

(7a)^[1c]). The conjugative stabilization accompanying the formation of the pyrromethenic partial structure in the C,D-ring region presumably promotes an eventual didehydrogenation step^[11] to (6). The same partial structure also occurs in the hexahydroporphinoid ligand system (1).

The transformation (5)→(6) is another experimental variant of Johnson's synthesis of corrinoid structures from tetrapyrrolic precursors^[3].



Fig. 2. Crystal structure of *cttt*-(6). Projection at right angles to the plane of atoms N-21, N-22 and N-23; ring-D in foreground (ligand system without substituents).



Fig. 3. Crystal structure of *tctcc*-Ni^{II}-2,3,7,8,12,13,17,18-octaethyl-2,3,7,8,12,13-hexahydroporphyrinate (cf. *tctcc*-(5) in [1d]). Same projection and scale as Fig. 2.

Figure 2 shows the molecule *cttt*-(6) (cf. Fig. 1) in side view. The four coordination centres and the metal ion have essentially a coplanar arrangement; the characteristic macro-ring deformation observed in the nickel(II) complexes of the tetrahydro-^[12] and hexahydroporphyrin^[1a,d] series is absent (for comparison see Fig. 3). This observation corroborates our contention that the coordination cavity of corrinoid ligand systems is closer to the spatial coordination optimum of transition metal ions such as Ni²⁺ than the cavity of hydrophorinoid ligand systems.

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- [5] Colorless needles, m.p. = 166 °C (under N₂ in evacuated capillary) characterized by MS, ¹H- and ¹³C-NMR; prepared by reduction of 1,2,3,7,8,12,13,17,18-nonamethyl-10,23-dihydrobilin dihydrobromide with NaBH₄ in 80% methanol (yield 51%). For the synthesis of the starting material, a modified procedure of that described by A. F. Mironov, O. D. Popova, Kh. Kh. Alarkon, V. M. Bairamov, R. P. Eustigneevea, *Zh. Org. Khim.* 15, 1086 (1979); *J. Org. Chem. USSR* 15, 970 (1979) was used. For details, cf. [1c].
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- [7] a) Identified by comparison of UV/VIS and mass spectra with those of (9) [7b]; this compound was prepared [1c] from nonamethyl-10,23-dihydrobilin

dihydrobromide by Johnson-cyclization [3b]; b) D. A. Clarke, R. Grigg, R. L. N. Harris, A. W. Johnson, I. T. Kay, K. W. Shelton, *J. Chem. Soc. C* 1967, 1648.

- [8] UV/VIS spectrum (CH₂Cl₂) of a crystalline precipitate characterized by MS and ¹H-NMR spectroscopy; for isolation and constitutional assignment cf. [1c]; a) binary mixture of diastereomers (10): λ_{max} = 295 nm (lg ε = 4.20), 330 sh (4.11), 360 sh (4.23), 408 (4.57), 476 sh (3.72), 545 (3.52), 625 sh (3.60), 657 sh (3.72), 695 (3.86), 758 (4.23); b) diastereomer (11) (from nonamethyl-5,15,21,24-tetrahydrobilin; cf. [11]): λ_{max} = 303 nm (lg ε = 4.25), 399 (4.33), 455 (4.03), 508 (3.87), 675 (3.90).
- [9] a) We thank Dr. R. Schwesinger for a sample of TBD; cf. also [1d], reference [4]; b) R. Schwesinger, unpublished results.
- [10] E.g. using 1.5 · 10⁻² M (5) in *p*-xylene, 1.5 mole equivalents DBU/HOAc (2:1), 5 mole equivalents Ni(OAc)₂ · 4H₂O, anaerobic conditions, 16 h, 140 °C, produced *inter alia*, a mixture of diastereomeric Ni^{II}-octamethylisobacteriochlorinates (!) in 45% yield; using the same conditions, but with four times as much buffer, led [apart from ca. 20% isobacteriochlorinate, ca. 10% chlorinate and traces of (6)] to 16% of a product fraction, which according to UV/VIS, MS and ¹H-NMR data surprisingly must be a Ni^{II}-1,2,3,7,8,12,13,17,18-nonamethyl (!)-1,7,8,20-tetrahydroporphyrinate; for details cf. [1c].
- [11] The nature of the hydrogen acceptor remains unknown. The reaction sequence does not proceed *via* the didehydrogenated nonamethyl-5,15,21,24-tetrahydrobilin, because this gives practically no (6) under the reaction conditions of Scheme 2; under milder conditions (11 mole equivalents TBD, 1 mole equivalent Ni(OAc)₂ · 4H₂O, benzene, anaerobic, 2.5 h, 60 °C), diastereomers of types (11) and (6) are formed, yields ca. 15 and 12%, respectively (cf. [1c]).
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Electrophilic Reactions of Aryl- and Heteroaryl(trimethyl)silanes with a Remarkable Nucleophilic Catalysis^[**]

By Franz Effenberger and Wolfgang Spiegler^[*]

Dedicated to Professor Gerhard Pfeleiderer on the occasion of his 60th birthday

Eaborn *et al.*^[1] have shown that the facile displacement of the trimethylsilyl moiety by electrophiles is a decisive factor in the protodesilylation of aryl(trimethyl)silanes; on the basis of kinetic data, they have proposed a mechanism for this reaction analogous to that for electrophilic aromatic substitution. The very high *ipso* rate factors for a series of electrophilic desilylation processes^[2] gave rise to the expectation that aryl(trimethyl)silanes^[3] might also be successfully employed for synthetic purposes; this was confirmed by a regio-specific route to polysubstituted benzenes *via* aryl(trimethyl)silanes reported recently^[4].

Our own investigations of the acylation of aryl(trimethyl)silanes^[5], and reports in the literature on reactions of aldehydes with trimethylsilyl(pentahalogen)benzenes^[6a] and heteroaryl(trimethyl)silanes^[6b], have led us to the assumption that a mechanism different from that formulated by Eaborn^[1] might be operative in these cases. For this pathway, the breaking of the aryl-silyl bond—with at least partial evolution of aryl anions—would be rate-limiting; substituents which stabilize negative charges should therefore enhance the reactivity of aryl(trimethyl)silanes towards electrophiles.

But 2-nitrophenyl(trimethyl)silane (1a) does not react with benzaldehyde even upon heating to 100 °C in dimethylformamide (DMF) for three days. If, however, potassium *tert*-butanolate is added in catalytic amounts, electrophilic

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substitution proceeds smoothly even at -60°C , (*2a*) being formed within 1 h in 92% yield. Analogously, from a series of substituted phenyl(trimethyl)silanes (*1a*)–(*1h*) and benzaldehyde, the benzhydrylsilyl ethers (*2a*)–(*2h*) or, after hydrolysis, the benzhydrols (*3*) were obtained (Table 1).

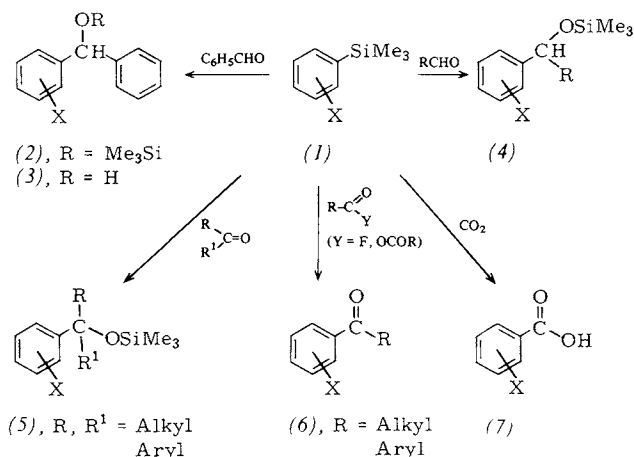


Table 1. Benzhydrylsilyl ethers (*2*) and benzhydrols (*3*) from mono-substituted phenyl(trimethyl)silanes (*1*) and benzaldehyde.

Educt	(1) X	KOC(CH ₃) ₃ [mol-%]	Conditions Solvent	[h]	[°C]	Prod- uct	Yield [%]
(1a)	<i>o</i> -NO ₂	10	DMF	1	-60	(2a)	92 [a]
(1b)	<i>o</i> -Cl	20	DMF	1	-30	(2b)	80 [a]
(1c)	<i>o</i> -F	5	DMF	1	+20	(2c)	76 [b]
(1d)	<i>o</i> -C ₆ H ₅ O	14	DMF	2	+20	(2d)	68 [b]
(1e)	<i>o</i> -C ₆ H ₅ SO ₂	7	DMF	1	+20	(2e)	97 [b]
(1f)	<i>o</i> -CH ₃ O	25	HMPT [c]	0.3	+20	(2f)	trace [a]
(1g)	<i>m</i> -Cl	30	HMPT [c]	4	+100	(3g)	78 [d]
(1h)	<i>p</i> -Cl	30	HMPT [c]	3	+100	(3h)	42 [d]

[a] Determined by gas chromatography. [b] Isolated. [c] Hexamethylphosphor triamide. [d] Determined by gas chromatography after acid hydrolysis.

For the nitro- and chlorophenyl(trimethyl)silanes, the relative reactivity correlates well with the σ^1 -substituent constants^[7a], but diverges significantly from the order of stabilization of the phenyl anions which would be essential intermediates for a nucleophilic desilylation^[7b]. The σ^1 correlation holds also for the other arylsilyl substrates (*1c*)–(*1f*) in Table 1; the remarkable increase in reactivity from (*1d*) to (*1f*) is similarly mirrored in the substituent constants. This clearly indicates that the electrophile participates significantly in the rate-limiting step of the reactions reported here—in contrast to normal nucleophilic desilylation^[7b]. Since “hard” bases have proven especially effective nucleophilic catalysts (KOC(CH₃)₃, KF, CsF, tetraalkylammonium fluoride, KOAc)^[8], one must assume that interaction of the catalyst with the silicon is the decisive factor for the reaction.

We have also extended the reaction to substituted benzaldehydes and aliphatic aldehydes, to ketones, acyl fluorides and carboxylic acid anhydrides as well as to carbon dioxide; the respective products, secondary (*4*) and tertiary benzyl alcohols (*5*), aryl ketones (*6*) and substituted benzoic acids (*7*), are obtained, at least in part, in excellent yields.

The scope of the procedure can be further widened by variation of the arylsilyl substrate. From 2-trimethylsilylbenzothiazole and benzaldehyde, for instance, the substitution product is formed in 78% yield, only after heating to 160 °C for 40 h^[6b]; in the presence of 1 mol-% of potassium *tert*-butanolate, 91% of the product is obtained after 15 min at

-60°C . Since the heteroaryl(trimethyl)silanes are readily accessible *via* cycloaddition reactions^[9], this method allows the introduction of substituents into heterocyclic substrates with high regioselectivity^[9].

The reaction will be of special preparative advantage in those cases where organometallic derivatives cannot be employed because of the presence of reactive functional groups in the molecule (nitro or carbonyl compounds) or because of secondary reactions, *e.g.* formation of dehydroarenes from halogen compounds or isomerization to more stable anions.

Experimental:

(*2a*): Potassium *tert*-butanolate (83 mg, 0.74 mmol) is added to a constantly stirred mixture of (*1a*)^[10] (3.91 g, 20 mmol) and benzaldehyde (2.12 g, 20 mmol) in 25 cm³ DMF at room temperature. The solutions warm slightly and turn red; as indicated by GLC, the reaction is complete after 1 h. The catalyst is filtered off, and the DMF distilled off. Upon fractional distillation, the oily residue yields 4.81 g (80%) (*2a*), b.p. 136–138 °C/0.1 torr. ¹H-NMR (CDCl₃): δ =0.07 (s, 9H), 6.57 (s, H), 7.20–8.00 (m, 9H).

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Nucleophilic Catalysis of Reactions of Tricarbonyl(trimethylsilylarene)chromium Complexes with Electrophiles^[**]

By Franz Effenberger and Klaus Schöllkopf^[*]

Dedicated to Professor Gerhard Pfeleiderer on the occasion of his 60th birthday

Electrophilic substitution of aryl(trimethyl)silanes having electron-donating substituents, *e.g.* alkyl- or aminophenyl(trimethyl)silanes, is not amenable to nucleophilic catalysis^[1]; Friedel-Crafts catalysts, on the other hand, specially facilitate reactions of such substrates with electrophiles. In this case, however, the directing influence of the substituents often overrides the tendency of the trimethylsilyl moiety to *ipso*-substitution, and regular H-substitution results^[2]. Recent investigations have established the electron-withdrawing effect

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