; lithio *N,N*-dimethylbutyramide, 55259-71-7; *N,N*-diethylacetamide, 685-91-6; lithio *N,N*-diethylacetamide, 62702-96-9; *N,N*-diisopropylpropanoamide, 1113-75-3; lithio *N,N*-diisopropylpropanoamide, 64728-06-9; *N*-methyl-2-piperidone, 931-20-4; lithio *N*-methyl-2-piperidone, 64728-05-8; TMCS, 75-77-4; TBCS, 18162-48-6; lithium diisopropylamide, 4111-54-0.

References and Notes

(1) Cf. H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, New York, N.Y., 1972, chapter 9.
(2) (a) Y.-N. Kuo, F. Chen, C. Ainsworth, and J. J. Bloomfield, *J. Chem. Soc., Chem. Commun.*, 136 (1971); (b) M. W. Rathke and D. F. Sullivan, *Synth. Commun.*, **3**, 67 (1973).
(3) J. F. Klebe, J. B. Bush, Jr., and J. E. Lyons, *J. Am. Chem. Soc.*, **86**, 4400 (1964).
(4) B. M. Trost and R. A. Kunz, *J. Org. Chem.*, **39**, 2475 (1974).
(5) P. F. Hudrlik, D. Peterson, and D. Chou, *Synth. Commun.*, **5**, 359 (1975).
(6) R. P. Woodbury and M. W. Rathke, *J. Org. Chem.*, **42**, 1688 (1977).
(7) (a) M. W. Rathke and D. F. Sullivan, *Tetrahedron Lett.*, 1297 (1973); (b) K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **96**, 1620 (1974); (c) S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, *Tetrahedron Lett.*, 1403 (1974).
(8) A. S. Kostyuk, Yu. I. Baukov, and A. S. Lutsenko. *J. Gen. Chem. USSR*, **40**, 598 (1970).
(9) The formation of ketene on thermolysis of *O*-silyl derivatives of esters has been reported: I. F. Lutsenko, Yu. I. Baukov, G. S. Burlachenko, and B. N. Khasapov, *J. Organometal. Chem.*, **5**, 20 (1966).
(10) S. C. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).
(11) *tert*-Butyldimethylchlorosilane was prepared according to a procedure outlined by Corey: E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972). The material is available commercially from several sources.

Mass Spectral Fragmentation of Substituted Pentaphenylcyclopentadienols

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The mass spectral decomposition pathway for a series of pentaphenylcyclopentadienols substituted in the para position of the 1- or 3- and 4-phenyl rings has been observed to consist of a continuum of two superimposed pathways with the choice of the major decomposition mode being determined by the electron-donating or -withdrawing ability of the substituents. Attempts to establish a linear-free-energy relationship for the mass spectral decomposition of the 1-para-substituted phenylcarbinols were unsuccessful, whereas similar attempts with the 3- and 4-para-substituted phenylcarbinols were successful.

The mass spectral fragmentations of tetracyclone, tetraarylquinones, and tetraphenylthiophene dioxides have been extensively studied by Bursey et al.[1-5] who has also published extensively on the use of fluorine as a "dead label" in the decomposition of pentaphenylcyclopentadienols.[1,3,5] The most interesting aspect of their work is the mass spectral production and decomposition of the parent and fluorosubstituted tetraphenyltetrahedrane radical cations from the decomposition of 1,2,3,4,5-pentaphenylcyclopentadien-2,4-ol-1 (**1**, R = H) and its *p*-fluoro derivatives.[5]

Since a large number of mono- and disubstituted pentaphenylcyclopentadienols have been prepared in our laboratories for a kinetic study of the electronic effects involved in a [1,5]-sigmatropic phenyl shift in such systems,[6-8] it became of interest to study the mass spectral fragmentations[9] of the complete family of 1-(para-substituted phenyl)-2,3,4,5-te-

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