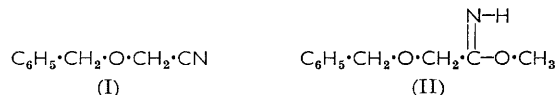# Benzyloxyacetonitrile and Methyl Benzyloxyacetimidate

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In addition to the previously reported benzyloxyacetonitrile, methyl benzyloxyacetimidate has been shown to be a major product in the reaction of benzyl chloride, formaldehyde, and sodium cyanide in methanol. Pyrolytic elimination of methanol from the acetimidate occurs readily to yield the acetonitrile.

STEVENS and his co-workers [1,2] achieved the synthesis of benzyloxyacetonitrile (I) by the reaction of sodium cyanide, formaldehyde, and benzylchloride in methanol; compound (I) was successfully converted into benyloxy-acetophenone by reaction with phenyl magnesium bromide. An acceptable analysis was obtained for the acetonitrile, but, in a repetition of this experiment, Chang and Wu [3] obtained a product which analysed 1% lower for nitrogen, although its b. p. was quite similar to that reported by Stevens.[1]

During the course of a study of the photolysis of alkoxyacetophenones,[4] a sample of benzyloxyaceto-phenone was required and the Stevens preparation of benzyloxyacetonitrile was repeated. The b. p. of the product was similar to those reported [1,3] and the major infrared (i.r.) features were compatible with the assigned structure. However, the appearance of intense absorptions at 3300 (O–H or N–H stretch [5]) and 1650 cm.$^{-1}$ (C=O or C=N stretch [5]) indicated the presence of a second major constituent. This conclusion was substantiated by the proton magnetic resonance (p.m.r.) spectrum of the product, which indicated it to be a mixture of compound (I)

$$C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot CN$$
(I)

$$C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot \overset{\overset{\displaystyle N-H}{\|}}{C} - O \cdot CH_3$$
(II)

and methyl benzyloxyacetimidate (II). Schaefer and Peters [6] have shown that nitriles undergo a reversible, alk-oxide- or cyanide-catalysed alcoholysis to yield imidates. On this basis, the acetonitrile is presumed to be the precursor of the acetimidate. The spectrum showed a broad N–H singlet at $\tau = 2 \cdot 42$, an aromatic singlet at $2 \cdot 83$, four methylene singlets at $5 \cdot 52$ (A), $5 \cdot 58$ (B), $6 \cdot 00$ (C), and $6 \cdot 27$ (D) and a methoxy singlet at $6 \cdot 37$ p.p.m. The relative integrated intensities of peaks C and D, the elemental analysis, and the molecular weight of the mixture indicated it to consist of 46—52% compound (I) and 48—54% compound (II).

Confirmation of these assignments was provided by the following observations. Chromatography of the mixture on silicic acid led to the isolation of pure benzyl-oxyacetonitrile (52%) and methyl benzyloxyacetate (40%); the hydrolysis of acetimidate to acetate would be expected under these conditions.[7] G.l.c. of the mixture led to pyrolytic elimination of methanol from methyl benzyloxyacetimidate; benzyloxyacetonitrile

and methanol were the only products detected. Finally, heating a sample of the mixture to 170° for 4 hr. led to pyrolysis and quantitative conversion of the mixture into the acetonitrile. In view of the pyrolysis results, it is probable that the composition of the initial mixture depends upon the distillation temperature and time employed in isolation.

EXPERIMENTAL

Infrared spectra were determined on a Perkin-Elmer model 21 spectrophotometer calibrated with a polystyrene film; all spectra were recorded as solutions in chloroform and only bands of medium–strong intensity are reported. P.m.r. spectra were determined on carbon tetrachloride solutions using a Varian Associates A-60 spectrometer; internal tetramethylsilane was used as a reference. All signals reported were singlets at 37°.

Formation of Benzyloxyacetonitrile (I) *and Methyl Benzyl-oxyacetimidate* (II).—Sodium cyanide (25 g., 0·51 mole) was added in portions to a cooled solution of 40% form-aldehyde (50 ml., 0·62 mole) in methanol (50 ml.); the rate of addition was adjusted so that the temperature of the mixture remained below 25°. After addition was complete, a solution of 60·5 g. (0·478 mole) of benzyl chloride in 100 ml. of methanol was added; no change in temperature was observed. The mixture was warmed on the steam-bath to 48°. At this point the solution became cloudy, and the reaction mixture was removed from the bath and stirred while a mild exothermic reaction (50°, 0·5 hr.) occurred. When the temperature began to decrease, the mixture was heated under reflux for 5 min., left to cool to room tempera-ture, and diluted with 100 ml. of light petroleum (b. p. 30—60°)–diethyl ether (1 : 1). Water (150 ml.) was added and the organic layer was separated. The aqueous layer was extracted four times with the solvent mixture and the combined organic layers were dried (MgSO₄). After filtration and removal of solvent, the residue was distilled (6 in. Vigreux column) to yield 35·5 g. of crude product, b. p. 78—80°/0·02 mm. A 20 g. forerun and a 14 g. residue were obtained. On cooling, the residue deposited 2 g. of crystalline benzyloxyacetamide, m. p. 88—91° (from water) (lit.,[1] m. p. 89—91°). This compound had also been isolated by Stevens and co-workers [1] in comparable yield. The p.m.r. spectrum consisted of a multiplet at $\tau = 2 \cdot 77$ (–C₆H₅), a broad singlet at 3·30 (–NH₂), and singlets at 5·54 (C₆H₅CH₂–) and 6·23 (–CO–CH₂–) p.p.m.

The crude product was redistilled (12 in. Vigreux column) to give 31·7 g. of a mixture of compounds (I) and (II), b. p. 144—146°/23·0 mm. [lit., b. p. for (I): 140°/20·0 mm.,[1]

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[3] P. Chang and S. L. Wu, *Sci. Sinica*, 1957, **6**, 279 (*Chem. Abs.*, 1957, **52**, 2022).

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[5] C. N. R. Rao, " Chemical Applications of Infrared Spectro-scopy," Academic Press, New York, 1963, pp. 178, 192, 245, 265.
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[7] R. Roger and D. G. Neilson, *Chem. Rev.*, 1961, **61**, 179.

136—137°/14·0 mm.³]. The i.r. spectra of the crude and redistilled products were identical; $\nu_{max.}$ 3300, 2959, 2865, 1667, 1502, 1453, 1397, 1302, 1261—1206, 1193, 1124—1086, 1032, 978, 942, 894, 871—866, 695 cm.$^{-1}$ [Found: C, 69·9, 69·7; H, 6·3, 6·6; N, 8·4, 8·6%; M (vapour pressure osmometer), 166, 160, 159. Calc. for C_9H_9NO (I): C, 73·5; H, 6·2; N, 9·5%; M, 147. $C_{10}H_{13}NO_2$ (III) requires C, 67·0; H, 7·3; N, 7·8%; M, 179. Calc. for 46% (I) + 54% (III): C, 70·0; H, 6·8; N, 8·6%; M, 164].

A portion (1·0 g.) of the mixture was chromatographed on a 6·4 × 2·5 cm. column containing 10 g. of silicic acid. Elution with a 10 : 3 mixture of carbon tetrachloride and methylene chloride (210 ml.) gave 0·52 g. of benzyloxy-acetonitrile (I), $\nu_{max.}$ 3067, 3012, 2899, 2865, 1502, 1458, 1435, 1393, 1353, 1232—1203, 1094, 1031, 902, 884, 697 cm.$^{-1}$

(Found: C, 73·3; H, 6·4; N, 9·8. Calc. for C_9H_9NO: C, 73·5; H, 6·2; N, 9·5%). The p.m.r. spectrum consisted of a multiplet at $\tau = 2·80$ (−C_6H_5) and singlets at 5·50 ($C_6H_5CH_2$−) and 5·98 (−CH_2CN) p.p.m.

Continued elution with the same solvent mixture gave 0·40 g. of methyl benzyloxyacetate, $\nu_{max.}$ 3049, 3003, 2941, 2857, 1751, 1456, 1441, 1285, 1227, 1199, 1117, 1030, 1003, 797—781, 696 cm.$^{-1}$ (Found: C, 66·9; H, 6·9. Calc. for $C_{10}H_{12}O_3$: C, 66·7; H, 6·7). The p.m.r. spectrum consisted of a multplet at $\tau = 2·83$ (−C_6H_5) and singlets at 5·51 ($C_6H_5CH_2$−), 6·08 (−CH_2CO−), and 6·38 (CH_3O−) p.p.m.

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