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.

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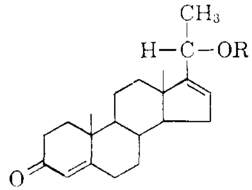
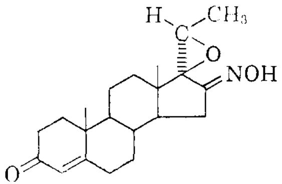
THE PHOTOLYSIS OF ORGANIC NITRITES. V. INTRAMOLECULAR ALKOXIDE RADICAL ADDITION TO A DOUBLE BOND

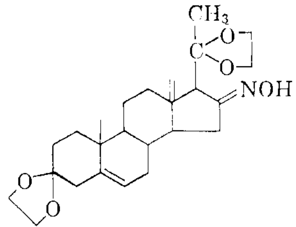
Sir:

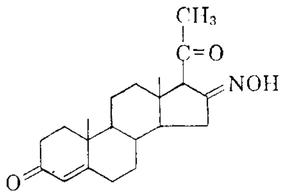
Recent work in the photolysis of organic nitrites[1] indicates that all the observed events can be rationalized by postulating the reaction to proceed *via* alkoxide free radicals. The further fate of such fragments has been discussed by Gray and Williams,[2] who detail, as one possible course of action, 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°), $\epsilon_{241}^{\max}$ 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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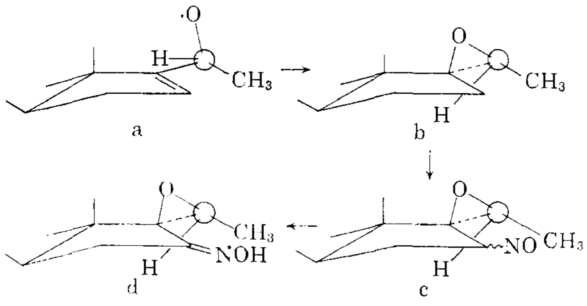
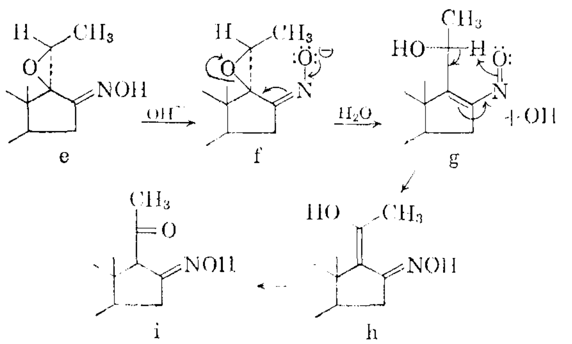
A corresponding bis-ketal (VII) already had been described[6] and we proceeded to synthesize it by a combination of the methods of Julian[7] and Bernstein.[6,8] When this material was subjected to a mild acetic acid ketal cleavage, a spectrum of six paper spots appeared which also could be observed in an identical control experiment with VI. A preparative deketalization of VII then resulted in the actual isolation of VI by absorption chromatography.

We rationalize the photolysis as depicted in (a) to (d): an alkoxide free radical would be expected to have the same conformation during its short life-time as its nitrite precursor. The close proximity of the single electron to the π system of the double bond would make the reaction described probable, and the other π electron would then undergo chain termination with NO.



The alkaline rearrangement of V to VI can be considered to involve the conjugate base (f) of the oxime, which experiences an electron shift involving oxide opening, and cyclic collapse as shown in (g)



On the basis of these considerations, the irradiation product has been assigned structure and stereochemistry as in V. It would be difficult to explain its formation without resorting to an intermediate alkoxide free radical.[9]

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[9] We wish to thank Dr. P. Kabasakalian and his staff for the analytical data.

NEW REAGENT FOR LABELING ORGANIC COMPOUNDS WITH TRITIUM[1]

Sir:

Though numerous forms of acid catalysis are known[2] for promoting hydrogen isotope exchange labeling, evaluation of the powerful acid complex $TH_2PO_4 \cdot BF_3$ for this purpose has revealed significant advantages. Its proficiency for very rapid exchange without side reactions makes it useful both for labeling and fundamental studies of reactivity of various forms of bound hydrogen. $H_3PO_4 \cdot BF_3$ has been used for some time strictly as a catalyst,[3] especially for alkylating aromatics. However, there is apparently no previous description of its utility as a hydrogen isotope exchange reagent when its hydrogen is partially replaced with tritium or deuterium. Because of easier detection, the radioactive tritium was preferred over stable deuterium.

Like the Wilzbach method[4,5,6] of radiation induced self-labeling with tritium, this method also can be applied where radio-chemical synthesis is not possible.

The tritiating reagent is $TH_2PO_4 \cdot BF_3$ nominally, *i.e.*, the tritium–hydrogen ratio is arbitrary. This complex is made very easily by stoichiometric admixture of tritiated water and P_2O_5 and saturation with BF_3 gas. It is a dense liquid that should be stored only in polyethylene containers, though glassware can be used for experiments of less than twenty hours.

Labeling of many organics is effected by simply contacting them with the reagent in a stirred flask at ambient temperature. The exchange mechanism very likely is initiated by transfer of a triton from the acid to the organic molecule. The resultant cation undergoes loss of a proton, yielding the tagged molecule. Hydrocarbons are insoluble in the reagent and are recovered by decantation of liquids or filtering of solids. Organic compounds containing oxygen dissolve but are separated out after tagging by addition of a small amount of water. The exchange reaction is quite rapid and equilibrium distribution of the tritium is effected readily in many cases. It is easy to show, if the tritium atoms are statistically distributed among all exchangeable hydrogen positions including the three of the phosphoric acid complex, that equation 1 applies

$$S_x = \frac{S_r}{3/166 \cdot M/N_H + W_x/W_r} \qquad (1)$$

where S_x is the ultimate specific activity of the tracer, M its molecular weight, and N_H the number of exchangeable hydrogen positions in it. S_r is the original specific activity of the reagent. W_x/W_r is the weight ratio of tracer to reagent. Thus,

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[1] This work was supported in part by the Division of Isotopes Development, U. S. Atomic Energy Commission under Contract No. AT (30–1)–2350.

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