REARRANGEMENTS OF BENZIMINAZOLE *N*-OXIDE: THE STRUCTURE OF DIACYLBENZIMINAZOLONES*

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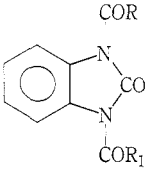
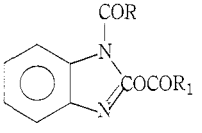
The rearrangement of benziminazole *N*-oxide with cold and with hot acetic anhydride to give *N*-acetylbenziminazolone and a diacetylbenziminazolone respectively was discussed in a previous communication.[1] The structures of the latter compound and of the related dipropionyl-, dibenzoyl-, and acetylbenzoylbenziminazolones were uncertain at that time, since two kinds of structure are possible for a diacylbenziminazolone: (I), an *NN'*-diacyl structure or (II), an *ON*-diacyl structure (1-acyl-2-acyloxybenziminazole).



(I) *NN'*-Diacylbenziminazolone



(II) 1-Acyl-2-acyloxybenziminazole

(Ia; R = R_1 = CH_3)

(Ib; R = R_1 = C_2H_5)

(Ic; R = R_1 = C_6H_5)

(Id; R = CH_3, R_1 = C_6H_5)

Evidence is now reported which shows these compounds to be *NN'*-diacylbenziminazolones.

Experimental

Diacetyl-, dipropionyl-, dibenzoyl-, and acetylbenzoylbenziminazolones were prepared as described previously.[1] Reference compounds were either prepared by standard methods or obtained from commercial sources; all compounds were purified by recrystallization until melting point determination, elementary analysis, and infrared analysis showed them to be sufficiently pure.

Infrared spectra were determined on a Perkin–Elmer 137 Infracord and on a Beckman IR7 spectrometer using 0·5 mm NaCl cells. Frequency measurements are believed to be accurate to within ± 1 cm^{-1}. The spectra were determined in a saturated solution of carbon tetrachloride.

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[1] Kew, D. J., and Nelson, P. F. (1962).—*Aust. J. Chem.* **15**: 792.

Ultraviolet absorption spectra were determined in 1 cm cells using a Unicam SP500 and a Beckman DK2 spectrophotometer. For each compound at least two independent sets of observations were made. The precision of $\lambda_{max.}$ values is estimated to be ± 1 mμ and the precision of $\epsilon_{max.}$ values $\pm 5\%$ or better; values were reproducible for most compounds to $\pm 2\%$.

TABLE 1

MAIN ULTRAVIOLET ABSORPTION MAXIMA OF COMPOUNDS (I), AND OF SUITABLE REFERENCE COMPOUNDS, IN VARIOUS SOLVENTS

Compound	Solvent	*B*-Band* (mμ)		*C*-Band* (mμ)	
		$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
(Ia)	Ethanol	236	11,700	*c. 265* 272·5 280·5	*2300* 2100 1750
(Ib)	Ethanol	235·5	11,700	*c. 266* 272·5 280·5	*2200* 2100 1800
(Ib)	Cyclohexane	233·5	12,000	*c. 265* 272·5 280	*2150* 2050 1850
(Ib)	Diethyl ether	232	11,700	*c. 266* 272·5 280	*2000* 2100 1850
(Ic)	Ethanol	224 241	24,000 23,000	*c. 274* *c. 281*	*11,000* *9500*
(Id)	Ethanol	246	17,500	*c. 280* *c. 290*	*5000* *3500*
N-Acetylbenziminazole-thione (III)	Cyclohexane	234·5	9000	272·5 280	1600 1450
Acetanilide	Ethanol	242	14,500	*c. 274* 280	*825* 500
Acetanilide	0·1N aqueous HCl	239	10,000	*c. 278*	*325*
NN'-Diacetyl-*o*-phenylene-diamine	Ethanol	*c. 243*	*12,000*	*c. 280*	*900*
Benziminazole	Ethanol	243 *c. 250*	6100 *5500*	*c. 265* 272 278	*4000* 5700 5800
2-Methylbenziminazole (IV)	Ethanol	242 *c. 248*	7000 *6500*	*c. 269* 273 280	*5000* 6800 7500
2-Phenylbenziminazole[3]	Ethanol	242	12,000	302 *313*	24,000 *14,200*
2-Phenylbenziminazole[3]	0·1N EtOH HCl	244	15,500	300	21,500
2-Phenylbenziminazole[3]	0·1N EtOH NaOH	228 251	18,500 11,000	311	22,500
2-(α-Hydroxycyclohexyl methyl) benziminazole[4]	75% Ethanol	245	6600	274 281	7650 7900

* For band nomenclature used, see Forbes and Shilton.[2]

[2] Forbes, W. F., and Shilton, R. (1959).—Symposium on spectroscopy. A.S.T.M. Spec. Tech. Publ. No. 269, p. 176.

[3] Cooper, F. C., Forbes, W. F., and Partridge, M. W., unpublished data.

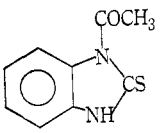
[4] Wagner, A. F., Wittreich, P. E., Lusi, A., and Folkers, K. (1962).—*J. Org. Chem.* **27**: 3236.

Solvents used were spectroanalysed carbon tetrachloride (Fisher) or other commercially available spectroanalysed solvents.

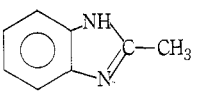
Discussion

(*a*) *Infrared Data.*—The carbonyl band data fit in well with the postulated structures (Ia)–(Id).

Compounds with an aliphatic acyl group (Ia, Ib, and Id) all gave a band at 1730 ± 1 cm^{-1} (cf. Jones and Sandorfy[5] and the carbonyl band of (III) at *c.* 1730 cm^{-1}) while compound (Ic), containing an aromatic acyl group, afforded a band at 1705 cm^{-1}. Only compound (Id) containing both groups, afforded both bands, at 1729 and 1706·5 cm^{-1}. In addition, all compounds gave a band at 1761–1771·5 cm^{-1} ((Ia), 1768·5 cm^{-1}; (Ib), 1761 cm^{-1}; (Ic), 1768·5 cm^{-1}; and (Id), 1771·5 cm^{-1}) which can best be explained by structure (I) (cf. Jones and Sandorfy[5]).



(III) *N*-Acetylbenziminazolethione



(IV) 2-Methylbenziminazole

(*b*) *Ultraviolet Data.*—The data in Table 1 show that compounds (I) have approximately similar ultraviolet spectra to those of *N*-acetylbenziminazolethione (III), acetanilide, and *NN'*-diacetyl-*o*-phenylenediamine, particularly in the sense that the intensities of the *B*-bands are considerably greater than those of the corresponding *C*-bands. All these compounds contain the chromophoric system Ph–N(COR)– and an absorption pattern of this type may therefore be associated with this particular chromophoric system. On the other hand, benziminazole, 2-methyl-(IV) or 2-phenylbenziminazole—compounds which contain the chromophoric system Ph–N = CH in a bicyclic system—show *B*- and *C*-bands of comparable intensity. Hence the ultraviolet spectral data confirm that compounds (I) in fact possess the structures assigned to them on the basis of the infrared data.

The authors are indebted to Miss V. R. Jellett, Mrs. Carole T. Schmidt, and Miss M. A. Shadbolt for the careful determination of the ultraviolet spectra.

[5] Jones, R. N., and Sandorfy, C. (1956).—"Technique of Organic Chemistry." (Ed. A. Weissberger.) Vol. 9. p. 247. (Interscience: New York.)