The conjugative stabilization accompanying the formation of the pyrromethenic partial structure in the C,D-ring region presumably promotes an eventual dehydrogenation step [11] to (f). The same partial structure also occurs in the hexahydropriopheniod ligand system (f).

The transformation (5)→(6) is another experimental variant of Johnson's synthesis of corrinoid structures from tetrapyrrolic precursors [12].

Fig. 2 Crystal structure of cttt-(f). 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 tetco-Ni1,2,3,7,8,12,13,17,18-octahethyl-2,3,7,8,12,13-hexahydropriophyrinate (cf. cttt-(f) in [1d]). Same projection as scale like Fig. 2.

Figure 2 shows the molecule cttt-(f) (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- [17] and hexahydropriophyrin [14, 15] 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 hydroporphinoid ligand systems.

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(5), 76879-12-4; cttt-(f), 76880-04-1; (9), 76880-03-9; (10), 76880-02-9; (11), 76880-01-8


[2] This type of ligand was first observed in our laboratory by S. Offer during his work on a synthesis of isobiotrichlorins. A de novo synthesis of metal-free C,D-tetrahydrocorinands will be published later (cf. S. Offer, Dissertation, ETH Zürich 1981).


[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-nonanethiyl-10,13-bicycloctadienobromide with NaNH in 80% methanol (yield 5%). For the synthesis of the starting material, a modified procedure of that described by A. F. Stewart, O. D. Popova, Kh. Kh. Alakon, V. M. Baitaev, R. P. Eustignezeu, Zh. Org. Khim. 15, 1085 (1979); J. Org. Chem. USSR 15, 970 (1979) was used. For details, cf. [1c].

[6] a) HPLC Partial 3; pentane-dimethoxysyntane-1,2,3,4-tetrahydroxybenzamine 200:2:1; b) present to 21% in the mixture of diastereomers (6).


[8] UV/VIS spectrum of (CH2Cl2)2 of a crystalline precipitate characterized by MS and 1H-NMR spectroscopy; for isolation and constitutional assignment cf. [1c]; a) binary mixture of diastereomers (10); Amax = 295 nm (lg ε = 4.20), 330 sh (4.11), 360 sh (4.23), 408 (4.57), 476 sh (3.72), 543 (3.52), 625 sh (3.60), 657 sh (3.72), 695 (3.65), 758 (4.23); b) diastereomer (11) (from nonanethiyl-15,21,24-tetrahydrochlorobin; cf. [11]: Amax = 300 nm (lg ε = 4.25), 399 (3.33), 455 (4.03), 508 (3.87), 675 (3.90).

[9] a) We thank Dr. R. Schweizer for a sample of TBD, cf. also [1d], reference [4]; b) R. Schweizer, unpublished results.

[10] E. g, using 1.5·10—7 mol (5) in pyridine, 1.5 mol equivalents DBU/HOAc (2:1), 5 mol equivalents, Ni(OAc)2.4H2O. anaerobic conditions. 160 °C, produced inter alia, a mixture of diastereomeric 11·tetrahydropriophyrin dichlorobin (5%); in 45% yield, using the same conditions, but with four times as much buffer, led [apart from ca. 20% isobiotrichlorin. ca. 10% chlorine; and traces of (6)] to 16% of a product fraction, which according to UV/VIS and 1H-NMR data surprisingly must be a Ni(II)-1,2,3,7,8,12,13,17,18-nonanethiyl-(5)-17,8,20-tetrahydrochlorobin; for details cf. [1e].

[11] The nature of the hydrogen acceptor remains unknown. The reaction sequence does not proceed via the dihydrogenated nonanethiyl-15,21,24-tetrahydrochlorobin, because this gives practically no (6) under the reaction conditions of Scheme 2; under milder conditions (11 mole equivalents TBD, 1 mol equivalent Ni(OAc)2.4H2O. anaerobic, 25 °C, 26 h), diastereomers of types (11) (and (6) are formed, yields ca. 15 and 12%, respectively (cf. [1c]).


Electrochemical Reactions of Aryl- and Heteroaryl( trimethyli) S ilanes  with a Remarkable Nucleophilic Catalysis[*]

By Franz Effenberger and Wolfgang Spiegler[**]

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

Eaborn et al.[11] have shown that the facile displacement of the trimethylsilyl moiety by electrophiles is a decisive factor in the protodesilylation of ary1(trimethyli)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[12] gave rise to the expectation that ary1(trimethyli)silanes[13] might also be successfully employed for synthetic purposes; this was confirmed by a regiospecific route to polysubstituted benzenes via ary1(trimethyli)silanes reported recently[14].

Our own investigations of the acylation of ary1(trimethyli)silanes[15], and reports in the literature on reactions of aldehydes with trimethylsilyl(pentahalo)benzenes[16] and heteroaryl(trimethyli)silanes[17], have led us to the assumption that a mechanism different from that formulated by Eaborn[11] might be operative in these cases. For this pathway, the breaking of the ary1-silyl bond—with at least partial evolution of ary1 anions—would be rate-limiting; substituents which stabilize negative charges should therefore enhance the reactivity of ary1(trimethyli)silanes towards electrophiles.

But 2-nitrophenyl(trimethyli)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 \(-60^\circ\)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).

![Chemical structures](image)

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

<table>
<thead>
<tr>
<th>Educt (1)</th>
<th>X</th>
<th>KOC(CH₃)₂</th>
<th>Conditions</th>
<th>Product</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(la)</td>
<td>OₙO₂</td>
<td>10</td>
<td>DMF</td>
<td>1–60</td>
<td>(2a) 92 [a]</td>
</tr>
<tr>
<td>(lb)</td>
<td>OCl</td>
<td>20</td>
<td>DMF</td>
<td>1–30</td>
<td>(2b) 80 [a]</td>
</tr>
<tr>
<td>(lc)</td>
<td>FH</td>
<td>5</td>
<td>DMF</td>
<td>1–20</td>
<td>(2c) 76 [b]</td>
</tr>
<tr>
<td>(ld)</td>
<td>O,H₂O</td>
<td>14</td>
<td>DMF</td>
<td>2–10</td>
<td>(2d) 68 [b]</td>
</tr>
<tr>
<td>(le)</td>
<td>O,H₃SO₂</td>
<td>7</td>
<td>DMF</td>
<td>1–20</td>
<td>(2e) 97 [b]</td>
</tr>
<tr>
<td>(lf)</td>
<td>O,H₃O</td>
<td>25</td>
<td>HMPT</td>
<td>0.3</td>
<td>(2f) trace [a]</td>
</tr>
<tr>
<td>(lg)</td>
<td>mCl</td>
<td>30</td>
<td>HMPT</td>
<td>4</td>
<td>(2g) 78 [d]</td>
</tr>
<tr>
<td>(lh)</td>
<td>pCl</td>
<td>30</td>
<td>HMPT</td>
<td>3</td>
<td>(2h) 42 [d]</td>
</tr>
</tbody>
</table>


For the nitro- and chlorophenyl(trimethyl)silanes, the relative reactivity correlates well with the \(n\)-substituent constants\[^{[14]}\], but diverges significantly from the order of stabilization of the phenyl anions which would be essential intermediates for a nucleophilic desilylation\[^{[16]}\]. The \(n\)-correlation holds also for the other arylsilanes (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\[^{[16]}\]. Since “hard” bases have proven especially effective nucleophilic catalysts (KOC(CH₃)₂, KF, CsF, tetraalkylammonium fluoride, KOAc)\[^{[16]}\], 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; 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 arylsilane substrate. From 2-trimethylsilylbenzthiazole and benzaldehyde, for instance, the substitution product is formed in 78% yield, only after heating to 160\°C for 40 h\[^{[16]}\] in the presence of 1 mol-% of potassium tert-butanolate. 91\% of the product is obtained after 15 min at \(-60^\circ\)C. Since the heteroaryl(trimethyl)silanes are readily accessible via cycloaddition reactions\[^{[15]}\], this method allows the introduction of substituents into heterocyclic substrates with high regioselectivity\[^{[20]}\].

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 dehydroarrenes 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 warms slightly and turns 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 oil residue yields 4.81 g (80\%) (2a), b.p. 136–138\°C/0.1 torr. \(^1\)H-NMR (CDCl₃): \(\delta=0.07\) (s, 9 H), 6.57 (s, H), 7.20–8.00 (m, 9 H).

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**Nucleophilic Catalysis of Reactions of Tricarbonyl(trimethylsilylarene)chromium Complexes with Electrophiles**[^{[12]}]

By Franz Effenberger and Klaus Schöllkopf[^{[13]}]

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

Electrophilic substitution of aryl(trimethyl)silanes having electron-denaturing substituents, e.g. alkyl- or aminophenyl(trimethyl)silanes, is not amenable to nucleophilic catalysis[^{[14]}; 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[^{[15]}]. Recent investigations have established the electron-withdrawing effect