The reduction of chlorides **4** and **5** with tri-*n*-butyltin hydride in the presence of di-*tert*-butyl peroxide produced the *n*-alkylsilanes, *but rearranged silanes were also observed.* Thus, from **4**, phenyldimethyl-*n*-propylsilane (**6**)[1] and the rearranged (γ-phenylpropyl)dimethylsilane (**7**; λ_{neat} 4.74 (Si–H), 8.0 (CH_3–Si–CH_3); $\delta_{CCl_4}^{TMS}$ 3.88 nonet (Si–H), 2.59 t (Ph–CH_2))[8] were formed. Similarly, from **5**, phenyldimethyl-*n*-butylsilane (**8**)[6,9] and the rearranged (δ-phenylbutyl)dimethylsilane (**9**;[6] λ_{neat} 4.75 (Si–H), 8.0 (CH_3–Si–CH_3); $\delta_{CCl_4}^{TMS}$ 3.90 nonet (Si–H), 2.58 t (Ph–CH_2)) were produced. Silaneophyl chloride under the same conditions gave no rearrangement.[10]

Control studies of these reactions indicated that the products were stable under the reaction conditions and that no reaction occurred in the absence of the tin hydride at the concentrations employed.

An increase in rearrangement was observed with dilution of the chlorides **4** and **5**, as shown in Table I.

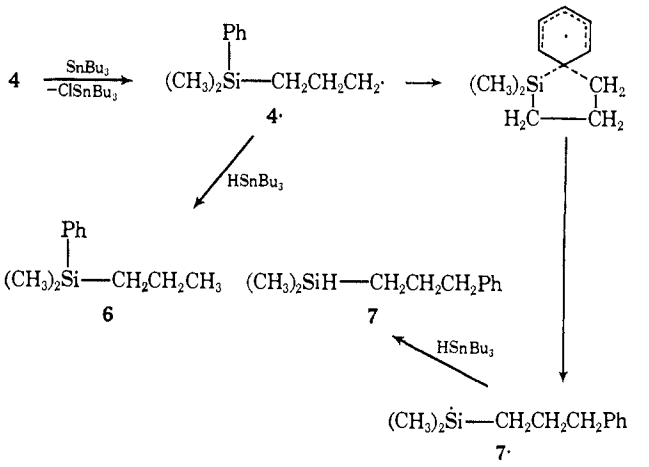
Table I

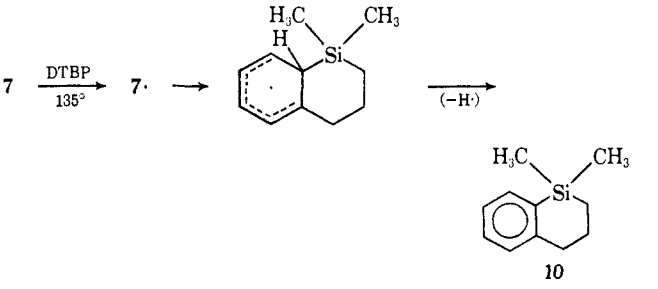
Chloride	M^a	Rearranged product[b]	%[c]
4	1.0	**7**	0
4	0.1	**7**	2.5
4	0.01	**7**	23.5
5	1.0	**9**	0
5	0.1	**9**	4.5
5	0.01	**9**	13.0

[a] The reactions were performed in purified benzene in the presence of di-*tert*-butyl peroxide (DTBP) at 130–135°. The solutions were placed in ampoules and sealed *in vacuo* after three freeze–thaw cycles. The ratio of reactants was **4**(**5**):tri-*n*-butyltin hydride:DTBP = 30:10:3. The reactions were conducted for 15 hr and all the tin hydride was consumed. [b] The reactions were apparently quite clean. The only other products were the unrearranged silanes **6** and **8**, along with tri-*n*-butyltin chloride. [c] Percentage composition as determined by glpc on a polypropylene glycol adipate column at 150°. Duplicate runs indicated a precision of ±3%.

The present data suggest that, unlike their α-silyl counterparts,[1,2] γ- and δ-silyl radicals rearrange with no difficulty. Clearly, neither d_π–p_π back-bonding nor serious steric hindrance to transition state formation is now present, so the disparity between the organic and organosilyl systems, previously so apparent in the α radicals, disappears.[11] A plausible mechanistic scheme involving an Ar_1-5 phenyl shift is illustrated below for chloride **4**. An analogous one involving an Ar_1-6 phenyl shift would apply to **5**.

It should be noted that the reverse rearrangement of radical **7**· to radical **4**· does not occur. Rather, the decomposition of equimolar **7** and di-*tert*-butyl peroxide without solvent takes an Ar_2-6 course and leads to the silatetralin **10** at 135°.[12] No **10** was detected in our study of chloride **4**, nor was a similar ring-closed product found from chloride **5**.[13] In another study, Kumada and coworkers[14] reported the isomerization of **7** to **6** at 370°. If this thermal process involves radical **7**·, then the above change **4**· → **7**· must be reversed under these conditions.





While further study must be done to sort out these differing processes, the present results indicate that organosilyl analogs of carbon neophyl radical rearrangements are not *per se* interdicted. The failures experienced in α-silyl radical investigations may now be more securely blamed upon back-bonding and steric factors.

(8) (a) Silane 7 was identical with a sample prepared by the method of Kumada and coworkers:[5] H. Sakurai, A. Hosami, and M. Kumada, *Tetrahedron Lett.*, 1757 (1969).

(9) The properties of **8** corresponded to those reported by V. D. Tyurin, N. U. Ushakov, S. D. Gubin, and N. S. Nametkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1407 (1968).

(10) This is the third radical process that gave no rearrangement in α-silyl radical species. Earlier studies involved decarbonylation of an aldehyde[1] and decomposition of organometallics in the presence of transition metal ions.[1,2]

(11) Analogous phenyl shifts in organic systems are well known; *cf.* S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(12) See Kumada, *et al.*[5]

(13) In our case 7· is trapped out by the tin hydride. In Kumada's case, 7· would have a longer lifetime (hence it could cyclize) because chain transfer with silane 7 is an identity reaction. Kumada's group looked for the rearrangement to **4**· but did not oberve it from 7·.

(14) H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 521 (1969).

(15) National Science Foundation Trainee, 1968–1970.

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Photolysis of *N*-Alkoxy Quaternary Ammonium Salts. A Potential New Method of Aromatic Methoxylation

Sir:

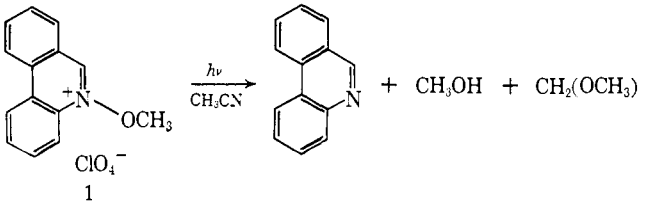
The photochemistry of heterocyclic tertiary amine *N*-oxides has been the subject of extensive investiga-

Table I. Photolysis of *N*-Methoxyphenanthridinium Perchlorate in the Presence of Aromatic Compounds

Aromatic compd	% yield of methoxylation product	Isomer distribution ortho	meta	para	% yield of of $CH_2(OCH_3)_2$	% yield of of CH_3OH
Anisole	21.6	79	Trace	21	17	54
Toluene	4.9	70	13	17	0	72
Benzene	4.4				15	33
Benzonitrile	7.6	73	5	22	15	25

tion.[1] We now wish to report on a new reaction, the photolytic cleavage of *N*-alkoxy quaternary ammonium salts, which may be potentially useful for direct alkoxylation of aromatic substrates.

N-Methoxyphenanthridinium perchlorate (**1**) was prepared by fusion of phenanthridine *N*-oxide with methyl *p*-toluenesulfonate at 100°, followed by conversion of the crude salt to the perchlorate with aqueous sodium perchlorate. Recrystallization from methanol gave the pure salt (71%), mp 179–180°. A 0.125 *M* solution of **1** in acetonitrile was photolyzed for 1 hr in a 1.0-mm quartz cell, using a Rayonet photochemical apparatus fitted with 3500-Å lamps. Analysis of the photolyzed solution revealed the presence of phenanthridine (~80%), methanol, and formaldehyde dimethyl acetal.



1

Photolytic cleavage of the N–O bond in **1** might have occurred homolytically to yield, initially, a methoxy radical and a phenanthridinium cation radical, or heterolytically, with the formation of a methoxy cation and phenanthridine. In an attempt to clarify this point, we investigated the possibility of reaction of a primary photolysis product with an aromatic substrate. Again with acetonitrile as solvent, solutions 0.125 *M* in **1** and 5 *M* in a monosubstituted benzene were photolyzed as described above and the resulting solutions analyzed by glpc. In each case, as summarized in Table I, methoxylation of the aromatic nucleus was observed.

The observed isomer distributions are consistent with the assumption that the active species is a methoxy radical. The results obtained with benzonitrile, where substitution occurred predominantly in the ortho and para positions, are particularly noteworthy; a methoxy cation would be expected to have the characteristics of a powerful electrophile and give rise to predominant meta substitution. Preferential substitution into the ortho and para positions of a benzene carrying an electron-withdrawing group has been demonstrated for methyl,[2] phenyl,[2] and hydroxyl[3] radicals. The observed almost exclusive substitution into the ortho and para positions of anisole (see Table I) is consistent with the assumption that the methoxy radical, like the hydroxyl radical,[3] should be more electrophilic than a methyl or a phenyl radical. Photolysis of **1** in the presence of anisole also gave rise to the formation of some phenol, consistent with the known radical-induced demethylation of ethers.[4]

It is known[5] that photolysis of dimethyl peroxide in the gas phase proceeds *via* methoxy radicals and gives methanol, carbon monoxide, and formaldehyde. Hence it seems probable that, under the reaction conditions employed here, formaldehyde dimethyl acetal results from a secondary reaction of methanol and formaldehyde.

Further evidence in support of a radical mechanism in the photolysis of **1** is found in the examination of products formed when the irradiation is carried out in the presence of toluene. *No* formaldehyde dimethyl acetal is formed, but the yield of methanol increases sharply, presumably as a result of facile hydrogen abstraction from the side-chain methyl group of toluene. The isolation of both bibenzyl and of several methyldiphenylmethanes by preparative glpc strongly supports the intermediacy of benzyl radicals. Photolysis of **1** in acrylonitrile leads to the formation of polyacrylonitrile; acrylonitrile is polymerized by radicals but not by cations.[6]

Direct alkoxylation of aromatic substrates has previously been observed only in the electrolytic methoxylation of toluene, which produced traces of *o*- and *p*-methoxytoluenes *via* the demonstrated intermediacy of methoxy radicals.[7] We are currently examining the photolysis of other *N*-alkoxy quaternary ammonium salts in an attempt to develop a practical aromatic alkoxylation method.

The photolysis of *N*-ethoxyquinolinium perchlorate in methanol has recently been reported to give rise to quinoline, 2-quinolinemethanol, and 4-quinolinemethanol.[8] In the light of our results, a possible course of this reaction is through the photolytic cleavage of the quaternary salt to yield an ethoxy radical. Hydrogen atom abstraction from solvent methanol, followed by

(1) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 70, 231 (1970).
(2) These data are listed in G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.
(3) R. O. C. Norman and G. K. Radda, *Proc. Chem. Soc.*, 138 (1962).
(4) M. S. Kharasch and R. L. Huang in "Vistas in Free-Radical Chemistry," W. A. Waters, Ed., Pergamon Press, London, 1959, pp 131–138.
(5) L. M. Toth and H. S. Johnston, *J. Amer. Chem. Soc.*, 91, 1276 (1969), and references cited therein.
(6) B. Golding, "Polymers and Resins," Van Nostrand, Princeton, N. J., 1959, p 465.
(7) T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka, and S. Tsutsumi, *Kogyo Kagama Zasshi*, 66 (11), 1659 (1963).
(8) M. Hamana and H. Noda, *Chem. Pharm. Bull. (Tokyo)*, 17, (12), 2663 (1969).

reaction of the resulting hydroxymethyl radical could then lead to the observed products.

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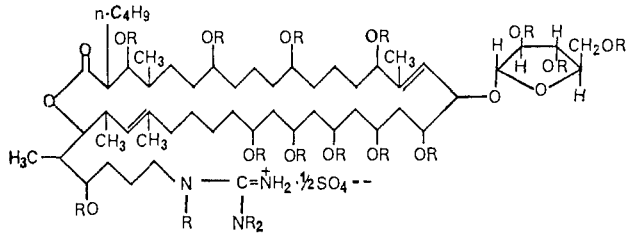
Primycin[1]

Sir:

The antibiotic primycin was first isolated in 1954[2] from cultures of actinomycetes from the intestinal tract of the wax moth. It has activity against gram-positive pathogens and human and bovine *M. tuberculosis*. We have found primycin to consist of a number of closely related structures, and report here the structure of the major constituent.[3]

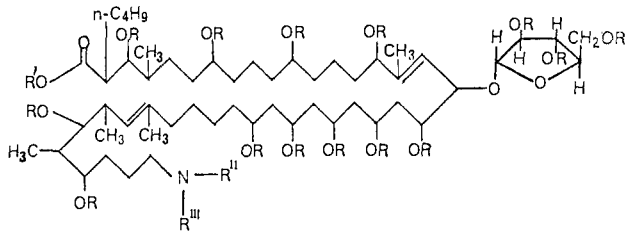
Primycin (**1**, R = H) is a white microcrystalline



1

powder. It is a guanidine sulfate and these two functions are responsible for all the sulfur and nitrogen contained in the molecule.[4] It is unsaturated but shows no evidence of conjugation in the ultraviolet. Mild acid hydrolysis gave D-(−)-arabinose.[5]

Alkaline hydrolysis (5 *N* KOH at 135°) gave the amino acid (**2**, R = R′ = R″ = R‴ = H). The corre-



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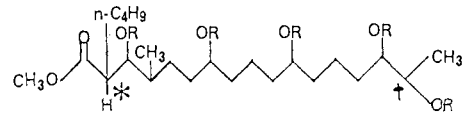
sponding polyether (**2**, R = R′ = R″ = Me; R‴ = Ac), $C_{72}H_{137}NO_{19}$ (mol wt calcd, 1319; found, 1319[6]), was the largest moiety volatile enough for molecular weight determination by mass spectrometry.[7] The spectrum also revealed the presence of much weaker peaks at higher mass which were homologous. The polyacetate (**2**, R = R‴ = Ac; R′ = Me; R″ = H) on ozonolysis followed by sodium borohydride reduction and reacetylation gave secoprimycin A acetate (**3**, R =



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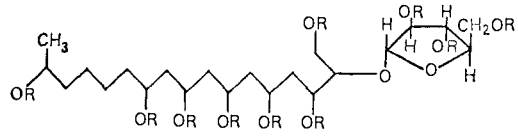
Ac), $C_{21}H_{38}(OAc)_5COOMe$, secoprimycin B acetate (**4**,



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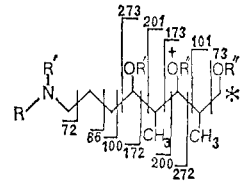
R = Ac), $C_{22}H_{34}O_2(OAc)_{10}$, and secoprimycin C acetate (**5**, R = H; R′ = R″ = Ac), $C_{10}H_{18}(OAc)_3NHAc$.



5

The structure of secoprimycin C acetate (**5**, R = H; R′ = R″ = Ac) could be determined entirely from nmr data since double irradiation revealed the contiguity of all the relevant atoms. Independent, and also complete, structure proof came from the mass spectrometric fragmentation pattern.[8] Some of the primary cleavages are indicated in the formula. Replacement of sodium borohydride by the borodeuteride gave a deuterium at the asterisked carbon. This, therefore, represented the site of attachment of secoprimycin B.

Similar degradation of **1** (R = Me) gave **5** (R = $CONMe_2$; R′ = Me; R″ = Ac). The chemical shift of the methine proton geminal to the methoxyl was readily detected. The hydroxyl group indicated with a dagger, protected from methylation in **1** (R = Me), was that involved, therefore, in lactone formation.

Secoprimycin B acetate (**4**, R = Ac) on hydrolysis gave the free alcohol **4** (R = H), and this on mild acid hydrolysis gave D-(−)-arabinose and the alcohol $C_{17}H_{36}O_8$. The presence of the grouping R–CH(OH)-CH(OH)CH_2OH was shown by periodate oxidation and that of the function $CH_3CH(OH)$– from nmr data. Isolation of the corresponding fragment from permethylated primycin gave, after hydrolysis of the arabinose and periodate oxidation, an aldehyde ($C_{21}H_{42}O_7$). The structure of this substance (**6**, R = Me) followed

(1) The work in London was supported by Grant No. RO1-A106649 from the U. S. National Institute of Allergy and Infectious Diseases and at McMaster by a grant from the National Research Council of Canada.

(2) T. Vályi-Nagy, J. Uri, and I. Szilágyi, *Nature (London)*, 174, 1105 (1954); T. Vályi-Nagy and B. Kelentei, *Arch. Int. Pharmacodyn.*, 124, 466 (1960); J. J. Blum, *Arch. Biochem. Biophys.*, 111, 635 (1965).

(3) In the work described only the most essential data are reported.

(4) Titration with barium perchlorate gave an equivalent weight of 1143 ± 2 (calcd, 1127). The sulfate ion was identified (infrared) as barium sulfate and all the sulfur was removed from the molecule by ion exchange. The base had pK_a = 11.2 (MeOH) and gave ammonia with hot alkali. It gave a positive Sakaguchi test.

(5) Identified as the *p*-nitrophenylhydrazone, by comparison with an authentic specimen.

(6) We are very much indebted to Dr. B. C. Das (Gif-sur-Yvette) for this most valuable determination.

(7) Although our evidence renders it unlikely, it is not absolutely excluded that a small fragment may have been lost in the conversion of **1** to compounds of type **2**.

(8) The masses of the primary fragment ions of the seco compounds were determined by high-resolution mass spectrometry and agreed with the calculated values within acceptable limits.