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N - ACYL BENZALDIMINES

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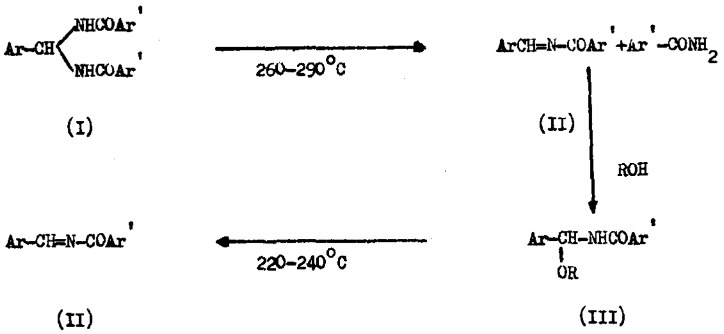
Thermal decomposition of alkylidenebisamides led to the formation of enamides(1). In a parallel study the pyrolysis of arylidenebisamides(2) (I) was examined, as these, not having hydrogens β to the amide group, could not form enamides. It was found that all the benzylidenebisbenzamides (I) decomposed on heating, giving benzamides and N-benzoylbenzaldimines (II). The N-acyl imines were very reactive, as had been found with the N-acyl benzophenone(3,4) trifluoroacetaldehyde, and chloral imines(5). This made their separation from the starting material (I) and benzamide difficult, but reaction with methanol(3) gave crystalline adducts (III; $R=CH_3$) which were more stable and were easily separated and purified (Table I).

The reaction, if care is taken to exclude moisture, is smooth, giving clean products in good yields. For example the sequence: Ia $\longrightarrow$ IIa $\longrightarrow$ IIIa, ($R=CH_3$), pyrolysis at 260°C/25mm, sublimation of products followed by reaction with methanol, chromatography over neutral Al_2O_3 deactivated by 15% methanol, and crystallization gave 85% yield of pure material. Similar results were obtained with the substituted bisamides (I, b-f) but lower pressures (0.3mm) were necessary to complete sublimation of the imines (II,b-f).



	Ar	**Ar'**
a)	C_6H_5	C_6H_5
b)	$4\text{-}C_6H_5CH_2O\text{-}C_6H_4$	C_6H_5
c)	$4\text{-}CH_3O\text{-}C_6H_4$	C_6H_5
d)	$4\text{-}O_2N\text{-}C_6H_4$	C_6H_5
e)	C_6H_5	$4\text{-}CH_3O\text{-}C_6H_4$
f)	C_6H_5	$4\text{-}O_2N\text{-}C_6H_4$

As the addition of methanol (II $\longrightarrow$ III; $R=CH_3$) is reversible by heating(3) the imines (II,a-f) were stored as their methanol adducts (III, a-f; $R=CH_3$) from which they were recovered when needed, by heating above their melting point under vacuum.

The reactivity of the N-acyl imine system towards nucleophiles possessing an active hydrogen or its equivalent, e.g. alcohols, amines(3,5) and Grignard reagents(4) has been demonstrated. Accordingly N-benzoylbenzaldimine (II a) reacted with alcohols: primary (III a, $R=CH_3$; m.p. 102-104°C), secondary (III a, R=i-Pr; m.p. 117-118°C) and tertiary (III a, R=t-Bu; m.p. 140-143°C). The <u>tert</u>. butanol adduct was not stable, and was characterized by infrared and NMR spectra alone. Similarly, a 1:1 adduct was formed with piperidine (m.p. 142.5-143.5°C). Water hydrolysed the imine (II a) to benzaldehyde and benzamide, and addition of benzamide to the imine (II a) required acid catalysis (BF_3) to re-form the original bisamide (I a). Sodium borohydride reduction of the imine

TABLE I

$Ar-CH(OCH_3)-NH-CO-Ar'$ (III)

Compound	Yield(%)	m.p.(°C)	Infrared^a	NMR $-CH(OCH_3)-$(τ)	
			$\nu_{C=O}$ (cm^{-1})	δ_{CH} (d)^b	δ_{OCH_3}(s)
IIIa	85	102-104	1675	3.78	6.61
IIIb	56	141-143	1670	3.68	6.48
IIIc	79	117-118	1670	3.71	6.53
IIId	75	142-143	1674	3.50	6.47
IIIe	76	97-99	1668	3.67	6.50
IIIf	65	146-149	1680	3.70	6.50

a) In the infrared (III a-f) all showed absorption at 3440 and 1510 cm^{-1} (NH). Spectra were taken in $CHCl_3$.

b) In the NMR the -CH- appeared as an unequal doublet, J=9-9.5 c.p.s. Spectra taken in $CDCl_3$ with TMS as internal standard.

TABLE II

$Ar-CH=N-CO-Ar'$ (II)

Compound	Infrared^a $\nu_{C=O}$ (cm^{-1})	NMR^b $\delta_{-CH=N-}$ (τ)
IIa	1679	1.27
IIb	1675	1.25
IIc	1675	1.24
IId	1689	1.16
IIe	1679	1.23
IIf	1686	1.13

a) In CCl_4

b) In $CDCl_3$ with TMS as internal standard.

(IIa) in dioxan yielded N-benzyl-benzamide and reaction with an excess of methyl magnesium iodide gave N-benzoyl-α-phenylethylamine as the sole product in 85% yield.

The infrared spectra of the N-acyl imines showed carbonyl absorption in the region 1675 - 1690 cm^{-1} (Table II), the exact position varying somewhat according to the substituents on the aromatic groups. None of the compounds absorbed in the NH region. In the ultraviolet the unsubstituted compound (II a) absorbed at 268 mμ (log ϵ : 4.25). In the NMR, apart from the aromatic absorption (1.6 - 3 τ) only one sharp singlet appeared in the region 1.1 - 1.3 τ, the exact position of which varied with the substituents (Table II).

Satisfactory elemental analyses, infrared and NMR spectra have been obtained for all the new compounds mentioned above, unless specified otherwise.

REFERENCES

1) D. Ben-Ishai and R. Giger, Tetrahedron Letters, (1965) , 4523.

2) H.E. Zaugg and W.B. Martin, Org. Reactions, 14, 52, (1965).

3) J.E. Banfield, G.M. Brown, F.H. Davey, W. Davies and T.H. Ramsey, Austral. J. Sci. Research, A1, 330, (1948).

4) K. Ivanov, Doklady Akad. Nauk. S.S.S.R., 109, 537, (1956). C.A., 51, 4997, (1957).

5) F. Weygand, W. Steglich, I. Lengyel, F. Fraunberger, A. Maierhofer and W. Oettmeier, Chem. Ber., 99, 1944, (1966).