Homoconjugation in *N*-Alkylketimines

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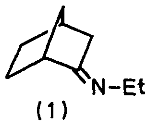
Summary U.v. spectral data indicate that homoconjugation in ketimines may occur when there are π-orbitals β to the carbon or the nitrogen atom of the C=N bond.

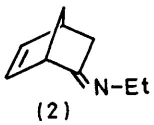
THE concept of homoconjugation has been used to account for the marked stability and solvolysis products of various non-classical carbonium ions,[1] and also for certain photochemical,[2] ultraviolet,[3] optical rotatory,[4] and photoelectron spectral[5] effects in molecules. It is expected that similar effects would be observed for β,γ-unsaturated ketimines. This research was undertaken to test this expectation and to determine whether or not homoconjugation can occur from either side of the C=N bond.

The u.v. spectral constants for (1) and (2) (Table 1) provide evidence for homoconjugation in (2). Thus, the C=N $n \rightarrow \pi^*$ band of (2) (λ_m), recognized by the blue-shift when in a more polar solvent, is more than twice as intense as that of (1). The $\pi \rightarrow \pi^*$ band (λ_m') undergoes an even greater enhancement. These spectral changes are an excited-state effect, as confirmed by the two compounds having similar i.r. C=N stretching frequencies, an electronic ground-state property.

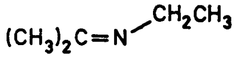
Some alicyclic ketimines were studied too. Comparison of the $\pi \rightarrow \pi^*$ band intensities for compounds (7) and (8) (Table 2) reveals that homoconjugation can occur also in a β-phenylketimine system. Although a small homoconjugation takes place between the C=N group and a vinyl group β to the nitrogen atom, [compound (3) as compared with (4), and (5) as compared with (6)], none occurs with a phenyl group β to the nitrogen [compound (10) as compared with (11)]. The combined effects of homoconjugation on both sides of the C=N bond [compound (9)] increases still more the intensity enhancement of the $\pi \rightarrow \pi^*$ band [compounds (7) and (8) as compared with (9)]. Again, it is to be noted that the C=N i.r. bands of the nonconjugated [(3), (5), and



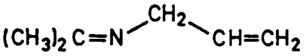
(1)



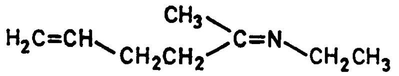
(2)


$(CH_3)_2C{=}N{-}CH_2CH_3$

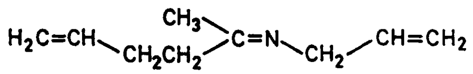
(3)


$(CH_3)_2C{=}N{-}CH_2{-}CH{=}CH_2$

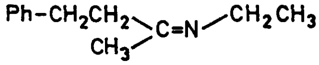
(4)


$H_2C{=}CH{-}CH_2CH_2(CH_3)C{=}N{-}CH_2CH_3$

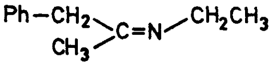
(5)


$H_2C{=}CH{-}CH_2CH_2(CH_3)C{=}N{-}CH_2{-}CH{=}CH_2$

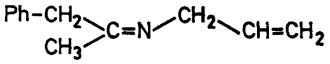
(6)


$Ph{-}CH_2CH_2(CH_3)C{=}N{-}CH_2CH_3$

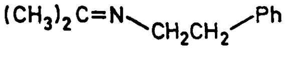
(7)


$Ph{-}CH_2(CH_3)C{=}N{-}CH_2CH_3$

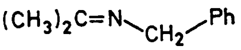
(8)


$Ph{-}CH_2(CH_3)C{=}N{-}CH_2{-}CH{=}CH_2$

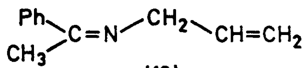
(9)


$(CH_3)_2C{=}N{-}CH_2CH_2{-}Ph$

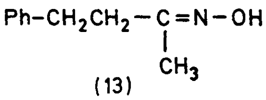
(10)


$(CH_3)_2C{=}N{-}CH_2{-}Ph$

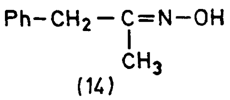
(11)


$Ph(CH_3)C{=}N{-}CH_2{-}CH{=}CH_2$

(12)


$Ph{-}CH_2CH_2{-}C(CH_3){=}N{-}OH$

(13)


$Ph{-}CH_2{-}C(CH_3){=}N{-}OH$

(14)

TABLE 1.

U.v. and i.r. spectral data for bicyclo ketimines

	Iso-octane Solvent				Methanol Solvent				I.r.
Compound	λ_m (nm)	ϵ	λ'_m (nm)	ϵ'	λ_m (nm)	ϵ	λ'_m (nm)	ϵ'	ν (cm^{-1})
(1)	209	127	249	200	210	105	235·5	240	1685
(2)	214	1695	249·5	495	215	1515	241·5	810	1685

TABLE 2.

U.v. and i.r. spectral data for some ketimines

	Hydrocarbon Solvent				Methanol Solvent				I.r.	
Compound	λ_m (nm)	ϵ	λ'_m (nm)	ϵ'	λ_m (nm)	ϵ	λ'_m (nm)	ϵ'	$\nu_{C=N}$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})
(3)	248	205			233	198			1666	
(4)	235	353			233	370			1668	1644
(5)	245	101			236	146			1663	1641
(6)	238	190			236	221	212	138	1655	1640
(7)	259·5	219	221	467	258·5	204	222	248	1655	
(8)	255	1240	219	3660			220	2840	1650	
(9)	260	1510	219	5450	260	671	219	3950	1660	1643
(10)			218	2460			219	1560	1663	
(11)			220	2070			219	1720	1664	
(12)	241	12,980			238				1634	1645
(13)	295·5	185	224	224	260	185	227	227	1655	
(14)	260	255	225	577	259	243	225·5	617	1660	

(7)] and homoconjugated ketimines [(4), (6), (8), and (9)] have approximately the same frequencies. In contrast, the frequency is substantially lower for the classically conjugated ketimine (12).

The presence of an OH group on the imino nitrogen atom, as in an oxime, reduces but does not eliminate the effect of homoconjugation. For instance, the $n \rightarrow \pi^*$ band of oxime (14) (λ'_m *ca.* 225 nm) is three times more intense than that of (13).

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[4] H. T. Thomas and K. Mislow, *J. Amer. Chem. Soc.*, 1970, **92**, 6292. D. A. Lightner and W. A. Beavers, *ibid.*, 1971, **93**, 2677.

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