The Structure of *N*-Alkylidine-*N*-phenylnitrones

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WHILST working on the structure of Banfield and Kenyon's radical which has recently been reformulated as a result of *X*-ray analysis,[1] we prepared the compound described at the *N*-butylidenenitrone (I),[2,3] by direct condensation of n-butyraldehyde and *N*-phenylhydroxylamine. The original structure assignment was based on its composition and ready hydrolysis to n-butyraldehyde,[2] but we observed that the mass spectrum indicated a dimeric constitution, $C_{20}H_{26}N_2O_2$ and, further, the i.r. showed a hydroxy-group, ν_{max} 3400 cm.$^{-1}$. Since this function was acetylated to a monoacetyl derivative ν_{max} 1775 cm.$^{-1}$, we inferred the presence of an *N*-disubstituted hydroxylamine residue[4] in the so-called *N*-butylidenenitrone. As the u.v. spectrum was virtually identical to that of the Banfield and Kenyon radical precursor (II; R = OH) it seemed likely that (I) was in fact also an isoxazoline, *i.e.* (III; R = OH), and on this basis the n.m.r. spectrum was readily interpreted. Thus H_A occurred as a doublet δ 5·23 (*J* 5·5 Hz), coupled to a single proton H_B, 154 Hz. upfield,† while H_C was a broad multiplet δ 3·30 the result of splitting by H_B and the adjacent nonequivalent methylene group. Proof of the new carbon–carbon bond of structure (III; R = OH) was obtained by reduction with sodium in liquid ammonia to aniline and the amino-alcohol (IV; $R^1 = R^2 = H$)‡ characterized as monoacetate (IV; R^1 = Ac, R^2 = H), ν_{max} 3300 and 1735, and diacetate (IV; $R^1 = R^2$ = Ac), ν_{max} 1735 and 1650 cm.$^{-1}$. The n.m.r. spectrum of the alcohol showed the primary methylene group as a doublet, δ 3·60

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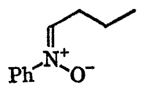
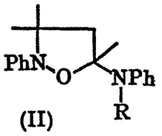
† Spin decoupling carried out at 100 MHz by Dr. D. W. Turner, whom we thank.
‡ Satisfactory analyses have been obtained for all new compounds.

(J 6·0 Hz) shifted downfield in the monoacetate, δ 4·16. The mass spectrum of (IV; $R^1 = R^2 = H$) showed the loss of a propyl group to m/e 178 (V) (amine fragmentation)[5] and sequential loss of formaldehyde to m/e 148 (VI) (McLafferty rearrangement).[6] In keeping with the new formulation as the isoxazolidine (III; R = OH), it was oxidized with silver oxide to an unstable nitroxide (III; R = O) λ_{max} (EtOH) 277, 284, 292, and 302 nm., equivalent to that of the more stable (II; R = O), We suspect that this type of aldol product will be commonly observed in the condensation of *N*-phenylhydroxylamine with carbonyl compounds, the acid-catalysed reversal of which affords ready explanation of the formation of n-butyraldehyde used in the original structure proof.[2]


(I)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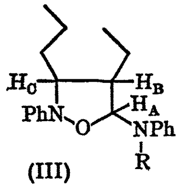
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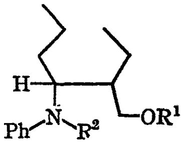
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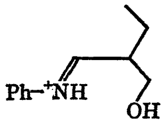
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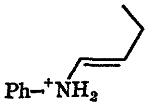
(VI)

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[6] K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, 1962, p. 125.