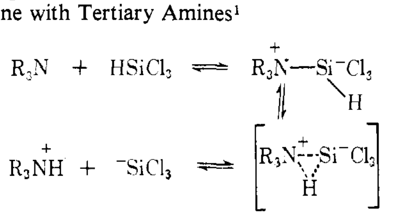
On the Mechanism of Interaction between Tertiary Amines and Trichlorosilane

Sir:

We wish to report confirmation for the mechanism suggested by Benkeser[1] for the interaction of tertiary amines with trichlorosilane.[2] The trichlorosilyl anion has been postulated[2] as the reactive intermediate produced from this interaction by the mechanism shown in Chart I. Support for this proposal is gained from the observation that trichlorosilane undergoes amine-catalyzed hydrogen–deuterium exchange with tri-*n*-butylamine deuteriochloride.[3]

Chart I. Proposed Mechanism for the Interaction of Trichlorosilane with Tertiary Amines[1]



We have measured the kinetics of this reaction in methylene chloride at 30°. The reaction was followed by Si–H line diminution and N–H line growth in the nmr. If the pathway for exchange is given by eq 1 and 2, if the initial concentrations of amine deuteriochloride and silane are both 1.00 *M*, and if there is no equilibrium isotope effect, the concentration–time dependency is[4]

$$R_3N + HSiCl_3 \underset{k_{RH}}{\overset{k_{FH}}{\rightleftharpoons}} R_3NH^+ + {}^-SiCl_3 \tag{1}$$

$$R_3N + DSiCl_3 \underset{k_{RD}}{\overset{k_{FD}}{\rightleftharpoons}} R_3ND^+ + {}^-SiCl_3 \tag{2}$$

$$4AIk_{FD}t = 2(I - 1)(1 - x) - (I + 1)\ln(2x - 1)$$

where A = amine concentration, I = kinetic isotope effect, t = time, and x = $HSiCl_3$ concentration. The reaction was followed twice using two different concentrations of tri-*n*-butylamine (0.0152 and 0.0185 *M*). In both cases the initial concentrations of amine deuteriochloride and silane were identically 1.00 *M*, and in both cases the equilibrium concentrations of Si–H and N–H were identically 0.50 *M* (no equilibrium isotope effect). Under these conditions equilibrium was reached after 5–6 hr. The nmr spectra were constant over at least several days indicating that there were no competing reactions (notably disproportionation of trichlorosilane[5,6]) interfering with the isotope exchange.

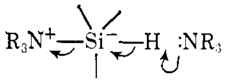
A nonlinear least-squares determination of k_{FD} and I from the data of both runs was made by the function minimization subroutine, GRID4.[7] The kinetic isotope effect, I, is 0.83 ± 0.21, and the forward rate constant, k_{FD}, is 11. ± 3 l. (mol hr)$^{-1}$. The experimental data are summarized in Table I.

Table I. Kinetic Data for the Tri-*n*-butylamine-Catalyzed Hydrogen–Deuterium Exchange between Trichlorosilane and Tri-*n*-butylamine Deuteriochloride

Obsvd Si–H concn, *M*[a]	Obsvd time, hr	Calcd time, hr[b]	Deviation squared
1.000[c]	0.00	0.000	0.000
0.924	0.20	0.593	0.154
0.896	0.33	0.837	0.257
0.911	0.47	0.704	0.055
0.849	0.61	1.284	0.454
0.875	0.92	1.030	0.012
0.866	1.27	1.116	0.024
0.776	1.73	2.107	0.142
0.778	2.05	2.082	0.001
0.738	2.30	2.622	0.103
0.733	2.60	2.695	0.009
0.768	2.96	2.209	0.563
0.763	3.20	2.275	0.856
0.746	3.52	2.507	1.03
0.703	3.93	3.171	0.577
0.685	4.24	3.490	0.563
0.645	4.52	4.322	0.039
0.621	4.80	4.937	0.019
0.621	5.12	4.937	0.033
0.594	5.43	5.792	0.131
1.000[d]	0.00	0.000	0.000
0.803	0.26	1.467	1.46
0.791	0.41	1.584	1.38
0.823	0.67	1.283	0.375
0.812	0.88	1.383	0.253
0.807	1.11	1.429	0.102
0.824	1.44	1.274	0.028
0.717	2.04	2.423	0.146
0.714	2.42	2.462	0.002
0.638	2.98	3.700	0.518
0.677	3.14	3.000	0.020
0.719	3.34	2.397	0.890
0.636	3.74	3.741	0.000
0.645	4.01	3.561	0.202
0.607	4.30	4.411	0.012
0.585	4.76	5.051	0.085

[a] From integrated nmr peak areas. [b] From GRID4 (ref 7). [c] The amine concentration was 0.0152 *M* for the data in this section. [d] The amine concentration was 0.01845 *M* for the data in this section.

Within experimental error, there is no kinetic isotope effect, *i.e.*, $k_{FH} = k_{FD}$. Therefore, the Si–H bond may not break during or before the rate-determining step. There is ample evidence that tertiary amines react with trichlorosilane to form complexes containing nitrogen bound to silicon.[6,8] Complex formation is, then, most likely the first and slow step. Concerted removal of the hydrogen and the amine from the silicon probably occurs next for the following reasons. Simple proton removal would add a further negative charge to the silicon atom. If a free hydride ion were lost it would react with the protonated (or deuterated) amine to give hydrogen gas. Loss of a hydrogen atom is not consistent with the ionic nature of Benkeser's[2] reactions. It is possible that a second amine molecule removes the proton; however, this seems unlikely in view of the very low amine concentrations used in our studies. The mechanism



---

(1) R. A. Benkeser, presented at the Second International Silicon Symposium, Bordeaux, France, July 1968. Dr. Benkeser has informed us that this presentation will appear in *Pure Appl. Chem.* this year.

(2) R. A. Benkeser, K. M. Foley, J. M. Gaul, G. S. Li, and W. E. Smith, *J. Amer. Chem. Soc.*, **91**, 4578 (1969), and earlier papers in the series.

(3) R. A. Benkeser, J. M. Gaul, and W. E. Smith, *ibid.*, **91**, 3666 (1969).

(4) The steady-state assumption was used for the concentration of the trichlorosilyl anion.

(5) D. Weyenberg, A. E. Bey, and P. J. Ellison, *J. Organometal. Chem.*, 3, 489 (1965).

(6) A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 2674 (1954).

(7) J. G. Becsey, L. Berke, and J. R. Callan, *J. Chem. Educ.*, **45**, 728 (1968).

(8) V. U. Wannagat and R. Schwarz, *Z. Anorg. Allg. Chem.*, **277**, 73 (1954); H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc.*, *A*, 1508 (1966).

suggested by Benkeser and shown in Chart I appears to be the simplest scheme that is consistent with all observations.

We have observed that no exchange occurs between methyldichlorosilane and tri-*n*-butylamine deuteriochloride in the presence of *ca.* 1 *M* tri-*n*-butylamine. This is of interest especially since Benkeser has not been able to substitute methyldichlorosilane for trichlorosilane in his reactions.[9] We are currently investigating other systems in order to sort out the factors that are and are not responsible for the success of the exchange reaction.

Acknowledgment. We are extremely grateful to Dr. Leonard Spialter for many thought-provoking discussions of this material. In addition, we wish to express our thanks to Dr. Robert A. Benkeser for sharing his results and ideas with us.

---

[9] R. A. Benkeser, Purdue University, personal communication, 1969.

[10] Part of this work was done while the author was a Visiting Research Associate at Aerospace Research Laboratories, Wright-Patterson Air Force Base, under University of Cincinnati Contract No. AF 33(615)2272.

Stanley C. Bernstein[10]
Department of Chemistry
Wright State University, Dayton, Ohio 45431

Received October 30, 1969

The Structure of Solaphyllidine, a Novel 4-Ketosteroidal Alkaloid

Sir:

We wish to report the structure of a new steroidal alkaloid isolated from the leaves and green berries of *Solanum hypomalacophyllum Bitter*,[1] a tree native to the Venezuelan Andes. The most abundant alkaloid solaphyllidine (I) was obtained pure after repeated crystallization from methanol, mp 165–170°, $[\alpha]^{20}\mathrm{D}$ −25.4° (*c* 0.887, MeOH).

Table I. Nuclear Magnetic Resonance Data (CDCl$_3$) on Solaphyllidine and its Derivatives[a]

	(C-18) C*H*$_3$	(C-19) C*H*$_3$	(C-27) CH–C*H*$_3$	(C-21) CH–C*H*$_3$	(C-22) H CH | | C–C*H*NH–	(C-23) CH | –CH$_2$–C*H*–OH	(C-3) –CO | \\CH–C*H*–OH /	(C-16) \\C*H*–OAc /	O || C–C*H*$_3$
I	0.69	0.72	0.82	0.91	2.95	3.43	4.10	4.96	2.03
II	0.70	0.78	0.82	0.96	3.35	4.95	5.26	5.11	2.05, 2.13
III	0.75	1.01	0.82	0.91	2.93	3.40	3.63	4.87	2.01
IV	0.69	0.69	0.82	0.91	2.87	3.48	4.09	4.17	

[a] Chemical shifts in δ; TMS internal reference; I, II, IV in CDCl$_3$, III in CD$_3$OD.

High-resolution mass spectrometry indicated the molecular formula of I to be $C_{29}H_{47}NO_5$. The base peak at *m/e* 114 suggested a hydroxytetrahydropyridinium ion.[2] Fragments at *m/e* 447 (M − 42) and *m/e* 429 (M − 60) and ir bands at 1255 and 1730 cm^{-1} suggested the presence of an O-acetyl group. A hydroxyl band at 3430 cm^{-1} and a small band at 1670 cm^{-1} were also present. The 100-Mc nmr spectrum (Table I) showed the presence of two tertiary C-methyls, two secondary methyls, an acetoxy group, and four downfield protons in addition to an OH peak.

Acetylation of I with acetic anhydride–pyridine introduced three additional acetyl groups to yield II, mp 204–206° (from isopropyl alcohol), $[\alpha]^{20}\mathrm{D}$ −25.4° (*c* 0.75, MeOH), whose mass spectrum showed a parent ion at *m/e* 615. Major fragments at *m/e* 156 and 198 and the lack of fragment *m/e* 114 indicated conversion of the $C_6H_{12}NO$ moiety to an N,O-diacetyl derivative.

Hydrogenation of I in acetic acid solution with PtO$_2$ led to the dihydro base III, mp 246–248° (from acetone), $[\alpha]^{20}\mathrm{D}$ −46.5° (*c* 0.28, MeOH).

Mild hydrolysis of I with K$_2$CO$_3$–MeOH produced the deacetyl base IV, mp 272–276°, $[\alpha]^{20}\mathrm{D}$ +48.3° (*c* 0.258, MeOH). The mass spectrum of IV has a molecular ion at *m/e* 447 ($C_{27}H_{45}NO_4$) and the same base peak at *m/e* 114. The ir spectrum still exhibited a sharp band at 1730 cm^{-1}. It was concluded that, in addition to the original acetyl group, I must have a ketonic carbonyl group. A keto group α to the C-3 hydroxyl group[3] would explain the peak at 1670 cm^{-1} in the ir spectrum of I and the strong diamagnetic shift (0.3 ppm) shown by the C-19 methyl group of III.

Reduction of I with LiAlH$_4$ in ether afforded the tetraol V, $C_{27}H_{49}NO_4$, resulting from reduction of the carbonyl and hydrolysis of the O-acetyl group. The ir spectrum of V showed no absorption at all between 1800 and 1500 cm^{-1}. Acetylation of III with acetic anhydride–pyridine rendered a pentaacetylated derivative VI, mp 210–211° (from acetone–petroleum ether).

An X-ray diffraction analysis of a single crystal of I which contained no heavy atoms has confirmed and supplemented these observations and established the stereochemistry, except for the absolute configuration which has been assumed to be the same as that determined for cholesterol. The atoms in the unit cell were located by means of the E map computed with phase angles derived directly from structure factor magnitudes using the symbolic addition procedure for noncentrosymmetric crystals.[4,5]

The space group is P2$_1$2$_1$2$_1$ with four molecules in the unit cell with a = 15.24, b = 10.32, and c = 17.50 Å. Independent reflections (2600) were recorded with Cu Kα radiation by the multiple-film, equiinclination Weissenberg technique and their intensities were estimated visually. Initial phases for the E_{hkl} were obtained by means of a sum of angles formula[5] and were

---

[1] The authors are indebted to Dr. Ruiz-Teran, who identified the botanical material.

[2] H. Budzikiewicz, *Tetrahedron*, **20**, 2267 (1964).

[3] *Cf.* Pachystermine A: T. Kikuchi and S. Ueyo, *Chem. Pharm. Bull.* (Japan), **15**, 549 (1967).

[4] J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

[5] I. L. Karle and J. Karle, *ibid.*, **17**, 835 (1964).