72. Synthesis, Properties, and Crystal Structure of Silyl Nitronates (Silyl Esters of *aci*-Nitroalkanes): Towards the S_N2 Reaction Path with Retention of Configuration at Silicon

by **Ernest W. Colvin**[1], **Albert K. Beck**, **Bahram Bastani**[2], **Dieter Seebach**[3], **Yasushi Kai**[4], and **Jack D. Dunitz**[3]

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich

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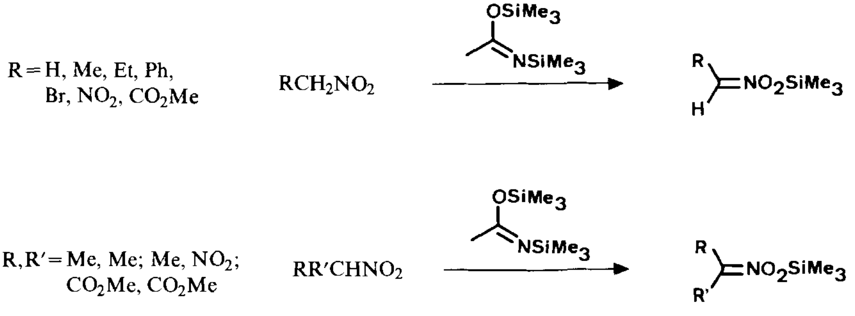
Summary

An efficient and flexible method for the preparation of silyl nitronates is described (see **1**-**10**). NMR. spectral investigations indicate a rapid 1,3-silyl migration process, with an activation energy of about 10 kcal mol^{-1}. X-ray crystallographic studies on the silyl nitronates **3** and **8** show structures that lean towards an S_N2 retention pathway at silicon.

Silyl nitronates (the trialkylsilyl esters of nitronic acids (=*aci*-nitroalkanes)) have been prepared and their chemistry as 1,3-dipolar reagents has been studied by *Joffe et al.* [1] and *Torsell et al.* [2]. The method of synthesis employed by *Joffe* [1] was to heat the appropriate nitroalkane in *N,O*-bis(trimethylsilyl)acetamide; close to quantitative yields were claimed, but product purification proved to be a problem, with unavoidable contamination by excess silylating agent and acetamide by-products. Although only a limited range of compounds was described, both primary and secondary nitroalkanes could be employed [Equation (1)].



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[1] On leave from the University of Glasgow (Scotland), 1978.

[2] On leave from the University of Esfahan (Iran), 1978/79.

[3] Correspondence authors.

[4] On leave from Osaka University (Japan), 1978/79.

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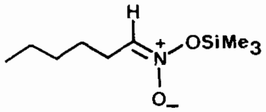
Torsell et al. [2], on the other hand, used both this method and the reagent trimethylsilyl chloride/triethylamine in benzene. The latter method is only successful with primary nitroalkanes up to nitropropane; it fails with higher or sterically hindered primary nitroalkanes and with secondary nitroalkanes.

We wish to report a simple method of wide applicability and high efficiency for the preparation and isolation of silyl nitronates in pure form. As an additional advantage, both trimethylsilyl esters and the more stable (*t*-butyl)dimethylsilyl esters can equally well be prepared.

A) Preparation and Properties of Silyl Nitronates. - Treatment of primary or secondary nitroalkanes with a solution of lithium diisopropylamide in THF, followed by quenching of the resulting lithium nitronates with the appropriate trialkylsilyl chloride, gave THF solutions of the desired silyl nitronates. Non-aqueous isolation (see exper. part) and bulb-to-bulb distillation provided pure silyl nitronates, normally in good yields. Some distillation losses were experienced with nitronates derived from secondary nitroalkanes, although ^{1}H-NMR. spectra of the crude products prior to distillation showed virtually quantitative conversion in all cases investigated. In general, the silyl nitronates studied proved to be remarkably stable thermally, in contrast to the thermal lability [3] of the corresponding alkyl analogues. The range of silyl nitronates so far prepared can be seen in formulae **1-10**.



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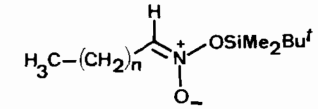
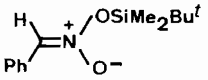


2 a n=4
b n=6
c n=16



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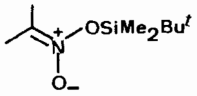

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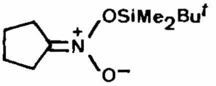

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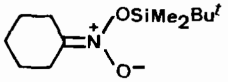

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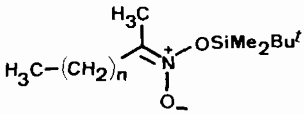
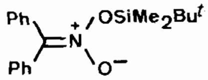


7 a n=4
b n=5
c n=6



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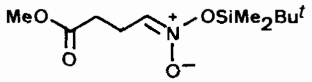

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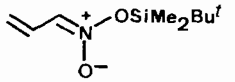

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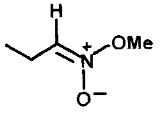
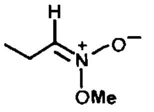
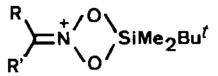
The ready availability of such a wide variety of silyl nitronates allowed a detailed investigation of their chemistry [4], which will be reported separately, and of their physical properties. Silyl nitronates are moisture-labile: as expected, the (*t*-butyl)dimethylsilyl esters are much more stable than the corresponding trimethylsilyl species and are therefore used for the studies reported herein. Their IR. and UV. spectra are similar to those reported for simple alkyl nitronates [3], with C=N absorption at 1615 cm^{-1} for open chain derivatives (1645 cm^{-1} for **5**, 1550 cm^{-1} for **8**) in the IR., and near 230 nm in the UV. (of **1** and **5**).

NMR. studies on silyl nitronates. All of the silyl nitronates **1–10** appear to be single compounds. Those derived from primary nitroalkanes show only one triplet for the olefinic proton in their ^{1}H-NMR. spectra at around 6 ppm. Those derived from symmetrical secondary nitroalkanes show no evidence of non-equivalence of the *a*- and *a'*-positions: for example the silyl nitronate **4** exhibits a six-proton singlet at 2.0 ppm in its ^{1}H-NMR. spectrum, and a corresponding singlet at 17.6 ppm in its ^{13}C-NMR. spectrum for the isopropylidene methyl groups. Similarly, compounds **5** and **6** derived from nitrocyclopentane and -hexane, respectively, possess isochronous *a*-methylene groups. These observations are in dramatic contrast to those obtained with alkyl nitronates [3]: for example, the methyl nitronate **11** was clearly shown by ^{1}H-NMR. to exist as two isomers, the N=CH protons appearing as triplets centred at 5.75 and 6.04 ppm [5].


E-**11**


Z-**11**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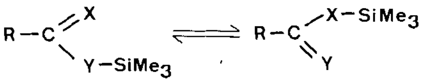
(2)

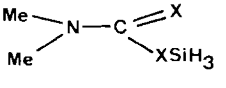
Such apparent magnetic equivalence in the silyl nitronates could be accounted for either by a symmetrical pentacovalent silicon species [6] **12** or by rapid exchange of the silyl group between the two O-atoms [equilibrium (2)] (only intramolecular mechanisms are considered here, as no dilution effect could be observed). The possible involvement of a species such as **12** stimulated an X-ray structural investigation of the crystalline nitronates **3** and **8**, as will be discussed below. The alternative bond-switching mechanism has considerable precedent.

It has been studied extensively in the amide derivatives **13** [7], **14** [8], **15** [9], and **16** [10] [equation (3)]. In the last case, the activation energies for bond-switching were estimated [10] from ^{1}H-NMR. coalescence temperatures for the Me_3Si signals to lie between 10 and 20 kcal mol^{-1}, the lowest values being observed with electron donating R groups. 1,3-Silyl migration has also been invoked to account for features in the ^{1}H-NMR. spectra of the carbamates **17** and **18** [11], and of the acetate derivatives **19** and **20** [12].

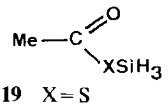


(3)

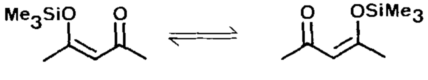
13 X=NSiMe$_3$, Y=O
14 X=O, Y=NMe
15 X=Y=NMe
16 X=O, Y=NPh



17 X=O
18 X=S



19 X=S
20 X=Se



(4)

β-Diketone silyl enol ethers also exhibit bond-switching. For the case shown in equation (4), an activation energy of *ca.* 13 kcal mol^{-1} was estimated [13], again from ^{1}H-NMR. coalescence temperatures. This particular intramolecular reaction has been shown to proceed with retention of configuration at silicon [14].

In order to evaluate the activation energy for the process of equation (2), low-temperature ^{13}C-NMR. studies were performed on the nitronates **4** and **5**. In carbon disulfide/tetrahydrofuran no discernable splitting of the isopropylidene methyl signal of **4** could be detected, even at −125°; at this temperature, the only observable effect was broadening of the signal due to the *t*-butyl methyl groups, probably because of slow rotation. In the same solvent mixture, at −110°, the α/α'-CH$_2$-signal of the five-membered ring derivative **5** broadened to about the same extent as the *t*-butyl methyl signal. On the other hand, a solution of **5** in *Frigen*-22 (CHClF$_2$) showed a sharp singlet signal at −60° and two almost base-line separated signals 10 Hz apart below −75°, with coalescence at *ca.* −65°. This corresponds to an activation energy for a first order process of 10 kcal/mol[5]).

B) Crystal Structures of Silyl Nitronates 3 and 8. - Indications concerning the reaction path leading to bond switching in silyl nitronates [s. equation (2)] are provided by low-temperature crystal structure analyses of molecules **3** and **8** (for details see exper. part).

The molecular structures of **3** and **8** are so alike that we shall discuss them together, drawing attention to points of similarity and of difference as we proceed.

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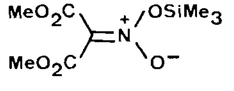
[5]) Related results have been described by *Joffe* [15]. The trimethylsilyl analogue of **4** showed magnetic equivalence of the isopropylidene methyl groups in the ^{13}C-NMR. spectrum down to −80°. The diester **21**, on the other hand, showed separate signals for the ester methyl groups at temperatures below −23°, although this may very well be due to restricted rotation in the methoxycarbonyl groups.



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The overall similarity in conformation is apparent from comparison of the stereoviews shown in *Figure 1.* Evidently the introduction of the second phenyl group in **8** has only a minimal effect on the molecular conformation; the plane of this phenyl group lies nearly perpendicular to the plane of the other phenyl group which is roughly coplanar with the atoms comprising the nitronate grouping in both molecules. *Figure 2* gives an impression of the nature and extent of the deviations of the various atoms from the NO_2 plane. It is clear that in **3** the terminal chain of the substituted silyl group is tipped more out of this plane than in **8**; the torsion angle O(2)–N–O(1)–Si is 31° in **3** and 8° in **8**; nevertheless the description of the molecules as having approximate mirror symmetry holds quite well in both cases.

Turning now to details, we note that both molecules share a close similarity in corresponding bond lengths and angles *(Fig. 3)*. We draw special attention to the following points (in the following the first value refers to **3**, the second (in brackets) to **8**). 1) the asymmetry in the exocyclic bond angles at C(2), the *ipso*

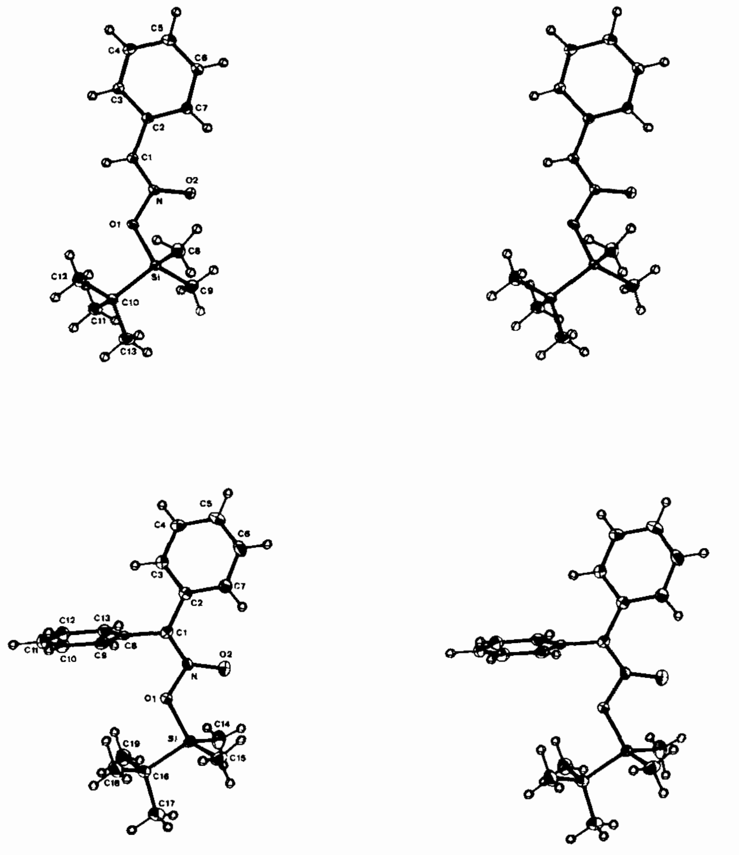

Fig. 1. *Stereoviews of* **3** *and* **8**. Non-hydrogen atoms are drawn with thermal ellipsoids at the 50% probability level, hydrogen atoms are shown by circles of radius 0.1 Å.

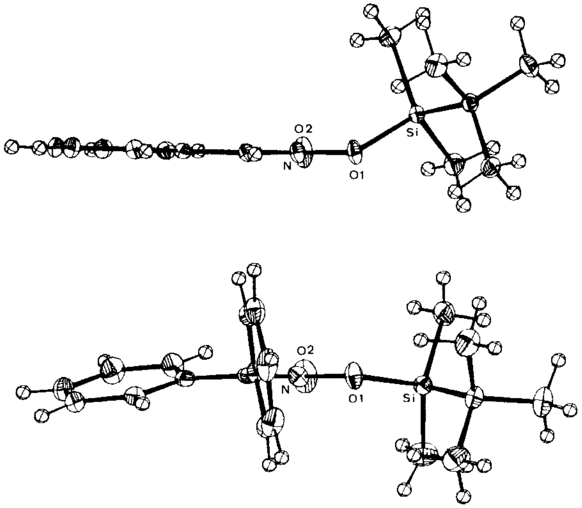

Fig. 2. *Molecules* **3** *and* **8** *shown in projection perpendicular to the plane of the nitronate group*

carbon atom of the phenyl group lying in the plane of the NO_2 group; C(7)–C(2)–C(1) = 124.9 (124.2)°; C(3)–C(2)–C(1) = 116.0 (117.7)°; 2) the unusually large bond angle C(1)–N–O(2) = 129.7 (130.0)°; 3) the nonbonded O(2)···Si distance of 2.832 (2.800) Å is markedly shorter than the sum of the *van der Waals* radii, 1.52 and 2.10 Å for O and Si, respectively [16], although it is still much longer than the bonded O(1)–Si distance of 1.716 (1.709) Å; 4) the $Si-C(CH_3)_3$ distance of 1.883 (1.892) Å is slightly longer than the $Si-CH_3$ distances (1.856–1.859 (1.852–1.858) Å); 5) the $O(2)\cdots Si-C(CH_3)_3$ angle (153.7 (150.4)°) is much closer to colinearity than any of the other $O(2)\cdots Si-CH_3$ angles; 6) the $O(1)-Si-C(CH_3)_3$ angle is 100.6 (97.5)°, markedly less than the tetrahedral angle, whereas the other five angles between atoms bonded to Si are all slightly greater than the tetrahedral angle (109.8–112.7 (110.9–112.7)°).

The first two features are obviously connected with the nonbonded repulsion between the phenyl *o*-hydrogen atom H(7) and O(2). The H(7)···O(2) distance (2.30 (2.26) Å) is already shorter than normal (~2.6–2.7 Å) and it would become even shorter in the absence of these bond-angle distortions.

Although this nonbonded repulsion will tend to reduce the O(2)···Si distance, there are good reasons to believe that the observed nonbonded O(2)···Si distance (point 3) is an expression of a specific attraction between these atoms. According to the NMR. evidence discussed in part A, the activation energy for switching the Si–O bond from O(1) to O(2) is *ca.* 10 kcal mol^{-1}. As mentioned above, quite analogous rapid bond switching of silyl groups has been reported to occur in *N,N*-dimethylcarbamate and *N,N*-dimethyldithiocarbamate [11] as well as in silyl thioacetate and selenoacetate [12]. Also, recent X-ray and electron-diffraction studies of silyl formate and acetate show that these molecules occur in the same (*E*)-conformation as observed in the present study with O···Si distances of 2.86 and 2.83 Å [17], close to the values found here. It seems not unreasonable to interpret these

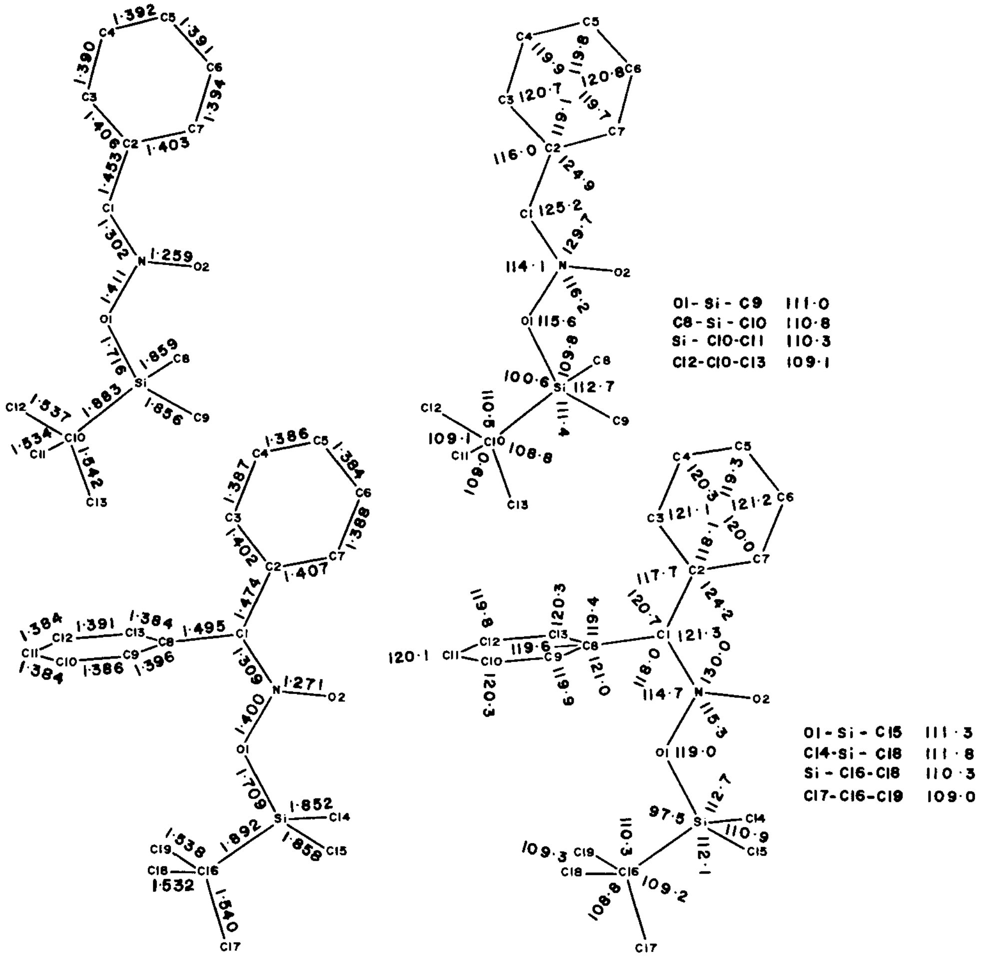

Fig. 3. *Selected bond lengths and angles in* **3** *and* **8**. Estimated standard deviations are 0.001–0.004 Å in distances, 0.05–0.23° in angles, with the lower ranges referring to parameters involving the Si atom. Thermal motion corrections have not been applied but should be small.

short nonbonded distances as corresponding to a slight displacement of the molecular system along the reaction path towards the transition-state for O–Si···O bond switching.

Nucleophilic attack of the non-bonded oxygen atom O(2) could, in principle, proceed along two paths, one leading to expulsion of one of the alkyl substituents (chemically unreasonable!), the other to O–Si···O bond switching. The first path would correspond to an S_N2 displacement with inversion, the second to S_N2 displacement with retention of configuration at Si. At first sight, the observed lengthening of the Si–C(CH$_3$)$_3$ bond and the approach of the O(2)···Si–C(CH$_3$) angle towards linearity (points 4 and 5) might suggest that the structural data are more consistent with the first path, the one leading ultimately to inversion at Si.

However, the difference in length between the Si–C bonds is quite in line with what one would expect for the difference between primary and quaternary carbon substituents and requires no special explanation in terms of a specific weakening of the $Si-C(CH_3)_3$ bond associated with the approach of the nucleophile. Similarly, the large $O(2)\cdots Si-C(CH_3)_3$ angle is easily accounted for on the assumption that the bulky *t*-butyl group has to be as far as possible from O(2), in a position where steric hindrance with the rest of the molecule is minimized.

It is point 6 that provides the most clear-cut evidence that the structural parameters are leaning towards the S_N2 retention path. We would expect an isolated R_3SiO- fragment to have approximate C_{3v} symmetry with the SiR_3 pyramid perhaps slightly flattened compared with regular tetrahedral geometry, *i.e.* the three O–Si–R angles should be approximately equal and slightly smaller, on the average, than 109.5° [18]. If anything, the $O-Si-C(CH_3)_3$ angle might be expected to be slightly larger than the $O-Si-CH_3$ angles. In molecules **3** and **8** the O–Si–R angles show a quite different pattern: the $O-Si-C(CH_3)_3$ angle is about 10° smaller than the other two $O-Si-CH_3$ angles, a deformation that is clearly quite at variance with expectations based on purely steric arguments. As a result of this deformation, the approximate threefold axis of the SiR_3 group (defined as the resultant of the three normalized Si–C vectors) is no longer coincident with the Si–O(1) axis but points between Si–O(1) and $Si\cdots O(2)$, making an angle of about 8° with the former and about 45° with the latter in both molecules. However, the threefold axis still lies within a degree or two of the O(1)SiO(2) plane.

We interpret this movement of the SiR_3 axis as an important component of the reaction coordinate leading to the S_N2 retention transition-state. Further movement along this path leads to a situation where the SiR_3 axis is equally inclined to the two Si–O directions (symmetric transition state or intermediate) and ultimately to the bond switching detected by the NMR. experiments. Note in passing that the symmetric intermediate situation, with the threefold axis of the SiR_3 group coincident with the bisector of the O–Si–O group, represents the same kind of deformation of a trigonal bipyramid as has been postulated to occur in the course of the turnstile rotation mechanism [19].

Experimental Part

General Remarks. All preparations of silyl nitronates were carried out in an atmosphere of argon, employing a pre-dried two-necked round-bottomed flask, one neck of which was equipped with a rubber septum. THF was freshly distilled from lithium aluminium hydride prior to use. All introductions of reagents and solvents were performed with a hypodermic syringe. Butyl lithium (1.5M) in hexane was obtained from *Metallgesellschaft AG*. Bulb-to-bulb distillations were carried out either on a *Büchi* GKR 50 or on an *Aldrich* 'Kugelrohr', depending on scale, and distillation temp. refer to air-bath temp. IR. spectra were recorded with a *Perkin-Elmer* Spectrophotometer 297, UV. spectra with a *Perkin-Elmer* Spectrophotometer 555 (λ_{max} given in nm), ^1H-NMR. spectra with a *Varian* EM390, ^{13}C-NMR. spectra with an XL-100 spectrometer.

^1H-NMR. chemical shifts of some (*t*-butyl)dimethylsilyl nitronates are based on the Me–Si resonance of Me_2Bu^tSi, which was consistently 0.25-0.3 ppm downfield of the Me_4Si signal.

Preparation of Nitroalkanes. – 1-Nitrohexane, 1-nitrooctane, 1-nitrooctadecane, phenylnitromethane, 2-nitrooctane, and nitrocyclopentane were prepared from the corresponding bromides and sodium nitrite in DMF, as described by *Kornblum et al.* [20]. Nitropropene was obtained by reaction of allyl bromide with silver nitrite [21]. Nitrocyclohexane, 2-nitropropane, and methyl 4-nitrobutyrate were obtained commercially.

2-Nitroheptane. A mixture of 71.64 g of 2-bromoheptane, 48.3 g of sodium nitrite, 42 g of urea, 40 g of 1,3,5-benzenetriol (= phloroglucinol), and 700 ml of dimethylformamide was stirred in a 1-l flask at room temp. for 3.5 days. The dark brown solution was poured into 1.5 l of ice/water. Six pentane extractions with 100 ml of pentane, washing of the combined organic layers with six 75 ml portions of water, drying with $MgSO_4$, evaporation of the solvent, and distillation through a 30-cm *Vigreux* column gave after a 15 g forerun 28.1 g (48%) of colourless 2-nitroheptane, b.p. 74°/10 Torr. - ^{1}H-NMR. (CCl_4): 0.95 (*m*, 3 H); 1.2–2.2 (*m*, 8 H); 1.5 (*d*, 3 H, 3 H–C(1)); 4.5 (*m*, 1 H, H–C(2)).

$C_7H_{15}NO_2$ (145.20) Calc. C 57.90 H 10.41 N 9.65% Found C 58.19 H 10.60 N 9.32%

2-Nitrononane. Using the previous procedure, 82.86 g (0.4 mol) of 2-bromononane and 48.30 g (0.7 mol) of $NaNO_2$ gave 28.9 g (42%) of 2-nitrononane, b.p. 63°/0.4 Torr. - ^{1}H-NMR. (CCl_4): 0.85 (*m*, 3 H); 1.25 (br.*s*, 10 H); 1.42 (*d*, 3 H, 3 H–C(1)); 1.5–2.2 (*m*, 2 H); 4.4 (*sextuplett*-like signal, 1 H, H–C(2)):

$C_9H_{19}NO_2$ (173.25) Calc. C 62.39 H 11.05 N 8.09% Found C 62.50 H 11.10 N 8.15%

Nitro-diphenyl-methane. To a solution of 3.36 g (20 mmol) of diphenylmethane in 40 ml of THF were added, at 0°, 13 ml (21.7 mmol) of butyl lithium in hexane. The resulting blood-red solution was stirred at 0° for 1.5 h, cooled to −78°, and 5.5 ml (40 mmol) of isoamyl nitrite added. Stirring was continued at −78° for 45 min. The now pale yellow solution was added to 100 ml of water containing 2 g (50 mmol) of sodium hydroxide, and the whole extracted with 4 times 50 ml of pentane. The organic extracts were back-extracted with 2 times 50 ml of water, and the total combined aqueous extracts acidified at $< 5°$ with 4M H_2SO_4 to pH 5. The resulting precipitate was collected by filtration through a glass sinter; it was then washed with ice/water, and dried i.V. over P_2O_5, to give 1.7 g (40%) of a highly unstable [22] pale pink powder which was used without further purification for conversion into the silyl nitronate **8**. - ^{1}H-NMR. ($CDCl_3$): 7.1 (*s*, 1 H); 7.3 (*m*, 10 H). The ^{1}H-NMR. also showed a broad peak of variable shift and intensity, probably due to water of crystallisation.

Careful drying of an ether solution of nitro-diphenyl-methane with Na_2SO_4 yielded the tautomeric *aci*-nitroalkane. - ^{1}H-NMR. ($CDCl_3$): 7.4 (*m*, 10 H); 9.9 (*s*, 1 H, N–OH).

Preparation of silyl nitronates. - *Trimethylsilyl ester of 1-*aci*-nitrohexane* (**1**). To a stirred solution of 1.6 g (2.24 ml, 16 mmol) of diisopropylamine in 50 ml of THF were added, at −78°, 10.4 ml (15.6 mmol) of butyl lithium in hexane. The cooling bath was removed, and stirring continued for 30 min, after which time the cooling bath was replaced. To this solution of lithium diisopropylamide were added, at −78°, 1.99 g (15 mmol) of 1-nitrohexane within 1 min. The resulting unstirrable jelly was kept at −78° for 20 min; then 2.39 g (2.8 ml, 22 mmol) of trimethylsilyl chloride were added. Stirring was recommenced, and the mixture kept at −78° for 30 min. The cooling bath was then removed, and stirring continued for 1 further h. Isolation as described for **2a** (s. below) and bulb-to-bulb distillation gave 2.1 g (69%) of pure **1** as a moisture-sensitive colourless oil, b.p. 65°/0.01 Torr. - UV. (hexane): 231. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 9 H); 0.95 (br. *t*, 3 H); 1.45 (*m*, 6 H); 2.35 (br. *qa*, 2 H); 6.05 (*t*, $J = 4$, 1 H).

*(t-Butyl)dimethylsilyl ester of 1-*aci*-nitrohexane* (**2a**). - *General procedure.* To a stirred solution of 11.3 g (15.5 ml, 111 mmol) of diisopropylamine in 200 ml of THF were added, at −78°, 70 ml (105 mmol) of butyl lithium in hexane. The cooling bath was removed and stirring continued for 30 min, after which time the cooling bath was replaced. To this solution of lithium diisopropylamide were added, at −78°, 13.2 g (100.7 mmol) of 1-nitrohexane within 5 min. The resulting unstirrable jelly was left at −78° for 30 min, then a solution of 18.1 g (120 mmol) of (*t*-butyl)dimethylsilyl chloride in 20 ml of THF was added. Stirring was recommenced, and the mixture kept at −78° for 30 min. The cooling bath was then removed, and the mixture allowed to warm up to room temp. overnight[6]). After removal of the magnetic stirring bar, the mixture was evaporated

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[6]) General procedure: depending on the particular concentrations employed, the resulting mixture was either a clear, yellowish solution, or a milky suspension (of lithium chloride).

directly in the reaction flask at <35°/>10-20 Torr (oil pump). The residual semi-solid was suspended in 250 ml of pentane, and the suspension filtered through a *Celite* pad on a glass sinter; the pad was washed with 4 times 50 ml of pentane. The pentane filtrates were combined and evaporated at <35°/>10-20 Torr (oil pump). Bulb-to-bulb distillation of the residue gave 19.25 g (78.5%) of pure **2a** as a colourless oil, b.p. 80-90°/0.02 Torr. - IR. (film): 3100 (HC=C), 1615 (C=N), 1250 (Si–CH_3), 1110 (Si–O), 835 and 790 (Si–C). - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 6 H, $(CH_3)_2Si$); 1.1 (br. *s*, 12 H, $(CH_3)_3Si$, 3 H–C(6)); 1.6 (*m*, 6 H); 2.4 (br. *qa*, 2 H, 2 H–C(2)); 6.15 (*t*, *J* = 4, 1 H, H–C(1)).

*(*t*-Butyl)dimethylsilyl ester of 1-*aci*-nitrooctane* (**2b**) was prepared from 1-nitrooctane by the general procedure (s. **2a**), and obtained prior to distillation in 95% yield as a pale yellow oil. Although its NMR. indicated almost complete purity, considerable thermal decomposition occurred on bulb-to-bulb distillation giving pure **2b** in 47% yield as a colourless oil, b.p. 140°/0.005 Torr. - IR. (film): 3100, 1615, 1250, 1110, 835 and 790. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 3 H); 1.0 (br. *s*, 12 H); 1.45 (*m*, 10 H); 2.35 (*m*, 2 H); 6.05 (*t*, *J* = 4, 1 H).

$C_{14}H_{31}NO_2Si$ (273.49) Calc. C 61.48 H 11.44 N 5.13% Found C 61.72 H 11.28 N 5.01%

*(*t*-Butyl)dimethylsilyl ester of 1-*aci*-nitrooctadecane* (**2c**) was prepared from 1-nitrooctadecane (s. **2a**). Usual isolation procedures gave crude **2c** as a pale yellow oil in 51% yield. Due to its extremely high b.p., it could not be purified by distillation, but volatile impurities were removed i.V. (25°/0.1 Torr/12 h) to give **2c** in 43% yield as a slowly crystallizing pale yellow oil. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 3 H); 0.98 (br. *s*, 12 H); 1.3 (br. *s*, 30 H); 2.3 (*m*, 2 H); 6.02 (*t*, *J* = 4, 1 H).

*(*t*-Butyl)dimethylsilyl ester of *aci*-nitro-phenyl-methane (*aci*-α-nitrotoluene)* (**3**) was prepared from nitro-phenyl-methane (s. **2a**). Usual isolation and purification procedures gave **3** in 90% yield as white crystals, m.p. 68-69°, b.p. 150°/0.01 Torr. - ^{1}H-NMR. (CCl_3): 0.3 (*s*, 3 H); 0.9 (*s*, 9 H); 6.95 (*s*, 1 H); 7.25 (*m*, 3 H); 7.75 (*m*, 2 H).

$C_{13}H_{21}NO_2Si$ (251.39) Calc. C 62.11 H 8.42 N 5.57% Found C 61.53 H 8.29 N 5.63%

*(*t*-Butyl)dimethylsilyl ester of 2-*aci*-nitropropane* (**4**) was obtained from 2-nitropropane (s. **2a**) in 30% yield after bulb-to-bulb distillation as a colourless oil, b.p. 120-140°/10 Torr. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 6 H); 0.95 (*s*, 9 H); 2.0 (*s*, 6 H). - ^{13}C-NMR. ($CDCl_3$): 120.1 (*s*, C(2)); 25.4 (*qa*, $(CH_3)_3C$); 17.6 (*qa*, C(1), C(3)); 17.1 (*s*, $(CH_3)_3C$); -4.5 (*qa*, $(CH_3)_2Si$). Selective proton decoupling at 0.7 ppm resulted in collapse of the original *qa* at 25.4 into a *s*. Cooling of a sample to −125° (CS_2/THF 3:1) did not cause any discernable broadening of the signal at 17.6 ppm; the signal at 25.4 ppm showed significant broadening.

*(*t*-Butyl)dimethylsilyl ester of 1-*aci*-nitrocyclopentane* (**5**) was prepared from nitrocyclopentane (s. **2a**), with final room temp. stirring for 1 h rather than overnight. Usual isolation furnished crude **5** in quantitative yield, and after bulb-to-bulb distillation 62% of a greenish oil which solidified at −20°, b.p. 90-100°/0.01 Torr. - UV. (hexane): 233 (11,900). - IR. (film): 1645, 1250, 835, 790. - ^{1}H-NMR. (CCl_4): 0.25 (*s*, 6 H); 0.88 (*s*, 9 H); 1.8 (*m*, 4 H); 2.45 (*m*, 4 H). - ^{13}C-NMR. ($CDCl_3$, room temp.): -3.95 (*qa*, $(CH_3)_2Si$); 17.78 (*s*, $(CH_3)_3C$); 25.57 (*t*, C(3), C(4)); 26.03 (*qa*, $(CH_3)_3C$); 29.85 (*t*, C(2), C(5)); 132.15 (*s*, C(1)). - ^{13}C-NMR. (CS_2/THF-d_8 3:1, room temp.): -3.01, 18.64, 26.74, 26.98, 30.68, 129.71. - ^{13}C-NMR. (CHF_2Cl, −85°): -3.83, 18.53, 26.14 ($(CH_3)_3C$); 26.39 (C(3), C(4)); 30.62 and 31.02 (C(2), C(5)).

$C_{11}H_{23}NO_2Si$ (229.38) Calc. C 57.59 H 10.11 N 6.11% Found C 57.80 H 10.13 N 5.84%

*(*t*-Butyl)dimethylsilyl ester of 1-*aci*-nitrocyclohexane* (**6**) was prepared from nitrocyclohexane like **5**. It was obtained in 33% yield as a colourless oil which solidified at −20°, b.p. 150°/0.01 Torr. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 6 H); 1.0 (*s*, 9 H); 1.7 (*m*, 6 H); 2.6 (*m*, 4 H).

*(*t*-Butyl)dimethylsilyl ester of 2-*aci*-nitroheptane* (**7a**). From 11 mmol of lithium diisopropylamide, 10 mmol (1.45 g) of 2-nitroheptane, and 12 mmol (1.80 g) of (*t*-butyl)dimethylsilyl chloride, 2.50 g (96%) of crude **7a** was obtained, following the general procedure (s. **2a**), purity >95% according to ^{1}H-NMR. The material can be used without further purification for subsequent reactions. - ^{1}H-NMR. (CCl_4): 0.25 (*s*, 6 H, $(CH_3)_2Si$); 0.9 (*s*, 9 H, $(CH_3)_3C$); 0.80-1.65 (*m*, 9 H, $CH_3(CH_2)_3$); 1.90 (*s*, 3 H, 3 H–C(1)); 2.25 (*m*, 2 H, 2 H–C(3)).

*(*t*-Butyl)dimethylsilyl ester of 2-*aci*-nitrooctane* (**7b**) was prepared from 2-nitrooctane by the general procedure (s. **2a**) up to and including the addition of (*t*-butyl)dimethylsilyl chloride. The resulting mixture was stirred at −78° for 30 min, then stored for 20 h at −30° (deep freezer). Usual

room temp. isolation procedures gave virtually pure **7b** in 95% yield as a pale yellow oil. Bulb-to-bulb distillation was accompanied by unavoidable thermal decomposition, and gave pure **7b** in 80% yield as a colourless oil, b.p. 90-100°/0.01 Torr. - IR. (film): 1615, 1250, 1100, 835, 790. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 6 H); 0.95 (br. *s*, 12 H); 1.35-1.6 (br. *m*, 8 H); 1.95 (*s*, 3 H); 2.4 (*m*, 2 H).

$C_{14}H_{31}NO_2Si$ (273.48) Calc. C 61.48 H 11.43 N 5.12% Found C 62.81 H 11.12 N 4.77%

*(*t*-Butyl)dimethylsilyl ester of 2-*aci*-nitrononane* (**7c**). In a 10 mmol batch, 2-nitrononane was converted to **7c** as described for **7a** and **7b**. Yield of crude product 2.86 g (100%), purity >95%. - ^{1}H-NMR. (CCl_4): 0.25 (*s*, 6 H, $(CH_3)_2Si$); 0.95 (*s*, 9 H, $(CH_3)_3C$); 0.75-1.75 (*m*, 13 H, $CH_3(CH_2)_5$); 1.90 (*s*, 3 H), 3 H-C(1)); 2.3 (*m*, 2 H, 2 H-C(3)).

*(*t*-Butyl)dimethylsilyl ester of *aci*-nitro-diphenyl-methane* (**8**) was prepared from nitro-diphenylmethane (s. **2a**). Usual isolation procedures gave crude **8** in 75% yield as air- and heat-sensitive yellow crystals; crystallization from pentane at -78° gave pure **8** as a pale yellow powder which decomposed spontaneously on contact with air, evolving nitrous gases. - IR. (CCl_4): 1550, 1255, 1140. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 6 H); 0.7 (*s*, 9 H); 7.3-7.7 (*m*, 10 H).

$C_{19}H_{25}NO_2Si$ (327.49) Calc. C 69.68 H 7.69 N 4.28% Found C 68.75 H 7.64 N 4.03%

*(*t*-Butyl)dimethylsilyl ester of 1-methoxycarbonyl-3-*aci*-nitropropane* (**9**) was prepared from methyl 4-nitrobutyrate (s. **2a**). It was obtained, after bulb-to-bulb distillation, in 44% yield as a colourless oil, b.p. 140-150°/0.01 Torr. - ^{1}H-NMR. (CCl_4): 0.3 (*s*, 6 H); 1.1 (*s*, 9 H); 2.55 (br. *s*, 4 H); 3.65 (*s*, 3 H); 6.15 (br. *t*, 1 H).

*(*t*-Butyl)dimethylsilyl ester of 3-*aci*-nitro-1-propene* (**10**) was prepared from 3-nitro-1-propene by the general procedure (s. **2a**) with final room temp. stirring for 1 h rather than overnight. Pure

Table 1. *Crystal structure of compound* **3**. Positional and thermal parameters (with standard deviations in parentheses). The temperature factor is expressed in the form

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* \ldots)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
SI	.36437(4)	.21028(2)	.76705(2)	.0120(1)	.0138(1)	.0127(1)	.0023(1)	.0010(1)	.0075(1)
O1	.62193(11)	.27618(8)	.73131(7)	.0151(3)	.0294(3)	.0197(3)	.0006(2)	.0002(2)	.0190(3)
O2	.46821(12)	.35185(9)	.61630(8)	.0178(3)	.0419(4)	.0300(4)	.0134(3)	.0067(3)	.0267(3)
N	.63582(13)	.31086(8)	.63009(7)	.0153(3)	.0196(3)	.0170(3)	.0031(3)	.0010(3)	.0126(3)
C1	.82347(14)	.29569(9)	.56486(8)	.0140(4)	.0158(3)	.0154(4)	.0022(3)	.0001(3)	.0092(3)
C2	.87826(14)	.32004(8)	.45378(8)	.0148(4)	.0118(3)	.0133(3)	.0011(3)	-.0001(3)	.0062(3)
C3	1.08769(14)	.29251(9)	.39444(9)	.0154(4)	.0179(4)	.0164(4)	.0033(3)	.0006(3)	.0089(3)
C4	1.15622(15)	.31187(10)	.28723(9)	.0182(4)	.0206(4)	.0162(4)	.0038(3)	.0035(3)	.0087(3)
C5	1.01714(16)	.35954(9)	.23795(8)	.0235(4)	.0187(4)	.0138(4)	.0019(3)	.0013(3)	.0084(3)
C6	.80963(15)	.38729(9)	.29615(9)	.0210(4)	.0176(4)	.0158(4)	.0027(3)	-.0021(3)	.0092(3)
C7	.73863(14)	.36780(9)	.40344(8)	.0157(3)	.0149(3)	.0156(4)	.0027(3)	.0000(3)	.0077(3)
C8	.23196(16)	.07401(10)	.61604(9)	.0232(4)	.0223(4)	.0180(4)	.0027(3)	-.0043(3)	.0077(3)
C9	.19584(16)	.35341(10)	.86580(10)	.0223(4)	.0198(4)	.0229(4)	.0084(3)	.0048(3)	.0103(3)
C10	.43625(14)	.12819(9)	.86279(8)	.0163(4)	.0162(3)	.0148(4)	.0019(3)	.0006(3)	.0090(3)
C11	.59000(18)	.01817(11)	.78232(10)	.0278(5)	.0235(4)	.0239(4)	.0116(3)	.0019(4)	.0127(4)
C12	.55009(16)	.24096(10)	.98601(9)	.0221(4)	.0244(4)	.0166(4)	-.0004(3)	-.0028(3)	.0104(3)
C13	.22270(17)	.05556(11)	.89993(10)	.0230(4)	.0247(4)	.0260(4)	-.0031(3)	-.0002(4)	.0178(4)

	x	y	z	U
H1	.922(3)	.266(2)	.593(2)	.024(3)
H3	1.182(3)	.264(2)	.432(2)	.025(3)
H4	1.300(3)	.295(2)	.252(2)	.022(3)
H5	1.067(3)	.373(2)	.163(2)	.030(4)
H6	.717(2)	.422(2)	.266(2)	.021(3)
H7	.594(3)	.390(2)	.442(2)	.027(4)
H81	.221(4)	.110(2)	.559(2)	.051(5)
H82	.323(4)	-.002(2)	.568(2)	.050(5)
H83	.095(4)	.030(2)	.629(2)	.052(6)
H91	.070(4)	.322(2)	.902(2)	.051(6)
H92	.154(4)	.394(2)	.819(2)	.052(6)
H93	.270(3)	.424(2)	.936(2)	.044(5)
H111	.518(3)	-.057(2)	.708(2)	.037(4)
H112	.632(3)	-.023(2)	.832(2)	.040(5)
H113	.727(3)	.060(2)	.758(2)	.031(4)
H121	.456(3)	.319(2)	1.043(2)	.032(4)
H122	.687(3)	.289(2)	.967(2)	.027(4)
H123	.580(3)	.196(2)	1.037(2)	.037(4)
H131	.140(3)	.021(2)	.823(2)	.040(5)
H132	.253(3)	.011(2)	.944(2)	.039(4)
H133	.116(3)	.118(2)	.950(2)	.031(4)

Table 2. *Crystal structure of compound* **8**. Details as in *Table 1*.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
SI	.15324(3)	.07786(8)	.15755(5)	.0176(3)	.0155(3)	.0163(3)	.0015(3)	.0003(2)	.0013(3)
OI	.22498(7)	.02434(19)	.23834(13)	.0188(7)	.0215(9)	.0242(8)	-.0061(6)	-.0038(6)	.0071(7)
O2	.27270(7)	.24559(23)	.16027(14)	.0342(9)	.0312(9)	.0348(9)	-.0047(8)	-.0030(8)	.0145(9)
N	.27952(8)	.12863(22)	.23510(15)	0220(9)	.0147(9)	.0176(9)	-.0037(7)	.0020(7)	.0026(8)
C1	.33010(9)	.08848(28)	.30887(16)	0175(9)	.0164(11)	.0134(9)	.0024(9)	.0011(8)	-.0029(9)
C2	.39050(10)	.18978(27)	.31921(18)	.0180(10)	.0151(11)	.0183(10)	.0008(9)	.0043(9)	-.0031(9)
C3	.43434(10)	.17253(28)	.41959(18)	.0211(11)	.0178(11)	.0180(11)	.0005(9)	.0039(9)	-.0009(9)
C4	.49116(10)	.26786(29)	.43726(19)	.0181(10)	.0233(12)	.0248(11)	-.0013(10)	.0009(9)	-.0044(10)
C5	.50613(10)	.38058(29)	.35445(20)	.0195(11)	.0259(13)	.0334(13)	-.0074(10)	.0065(10)	-.0053(11)
C6	.46392(11)	.39662(32)	.25394(20)	.0300(12)	.0326(14)	.0272(12)	-.0081(11)	.0094(10)	.0068(11)
C7	.40645(10)	.30381(29)	.23546(18)	.0237(11)	.0276(13)	.0193(11)	-.0041(10)	.0016(9)	.0027(10)
C8	.32472(9)	-.06292(27)	.38352(16)	.0118(9)	.0196(11)	.0140(9)	-.0035(9)	-.0013(8)	.0018(10)
C9	.29506(10)	-.05047(30)	.48261(18)	.0208(10)	.0304(14)	.0174(10)	.0008(10)	.0018(9)	-.0006(10)
C10	.29110(11)	-.19256(35)	.55079(19)	.0230(12)	.0494(17)	.0195(11)	-.0024(11)	.0046(10)	.0123(12)
C11	.31601(11)	-.34691(32)	.52067(21)	.0239(12)	.0320(14)	.0340(14)	-.0069(11)	-.0011(11)	.0191(12)
C12	.34580(11)	-.35974(29)	.42294(21)	.0248(11)	.0179(12)	.0343(13)	-.0019(10)	-.0023(10)	.0028(11)
C13	.35034(10)	-.21720(27)	.35470(18)	.0182(10)	.0210(11)	.0181(11)	-.0021(10)	.0009(9)	-.0006(10)
C14	.12949(12)	.30154(30)	.17858(21)	.0437(14)	.0195(12)	.0333(13)	.0049(11)	.0098(12)	.0021(11)
C15	.15582(10)	.03250(32)	.00398(19)	.0242(12)	.0369(15)	.0187(11)	.0004(10)	-.0019(9)	-.0012(10)
C16	09900(9)	-.07657(30)	.22364(18)	.0164(10)	.0222(11)	.0248(11)	-.0009(10)	.0020(8)	.0028(11)
C17	.02963(10)	-.06731(34)	.15834(22)	.0199(11)	.0370(14)	.0404(14)	-.0033(12)	-.0005(10)	.0041(13)
C18	.12454(11)	-.25864(32)	.21621(22)	.0298(12)	.0200(11)	.0436(14)	-.0029(11)	.0068(11)	.0059(12)
C19	.09658(12)	-.03075(33)	.34951(20)	.0340(13)	.0377(16)	.0263(13)	-.0002(11)	.0098(11)	.0040(11)

	x	y	z	U
H3	.425(1)	.094(3)	.478(2)	.017(5)
H4	.520(1)	.259(3)	.508(2)	.016(5)
H5	.546(1)	.446(3)	.365(2)	.022(6)
H6	.474(1)	.472(3)	.197(2)	.038(7)
H7	.379(1)	.318(3)	.167(2)	.026(6)
H9	.279(1)	.052(3)	.502(2)	.018(6)
H10	.272(1)	-.185(3)	.616(2)	.043(8)
H11	.313(1)	-.449(3)	.567(2)	.035(7)
H12	.359(1)	-.461(3)	.402(2)	.038(7)
H13	.370(1)	-.230(3)	.287(2)	.028(6)
H141	.083(1)	.317(4)	.152(3)	.068(9)
H142	.152(1)	.371(4)	.138(3)	.056(9)
H143	.136(1)	.334(4)	.255(3)	.068(9)
H151	.115(1)	.057(3)	-.036(2)	.031(6)
H152	.166(1)	-.086(4)	-.008(2)	.049(8)
H153	.187(1)	.107(3)	-.024(2)	.044(8)
H171	.013(1)	.046(3)	.163(2)	.039(7)
H172	.028(1)	-.110(3)	.078(2)	.038(7)
H173	-.001(1)	-.146(4)	.200(2)	.053(9)
H181	.097(1)	-.337(3)	.247(2)	.042(7)
H182	.170(1)	-.267(4)	.264(2)	.045(7)
H183	.127(1)	-.298(3)	.138(2)	.042(8)
H191	.069(1)	-.109(4)	.383(2)	.049(8)
H192	.139(1)	-.041(3)	.396(2)	.046(8)
H193	.077(1)	.087(3)	.359(2)	.041(7)

10 was obtained in 15% yield after bulb-to-bulb distillation as a relatively volatile colourless oil which polymerized on standing, but which was relatively stable in CCl_4 solution, b.p. 80-90°/20 Torr. - ^{1}H-NMR. (CCl_4): 0.25 (*s*, 6 H); 0.9 (*s*, 9 H); 5.1-5.5 (*m*, 2 H); 6.2-6.7 (*m*, 2 H).

X-Ray Structure Analyses. - *Crystal Structure Analysis of* **3**. Crystals of **3** were obtained by sublimation; they volatilize slowly at room temp. A specimen (dimensions about 0.25 × 0.35 × 0.40 mm) was mounted on an *Enraf-Nonius* diffractometer equipped with a graphite monochromator (Mo*Ka* radiation, $\lambda = 0.71069$ Å) and a cooling device. During the X-ray measurements the recorded temp. at the crystal was held at 101 K.

Crystallographic data: $C_{13}H_{21}NO_2Si$, triclinic, space group $P\bar{1}$, $a = 6.186$ (2), $b = 10.952$ (5), $c = 11.853$ (5) Å, $\alpha = 118.69$ (4), $\beta = 82.82$ (4), $\gamma = 100.52$ (3)°, $Z = 2$, $D_x = 1{,}206$ g cm^{-3}, $D_m = 1.143$ (at 20°) g cm^{-3}.

Of 3334 independent reflexions measured ($\theta_{\max} = 28°$) 2907 were regarded as observed ($I > 3\sigma_I$). The structure was solved by direct methods (MULTAN 77 programme [23]) and refined with the XRAY system [24] using a modified weighting system [25] with $p = 6.5$ Å^2 in the latter stages (final $R = 0.027$, observed reflexions). Atomic positions and vibrational parameters are listed in *Table 1*.

Crystal Structure Analysis of **8**. Crystalline material was obtained by cooling the reaction vessel to about −20°; the crystals melt below room temp. but could be examined and manipulated under the microscope on a cooled glass slide. A specimen (dimensions about 0.25 mm) was mounted on a glass fibre and transferred as quickly as possible to the diffractometer. All X-ray measurements were made with the crystal held at 101 K as described above ($\theta_{\max}=25°$, 3331 independent reflexions measured, 2111 observed with $I > 3\sigma_I$). Structure analysis and refinement were as in **3** (s. above) but with $p=5.0$ Å^2 and final $R=0.032$. Atomic positions and vibrational parameters are listed in *Table 2*.

Crystallographic data: $C_{19}H_{25}NO_2Si$, monoclinic, space group $P2_1/c$, $a=20.710$ (7), $b=7.861$ (1), $c=11.821$ (2) Å, $\beta=97.64$ (2)°, $Z=4$, $D_x=1.140$ g cm^{-3}.

Packing drawings of the crystal structure of **3** and **8** are shown in *Figures 4* and *5*, respectively. There are no unusually short intermolecular contacts.

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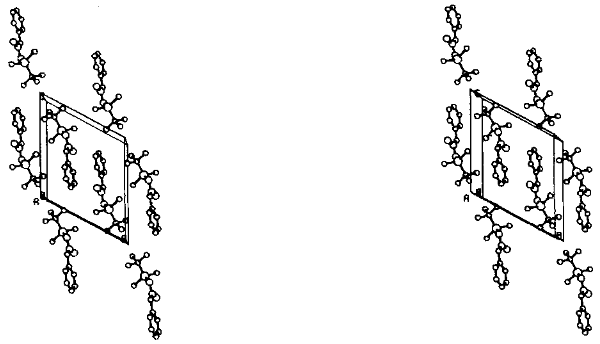

Fig. 4. *Stereoview of the crystal structure of* **3**. For clarity, hydrogen atoms are omitted.

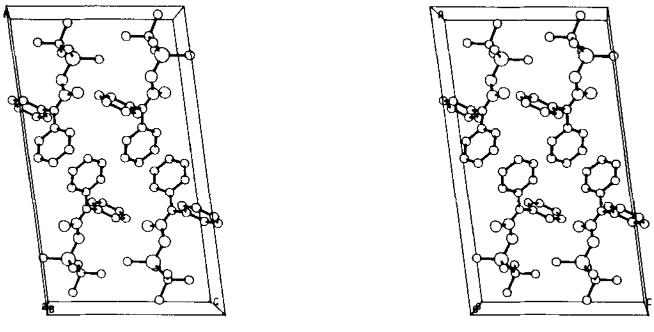

Fig. 5. *Stereoview of the crystal structure of* **8**. For clarity hydrogen atoms are omitted.

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