an increase in the extent of bridging of the Hg rather than to an increase in the extent of solvation.

Analyses of plots of $\delta\Delta S^*$ vs. σ and σ^+ reveal that in addition to the linear relationships found for solvent A^1, fairly linear ones also exist for solvent C ($r = 0.956$ and 0.947, respectively). The values of ρ (−1.38) and ρ^+ (−1.21) obtained from the correlation lines are 58% smaller than their corresponding standard values for this solvent. In this solvent, $\delta\Delta H^*$ is not a linear function of $\delta\Delta S^*$ nor σ (σ^+), thus these deviations probably indicate that the linearity of these plots are not significant.

In conclusion, these results show that the rates and the activation parameters for this reaction are functions of both the substituent and the solvent. The fact that ΔG^* for each styrene increases as the methanol concentration decreases reflects the destabilizing effect that a reduction in the solvent's polarity has on the polar transition state formed in step 2. However, the fact that ΔG^* for each styrene increases by the same amount in going from one solvent to another reflects the destabilizing effect that a reduction in the solvent's polarity has on the ion pair formed in step 1. Thus solvent effects on both steps are important. Unfortunately, it is not clear which, if either, step is the more sensitive to these effects. A part of the ambiguity arises from the fact that *p*-dioxane plays dual and competing roles—complexing agent vs. solvating agent—in this reaction. It is our hope that studies in progress, using solvents of the same dielectric constant as *p*-dioxane which cannot form a complex with the reactive Hg^{+2} species present in solution, will resolve this matter.

Experimental Section

Materials. All of the styrenes used in this study were prepared as previously described.[1] The mercuric acetate, methanol, and *p*-dioxane used were high grade commercial products which were purified as previously described.[1]

Kinetic Procedure. The rates of reaction were determined as previously described.[1]

Registry No. **3** (X = MeO), 637-69-4; **3** (X = Me), 622-97-9; **3** (X = H), 100-42-5; **3** (X = F), 405-99-2; **3** (X = Br), 2039-82-9; **3** (X = CN), 3435-51-6; **3** (X = NO_2), 100-13-0; Hg(OAc)$_2$, 1600-27-7; MeOH, 67-56-1.

Regioselective Halo- and Carbodesilylation of (Trimethylsilyl)-1-methylpyrazoles[1]

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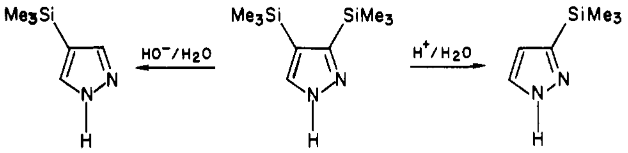
Received April 11, 1984

The isomeric 3-, 4-, and 5-(trimethylsilyl)- as well as the 3,4-, 3,5-, and 4,5-bis(trimethylsilyl)-1-methylpyrazoles (**2**, **7**, **3**, **5**, **9**, and **10**, respectively) are obtained by methylation of the corresponding (trimethylsilyl)-1*H*-pyrazoles or by silylation of Grignard or lithio derivatives of appropriate 1-methylpyrazoles with chlorotrimethylsilane. **5** and **10** are halodesilylated regioselectively by Br_2 or ICl in the 4-position, yielding **13** and **15**. With additional bromine, these monobromo compounds suffer exclusively bromodesilylation to give 3,4- and 4,5-dibromo-1-methylpyrazole (**14** and **16**, respectively). These findings are in accord with the electrophilic substitution reactivity indices for 1-methylpyrazole (**8**) and with ipso-directing influence of the Me_3Si group. The reaction of **5** with I_2, unexpectedly, attacks preferentially at the 3-position. Regioselective carbodesilylation in the 5-position is observed in the fluoride-catalyzed reactions of **3**, **9**, and **10** with carbon electrophiles. The high regiospecificity of this reaction is rationalized in terms of carbanion stabilization at the individual pyrazole positions.

Introduction

It has been recognized only in the last decade that the versatility of ipso reactions can be of preparative importance in electrophilic aromatic substitution.[3] Desilylation reactions, for instance, which have especially high ipso rate factors,[3,4] were used for the regioselective synthesis of some interesting disubstituted benzene derivatives.[5] Since, as a rule, the cleavage of the aryl silicon bond in such ipso reactions is believed to proceed as in normal electrophilic substitution, reactivity and orientation should be controlled by the well-established rule of aromatic substitution.[4a] For activated arenes, this has been verified in many cases.[4b,5] Acceptor-substituted aryltrimethylsilanes, on the other hand, react much faster in the presence of nucleophilic catalysts and thence must follow a different mechanistic route.[6]

Scheme I



It should be possible, therefore, to direct desilylation reactions of heteroaryltrimethylsilanes to different positions by adjusting the reaction conditions accordingly. Under regular Friedel–Crafts catalysis, the orientation should be governed by the relative stability of the re-

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[1] Electrophilic aromatic substitution. 26. For part 25 see: Effenberger, F.; Sohn, E.; Epple, G. *Chem. Ber.* **1983**, *116*, 1195.

[2] Krebs, A. Dissertation University Stuttgart, 1982.

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[4] (a) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43. (b) Häbich, D.; Effenberger, F. *Synthesis* **1979**, 841.

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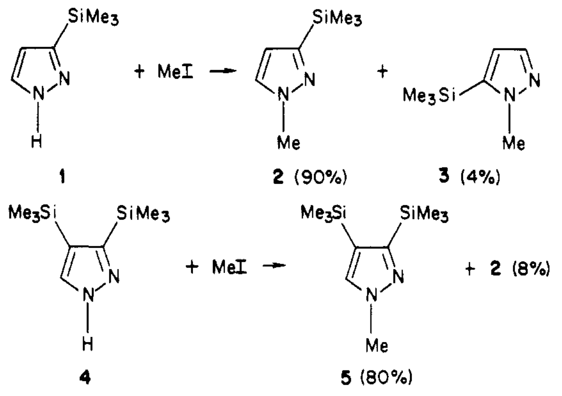
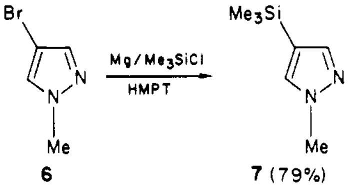
0022-3263/84/1949-4687$01.50/0

Scheme II



Scheme III



spective Wheland intermediates; in the presence of nucleophilic catalysts, however, reaction should occur at the position where a heteroaryl carbanion is most effectively stabilized.[6] Birkofer and Franz[7] found that 3,4-bis(trimethylsilyl)-1*H*-pyrazole, under acidic conditions, is protodesilylated only in the 4-position while in alkaline medium occurs exclusively at the 3(5)-position. The authors were unable at the time to explain this mechanistic behavior; it is right in line, though, with the rationale given above.

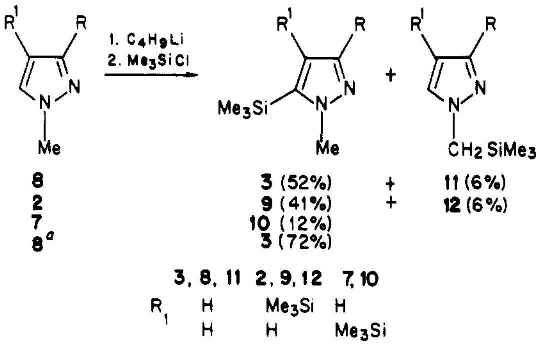
In the present paper, we report a number of regioselective electrophilic halodesilylation and nucleophilic-catalyzed electrophilic carbodesilylation reactions with different trimethylsilyl-substituted 1-methylpyrazoles.

Synthesis of 1-Methyl(trimethylsilyl)pyrazoles. Several routes are available for the synthesis of trimethylsilyl heteroarenes.[4b] Starting from acyclic precursors,[8] for instance, 3-(trimethylsilyl)-1*H*-pyrazole (1) and 3,4-bis(trimethylsilyl)-1*H*-pyrazole (4) are obtained in high yield by regiospecific cycloaddition of diazomethane to the respective (trimethylsilyl)acetylenes.[7-9] 1-Methyl(trimethylsilyl)pyrazoles are accessible either via methylation of (trimethylsilyl)-1*H*-pyrazoles or via introduction of the Me_3Si group into 1-methylpyrazoles. Thus, iodomethane reacts with compounds 1 and 4 under mild conditions to give predominantly the sterically less hindered 1-methyl derivatives 2 and 5. In the methylation of 4, simultaneous cleavage of the 4-trimethylsilyl group, forming 2, is a side reaction which cannot be suppressed completely.

1-Methyl-4-(trimethylsilyl)pyrazole (7) is obtained from 4-bromo-1-methylpyrazole (6) by an "in situ Grignard" synthesis (as described in reference 10); so far, 6 could not be converted into the Grignard compound even by the "entrainment method".[11]

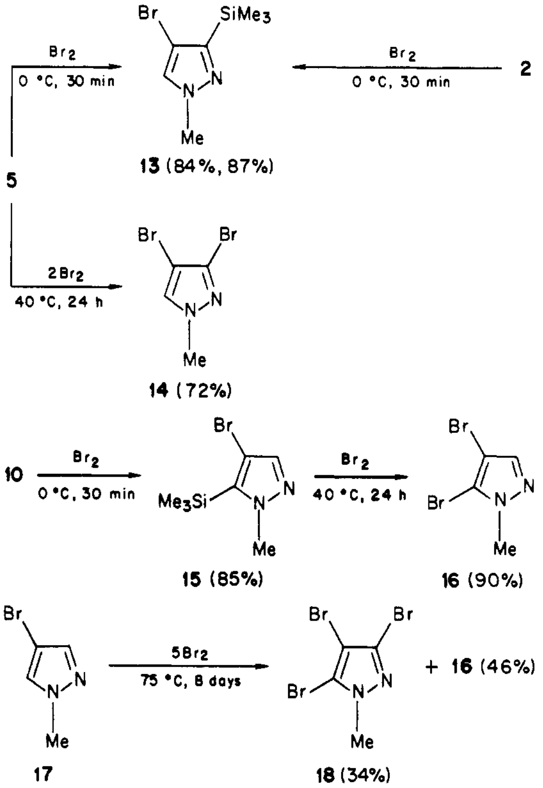
The 1-methyl-5-(trimethylsilyl)pyrazoles 3, 9, and 10 were prepared from the 1-methylpyrazoles 2, 7, and 8 via lithiation by *n*-butyllithium and subsequent silylation with chlorotrimethylsilane (Scheme IV). Competitive reaction at the *N*-methyl group of 2 and 8, as observed earlier by Butler and Alexander,[12] can be avoided by adding a complexing agent *N,N,N′,N′*-tetramethyl-1,2-ethanediamine.

Scheme IV



[a] With 1,2-bis(dimethylamino)ethane.

Scheme V



Halodesilylation of 1-Methyl(trimethylsilyl)pyrazoles. As expected from the known reactivity of pyrazole toward electrophiles desilylation by bromine preferentially occurs in the 4-position. The isomeric 3,4- and 4,5-bis(trimethylsilyl)-1-methylpyrazoles 5 and 10 were rapidly and selectively bromodesilylated at 0 °C to the 4-bromo compounds 13 and 15. In contrast, the subsequent bromodesilylations in the 3- and 5-position, respectively, required 24 h at 40 °C. By properly adjusting temperature and the molar ratio of bromine, both the products of single and double desilylations, i.e. 13 and 15 and 14 and 16, respectively, become individually accessible in good yield. Compound 13 may also be prepared by direct electrophilic bromination of 1-methyl-3-(trimethylsilyl)pyrazole (2). The parent compound 1-methylpyrazole (8) is brominated exclusively in the 4-position.[13] We succeeded in further brominating 4-

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(7) Birkofer, L.; Franz, M. *Chem. Ber.* **1972**, *105*, 1759.

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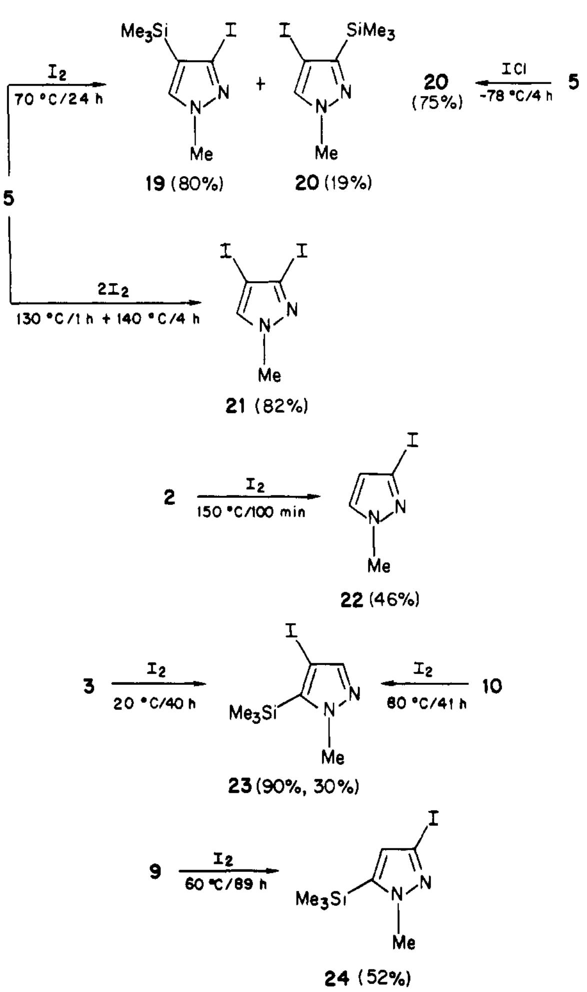
Scheme VI

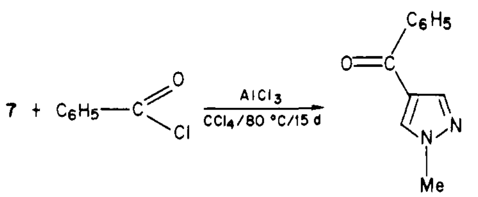


bromo-1-methylpyrazole (**17**), and obtained a mixture of 4,5-dibromo **16** and the 3,4,5-tribromo product **18** which could be separated by fractional distillation.

Unexpectedly, iodine reacts much less selectively with (trimethylsilyl)-1-methylpyrazoles than does bromine. Reaction of 3,4-bis(trimethylsilyl)-1-methylpyrazole (**5**) with an equimolar amount of iodine at 70 °C yields a mixture of 3-iodo-1-methyl-4- and 4-iodo-1-methyl-3-(trimethylsilyl)pyrazole (**19** and **20**, respectively); with 2 mol of iodine at 130–140 °C, 3,4-diiodo-1-methylpyrazole (**21**) is obtained. Compound **21** has previously been synthesized only in a mixture with the isomeric 4,5-diiodo compound by methylation of 3,4-diiodopyrazole[14] or by oxidative iodination of 4-iodo-1-methylpyrazole.[15] 3-Iodo-1-methylpyrazole (**22**), however, can be prepared selectively via iododesilylation of 1-methyl-3-(trimethylsilyl)pyrazole (**2**) at 150 °C.

With iodine monochloride, on the other hand, which is known for its high reactivity in desilylations,[16] compound **5** is selectively iododesilylated at −78 °C in the 4-position to give **20**. At higher temperatures, some competitive 3-desilylation takes place. The Me_3Si group in the 5-position of the 1-methylpyrazoles **3**, **9**, and **10** is inert toward iodine. Thus, compounds **3** and **10** can both be iodinated (electrophilically) in the 4-position to give 4-iodo-1-methyl-5-(trimethylsilyl)pyrazole (**23**); iododesilylation of **9** yields 3-iodo-1-methyl-5-(trimethylsilyl)pyrazole (**24**).

Scheme VII



25 (54%)

As becomes clearly apparent from the findings detailed above, the selectivity of electrophilic bromo- and iododesilylation depends not only on the effective electrophile but also on the reaction conditions.

Friedel–Crafts Benzoylation of 1-Methyl-4-(trimethylsilyl)pyrazole (7). The acylation reactions described by Grandberg et al. (Friedel–Crafts acylation with $AlCl_3$ catalysts,[17] heating with acyl chlorides[18] or mixtures of carboxylic acid anhydrides and sulfuric acid[19] to 200 °C) are confined to donor-substituted 1-alkylpyrazoles. 1-Methylpyrazole (**8**) so far has thwarted any attempt at acylation. 4-Benzoyl-1-methylpyrazole (**25**), for instance, could be synthesized neither by Friedel–Crafts benzoylation of **8** nor by reaction of 4-(chlorocarbonyl)-1-methylpyrazole with benzene.[20] It is known, though, that the ipso-directing effect of the Me_3Si group favors the acyldesilylation over the acyldeprotonation by a factor of 10^3, dependent upon the substrate.[4a] Reaction of 1-methyl-4-(trimethylsilyl)pyrazole (**7**) with benzoyl chloride/aluminum chloride indeed yielded 54% of the desired product **25** although the complexation of **7** requires a 2-fold molar amount of $AlCl_3$. More active Friedel–Crafts catalysts ($FeCl_3$, $SbCl_5$)[21] destroy the starting material **7** while less active catalysts ($TiCl_4$, $SnCl_4$)[21] effect little reaction.

Electrophilic Carbodesilylations of (Trimethylsilyl)-1-methylpyrazoles, Catalyzed by Nucleophiles. Prior investigations have shown potassium *tert*-butoxide or alkaline fluorides to be most effective in the nucleophilic catalysis of desilylation reactions.[6b] In the carbodesilylation of (trimethylsilyl)-1-methylpyrazoles, we therefore used KF or CsF as catalysts, and dimethylformamide as the solvent. The higher volatility of DMF facilitates a nonaqueous workup compared with hexamethyl phosphoric acid and triamide (HMPT) although requiring a longer reaction time. Both aldehydes and ketones (Scheme VIII) as well as acyl fluorides, carbonic acid fluorides, and *p*-toluenesulfonyl fluoride were employed (Scheme IX). The 5-(trimethylsilyl)pyrazoles **3**, **9**, and **10** without exception gave regioselective carbodesilylation at the 5-position. No carbodesilylation at the 3- or 4-position was observed under these conditions.

Side reactions, e.g., protodesilylation to 5-(1-hydroxybutyl)-1-methylpyrazole (**26′g**), and condensation reactions are obviously responsible for the low yields in the reactions of **3** with butenal and acetophenone. Aliphatic aldehydes are known to undergo condensation reactions in dipolar-

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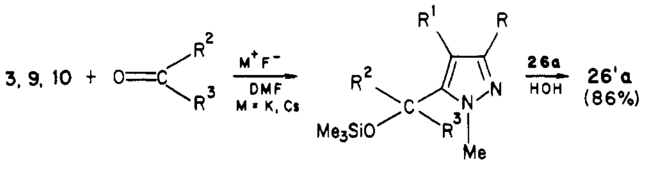
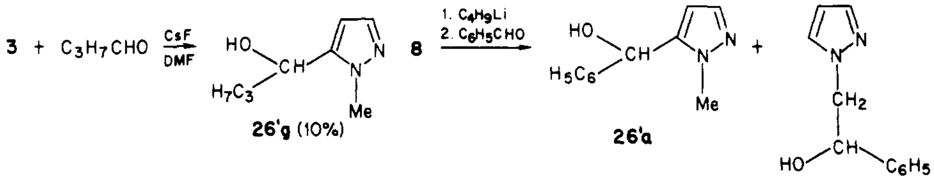
Scheme VIII



26-28

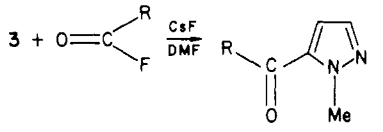
	26a	26b	26c	26d	26e	26f	27	28
R	H	H	H	H	H	H	$SiMe_3$	H
R^1	H	H	H	H	H	H	H	$SiMe_3$
R^2	H	H	H	CH_3	H	Ph	Ph	Ph
R^3	Ph	4-ClC_6H_4	4-$Me_2NC_6H_4$	Ph	CH=CHPh	CH=CHPh	H	H
yield %[a]	75	71	44				78	75
yield %[b]	87		67	14	39	33		



26'g (10%) **26'a** **26"a**

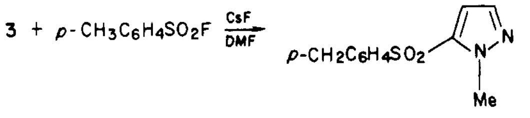
[a] With KF as catalyst. [b] With CsF as catalyst.

Scheme IX



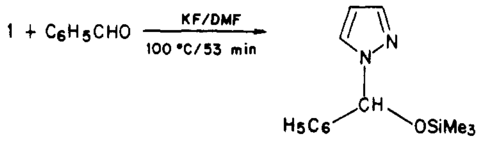
29

	a	b	c
R	C_6H_5	$OCH_2CH(CH_3)_2$	$N(CH_3)_2$
yield, %	64	66	67



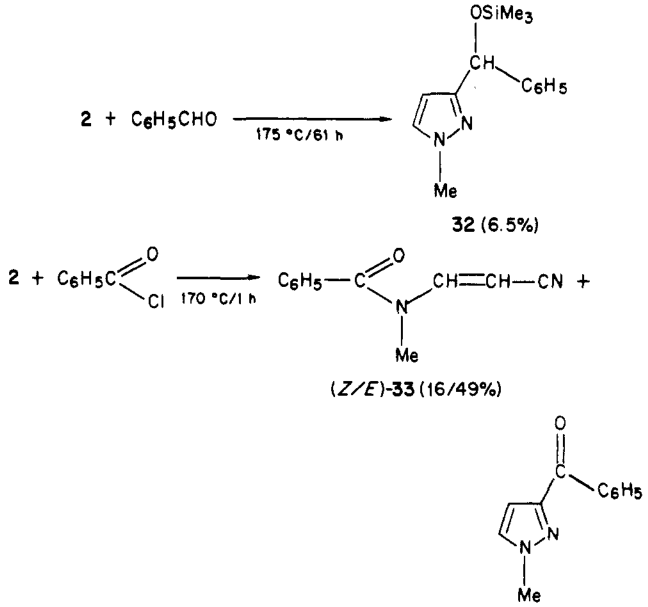
30 (48%)

Scheme X



31

Scheme XI



32 (6.5%)

(*Z/E*)-**33** (16/49%)

34 (2.6%)

aprotic solvents in the presence of fluoride ions.[22,23] For the CsF-catalyzed reaction of **3** with benzaldehyde, we could demonstrate that, by adding an equimolar amount of water at the end of the reaction, the trimethylsilyl ether **26a** is transformed into the corresponding alcohol, **26'a**. This offers a distinct preparative advantage over the lithiation of 1-methylpyrazole (**8**) with butyllithium, followed by reaction with benzaldehyde, as described in the literature.[12] This procedure always results in a mixture of **26'a** and 1-(2-hydroxy-2-phenylethyl)pyrazole (**26"a**) due to competitive deprotonation of the pyrazole nucleus and the 1-methyl group (Scheme VIII).[12] The carbodesilylations, as described above, are restricted to N-substituted (trimethylsilyl)pyrazoles. 1*H*-(trimethylsilyl)pyrazoles under these conditions rearrange to the corresponding 1-substituted pyrazoles, as demonstrated by the reaction of 5-(trimethylsilyl)-1*H*-pyrazole (**1**) with benzaldehyde which gives 1-[(phenyl)(trimethylsiloxy)methyl]pyrazole (**31**).

Attempts to react 1-methyl-3-(trimethylsilyl)pyrazole (**2**) with carbon electrophiles at the 3-position without nucleophilic catalysis are unsatisfactory. Me_3Si groups in the α-position to an azine lone pair are known to be activated.[24] Nevertheless, high reaction temperatures were necessary which led to numerous side reactions and increasing decomposition, and the reactions had to be

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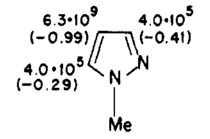
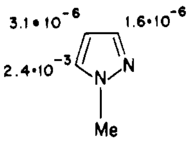
Chart I



8

partial rate factors (σ^+ values) for H/D exchange in acidic medium[27,29]



8

second order rate constants for H/D exchange in $CH_3OD/NaOCH_3$ at 139 °C[32]

quenched far from completion. Reaction of 2 with benzaldehyde (61 h at 175 °C) gave only 6% of the expected addition product **32**. With *p*-(dimethylamino)benzaldehyde, no reaction was observed even after 60 h at 175–195 °C.

Reaction of **2** with benzoyl chloride resulted in a preferential ring opening to a cis/trans mixture of the aminoacrylonitriles **33** which are formed via ring opening of 3-pyrazolyl carbanions;[25] only 3% of 3-benzoyl-1-methylpyrazole **34** could be isolated. Attempts to react benzaldehyde with 1-methyl-5-(trimethylsilyl)pyrazole (**3**) without a catalyst, in analogy to **2**, gave only traces of **26a**.

Discussion

Electrophilic Halodesilylation. On the basis of Eaborn's work,[4a] electrophilic reagents are presumed to cleave Ar–Si bonds via Wheland-type intermediates in the rate-determining step. The position of preferential halodesilylation might thus be estimated from the reactivity indices for electrophilic substitution of pyrazoles, although the significance of reactivity indices for heterocycles should not be overestimated.[26] In the case of 1-methylpyrazole (**8**), partial rate factors for the acid-catalyzed hydrogen exchange[27] and σ^+ values[28] both predict the 4-position to be the most reactive; 3- and 5-positions should be much less reactive.

This prediction is borne out by the fact that both 3,4- and 4,5-bis(trimethylsilyl)-1-methylpyrazole (**5** and **10**) are selectively bromosilylated in the 4-position (Scheme V) and that **5** suffers iododesilylation with iodine monochloride likewise in the 4-position to give **20** (Scheme VI).

Chan and Fleming[29] have proposed to assess the ipso-directing influence of the Me_3Si group by adding −0.6 to the σ^+ value. Thence, halodesilylation of both 1-methyl-3-(trimethylsilyl)pyrazole (**2**) and 1-methyl-5-(trimethylsilyl)pyrazole (**3**) should be feasible. Our experimental results, however, show that the Me_3Si ipso effect suffices only for iododesilylation of **2** by iodine, yielding 3-iodo-1-methylpyrazole (**22**). The reactions of **2** with bromine and of **3** with iodine gave only halodeprotonation in the 4-position, yielding **13** and **23**, respectively (Schemes V and VI). σ^+ values and the ipso-directing influence of the Me_3Si group also explain that in our experiments 4-bromo-1-methyl-3-(trimethylsilyl)pyrazole (**13**) and 4-bromo-1-methyl-5-(trimethylsilyl)pyrazole (**15**) are selectively brominated to the 3,4-dibromo and 4,5-dibromo compounds **14** and **16**, respectively (Scheme V). The extraordinary reactivity of **5** and of 1-methyl-3,5-bis(trimethylsilyl)pyrazole (**9**) in the 3-position toward iodine (Scheme VI) on the other hand, does not conform with the reactivity indices cited above.

Carbodesilylations Catalyzed by Nucleophiles. While there has been extensive investigation of the protodesilylation of trimethylsilyl heteroarenes with nucleophilic catalysis,[30] carbodesilylation with nucleophilic catalysis so far has been used only in a few cases to introduce carbon substituents into heteroarenes.[6a,c] Eaborn et al.[31] have proposed that carbanion formation usually is the rate-determining step in the nucleophilic cleavage of C–Si bonds. In this case, the reaction should depend on carbanion stabilization in the various ring positions.

According to Kohn,[32] the relative rate for the basic H/D exchange in the 5-position of **8** by far exceeds that in the 3- or 4-position (Scheme XII). The regioselective carbodesilylation in the 5-position of the (trimethylsilyl)pyrazoles **3**, **9**, and **10** under nucleophilic catalysis thus becomes plausible. The small H/D exchange rate in the 3-position is attributed to the so-called ATP effect,[33] i.e., carbanion destabilization by the adjacent lone pair of the azine nitrogen.

To sum up, substituents may be introduced regioselectively into the various positions of the pyrazole ring via desilylation reactions by combining straightforward electrophilic substitutions with reactions catalyzed by nucleophiles.

Direct electrophilic halogenation of the 4-position of pyrazole has been described in the literature. Compared with those older procedures, the halodesilylation reaction reported here offers advantages only in specific cases, e.g., in iodination or in dehalogenation. In the course of this work, however, we have for the first time achieved acylation and hydroxyalkylation, respectively, of pyrazols. Depending on the reaction conditions the reaction can be directed selectively either to the 4-position (with $AlCl_3$) or to the 5-position (with basic catalysts). This offers novel possibilities for the synthesis of pyrazole derivatives.

Experimental Section

Melting points were determined on a Büchi SMP 20 apparatus with a silicon bath and are uncorrected. ^1H NMR spectra were obtained on a Varian A 60 or T 60 and a Bruker WP 80 or HX 90. Chemical shifts are reported in parts per million relative to Me_4Si as an internal standard in $CDCl_3$. Mass spectral data were obtained by using a Varian Model MAT 711. Analytical gas chromatography was performed on a Hewlett Packard 5700 A instrument with a flame-ionization detector and a Spectrophysic Minigrator by using a glass column packed with OV-101 on Gas Chrom Q or OV-17 on Chromosorb W-HP (100–120 mesh), and a glass column (2 mm id × 2.3 m) packed with OV-17 on Chromosorb W-HP (100–120 mesh). Carrier gas: N_2, thermoregulation 16 °C/min, 100–300 °C. Preparative gas chromatography was performed by using a Dr. Hupe, Apparatebau, Karlsruhe, AGP 402 instrument with a glass column (13 mm id × 4.0 m) packed with 10% SE on Chromosorb P (60–80 mesh). Preparative column

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chromatography was done with silica gel S, 0.040–0.063 mm (Riedel-de Haen). MPLC was performed with a B. Glatz system[34] by using a silica gel column type C (2.4 cm id × 25 cm) packed with silica gel Lichroprep Si 60, 0.015–0.025 mm (E. Merck), ca. 6300 theoretical plates.

Dimethylformamide (DMF) was distilled, stirred with CaH_2 at 100 °C overnight, fractionally distilled, and stored over 3 Å molecular sieves.

Benzaldehyde was distilled twice under N_2 and stored in a glass flask, sealed off air tight with an air-tight septum. KF and CsF were dried over P_2O_5 at 300 °C in vacuo, powdered in a nitrogen box, again dried, and weighed into a flame-dried flask equipped with a stirring bar and glass beads; the fluorides then were stirred with 100 mL of DMF for 7 days. From the stirred suspension aliquots of KF or CsF were drawn via syringe (Method A). CsF was powdered twice in a ball mill and dried at 300 °C in vacuo, the process being carried out in a nitrogen box. All new substances showed satisfactory NMR spectra (see the paragraph at the end of paper about supplementary material).

General Method for Methylation of (Trimethylsilyl)pyrazoles with Iodomethane/Potassium Carbonate. (Trimethylsilyl)pyrazole, iodomethane, and anhydrous potassium carbonate were refluxed in the respective solvent at 40 °C and poured into a 2-fold amount of water. The aqueous layer was extracted with ether, the ether extract dried ($MgSO_4$) and concenrated at low pressure, and the residue fractionally distilled in vacuo.

Methylation of 3-(Trimethylsilyl)-1*H*-pyrazole (1).[7] **1** (15.4 g, 0.11 mol) and iodomethane (17.03 g, 0.12 mol) were stirred with 33.2 g (0.24 mol) of potassium carbonate and 160 mL of acetone for 92 h at 40 °C and worked up as described above. The crude product, containing 90% 1-methyl-3-(trimethylsilyl)pyrazole (**2**), 4% 1-methyl-5-(trimethylsilyl)pyrazole (**3**), and 6% **1** (FID-%, GLC), was purified by distillation to yield 11.5 g (68%) of **2**, bp 73.5 °C (16 torr). Anal. Calcd for $C_7H_{14}N_2Si$ (**2**): C, 54.49; H, 9.14; N, 18.15. Found: C, 54.31; H, 9.06; N, 18.41.

Methylation of 3,4-Bis(trimethylsilyl)-1*H*-pyrazole (4).[7] **4** (63.7 g, 0.3 mol), iodomethane (45.42 g, 0.32 mol), and potassium carbonate (88.4 g, 0.64 mol) in 430 mL of acetone were stirred for 65 h at 40 °C and then worked up by the general procedure to give 3.95 g (8%) of **2**, bp 66–67 °C (10 torr), and 54.4 g (80%) of 3,4-bis(trimethylsilyl)-1-methylpyrazole (**5**), bp 112–114 °C (10 torr). Anal. Calcd for $C_{10}H_{22}N_2Si_2$ (**5**): C, 53.03; H, 9.79; N, 12.36. Found: C, 53.30; H, 9.75; N, 12.08.

1-Methyl-4-(trimethylsilyl)pyrazole (7). A solution of 161.0 g (1.0 mol) of 4-bromo-1-methylpyrazole (**6**)[13] in 250 mL of HMPT was added dropwise to a stirred mixture of 135.8 g (1.25 mol) of chlorotrimethylsilane and 30.4 g (1.25 mol) of magnesium chips in 500 mL of HMPT at 90 °C within 2 h. 40 h stirring at 90 °C and workup analogous to the literature[10] yielded 121.3 g (79%) of **7**, bp 77–79 °C (12 torr). Anal. Calcd for $C_7H_{14}N_2Si$: C, 54.49; H, 9.14; N, 18.15. Found: C, 54.23; H, 9.13; N, 18.34.

Lithiation and Silylation of 1-Methylpyrazoles. General Workup Procedure. The resulting reaction mixture was poured into a 2-fold amount of 1 M $NaHCO_3$, ether was added, and the mixture stirred until solution occurred. In some cases it was necessary to adjust the mixture to ca. pH 7–8 with 0.5 M HCl. The organic layer was separated, and the aqueous layer extracted with ether. The combined organic phases were washed with water, dried ($CaCl_2$), concentrated under low pressure, and the resulting residue was purified by fractional distillation.

Reaction of 1-Methyl-3-(trimethylsilyl)pyrazole (2). A solution of 1.6 M butyllithium in hexane (24.5 mL, 39.2 mmol) was dropped into a stirred solution of 5.4 g (35.0 mmol) of **2** in 35 mL of ether at 0 °C under nitrogen. After an additional 1 h at 0 °C a solution of 3.95 g (34.6 mmol) of chlorotrimethylsilane in 14 mL of ether was added dropwise, and the mixture was stirred for 1 h more at 0 °C, was allowed to warm to room temperature, and was worked up as above to afford 0.48 g (6%) of 3-(trimethylsilyl)-1-[(trimethylsilyl)methyl]pyrazole (**12**), bp 87–90 °C (11 torr), and 3.26 g (41%) of 3,5-bis(trimethylsilyl)-1-methylpyrazole (**9**), bp 101–103 °C (11 torr), mp 55–56 °C (pentane). Anal. Calcd for $C_{10}H_{22}N_2Si_2$ (**9**, **12**): C, 53.03; H, 9.79; N, 12.36. Found (**9**): C, 53.01; H, 9.77; N, 12.22. Found (**12**): C, 53.26; H, 9.72; N, 12.60.

Reaction of 1-Methyl-4-(trimethylsilyl)pyrazole (7). The solution of 1.5 M butyllithium in hexane (33.3 mL, 50.0 mmol) was dropped into a stirred solution of 7.71 g (50.0 mmol) of **7** and 5.81 g (50.0 mmol) of *N,N,N′,N′*-tetramethyl-1,2-ethanediamine in 100 mL of ether at 0 °C under nitrogen within 20 min. After an additional 3 h at 0 °C a solution of 5.43 g (50.0 mmol) of chlorotrimethylsilane in 20 mL of ether was added dropwise at 0 °C, and the mixture then was allowed to warm to room temperature overnight and was worked up as above to yield 1.34 g (12%) of 4,5-bis(trimethylsilyl)-1-methylpyrazole (**10**), bp 48 °C (0.001 torr). Anal. Calcd for $C_{10}H_{22}N_2Si_2$: C, 53.03; H, 9.79; N, 12.36. Found: C, 52.98; H, 9.76; N, 12.45.

Reaction of 1-Methylpyrazole (8).[35] (a) A solution of 1.6 M butyllithium in hexane (197 mL, 0.315 mol) was dropped into a stirred solution of 24.2 g (0.295 mol) of freshly distilled **8** in 175 mL ether at −30 °C under nitrogen within 30 min. After an additional 3 h at −30 °C a solution of 34.3 g (0.316 mol) of chlorotrimethylsilane in 45 mL of ether was added dropwise at −30 °C within 15 min, and the mixture then was allowed to warm to room temperature overnight and was worked up as above to give 2.58 g (6%) of 1-[(trimethylsilyl)methyl]pyrazole (**11**), bp 61 °C (9 torr), and 23.8 g (52%) of 1-methyl-5-(trimethylsilyl)pyrazole (**3**), bp 78–80 °C (12 torr). Anal. Calcd for $C_7H_{14}N_2Si$ (**3**, **11**): C, 54.49; H, 9.14; N, 18.15. Found (**3**): C, 54.27; H, 8.91; N, 17.95. Found (**11**): C, 54.70; H, 9.30; N, 18.12.

(b) The same reaction was performed with addition of 34.4 g (0.295 mol) of *N,N,N′,N′*-tetramethyl-1,2-ethanediamine to the solution of **8** prior to the addition of butyllithium; yield: 32.7 g (72%) of **3**, bp 75–80 °C (12–13 torr).

Bromodesilylation of 3,4-Bis(trimethylsilyl)-1-methylpyrazole (5). (a) A 1 M solution of bromine in dichloromethane (6 mL) was dropped into a stirred solution of 1.36 g (6.0 mmol) of **5** in 6 mL of dichloromethane at 0 °C under a dry atmosphere within 15 min. After an additional 30 min at 0 °C the mixture was concentrated, and the residue distilled in vacuo to yield 1.17 g (84%) of 4-bromo-1-methyl-3-(trimethylsilyl)pyrazole (**13**), bp 104–106 °C (12 torr). Anal. Calcd for $C_7H_{13}BrN_2Si$: C, 36.05; H, 5.61; Br, 34.26; N, 12.01. Found: C, 36.00; H, 5.72; Br, 34.00, N, 12.18.

(b) A 1 M bromine solution in dichloromethane (12 mL) was added dropwise to the stirred solution of 1.36 g (6.0 mmol) of **5** in 6 mL of dichloromethane at 0 °C under a dry atmosphere. The orange colored solution was refluxed until the color disappeared (24 h) and concentrated, and the residue distilled in vacuo to give 1.04 g (72%) of 3,4-dibromo-1-methylpyrazole (**14**): bp 124–125 °C (13 torr): mp 57–58 °C; ^1H NMR ($CDCl_3$) δ 3.92 (s, NCH_3), 7.42 (s, H-5). Anal. Calcd for $C_4H_4Br_2N_2$: C, 20.02; H, 1.68; Br, 66.61; N, 11.67. Found: C, 20.00; H, 1.78; Br, 66.45; N, 11.93.

Bromodesilylation of 4,5-Bis(trimethylsilyl)-1-methylpyrazole (10). The reaction was performed by procedures similar to those described above (a). Reaction of 1.28 g (8.0 mmol) of bromine in 8 mL of dichloromethane with 1.81 g (8.0 mmol) of **10** in 8 mL of dichloromethane and workup resulted in a residue, which was extracted with ether; the extract was filtered and evaporated. The residue then was purified by sublimination (−20 °C) at 0.001 torr. Yield: 1.58 g (85%) of 4-bromo-1-methyl-5-(trimethylsilyl)pyrazole (**15**), mp 16–19 °C. Anal. Calcd for $C_7H_{13}BrN_2Si$: C, 36.05; H, 5.61; Br, 34.26; N, 12.01. Found: C, 36.26; H, 5.59; Br, 3.14; N, 11.93.

Bromodesilylation of 4-Bromo-1-methyl-5-(trimethylsilyl)pyrazole (15). The reaction was carried out similar to that described above (b). **15** (0.47 g, 2.0 mmol) in 2 mL of dichloromethane and 0.33 g (2.05 mmol) of bromine in 4 mL of dichloromethane yielded after 24 h at 40 °C and workup 0.43 g (90%) of 4,5-dibromo-1-methylpyrazole (**16**): mp 57–58 °C; ^1H NMR ($CDCl_3$) δ 3.93 (s, NCH_3), 7.51 (s, NCH_3). Anal. Calcd for $C_4H_4Br_2N_2$: C, 20.02; H, 1.68; Br, 66.61; N, 11.67. Found: C, 19.93; H, 1.58; Br, 66.45; N, 11.44.

Bromination of 1-Methyl-3-(trimethylsilyl)pyrazole (2). To a vigorously stirred mixture of 0.5 M bromine in dichloromethane (4 mL) and 424.0 mg (4.0 mmol) of anhydrous sodium

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carbonate was added 308.0 mg (2.0 mmol) of **2** via syringe at 0 °C. After an additional 20 min at 0 °C the orange colored mixture was poured into water, and the dichloromethane layer was separated, dried ($MgSO_4$), and evaporated. The residue, 414.0 mg (89%) of 4-bromo-1-methyl-3-(trimethylsilyl)pyrazole (**13**), showed the same ^1H NMR data as the product synthesized from **5** (see above).

Bromination of 4-Bromo-1-methylpyrazole (17).[13] **17** (16.1 g, 0.1 mol) and 79.9 g (0.5 mol) of bromine were refluxed in 400 mL of tetrachloromethane for 8 days under exclusion of light and moisture. The resulting mixture was added to a cooled (0 °C) and stirred mixture of 101 g (1.2 mol) of sodium bicarbonate and 124 g (0.5 mol) of sodium thiosulfate·$5H_2O$ in 1.5 L water. The water layer was separated from the discolored solution and extracted with dichloromethane, the combined organic phases were dried ($CaCl_2$) and evaporated, and the resulting residue was distilled in vacuo (maximum bath temperature 120 °C) to afford 11.1 g (46%) of 4,5-dibromo-1-methylpyrazole (**16**), bp 89–91 °C (9 torr); melting point and mixed mixed melting with **16** were obtained by bromodesilylation of **15**, 57–58 °C. The residue of this distillation was sublimed at 10^{-3} torr, and the sublimate was then twice recrystallized from methanol and sublimed again to yield 10.7 g (34%) of 3,4,5-tribromo-1-methylpyrazole (**18**), mp 90–91 °C (methanol) (lit.[36] mp 86–87 °C). Anal. Calcd for $C_4H_3Br_3N_2$: C, 15.06; H, 0.94; Br, 75.19; N, 8.78. Found: C, 15.00; H, 0.93; Br, 75.23; N, 8.94.

Iododesilylation of 3,4-Bis(trimethylsilyl)-1-methylpyrazole (5) with Iodine. (a) **5** (3.4 g, 15.0 mmol) and 3.8 g (15.0 mmol) of iodine were stirred in a flame-dried flask under a dry atmosphere for 1 h at room temperature. The mixture was then slowly warmed to 70 °C, stirred for another 24 h, cooled, and dissolved in ether. After adding of a solution of 1 M $NaHCO_3$/concentrated sodium thiosulfate the mixture was stirred until evolution of gas ceased and the mixture became colorless. The water layer was separated and extracted with ether, and the combined ether phases were dried ($MgSO_4$) and evaporated; the highly volatile parts were then removed at 0.01 torr in vacuo. The residue (4.17 g) consisted of 80% (FID of 3-iodo-1-methyl-4-(trimethylsilyl)pyrazole (**19**) and 18% (FID) of 4-iodo-1-methyl-3-(trimethylsilyl)pyrazole (**20**). This residue (3.12 g) was worked up by preparative gas chromatography. The main fraction of **19** (dark brown colored by decomposition products) was redistilled in high vacuo to give 1.29 g (41%) of **19** as 97% orange colored oil (as determined by GLC). Anal. Calcd for $C_7H_{13}IN_2Si$: C, 30.00; H, 4.67; N, 9.99. Found: C, 29.88; H, 4.47; N, 9.88.

(b) **5** (1.36 g, 6.0 mmol) and 3.30 g (13.0 mmol) of iodine were heated in a small vigreux column for 1 h at 130 °C and then for 4 h at 140 °C, whilst iodotrimethylsilane was removed. The residue was decolorized by using the procedure noted above, and the organic layer was separated, dried ($MgSO_4$), and evaporated. The crude product was purified by sublimination to yield 1.65 g (82%) of 3,4-diiodo-1-methylpyrazole (**21**), mp 58–60 °C (lit.[14] mp 56 °C).

Iododesilylation of 1-Methyl-3-(trimethylsilyl)pyrazole (2). **2** (1.54 g, 10.0 mmol) and 2.54 g (10.0 mmol) of iodine were treated by the same procedure (b) as above for 100 min at 150 °C. The crude product was purified by distillation to give 0.96 g (46%) of 3-iodo-1-methylpyrazole (**22**): bp 100–102 °C (11 torr); ^1H NMR ($CDCl_3$) δ 3.94 (s, CH_3), 6.45 (d, 4-H, ^3J = 2.2 Hz), 7.27 (d, 5-H). Anal. Calcd for $C_4H_5IN_2$: C, 23.09; H, 2.42; I, 61.01; N, 13.46. Found: C, 23.33; H, 2.66; I, 61.22; N, 13.43.

Iododesilylation of 1-Methyl-5-(trimethylsilyl)pyrazole (3). **3** (4.63 g, 30.0 mmol), 15.22 g (60.0 mmol) of iodine, 16.58 g (120.0 mmol) of potassium carbonate, and 90 mL of 1,2-dichloroethane were vigorously stirred for 40 h at room temperature. After workup with the procedure noted above (a) the water layer was separated and extracted with 1,2-dichloroethane. The combined organic extracts were dried ($MgSO_4$) and evaporated, and the residue was distilled to afford 7.53 g (90%) of 4-iodo-1-methyl-5-(trimethylsilyl)pyrazole (**23**): bp 72 °C (0.02 torr); mp 37 °C. Anal. Calcd for $C_7H_{13}IN_2Si$: C, 30.00; H, 4.67; I, 45.29; N, 9.99. Found: C, 29.92; H, 4.52; I, 45.29; N, 10.00.

Iododesilylation of 4,5-Bis(trimethylsilyl)-1-methylpyrazole (10). **10** (1.70 g, 7.5 mmol), 5.08 g (20.0 mmol) of iodine, and 40 mL of tetrachloromethane were stirred under a dry atmosphere for 41 h at 80 °C (bath temperature). After workup by using the procedure noted above (a) the combined organic layers were dried ($CaCl_2$), evaporated, and then concentrated in high vacuo to yield 0.64 g (30%) of **23**, mp 34–38 °C. **23** shows the same ^1H NMR data as the product synthesized from **3** (see above).

Iododesilylation of 3,5-Bis(trimethylsilyl)-1-methylpyrazole (9). **9** (2.26 g, 10.0 mmol), 3.04 g (12.0 mmol) of iodine, and 40 mL of tetrachloromethane were stirred for 89 h at 60 °C (bath temperature) under a dry atmosphere. After workup by using the procedure noted above (a) the combined ether layers were dried ($MgSO_4$) and evaporated. The residue was distilled in vacuo to give 1.47 g (52%) of 3-iodo-1-methyl-5-(trimethylsilyl)pyrazole (**24**): bp 139–142 °C (10 torr); mp 66–71 °C. Anal. Calcd for $C_7H_{13}IN_2Si$: C, 30.00; H, 4.67; I, 45.29; N, 9.99. Found: C, 30.29; H, 4.77; I, 45.32; N, 10.27.

Iododesilylation of 3,4-Bis(trimethylsilyl)-1-methylpyrazole (5) with Iodine Chloride. A solution of 1.94 g (12.0 mmol) of iodine chloride in 20 mL of dichloromethane was added to the stirred solution of 2.72 g (12.0 mmol) of **5** in 20 mL of dichloromethane at −78 °C under a dry atmosphere. After an additional 4 h at −78 °C the mixture was allowed to warm to room temperature overnight. After evaporation and contraction in high vacuo the residue was purified by column chromatography with ethyl acetate/ligroin (3/7) (bp 40–60 °C) as the eluant. Subsequent distillation yielded 2.53 g (75%) of 4-iodo-1-methyl-3-(trimethylsilyl)pyrazole (**20**), bp 66 °C (0.01 torr). Anal. Calcd for $C_7H_{13}IN_2Si$: C, 30.00; H, 4.67; N, 9.99. Found: C, 30.06; H, 4.61; N, 9.96.

Friedel–Crafts Benzoylation of 1-Methyl-4-(trimethylsilyl)pyrazole (7). In a flame-dried flask 34.2 mL of tetrachloromethane, 4.8 g (34.1 mmol) of benzoyl chloride, and 2.63 g (17.0 mmol) of **7** were added successively to 4.55 g (34.1 mmol) of freshly sublimed aluminum chloride under nitrogen atmosphere in an ice bath. The stirred mixture was refluxed (bath temperature 80 °C) for 15 days, neutralized with an ice-cooled 1 M solution of $NaHCO_3$, and rapidly extracted with tetrachloromethane five times. The combined organic layers were filtered and evaporated, and the residue was heated at 60 °C (bath temperature) (0.01 torr) to remove excess benzoyl chloride. The solid residue was then purified by recrystallization with hexane and sublimation in high vacuo to yield 1.73 g (54%) of 4-benzoyl-1-methylpyrazole (**25**): mp 81–82 °C; ^1H NMR ($CDCl_3$) δ 7.98 (s, 2 H, 3-H, 5-H), 7.75–7.95 (m, 2 H, $Ph^{2,6}$), 7.4–7.65 (m, 3 H, $Ph^{3,4,5}$), 3.95 (s, NCH_3). Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 71.11; H, 5.44; N, 15.07.

General Method for Fluoride-Catalyzed Carbodesilylation of the 1-Methyl-5-(trimethylsilyl)pyrazoles 3, 9, and 10 with Carbonyl Compounds in DMF. A round-bottomed two-necked flask equipped with a septum-closed quickfit on the lateral neck, a stirring bar, and a gas outlet tube with a stopcock was evacuated, heated, and allowed to cool again under nitrogen. The suspension of the catalyst in DMF was injected by syringe (Method A). Alternatively, the finely powdered CsF was weighed into the flask under nitrogen, and a given volume of DMF was added with a pipette (Method B). Subsequently, the carbonyl compound was injected, the reaction mixture stirred vigorously and warmed to the reacting temperature, and finally the trimethylsilyl compound was injected (neat or as DMF solution). The progress of the reaction was checked by GLC. For workup, 2–5 times the volume of ether was added, and the reaction mixture then cooled to 0 °C, filtered, and evaporated. The residue was distilled in vacuo.

Reaction of 1-Methyl-5-(trimethylsilyl)pyrazole (3) with Butyraldehyde. The reaction process was done by the general method described above. Butyraldehyde (1.58 g, 22.0 mmol) was dropped within 10 min into the mixture of 3.08 g (20.0 mmol) of **3**, 0.6 g (4.0 mmol) of cesium fluoride, and 20 mL of DMF at 50 °C. After an additional 80 min at 50 °C and workup DMF was removed by distillation. The first fraction (2.27 g) consisted

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Table I. Fluoride-Catalyzed Carbodesilylation of 1-Methyl-5-(trimethylsilyl)pyrazoles 3, 9, and 10

								anal.			
compd, g (mmol)	electrophile, g (mmol)	catalyst	DMF, mL	temp, °C	time	product, g (%), bp (°C/torr), mp (°C)	formula	C	H	N	
3, 2.31 (15.0)	benzaldehyde, 1.59 (15.0)	7.5 mL of 0.5 N KF in DMF	7.5	100	15 h	1-methyl-5-[phenyl-(trimethylsiloxy)methyl]-pyrazole (**26a**), 2.91 (75), 89–90 (0.01)	$C_{14}H_{20}N_2OSi$ (260.4)	calcd: 64.57 found: 64.54	7.74 7.67	10.75 10.83	
3, 15.42 (100)	benzaldehyde 10.62 (100)	CsF, 0.46 g (3.0 mmol)	100[a]	40 40–60 60	10 min 30 min 30 min	**26a**, 22.63 (87), 79–82 (0.004)					
3, 3.63 (23.5)	4-chloro-benzaldehyde, 3.3 (23.5)	4.2 mL of 0.56 N KF in DMF	19.3	100	5 h	5-[4-chlorophenyl-(trimethylsiloxy)methyl]-1-methylpyrazole (**26b**), 4.94 (71), 107–109 (0.001)	$C_{14}H_{19}ClN_2OSi$ (294.9)	calcd: 57.02 found: 56.79	6.49 6.79	9.50 9.65	Cl, 12.02 12.07
3, 2.02 (13.1)	4-(dimethylamino)-benzaldehyde, 1.95 (13.1)	2.3 mL of 0.56 N KF in DMF	10.8	100	46 h	5-[[4-(dimethylamino)phenyl]-(trimethylsiloxy)methyl]-pyrazole (**26c**), 1.77 (44), 154–156 (0.03)	$C_{16}H_{25}N_3OSi$ (303.5)	calcd: 63.32 found: 63.20	8.30 8.42	13.84 13.97	
3, 6.03 (39.1)	4-(dimethylamino)-benzaldehyde, 5.83 (39.1)	7.3 mL of 0.53 N CsF in DMF	31.8	100	1.4 h	**26c**, 7.96 (67), 116–120 (0.004)					
3, 8.64 (56.0)	acetophenone, 6.72 (56.0)	CsF, 0.85 g (5.6 mmol)	56	50	140 min	1-methyl-5-[1-phenyl-1-(trimethylsiloxy)ethyl]-pyrazole (**26d**), 2.10 (14), 60–85 (0.002)	$C_{15}H_{22}N_2OSi$ (274.4)	calcd: 65.64 found: 65.86	8.08 8.02	10.20 9.95	
3, 7.72 (50.0)	cinnamic aldehyde, 6.6 (50.0)	4.3 mL of 1.16 N CsF in DMF	45.7	50	45 min	1-methyl-5-[(*E*)-3-phenyl-1-(trimethyl-siloxy)-2-propenyl]-1-methylpyrazole (**26e**), 5.62 (39) 125–140 (0.005)[b]	$C_{16}H_{22}N_2OSi$ (286.4)	calcd: 67.08 found: 66.92	7.74 7.60	9.77 9.99	
3, 4.24 (27.5)	chalcone, 5.73 (27.5)	2.4 mL of 1.16 N CsF in DMF	25	50	77 min	5-[(*E*)-1,3-diphenyl-1-(trimethylsiloxy)-2-propenyl]-1-methylpyrazole (**26f**), 3.30 (33), 135–145 (0.001), 71–74	$C_{22}H_{26}N_2OSi$ (362.5)	calcd. 72.88 found: 72.76	7.22 7.21	7.72 7.59	
9, 2.26 (10.0)	benzaldehyde, 1.06 (10.0)	2.0 mL of 1 N KF in DMF	8	100	5.5 h	1-methyl-5-[phenyl-(trimethylsiloxy)methyl]-3-(trimethylsilyl)pyrazole (**27**), 2.59 (78), 100 (0.001)	$C_{17}H_{28}N_2OSi_2$ (332.6)	calcd: 61.39 found: 61.24	8.48 8.65	8.42 8.26	
10, 2.26 (10.0)	benzaldehyde, 1.06 (10.0)	2.0 mL of 1 N KF in DMF	8	100	46 h	1-methyl-5-[phenyl-(trimethylsiloxy)methyl]-4-(trimethylsilyl)pyrazole (**28**), 2.49 (75), 96–97 (0.001)	$C_{17}H_{28}N_2OSi_2$ (332.6)	calcd: 70.95 found: 61.16	5.41 8.53	15.04 8.63	
3, 3.08 (20.0)	benzoyl fluoride, 4.96 (40.0)	CsF, 0.6 g (4.0 mmol)	20	50	20 h	5-benzoyl-1-methylpyrazole (**29a**), 2.38 (64),[c] 41–42, 39–40][37]	$C_{11}H_{10}N_2O_2$ (186.2)	found: 71.05	5.28	14.77	
3, 3.08 (20.0)	isobutyl fluoroformiate,[38] 2.4 (20.0)	CsF 0.6 g (4.0 mmol)	20	50	6 h	5-isobutoxy-1-methyl-pyrazolecarboxylate (**29b**), 2.41 (66),[d] 105–107 (10.0)	$C_9H_{14}N_2O_2$ (182.2)	calcd: 59.32 found: 59.09	7.74 7.75	15.37 15.59	
3, 3.86 (25.0)	*N*,*N*-dimethylfluoro-formamide,[38] 2.28 (25.0)	CsF, 0.76 g (5.0 mmol)	25	70	16 h	1,*N*,*N*-trimethylpyrazole-5-carboxyamide (**29c**), 2.56 (67), 69 (0.02), 53–55	$C_7H_{11}N_3O$ (153.2)	calcd: 54.88 found: 54.70	7.23 7.36	27.43 27.37	
3, 3.08 (20.0)	4-toluenesulfonyl fluoride, 3.48 (20.0)	CsF, 0.6 g (4.0 mmol)	20	70	24 h	1-methyl-5-(4-toluene-sulfonyl)pyrazole (**30**), 2.29 (48),[d] 112 (0.005), 76–77	$C_{11}H_{12}N_2O_2S$ (236.3)	calcd: 55.91 found: 56.01	5.11 5.20	11.85 11.78	S, 13.54 13.34

[a] DMF was degassed by repeated boiling up in vacuo and saturated with dry N_2 prior to the reaction. [b] Redistilled for analyses, bp 98–102 °C (0.005 torr). [c] The crude product was chromatographed with CH_2Cl_2; the resulting colorless crystals (2.87 g, mp 32–34 °C) were recrystallized from *n*-pentane. [d] After gas evolution has ceased the mixture was poured into 100 mL of 0.1 M $NaHCO_3$ and repeatedly extracted with ether. The combined extracts were washed with water, dried with $MgSO_4$, and evaporated; the residue was distilled.

of ca. 30% 1-methylpyrazole (**8**) (determined by GLC and ^{1}H NMR). The residue was distilled in vacuo to give 0.51 g of crude 5-(1-hydroxybutyl)-1-methylpyrazole (**26′g**), bp 90–93 °C (0.008 torr), which was purified by chromatography with ethyl acetate/ligroin (1/1) as the eluent to yield 0.31 g (10%) of **26′g**: ^{1}H NMR ($CDCl_3$) δ 7.22 (d, 3-H), 6.10 (d, 4-H, ^3J = 2.0 Hz), ca. 4.9 (s, OH), 4.67 (t, C*H*OH), 3.76 (s, NCH_3), 0.8–2.0 (m, 7 H, n-C_3H_7). Anal. Calcd for $C_8H_{14}N_2O$: C, 62.30; H, 9.15; N, 18.16. Found: C, 61.49; H, 8.80; N, 18.12.

1-Methyl-5-(phenylhydroxymethyl)pyrazole (26′a). (a) The reaction was carried out as described above with 4.16 g (27.0 mmol) of 1-methyl-5-(trimethylsilyl)pyrazole (**3**), 2.86 g (27.0 mmol) of benzaldehyde, and 82.0 mg (0.54 mmol) of cesium fluoride in 27 mL of DMF, which was degassed prior to the reaction by repeatedly boiling up in vacuo and saturation with dry nitrogen. After the reaction was heated for 1 h at 50 °C and subsequently 1.5 h at 70 °C, water (0.49 mL, 27.0 mmol) was added by syringe. The resulting reaction mixture was stirred for 5 min at 50 °C, then treated with a diluted sodium bicarbonate solution, and extracted with ether/ethyl acetate (1/1). The extract was washed with water, dried ($MgSO_4$), and evaporated, and the residue recrystallized from ether/ethyl acetate (100/1) to afford 4.39 g (86%) of **26′a**, mp 111–112 °C (lit.[12] mp 106.5–110 °C).

(b) In a flame-dried flask a solution of 1.5 N butyllithium in hexane (20 mL) was dropped within 10 min into the stirred solution of 2.46 g (30.0 mmol) of 1-methylpyrazole (**8**) and 3.48 g (30.0 mmol) of *N*,*N*,*N′*,*N′*-tetramethyl-1,2-ethanediamine in 20 mL of ether at −30 °C under nitrogen. After an additional 3 h at −30 °C the solution of 3.18 g (30.0 mmol) of benzaldehyde in 4.5 mL of ether was added dropwise, and the mixture was then stirred for 1 h at −30 °C and allowed to warm to room temperature overnight. Subsequently 100 mL of 0.6 M $NaHCO_3$ was added, the resulting precipitate dissolved with ethyl acetate, and the separated water layer extracted with ethyl acetate/ether (1/1). The combined organic layers were dried ($MgSO_4$) and evaporated, and the crude residue was purified by fractional recrystallization to give 3.49 g (62%) **26′a** (first fraction), mp 110–111 °C, and 1.38 g, mp 102–104 °C (second fraction), of a mixture of two parts **26′a** and one part 1-(1-hydroxy-1-phenylethyl)pyrazole (**26″a**) (determined by GLC and ^{1}H NMR); ^{1}H NMR data were in agreement with literature[12] values.

Fluoride-Catalyzed Desilylation of 5-(Trimethylsilyl)-1*H*-pyrazole (1). The reaction process was done by procedures similar to the general method for carbodesilylation (see above). Reaction of 2.81 g (20.0 mmol) of **1**[7] (stored over P_2O_5) with 2.12 g (20.0 mmol) of benzaldehyde, 10 mL of a 0.5 N potassium fluoride suspension in DMF, and 10 mL of DMF yielded after 53 min at 100 °C and workup 0.9 g (18%) of 1-[phenyl(trimethylsiloxy)methyl]pyrazole (**31**), bp 78 °C (0.001 torr). Anal. Calcd for $C_{13}H_{18}N_2OSi$: C, 63.37; H, 7.36; N, 11.36. Found: C, 63.28; H, 7.19; N, 11.31.

Reactions of 1-Methyl-3-(trimethylsilyl)pyrazole (2) with Electrophiles. (a) With Benzaldehyde. **2** (3.08 g, 20.0 mmol) and 2.12 g (20.0 mmol) of benzaldehyde were heated under nitrogen in a sealed glass tube for 61 h at 175 °C. The mixture was then fractionally distilled in high vacuo to yield 2.98 g of a 1/1 mixture of **2** and benzaldehyde, bp 20–30 °C (0.01 torr), and 0.34 g (6.5%) of 1-methyl-3-[phenyl(trimethylsiloxy)methyl]pyrazole (**32**), bp 75 °C (0.0005 torr). Anal. Calcd for $C_{14}H_{20}N_2OSi$: C, 64.57; H, 7.74; N, 10.75. Found: C, 64.27; H, 7.46; N, 10.77.

(b) With 4-(Dimethylamino)benzaldehyde. Heating of 2.67 g (17.3 mmol) of **2** and 2.58 g (17.3 mmol) of 4-(dimethylamino)benzaldehyde under nitrogen for 3 days at 175 °C and subsequently for 3 days at 195 °C yielded no reaction (determined by GLC).

(c) With Benzoyl Chloride. **2** (1.54 g, 10.0 mmol) and 1.55 g (11.0 mmol) of benzoyl chloride were heated in a small vigreux column for 1 h at 170 °C, whilst chlorotrimethylsilane was removed. Subsequently, excessive benzoyl chloride was distilled off in high vacuo; the residue was filtered over a silica gel column (3 cm id × 10 cm) and separated by MPLC with ethyl acetate-/petroleum ether (1/9) as the eluent to yield 0.29 g (16%) of (*Z*)-3-(*N*-benzoyl-*N*-methylamino)acrylonitrile (**33a**), sublimation point 120 °C (0.01 torr), 0.92 g (49%) of (*E*)-3-(*N*-benzoyl-*N*-methylamino)acrylonitrile (**33b**), mp 66–67 °C (ether), and 48.0 mg (2.6%) of 3-benzoyl-1-methylpyrazole (**34**). ^{1}H NMR ($CDCl_3$) for **33a**: δ 7.53 (s, 5 H, Ph), 7.27 (d, NCH=), 4.50 (d, =CHCN, ^3J = 10.1 Hz), 3.68 (s, NCH_3). ^{1}H NMR for **33b**: δ 7.70 (d, NCH=), 7.51 (s, 5 H, Ph), 4.67 (d, =CHCN, ^3J = 14.5 Hz), 3.11 (s, NCH_3). ^{1}H NMR for **34**: δ 8.17–8.29 (m, 2 H, $Ph^{2,6}$), 7.45–7.67 (m, 3 H, $Ph^{3,4,5}$), 7.42 (d, 5-H), 6.93 (d, 4-H, ^3J = 2.3 Hz), 4.00 (s, NCH_3). Anal. Calcd for $C_{11}H_{10}N_2O$ (**33a**, **33b**, **34**): C, 70.95; H, 5.41; N, 15.04. Found for **33a**: C, 70.91; H, 5.41; N, 14.84. Found for **33b**: C, 71.20; H, 5.23; N, 15.27. MS (70 eV, 0.8 mA, 480 K source) calcd for 186.0793, found 186.0795.

5-Iodo-1-methylpyrazole. In a flame-dried flask a solution of 1.5 N n-butyllithium in hexane (20 mL, 30 mmol) was dropped within 10 min into a stirred solution of 2.46 g (30.0 mmol) of 1-methylpyrazole (**8**) and 3.48 g (30.0 mmol) of 1,2-bis(dimethylamino)ethane in 20 mL of ether at −30 °C under nitrogen. After an additional 3 h at −30 °C the solution of 7.61 g (30.0 mmol) of iodine in 40 mL of ether was added dropwise at −30 °C. The mixture was stirred 1 h more at −30 °C, allowed to warm to room temperature within 4 h, treated with a diluted solution of sodium bicarbonate, and decolored with sodium thiosulfate. The water layer was separated and extracted with ether, and the combined organic layers were dried ($MgSO_4$) and evaporated. The residue was purified by sublimation at 50 °C (0.001 torr) to yield 4.18 g (67%): mp 80 °C (pentane/hexane) (lit.[14] mp 76–76.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.56 (d, 3-H), 6.43 (d, 4-H, ^3J = 8.1 Hz), 3.98 (s, NCH_3).

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Supplementary Material Available: Full ^{1}H NMR data for compounds **2**, **3**, **5**, **7**, **9–14**, **19**, **20**, **23**, **24**, **26a–f**, **27**, **28**, **31**, and **32** and ^{13}C NMR data for compounds **2**, **3b**, **5**, **7**, **9**, **10**, **13–17**, **19–24** and 4-iodo- and 5-iodo-1-methylprazole respectively (4 page). Ordering information is given on any current masthead page.