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N-BENZOYLBENZALDIMINES AND N-α-ALKOXYBENZYLBENZAMIDES[1]

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Abstract—Thermal decomposition of benzylidenebisbenzamide (I) afforded N-benzoylbenzaldimines (II). Some of the chemical and spectroscopic properties of the aldimides and their methanol addition products (IV) are described.

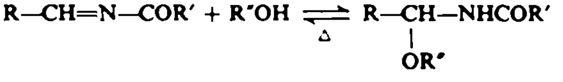
IN AN earlier communication[2] the pyrolysis of alkylidenebisamides formed from aldehydes containing an α hydrogen was reported, these gave enamides and the corresponding amide:

$$R_2CHCH(NHCOR')_2 \xrightarrow{\Delta} R_2C{=}CH{-}NHCOR + R'CONH_2$$

In a parallel study the pyrolysis of arylidenebisamides[3] was examined, as these, not having β hydrogens could not form enamides. When benzylidenebisbenzamides (I) were heated above their m.p. (250–280°) in a sublimation apparatus a decomposition took place forming N-benzoylbenzaldimines (II) and benzamides (Eq. 1):

$$\underset{\text{I}}{R{-}CH(NHCOR')_2} \overset{\Delta}{\rightleftharpoons} \underset{\text{II}}{R{-}CH{=}N{-}CO{-}R'} + \underset{\text{III}}{R'CONH_2} \qquad (1)$$

From the sublimate, the acylimine II (R, R′ = aryl) could be isolated through its greater solubility in nonpolar solvents than either the starting material I (R, R′ = aryl) or the primary amide III (R′ = aryl), or more conveniently, through the addition products with methanol[4,5] (Table 2) as in Eq. 2:



$$\underset{\text{II}}{R{-}CH{=}N{-}COR'} + R''OH \underset{\Delta}{\rightleftharpoons} \underset{\text{IV}}{R{-}\underset{\displaystyle OR''}{\underset{|}{CH}}{-}NHCOR'} \qquad (2)$$

The benzylidenebisbenzamides used in the pyrolyses were prepared (Table 1) by reacting the corresponding aldehydes with two equivalents of the benzamides in the presence of a sulfonic acid catalyst in benzene.[6,7] The water formed was removed by

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[1] Part of this work was reported in a preliminary communication: S. W. Breuer, T. Bernath and D. Ben-Ishai, *Tetrahedron Letters* 4569 (1966).

[2] D. Ben-Ishai and R. Giger, *Tetrahedron Letters* 4523 (1966).

[3] H. E. Zuagg and W. B. Martin, *Org. Reactions* Vol. 14; p. 52 (1965).

[4] J. E. Banfield, G. M. Brown, F. H. Davey, W. Davies and T. H. Ramsey, *Austral. J. Sci. Research* AI, 330 (1948).

[5] Y. Heng Suen, Alian Horeau and H. B. Kagan, *Bull. Soc. Chim. Fr*, 5, 1454 (1965).

[6] M. C. Paulson and J. M. Mersereau, *Trans. Illinois State Acad. Sci.* 47, 94 (1955); *Chem. Abstr.* 50, 233 (1956).

[7] U. Zehavi and D. Ben-Ishai, *J. Org. Chem.* 26, 1097 (1961).

TABLE 1. $RCH(NHCOR')_2$

R	R′	Yield (%)	Melting Point	Formula	Calc			Found		
					C	H	N	C	H	N
Ph	Ph	60	232 233[a]							
4-NO_2—C_6H_4	Ph	82	268 269[b]							
4-MeO—C_6H_4	Ph	65	234–236[c]							
4-Cl—C_6H_4	Ph	65	260–261	$C_{21}H_{17}N_2O_2Cl$	69·13	4·70	7·68	69·09	4·88	8·13
4-$PhCH_2$ -O—C_6H_4	Ph	56	229–231	$C_{28}H_{24}N_2O_3$	77·04	5·54	6·42	77·05	5·55	6·54
Ph	4-$NO_2C_6H_4$	59	249-251	$C_{21}H_{16}N_4O_6$	60·00	3·84	13·33	60·23	3·88	13·60
Ph	4-MeO -C_6H_4	66	229-231	$C_{23}H_{22}N_2O_4$	70·75	5·68	7·18	71·09	5·94	6·92
2-$PhCH_2$—O—C_6H_4	Ph	51	218 219	$C_{28}H_{24}N_2O_3$	77·04	5·54	6·42	76·95	5·41	6·48
2-OH -C_6H_4	Ph	[d]	193–195	$C_{21}H_{18}N_2O_3$	72·82	5·24	8·09	72·91	5·21	8·56

[a] E. Roth, *Liebigs Ann.* **154**, 72 (1870).

[b] R. K. Mehra and K. C. Pandya, *Proc. Ind. Acad. Sci.* **10**, 285 (1939).

[c] P. I. Ittyerah and K. C. Pandya, *Proc. Ind. Acad. Sci.* **15**, 258 (1942).

[d] Prepared by catalytic hydrogenolysis (Pd/C in DMF) from the corresponding benzyloxybisbenzamide.

In the IR, all bisamides had absorption at 3280 cm^{-1} (NH) and 1640 1660 cm^{-1} (CO). All spectra were measured as KBr discs.

TABLE 2. R—CH—NHCOR′ (with OR″ on CH)

$$\mathrm{R{-}\underset{\displaystyle OR''}{\underset{|}{CH}}{-}NHCOR'}$$

R	R′	R″	Yield	M.p.	Formula	Calc C	Calc H	Calc N	Found C	Found H	Found N
Ph	Ph	Me	85	102-104	$C_{15}H_{15}NO_2$	74·66	6·27	5·81	74·36	6·20	6·11
Ph	Ph	Me_2CH	55	117–118	$C_{17}H_{19}NO_2$	75·81	7·11	5·20	76·16	7·00	5·57
4-NO_2 C_6H_4	Ph	Me	75	142–143	$C_{15}H_{14}N_2O_4$	62·93	4·93	9·79	63·14	4·89	9·74
4-Cl-C_6H_4	Ph	Me	74	128–130	$C_{15}H_{14}NO_2Cl$	65·33	5·12	5·08	65·22	5·21	5·18
4-MeO-C_6H_4	Ph	Me	79	115–116	$C_{16}H_{17}NO_3$	70·83	6·32	5·16	70·85	6·32	5·16
4-$PhCH_2O$—C_6H_4	Ph	Me	56	141-143	$C_{22}H_{21}NO_3$	76·06	6·09	4·03	76·36	5·99	4·30
Ph	4-NO_2—C_6H_4	Me	65	149 150	$C_{15}H_{14}N_2O_4$	62·93	4·93	9·79	63·56	4·93	9·62
Ph	4-CH_3O Ph	Me	76	97-99	$C_{16}H_{17}NO_3$	70·83	6·32	5·16	70·63	6·48	5·36
Ph	Ph	Et*		87–88	$C_{16}H_{17}NO_2$	75·27	6·71	5·49	75·06	6·58	5·85
Ph	Ph	$Me(CH_2)_3$*		98–100	$C_{18}H_{21}NO_2$	76·29	7·47	4·94	76·11	7·31	4·81
Ph	Ph	Me_3—C*		133–135	$C_{18}H_{21}NO_2$	76·29	7·47	4·94	76·19	7·36	4·88

* These compounds were obtained by alcohol exchange from the corresponding methanol adduct; (R″ = Me). All the compounds absorbed in the infrared in $CHCl_3$ at 3440 cm^{-1} (NH) and in the region 1668-1680 cm^{-1} (CO). In the NMR, apart from the aromatic absorptions, the —CH— appeared as an unequal doublet (J = 9–9·5 c/s) in the region 3·4–3·8 τ. In the methanol adducts the Me appeared as a singlet in the region 6·5–6·6 τ.

azeotropic distillation. This method gave satisfactory yields of pure products; no systematic attempt was made to maximize yields. It is interesting to note that salicylaldehyde bisbenzamide (I; $R = 2\text{-HO—}C_6H_4$; $R' = Ph$) when subjected to pyrolysis under the standard conditions, yielded only benzamide III ($R' = Ph$) and polymeric material. This behaviour could be due to the fact that the N-benzoylsalicyladimine (II; $R = 2\text{-HO—}C_6H_4$; $R' = Ph$) may tautomerize and the tautomer, a benzamide quinone methide,[8] is very susceptible to polymerization under the conditions of pyrolysis.

Two other bisamides lacking α hydrogens were prepared and pyrolyzed to compare their behaviour with benzylidenebisamides. Formaldehyde bisbenzamide[9] (I; $R = H$, $R' = Ph$) was prepared and pyrolyzed under a variety of conditions. Apart from benzamide III ($R' = Ph$) only a polymer was formed. Pivalaldehyde bispivalamide (I; $R = R' = C(Me_3)$) was also prepared by a variant of the standard procedure. Its pyrolysis was carried out at atmospheric pressure by simply distilling the bispivalamide and treating the distillate with methanol. Under the standard conditions the pivalaldehyde bispivalamide simply sublimed.

To demonstrate the existence of the equilibrium under pyrolytic conditions, (Eq. 1), an exchange experiment was carried out. Benzylidenebisbenzamide was pyrolyzed in the presence of *p*-nitrobenzamide. The final product isolated, after treatment with methanol, was N-(α-methoxybenzyl) *p*-nitrobenzamide:

$$\mathrm{PhCH(NHCOPh)_2 + H_2NCOC_6H_4NO_2}(p) \xrightarrow[\text{2. MeOH}]{\text{1. }\Delta} \mathrm{PhCH(OMe)NHCOC_6H_4NO_2}(p) + \mathrm{H_2NCOPh}$$

We explored the possibility of decomposing the bisamide I ($R = R' = Ph$) according to Eq. 1 under conditions milder than those of the pyrolysis. When benzylidene bisbenzamide (I; $R = R' = Ph$) was reacted with benzaldehyde in boiling xylene in the presence of an acid catalyst, N-benzoylbenzaldimine (II; $R = R' = Ph$) was slowly accumulated. It was isolated and characterized as its methanol adduct. In a parallel experiment benzylidenebisbenzamide (I; $R = R' = Ph$) was heated in refluxing butanol for 10 days without any added catalyst. Under these conditions, any N-benzoylbenzaldimine (II; $R = R' = Ph$) formed according to Eq. 1 would immediately react with the solvent, butanol (Eq. 2) thus shifting the equilibrium away from the bisamide. From the reaction mixture N-(α-butoxybenzyl)-benzamide was isolated. While both these reactions were successful they did not match the pyrolytic method of decomposition for speed, convenience and yield.

Another method, reported,[10] of decomposing benzylidenebisbenzamide (I; $R = R'' = Ph$) and trapping the decomposition product, was its use as an amidomethylating agent of aromatic compounds by heating the bisamide in the presence of phenols or their esters at 190°. The amidomethylating agent in this reaction was almost certainly the N-benzoylbenzaldimine (II; $R = R' = Ph$).

The methanol adducts of the aromatic N-acylimines IV ($R = R' = \text{Aryl}$; $R'' = Me$) decomposed when heated to 200° under reduced pressure to methanol and the original N-acylimine (Eq. 2). This property[4,5] was exploited for the storage and

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[8] A. B. Turner, *Quart. Revs.* **18**, 347 (1964).

[9] A. Einhorn, E. Bischoff and B. Szelinsky, *Liebigs Ann.* **343**, 223 (1905).

[10] G. Stefanovic, J. Bojanovic, V. Vandjel, Z. Maksimovic, and M. L. Mihailovic, *Rec. Trav. Chim.* **76**, 24 (1957).

recover of the N-benzoylbenzaldimines (II) in the subsequent study of their physical and chemical properties. In contrast the N-(α-methoxyneopentyl) pivalamide (IV; R = R′—t-Bu; R″ = Me) was stable, in fact, under pyrolytic conditions we did not succeed in recovering the pivaloylpivalaldimine (II; R = R′—t-Bu).

In the IR spectra of the N-benzoylbenzaldimines (Table 3) the CO absorption appeared in the region 1657–1690 cm^{-1}.[5,11] The nature and magnitude of aromatic substituent affects on the position of CO absorption was very similar to those, found with other aromatic carbonyl compounds. The spectra of the N-benzoylbenzaldimines contained no bands attributable to N—H absorption and the C=N absorption appeared in the region 1620–1630 cm^{-1} but this sometimes masked by the aromatic absorption made accurate assignment difficult. The CO absorption of N-benzoylbenzaldimine (1680 cm^{-1}) was found to be higher by 20 cm^{-1} than the CO absorption of its carbon analogue, benzalacetophenone (1660 cm^{-1}). The UV spectra also showed a shift of 30 mμ to shorter wave length in going from benzalacetophenone (298 mμ log ε 4·4) to N-benzoylbenzaldimine (268 mμ log ε 4·25). The NMR spectra of the benzoylbenzaldimines (II) showed, apart from signals due to the aromatic groups or their substituents, one sharp singlet in the region 1·1–1·3 τ (Table 3). The position varied with substituent but there is no observable relationship between the chemical shift of the "aldehydic" proton and nuclear substituents.

TABLE 3. $(p)X—C_6H_4—CH=N—CO—C_6H_4\,Y(p)$

X	Y	$CO(cm^{-1})^a$	$CH=N^b$ (τ)
NO_2	H	1689	1·16
Cl	H	1681	1·15
H	H	1679	1·27
CH_3O	H	1675	1·24
$C_6H_5CH_2O$	H	1675	1·25
H	NO_2	1686	1·13
H	CH_3	1679	1·23

[a] measured in CCl_4
[b] measured in $CDCl_3$

The chemical reactions of N-benzoylbenzaldimine (I; R = R′ = Ph) were in accordance with those found with other compounds containing the N-acylimine group.[4,5,11] In addition reactions with alcohols (Eq. 2) it formed adducts with primary, secondary and even tertiary alcohols. Similarly a secondary amine e.g. piperidine formed a stable adduct. When treated with sodium borohydride, N-benzoylbenzaldimine (V) was completely reduced to N-benzylbenzamide (VIII), and when it was reacted with methyl magnesium iodide[12] the addition took place exclusively, on the imine carbon giving pure N-(α-phenylethyl) benzamide (VII) in 90% yield.

The reactivity of N-benzoylbenzaldimine compared with benzalacetophenone, its carbon analogue, and the relative stability of the alcohol addition products is

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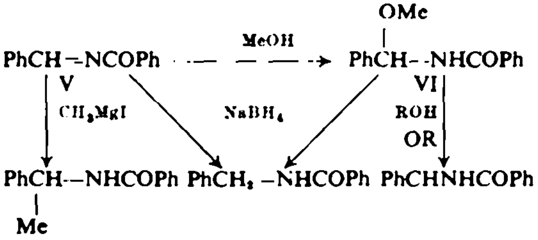
[11] F. Weygand, W. Steglich, I. Lengyel, F. Fraunberger, A. Maierhofer and W. Oettmeier, *Chem. Ber.* **99**, 1944 (1966).

[12] K. Ivanov, *Dokl. Akad. Nauk. SSSR.* **109**, 537 (1956); *Chem. Abstr*, **51**, 4997 (1957); but compare with Grignard reactions of amides: M. S. Knarasch and O. Rheinmuth, *Grignard reactions of Nonmetallic Substances* p. 870. Constable, London (1954).

probably due to change in hybridization. The unshared pair of electrons on nitrogen changes from sp^2 in the acylimine (V) to sp^3 like in the addition products (VI–IX). By this change the latter regain the resonance stabilization of the amide group which is absent in the acylimine.



VII VIII IX

In view of the recovery of N-benzoylbenzaldimine (V) from its methanol adduct VI (Eq. 2) we examined the possibility of substituting the methanol adduct VI for the imine V in the various reactions. Accordingly N-(α-methoxybenzyl)benzamide (VI) was subjected to the same reactions as those found characteristic of N-benzoylbenzaldimine (V). When treated with sodium borohydride in glyme solution, the methanol adduct underwent reduction to N-benzylbenzamide (VIII) and the same was observed when the isopropanol adduct was treated with sodium borohydride in isopropanol. In the reaction of the methanol adduct VI with methyl lithium the product VII was the same as the methyl magnesium iodide reaction with N-benzoylbenzaldimine (V). During the reaction the coloration of the reaction mixture indicated that the first step is the elimination of methanol by the strong base, methyl lithium, with the formation of the imine V which reacted further with the excess of the reagent. When N-(α-methoxybenzyl)benzamide (VI) was allowed to stand at room temperature in the presence of piperidine, after 3 days the sole product, after evaporating the solvent, was N-(α-1-piperidylbenzyl)benzamide. In all these cases, however, the reagents themselves could act as base catalyst. To eliminate this influence, the exchange of methanol with ethanol in the adduct VI was examined. At room temperature the exchange proceeded slowly, after a week the solution contained only about one third ethanol adduct IX (R = Et). As the temperature was raised, the exchange went faster, at reflux, it was complete in about 4 days. Under similar condition the exchange of methanol for butanol could also be achieved. Transetherification of ethers of N-α-alkylolamides has been known for a long time but it was carried out always in the presence of a catalyst, acid[13] or base.[14]

All these exchange reactions probably proceed through an elimination addition mechanism, and an attempt was made to separate the elimination and the addition part of the process. The methanol adduct VI was dissolved in toluene and the solution was heated under reflux with very slow take off of a distillate in the hope of removing the free methanol from the equilibrium system represented by Eq. 2, and leaving behind the N-benzoylbenzaldimine (V) in solution. When the distillation was completed, the residual solution was treated with ethanol and the product was found to be pure ethanol adduct IX; (R = Et), showing the equilibrium (Eq. 2) to have been

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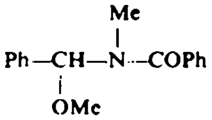
[13] R. D. Haworth, D. H. Peacock, W. R. Smith and R. MacGillivray, *J. Chem. Soc.* 2972 (1952).
[14] F. D. Chattway and E. J. F. James, *J. Chem. Soc.* 109 (1934).

driven completely to the imine form by the removal of the methanol.



$$\mathrm{Ph{-}\underset{\displaystyle OMe}{CH}{-}\overset{\displaystyle Me}{N}{-}COPh}$$

X

N-methyl N-(α-methoxybenzyl)benzamide (X) was prepared by heating benzaldehyde dimethyl acetal with N-methylbenzamide in the presence of sulfuric acid at 210°.[16] It was subjected to the borohydride reduction, ethanol and piperidine exchange reactions, and in all three cases it was recovered unchanged. This lends further support to the elimination-addition mechanism.

EXPERIMENTAL

M.ps are corrected. IR spectra were measured, in the phases specified, on Perkin–Elmer 21 and Perkin–Elmer 237 spectrophotometers. NMR spectra were taken on Varian A-60 spectrometer, in $CDCl_3$, with TMS as internal standard. Chemical shifts are given in τ units with TMS taken as 10·0.

TLC was carried out on microscope slides coated with alumina. For column chromatography Merck Neutral alumina was used; deactivated alumina refers to deactivation by the addition of 15% MeOH. Florisil was supplied by Nymco S.p.A., Milan.

Preparation of benzylidenebisbenzamides (I)

Typical procedure. A mixture of benzamide (0·1 mole) and benzaldehyde (0·05 mole) was heated under reflux with continuous stirring in benzene (600 ml) in the presence of *p*-toluenesulphonic acid (100 mg). The water formed in the reaction was removed by azeotropic distillation and collected in a Dean–Stark trap. The benzylidenebisbenzamide separated out, and after a total reaction time of 5 hr the mixture was cooled and the product was filtered and recrystallized from MeOH. In the case of the less soluble bisamides acetone was required as solvent for recrystallization. In all instances one recrystallization furnished analytically pure material (Table 1).

Pivalaldehyde bispivalamide. A mixture of pivalaldehyde (3·74 g) and pivalamide (8 g) was heated under reflux in benzene (500 ml) in the presence of *p*-toluenesulphonic acid (100 mg). The water formed in the reaction was removed by azeotropic distillation and collected in a Dean–Stark trap. The heating was continued for 96 hr, after which the benzene was evaporated and the residue (8·5 g) was recrystallized from AcOEt, M.p. 213–214°, yield 80%. ν_{max}^{KBr}: 3340 cm^{-1} (NH), 1655 cm^{-1} (CO) and 1390, 1362 cm^{-1} $C(Me_3)$. NMR_{CDCl_3}: 9·07 τ (s; 9H; Me_3C—CH), 8·82 τ (s; 18H; Me_3C CO), 4·96 τ (t; 1H; —CH(NH—$)_2$), (J = 8·5 c/s), 2·58 τ (2H v. broad peak, NH). (Found: C, 66·41; H, 11·03; N, 10·57; $C_{15}H_{30}N_2O_2$ requires: C, 66·62; H, 11·18; N, 10·36%.)

Pyrolysis of benzylidenebisbenzamides

The bisamides I were heated for 10–15 min in a dry sublimation apparatus, with the exclusion of moisture, above their m.p. (usually 260–280°) and the formed III were sublimed by reducing the press to 25–30 mm. The more volatile II also sublimed under these conditions but in some cases evacuation to 0·3–0·5 mm was necessary to complete the reaction. The material collected on the cold finger was dissolved in hot MeOH ,and the latter evaporated. The residue was dissolved in benzene (the starting material and the banzamide were usually insoluble) and chromatographed on alumina (Merck neutral, deactivated). The compounds IV, obtained from the chromatography were recrystallized from benzene–hexane. The yields in Table 2 refer to products after chromatography and crystallization.

N-(α-methoxyneopentyl)pivalamide. Pivalaldehydebispivalamide (500 mg) was heated in a small distillation apparatus with a low flame. The pyrolysis product distilled, and the distillate was dissolved in hot MeOH. The MeOH was evaporated and the product isolated by chromatography on Florisil.

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[15] H. Bohme and G. Berg, *Chem. Ber.* **99**, 2127 (1966); H. Bohme and K. Hartke, *Chem. Ber.* **96**, 600 (1963).

The pure product (192 mg. 55%) was recrystallized from hexane, m.p. 88–89°. $\nu_{max}^{CHCl_3}$: 3460 cm^{-1} (NH) and 1670 cm^{-1} (CO).

The NMR spectrum shows three singlets at 9·10 τ (9H), 8·77 τ (9H) and 6·70 τ (3H) corresponding to the two -Bu and the O-Me groups respectively as well as a doublet (J 9·5 c/s) at 5·20 τ from the methine hydrogen, and a very broad signal centred on 4·2 τ due to the NH. (Found: C, 65·39; H, 11·48; N, 7·24. $C_{11}H_{23}NO_2$ requires: C, 65·63; H, 11·52; N, 6·96%.)

Mixed pyrolysis of benzylidenebisbenzamide (I) *and* p-*nitrobenzamide*

Compound I (R = R′ = Ph; 320 mg) nad *p*-nitrobenzamide (310 mg) were pyrolyzed at 240° and 250 mm press for 15 min. The press then was reduced to 0·5 mm and the sublimation completed. The sublimed material was dissolved in hot MeOH (15 ml). The MeOH was evaporated and the residue was purified by chromatography on deactivated alumina, followed by rechromatography on Florisil (22 g). The fractions containing the main product pure were collected and the product was recrystallized from benzene–hexane, m.p. 149–150°. Its identity with authentic N-(α-methoxybenzyl) *p*-nitrobenzamide was shown by its m.p., mixed m.p. and IR spectrum.

Pyrolytic decomposition of N-(*α-methoxybenzyl*)*benzamides* (IV)

Compounds IV, were pyrolyzed in a sublimation apparatus without a cold finger at 200–210° and 25–30 mm press. The pyrolysis was usually complete in 10–15 min. Compounds II were cooled and used in soln in dry solvents for further spectroscopic or chemical study.

Reaction of benzylidenebisbenzamide (I) *with benzaldehyde*

Compound I (R = R′ = Ph; 1 g), freshly distilled benzaldehyde (950 mg) and catalytic amount of *p*-toluenesulfonic acid were refluxed in dry xylene (50 ml) for 43 hr with continuous stirring. The mixture was cooled, MeOH (2 ml) was added. The unchanged starting material (500 mg) was filtered off, and the mother liquor (according to TLC containing mostly N-α-methoxybenzylbenzamide) was purified by chromatography on deactivated alumina (100 g). From the collected fractions the chromatographically pure middle ones were taken (270 mg) and the product was recrystallized from benzene–hexane. Its m.p. mixed m.p. and IR spectrum was identical with authentic VI.

Reaction of benzylidenebisbenzamide (I) *with n-butanol*

Compound I (500 mg), was heated under reflux in abs. n-butanol (50 ml) for 10 days. The solvent was evaporated and the residue purified by chromatography on deactivated alumina (15 g). After recrystallization from benzene–hexane, pure N-(α-n-butoxybenzyl)benzmide (150 mg) was obtained in 35% yield, m.p. 97–99°.

N-(α-1-*piperidinylbenzyl*)*benzamide*.

Compound IV (200 mg) was pyrolyzed and the residue was cooled and dissolved in benzene (3 ml). Piperidine (300 mg) was added to the yellow soln resulting in immediate loss of color, and on addition of hexane (3 ml) the product separated out. It was filtered and recrystallized from benzene–hexane giving the pure piperidine adduct (145 mg), m.p. 142·5–143·5°. (Found: C, 77·05; H, 7·46; N, 9·51. Calc. for $C_{19}H_{22}N_2O$: C, 77·52; H, 7·53; N, 9·52%.)

Compound VI (130 mg) was dissolved in benzene (3 ml), piperidine (3 ml) was added and the soln was left for 75 hr at room temp. After evaporation of the solvents, the residue after crystallization from benzene–hexane proved to be N-(α-1-piperidenylbenzyl)benzamide.

Reduction of N-*benzoylbenzaldimine* (*V*) *with sodium borohydride*

Compound V prepared by the pyrolysis of its MeOH adduct (200 mg), was dissolved in dry dioxan and added to a dispersion of $NaBH_4$ (33 mg) in dry dioxan (10 ml). The dispersion was stirred at room temp overnight. The solvent was evaporated and the residue distributed between dil HCl and AcOEt. The organic layer was dried and evaporated and the residue (182 mg) was recrystallized from benzene–hexane. The product was identical with authentic VIII, prepared by benzoylation of benzylamine. (M.p. and mixed m.p. 103–104°, *R*$_f$ on TLC and IR spectra were identical.)

Grignard reaction on N-*benzoylbenzaldimine.* MeMgI was prepared from MeI (0·7 ml) and Mg (240 mg) in anhyd ether and heated under reflux with stirring. Compound V prepared by the pyrolysis of its MeOH- adduct (483 mg, 2 moles), was dissolved in ether and was added to the soln of the Grignard reagent, and the reaction mixture was refluxed a further ½ hr. 20% NH_4Cl aq (1·5 ml) was added to decompose the excess of reagent, the ether soln was decanted, dried and evaporated and the product (407 mg) was homogeneous on TLC. Its IR and NMR spectra correspond exactly to that of VII, as did the m.p. 118·5–119·5 (litt. m.p. 120°); yield 90%. Mixed m.p. with an authentic sample, prepared by benzoylation of α-phenylethylamine was not depressed.

Reaction of N-(*α-methoxybenzyl*)*benzamide with ethanol*

A sample of VI was dissolved in abs EtOH and allowed to stand for a week at room temp. The solvent was evaporated and the residue analysed by NMR. It was found to contain approximately 30–35% of IX (R = Et) besides starting material. When the reaction was repeated at reflux, the exchange proceeded faster, and was somplete after 100 hr.

Similar alcohol exchange reactions were carried out with n-butanol and t-butanol, refluxing for 1 and 4 days respectively to accomplish complete conversion. (The composition of reaction mixtures was analysed by TLC).

Stability of N-(*α-methoxybenzyl*)*benzamide* (VI) *in toluene at* 110°

Compound VI (225 mg) was dissolved in dry toluene (70 ml) and was heated under reflux with slow takeoff of the distillate. Over 20 hr 40 ml distillate were collected and the residual soln was yellow. After cooling, abs EtOH (2 ml) was added and the soln became colorless. The solvent was evaporated under reduced press and the residual solid examined by NMR. It was pure IX (R = Et), recrystallized from benzene–hexane, m.p. 85–86°.

Reaction of N-(*α-alkoxybenzyl*)*benzamides with sodium borohydride*

(a) A mixture of VI (83 mg) and $NaBH_4$ (37 mg) in dry glyme (6 ml) was left at room temp overnight, and then was distributed between ether and dil HCl aq. The ether layer was dried and evaporated and the residue (85 mg), after one recrystallization from benzene–hexane, was found to be identical with authentic VIII.

(b) A mixture of IV (R = $CH(Me_2)$) was treated with $NaBH_4$ in isopropanol. After 20 hr, TLC analysis of the reaction mixture showed only VIII and a complete absence of starting material.

Reaction of N-(*α-methoxybenzyl*)*benzamide* (VI) *with methyl lithium*

Compound VI (482 mg, 2 mmoles) was stirred in dry ether (50 ml) and was treated with MeLi (8 mmoles) in ether. The soln became yellow, orange and red in succession (over 20 sec!) and was stirred for 1 hr at room temp. The excess of reagent was decomposed by 20% NH_4Cl aq (5 ml), which was accompanied by the disappearance of the color. TLC analysis showed the product to be pure VII, which was confirmed by its isolation and recrystallization from benzene–hexane, m.p. 119–120°.