the monoterpene II labeled at the positions indicated by black dots.

However, our results do support a new hypothesis for the biosynthesis of ajmaline which is also adaptable to all the known indole alkaloids.[11] We suggest that the chain involving carbons 18, 19, 20, 15, 14, and 3 is formed by the linear condensation of three molecules of acetylcoenzyme A, C_{18} being the methyl end of the chain.[12] A one-carbon fragment is attached at C_{20} (a methylene position in the poly-β-ketoacid). At C_{15} condensation occurs with the methylene carbon of a molecule of malonylcoenzyme A. In ajmaline one of the carboxyl groups at C_{16} is lost, but in many other indole alkaloids, *e.g.*, macusine-A,[13] it is retained. We would thus expect the ajmaline derived from acetate-1-C^{14} to be labeled on carbons 3, 15, 17, and 19, indicated by black dots in formula I. Since only a small amount of radioactive ajmaline was at our disposal we were unable to carry out a more extensive degradation to locate the rest of the activity in the alkaloid. Feeding experiments will be carried out with malonic acid-1-C^{14} and larger amounts of acetate-1-C^{14}.

We thank Dr. W. I. Taylor of Ciba for the generous supply of ajmaline.

[11] This hypothesis was independently adumbrated by E. Schittler and W. I. Taylor, *Experientia*, **16**, 244 (1960). A. R. Battersby has also expressed similar ideas in private communications.

[12] It is probable that carboxylation of acetylcoenzyme A to malonylcoenzyme A will occur prior to condensation, *cf.* S. J. Wakil and J. Ganguly, *J. Am. Chem. Soc.*, **81**, 2597 (1960); R. Bentley J. G. Keil and D. S. Bhate, *ibid.*, **83**, 3716 (1961); R. Bentley, and J. G. Keil, *Proc. Chem. Soc.*, 111 (1961); A. J. Birch, A. Cassera, and R. W. Rickards, *Chemistry and Industry*, 792 (1961).

[13] A. T. McPhail, J. M. Robertson, G. A. Sim, A. R. Battersby, H. F. Hodson, and D. A. Yeowell, *Proc. Chem. Soc.*, 223 (1961).

SCHOOL OF CHEMISTRY EDWARD LEETE
UNIVERSITY OF MINNESOTA SHIBNATH GHOSAL
MINNEAPOLIS 14, MINNESOTA PHILIP N. EDWARDS

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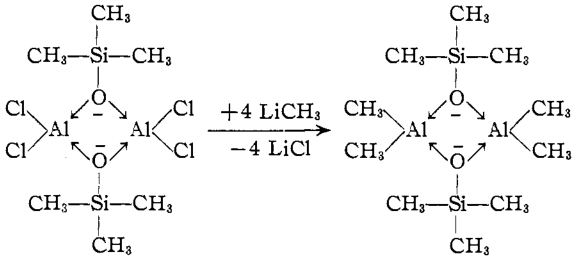
WEAKENING OF $d_\pi p_\pi$–BONDS BY COÖRDINATION

Sir:

In previous papers[1,2,3] we have reported some results of our current investigations on various types of alkyl-hetero-siloxanes containing elements of the IVb and Vb group. This communication now describes the synthesis of pentamethylsiloxalane, the first member of the *homologous* series of alkyl-alumino-siloxanes, and records our conclusions from physical studies on that new compound.

Both procedures for the preparation of aluminosiloxanes described in the literature are not applicable for the synthesis of pentamethylsiloxalane.[4,5] In the reaction of trimethylsiloxy-dichloro-alane (I), $Me_3SiOAlCl_2$,[6] with two moles of methyllithium in diethyl ether at 10°, we have found a simple method of preparation of the desired $Me_3SiOAlMe_2$. If the reaction is carried out in an atmosphere of dry nitrogen good yields of pentamethylsiloxalane (II) are recovered. By repeated vacuum distillation, fractional crystallization and sublimation *in vacuo* the pure compound is obtained in the form of dry, colorless crystals of several cm. length with m.p. +45.5°, which can be distilled without decomposition at b.p. +81.5° (10 mm.). The substance shows excellent solubility in all dry and proton-inactive organic solvents. Chemical analysis and assignment of the infrared spectrum confirm the composition and principles of structure, according to the formula $Me_3SiOAlMe_2$ (II).

Cryoscopic and dipole measurements of benzene solutions of the compounds I and II have shown, however, that both compounds are dimeric and have no dipoles within the experimental error of the apparatus. The dimerization demanded by these experiments takes place with formation of a planar four-membered ring, in which each siloxy-group forms coördinative bonds to two aluminum atoms



The unusual chemical and thermal stability of the inorganic four-membered ring II is evident from the facts that it cannot be split even by the strong donator trimethylamine at 30°, and that the compound can be distilled under ordinary pressure of dry nitrogen at about 200° with only slight decomposition.[7]

N.m.r. spectra[8] of I and II give rise to certain conclusions regarding the types of bondings in these compounds. Solutions of II in CCl_4 showed a spectrum with two singlet peaks, the areas of which are (in agreement with formula II) in the ratio 3:2. Using tetramethylsilane in CCl_4[8] as an external standard the protons of the Me_2Al-group appear at higher fields with a chemical shift of τ = 10.82 p.p.m., suggesting a comparatively high electron-density at these partly negative carbon atoms. The protons of the silyl group, however, are in resonance at lower fields with a chemical shift of τ = 9.80 p.p.m. Compared with hexamethyldisiloxane (chemical shift τ = 9.96 p.p.m., as an additional internal standard of equal concentration) this chemical shift is considerably high.[9]

The unusual small deshielding effect of the protons in the transition $Me_4Si \rightarrow Me_3SiOSiMe_3$ must be ascribed to the strong $d_\pi p_\pi$-bonds in the latter,[9] which increase the electron density at the carbon atoms and are nearly compensating the electron withdrawing effect of the new substituent oxygen.

[1] H. Schmidbaur and M. Schmidt, *Chem. Ber.*, **94**, 1138 (1961).

[2] H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **83**, 2963 (1961).

[3] H. Schmidbaur and M. Schmidt. *Angew. Chem.*, **73**, 655 (1961).

[4] W. A. Kriner, A. G. McDiarmid and E. Ch. Evers, *J. Am. Chem. Soc.*, **80**, 1546 (1958).

[5] H. Jenkner, *Z. f. Naturforschung*, **14b**, 133 (1959).

[6] N. F. Orlow, *Dokl. Akad. Nauk SSSR*, **114**, 1033 (1957); *C. A.*, **52**, 2742 (1958), and A. H. Cowley, F. Fairbrother and N. Scott, *J. Chem. Soc.* (London), 717 (1959).

[7] The analogous compound $[H_3SiOAlMe_2]_2$ slowly decomposes at room temperature, SiH_4 being formed.[4]

[8] Varian Associates 60, 60 Mc.; CCl_4 solutions with concentrations 5 ± 1%.

[9] M. P. Brown and D. E. Webster, *J. Phys. Chem.*, **64**, 698 (1960).

TABLE I

PROTON MAGNETIC RESONANCE SHIELDING VALUES OF Me_4Si, $Me_3SiOSiMe_3$, $Me_3SiOAlMe_2$ AND $Me_3SiOAlCl_2$[a]

	τ (p.p.m.)[b]	τ (p.p.m.)[c]
$(CH_3)_3SiCH_3$	10.00	...
$(CH_3)_3SiOSi(CH_3)_3$	9.96	...
$[(CH_3)_3SiOAl(CH_3)_2]_2$	9.80	10.82
$[(CH_3)_3SiOAlCl_2]_2$	9.54	...

[a] All compounds in CCl_4 soln. with concentrations of 5 ± 1%. [b] Protons of the silyl groups. [c] Protons of the Me_2Al group.

In the aluminosiloxane the formation of $d\pi p\pi$ bonds between silicon and oxygen is restricted by coördination of the oxygen atom to both neighboring aluminum atoms. This coördinative bonding is even stronger in compound I, where the acceptor character of the aluminum atoms is still increased by the negative field effect of the chlorine atoms. This weakening of $d_\pi p_\pi$-bonding by coördination in I results in high deshielding of the silyl-protons with a chemical shift of $\tau = 9.54$ p.p.m. (Table I).

Weakening of $d\pi p\pi$-bonds by coördination, which is evident from n.m.r.-spectra in compounds I and II, is responsible for the comparatively high reactivity of siloxane compounds with a series of Lewis acids. In all these cases the coördination compounds are not stable, however, but decompose spontaneously, following four center processes.[10–16] The authors are indebted to Mr. H. Keller and Mr. H. Lindner for n.m.r. and dipole measurements.

(10) E. Wiberg and U. Krüerke, *Z. f. Naturforschung*, **8b**, 608 (1953).

(11) H. J. Éméléus and M. Onyschuk, *J. Chem. Soc.* [London], 604 (1958).

(12) P. A. McCusker and T. Ostdick, *J. Am. Chem. Soc.*, **80**, 1103 (1958), and **81**, 5550 (1959).

(13) M. Schmidt and H. Schmidbaur, *Chem. Ber.*, **93**, 878 (1960).

(14) H. Schmidbaur and M. Schmidt, *ibid.*, **94**, 1349 (1961), and **94**, 2137 (1961).

(15) J. E. Griffith and M. Onyschuk, *Canad. J. Chem.*, **39**, 339 (1961).

(16) M. Onychuk, *ibid.*, **39**, 808 (1961).

INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT MÜNCHEN
MÜNCHEN 2, MEISERSTR. 1, GERMANY
HUBERT SCHMIDBAUR
MAX SCHMIDT

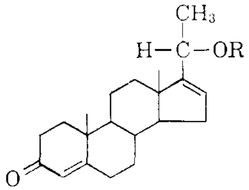
RECEIVED DECEMBER 27, 1961

THE PHOTOLYSIS OF ORGANIC NITRITES. V. INTRAMOLECULAR ALKOXIDE RADICAL ADDITION TO A DOUBLE BOND

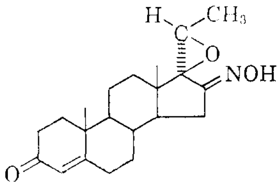
Sir:

Recent work in the photolysis of organic nitrites[1] indicates that all the observed events can be rationalized by postulating the reaction to proceed *via* alkoxide free radicals. The further fate of such fragments has been discussed by Gray and Williams,[2] who detail, as one possible course of action, addition of such an oxide radical to unsaturated compounds, but few instances of this kind actually have been observed. We now wish to report such a case: an intramolecular addition of alkoxide radical to a double bond, the process being effected by nitrite photolysis.

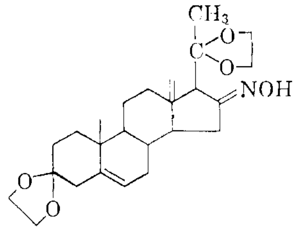
Selective conversion of 16-dehydroprogesterone (I) to the enol ether (II) of the Δ^4-3-ketone moiety,[3] followed by reduction of the C-20 carbonyl and removal of the protecting group, gave 20α-hydroxy-$\Delta^{4,16}$-pregnadien-3-one (III, R = H), m.p. 185–188° (transition at 175°), ϵ_{241}^{max} 15,400, $[\alpha]^{24}D$ + 110.2 ($CHCl_3$); (*anal.* Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.43; H, 9.87). This material also was obtained by a "microbiological Oppenauer"[4] reaction from the known $\Delta^{5,16}$-pregnadiene-3β-20α-diol[5] (IV). Conversion of III (R = H) to its nitrite with nitrosyl chloride in pyridine, then irradiation of III (R = NO) under nitrogen in benzene for a one-hour period, using a 200-watt mercury lamp, gave a more polar product V, m.p. 211–225°, $\epsilon_{239.5}^{max}$ 17,700, $[\alpha]^{22}D$ −42.8 ($CHCl_3$), λ^{Nujol} at 3.09, 6.08 and 6.24 μ (*anal.* Calcd. for $C_{21}H_{29}O_3N$: C, 73.43; H, 8.51, N, 4.08. Found: C, 73.65; H, 8.19; N, 4.00).



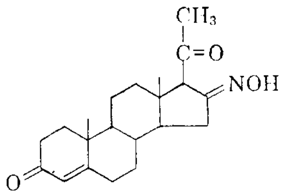
III



V



VII



VI

This material obviously was an oxime (color test, titration data) to which structure V was assigned on the basis of the evidence below. The spectroscopic data indicated survival of the original Δ^4-3-ketone structure, but the relatively negative optical rotation suggested a strong levorotatory influence. The double bond at C-16 was no longer present (disappearance of tetranitromethane test, failure of manganese dioxide to regenerate a Δ^{16}-20-ketone). The compound was devoid of alcoholic hydroxyl: a *monoacetate*, m.p. 173–177°, $\epsilon_{237.5}^{max}$ 18,500 (*anal.* Calcd. for $C_{23}H_{31}O_4N$: C, 71.66; H, 8.11, N, 3.63. Found: C, 71.33; H, 7.94; N, 3.49) had no remaining hydroxyl band, but a characteristic oxime acetate bond in the infrared. Photolysis product V was unstable to acid and base: treatment with aqueous potassium hydroxide and dioxane gave rise to a mixture from which oxime-dione VI, m.p. 244–248°, $\epsilon_{239.5}^{max}$ measd. (*anal.* Calcd. for $C_{21}H_{29}O_3N$: C, 73.43; H, 8.51; N, 4.08. Found: C, 73.35; H, 8.83; N, 3.53) was isolated. Structure of the latter followed from the typical 20-ketone band (5.87 μ) in the infrared, which persisted upon acetylation, the absence of any but oxime hydroxyl, the elementary composition, and an independent synthesis.

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(1) For a review, see A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, in press.

(2) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

(3) A. L. Nussbaum, E. Yuan, D. Dincer and E. P. Oliveto, *J. Org. Chem.*, **26**, 3925 (1961).

(4) A. L. Nussbaum, E. Yuan, E. P. Oliveto, C. Federbush and W. Charney, *Chem. and Ind.*, 836 (1960). We wish to thank Miss Federbush for carrying out this transformation.

(5) E. L. Shapiro, D. Gould and E. B. Hershberg, *J. Amer. Chem. Soc.*, **77**, 2912 (1955).