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

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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 reaction[1—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 $\mathrm{cm^{-1}}$,[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 $\mathrm{cm^{-1}}$, and at λ 305 (ε 130.5) and 303 nm (ε 87.8 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$), respectively.[6] All four values are inconsistent with those expected of iminium salts[8—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 compounds[6] and for their inability to transfer alkyl groups from nitrogen to oxygen[6] like 3-oxopyridinium betaines.[14] As a consequence of structural reassignments, the contention that alkyl iodides change α-hydroxyimines to betaines remains unproven.

$\mathrm{MeC(:NR^1)CH(OH)Me}$ $\mathrm{MeCH(NHR^1)COMe}$
(**1**) (**3**)
a; $\mathrm{R^1 = Pr^n}$
b; $\mathrm{R^1 = Pr^i}$
c; $\mathrm{R^1 = Bu^t}$

$\mathrm{MeC(:\overset{+}{N}R^1R^2)CH(O^-)Me}$ $\mathrm{MeCH(NR^1R^2)COMe}$
(**2**) (**4**)
a; $\mathrm{R^1 = Pr^n,\ R^2 = Me}$
b; $\mathrm{R^1 = Pr^n,\ R^2 = Et}$
c; $\mathrm{R^1 = Pr^n,\ R^2 = CH_2{:}CHCH_2}$
d; $\mathrm{R^1 = Pr^i,\ R^2 = Me}$
e; $\mathrm{R^1 = Pr^i,\ R^2 = CH_2{:}CHCH_2}$
f; $\mathrm{R^1 = Bu^t,\ R^2 = Me}$

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