

Alleged Alkylations of α -Hydroxyimines to Betaines: Revisions of the Structures of Educts and Products

Richard Friary*^a and Gordon W. Kirby^b

^a *Pharmaceutical Research Division, Schering-Plough Corporation, Bloomfield, New Jersey 07003, U.S.A.*

^b *Chemistry Department, The University, Glasgow G12 8QQ, Scotland, U.K.*

According to published spectral data, unnoticed Voigt reactions of acetoin yielded the expected α -(alkylamino)ketones which formed α -(dialkylamino)ketones on alkylation.

Knowledge of the Voigt reaction¹⁻⁵ compels us to criticize a recent communication by Akiyama.⁶ Occurring with rearrangement, the Voigt reaction forms α -aminoketones from amines and α -hydroxyketones.¹⁻⁵ In contrast, however, Akiyama reported that amines condensed with acetoin to give unrearranged α -hydroxyimines (**1a-c**).⁶ Furthermore, alkylations of (**1a-c**) reportedly formed betaines (**2a-f**).⁶

Inspection of published i.r. and u.v. data of Akiyama's products shows the data were misinterpreted. Compound (**1a**) absorbs at ν 1705 cm^{-1} ,⁶ a value inconsistent with that expected for the carbon-nitrogen double bond of an imine.⁷ Compounds (**2a**) and (**2c**) absorb at ν 1705 and 1710 cm^{-1} , and at λ 305 (ϵ 130.5) and 303 nm (ϵ 87.8 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), respectively.⁶ All four values are inconsistent with those expected of iminium salts⁸⁻¹⁰ and hence are not those to be expected of betaine structures (**2**). Measurements of dipole moments, which might have confirmed assignments of structures (**2**), were not reported.⁶

Akiyama's spectral data require revision of his structural assignments. I.r. absorptions of compounds (**1a**), (**2a**), and (**2c**) are those of the carbon-oxygen double bonds of ketones.^{11,12} Moreover, u.v. bands of (**2a-f**) are those of

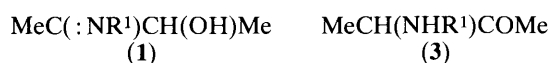
$n \rightarrow \pi^*$ transitions of ketones.¹³ Revised structures of compounds (**1a-c**) are those of α -(alkylamino)ketones (**3a-c**) and are also those of the expected Voigt products. Evidently resulting from alkylations, compounds (**2a-f**) have the α -(dialkylamino)ketone structures (**4a-f**). Revised structures (**4a-f**) account for the acid solubility of the compounds⁶ and for their inability to transfer alkyl groups from nitrogen to oxygen⁶ like 3-oxopyridinium betaines.¹⁴ As a consequence of structural reassignments, the contention that alkyl iodides change α -hydroxyimines to betaines remains unproven.

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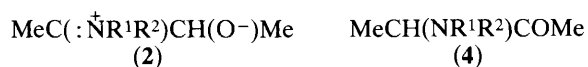
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- a; $\text{R}^1 = \text{Pr}^n$
b; $\text{R}^1 = \text{Pr}^i$
c; $\text{R}^1 = \text{Bu}^t$



- a; $\text{R}^1 = \text{Pr}^n$, $\text{R}^2 = \text{Me}$
b; $\text{R}^1 = \text{Pr}^n$, $\text{R}^2 = \text{Et}$
c; $\text{R}^1 = \text{Pr}^n$, $\text{R}^2 = \text{CH}_2\text{:CHCH}_2$
d; $\text{R}^1 = \text{Pr}^i$, $\text{R}^2 = \text{Me}$
e; $\text{R}^1 = \text{Pr}^i$, $\text{R}^2 = \text{CH}_2\text{:CHCH}_2$
f; $\text{R}^1 = \text{Bu}^t$, $\text{R}^2 = \text{Me}$