Ketimines. VIII. Infrared Spectra of Ketimines

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The literature includes much work on the absorption band due to the =N— group but in most instances this group is part of a ring. Randall[1] has published the spectra of a few oximes, imido ethers, thiazolidines, imidazolines, oxazolones and pyridines. His assignments for the C=N maximum range from 5.89–6.50 μ. In addition to these assigned maxima, Randall obtained the spectra of several guanidines and/or their salts, 1-phenyl-3-methylpyrazolone-5 and creatinine. From his spectra we have made assignments for the C=N ranging from 5.95–6.29 μ (Table I).

Table I

Compound	Wave length in μ for C=N band
Guanidine acetate	6.00
Aminoguanidine bicarbonate	5.95
Aminoguanidine sulfate	6.05
Guanidine carbonate	6.00
Guanidine thiocyanate	6.03
Methylguanidine hydrochloride	6.00
Methylguanidine sulfate	6.08
Triphenylguanidine	6.11
sym-Diphenylguanidine	6.10
1-Phenyl-3-methylpyrazolone-5	6.24
Creatinine	6.29

Lieber, *et al.*,[2] have published the spectra of 38 guanidine derivatives and assigned values from 5.8–6.15 μ for the C=N group.

In connection with a long range program of preparation and characterization of ketimines in this Laboratory it was desired to establish whether the imino group in these compounds showed characteristic absorption in the range obtained for the compounds investigated by other authors. During this study Fuson[3] published the absorption maxima for N-benzoylduryl phenyl ketimine (6.14 μ), N-methylduryl phenyl ketimine methiodide (6.14 μ) and N-methylduryl *p*-*t*-butylphenyl ketimine (6.11 μ).

A secondary aim of this investigation was to check the possibility of an ene–amine tautomerism in compounds containing hydrogen alpha to the imino group. This tautomeric equilibrium has been hypothesized by Moureau and Mignonac[4] and Weissberger and Glass[5] to explain certain reaction products of imines. In none of our spectra was there evidence of the band due to the olefinic linkage. However, the location of the imine maximum is found so near that expected for the olefin that, due to the probability of overlapping, no conclusion could be drawn as to eneaminization. Imines and the corresponding ketones are given in Table II.

Table II

Ketimine	=N—H	C=N	C=O in corresponding ketone
Bis-(*p*-chlorophenyl)	3.08	6.05	5.82
ω-Cyclohexylethyl *s*-butyl	3.09	6.09	..
ω-Cyclohexylamyl *s*-butyl	3.09	6.09	5.83
Diphenyl	3.09	6.24	..
o-Tolyl *s*-butyl	3.09	6.14	5.92
Phenyl *t*-butyl	3.10	6.18	..
o-Tolyl *i*-amyl	3.10	6.13	5.92
o-Tolyl *n*-propyl	3.10	6.14	5.93
Ethyl *n*-butyl	3.10	6.08	5.83
Di-*n*-propyl	3.10	6.08	..
ω-Cyclohexylpropyl *s*-butyl	3.10	6.10	..
α-Naphthyl phenyl	3.10	6.24	6.02
o-Tolyl ethyl	3.12	6.13	5.91
o-Tolyl *n*-butyl	3.12	6.14	5.92
o-Tolyl *i*-butyl	3.12	6.15	5.93

Five dialkyl ketimines were studied, showing strong bands assigned to the imino group in the region from 6.08–6.10 μ. Also, the N–H band occurred from 3.09 to 3.12 μ. One aryl alkyl ketimine, in which the alkyl group was tertiary, absorbed at 6.18 μ.

It is possible that this value might be more nearly that of the imine band and the lower values of 6.13–6.14 due to overlap with the olefin band from the eneamine form—the latter form being impossible with the tertiary group. However, the band assigned to the imine group is, in every case, quite sharp and shows no indication of being a doublet.

As was expected, the increase of wave length of absorption when the imine group is conjugated with a single aromatic nucleus, was greatly enhanced in diaryl ketimines. Diphenyl ketimine and α-naphthyl phenyl ketimine show strong bands at 6.24 μ. It was also expected that the presence on the aromatic nucleus of a "deactivating" group, such as the halogen, would decrease the extent of conjugation, and that absorption would occur at a shorter wave length than in other aryl ketimines. Bis-(*p*-chlorophenyl) ketimine absorbed at 6.05 μ.

All spectra were obtained with the Perkin–Elmer Model 12C, single beam instrument with NaCl optics, using NaCl cells. The compounds used were prepared in this Laboratory as reported in previous papers in this series.[6]

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[1] H. Randall, *et al.*, "Infrared Determination of Organic Structures," D. Van Nostrand, Inc., New York, N. Y., 1949.

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[5] A. Weissberger and D. Glass, This Journal, **64**, 1724 (1942).

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Steroids. LVIII.[1] Synthesis of Allopregnane-3β,6β,21-triol-20-one Triacetate

By J. Romo, G. Rosenkranz and F. Sondheimer

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For certain biological studies we required the triacetate V of allopregnane-3β,6β,21-triol-20-one, an isomer of Reichstein's substance R with the 11β-hydroxy group transposed to C-6. The Δ^4-unsaturated compound corresponding to V has been described,[2] but its hydrogenation does not

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[1] Paper LVII, G. Rosenkranz, M. Velasco and F. Sondheimer, This Journal, **76**, 5024 (1954).

[2] O. Mancera, G. Rosenkranz and C. Djerassi, *J. Org. Chem.*, **16**, 192 (1951).