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EVIDENCE FOR RATE LIMITING C-H BOND CLEAVAGE IN THE LEUCKART REACTION

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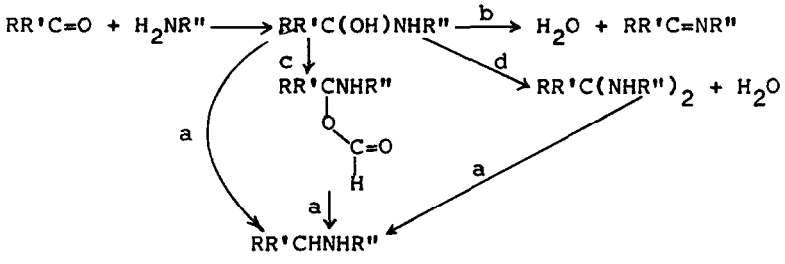
Abstract: A rho value of +0.21 is reported for the reaction of mono 4-substituted benzophenones with formamide. This, in conjunction with a kinetic isotope effect value of 1.80 obtained for the system, suggests a rate-limiting C-H bond cleavage.

The Leuckart reaction, a process for the alkylation of ammonia or amines or their formyl derivatives by aldehydes or ketones, is a facile route to a variety of amines[1]. Despite its versatility, there is yet no single universal mechanism for this reaction. There seems to be a general acceptance that the mechanism involves an initial addition of ammonium formate, formamide or substituted formamide to the carbonyl function derived from an aldehyde or ketone to yield an unstable carbinolamine intermediate which then suffers either reduction (step a, scheme 1), dehydration to an imine (step b) or formylation to the formic ester (step c). This intermediate may also suffer nucleophilic displacement (step d), for example, by formamide, to give an alkylidene diformamide intermediate. Any of these derived products may then undergo reductive transformation to the amine.



Scheme 1

There has been no general agreement, however, on the nature of the species involved in the final reductive step leading to the Leuckart product or on the mode of hydrogen transfer to the substrate. In one case, an activated complex of the quasi-ring type involving immonium and formate ions suffers hydride transfer[2]. The use of formic acid per se and in conjunction with certain hydrogenation catalysts such as nickel and cobalt, has been explained as necessary for the reduction of the intermediate carbinolamine, arylidene or alkylidene bisamine, imine or enamine to the amine. The most current hypothesis assumes a free-radical mechanism involving the formic ester of an α-aminoalcohol (i.e. carbinolamine) and formic acid to yield the reduction product and carbon dioxide. This assumption is based on the finding that the rate of reac-

tion in this system is influenced by the nature of the solvent (but not its polarity)and temperature, as well as by added hydroquinone or diphenylamine, known radical reaction inhibitors[3].

In spite of the above attempts to explain the course of the Leuckart reaction, there are still cases in the literature which cannot be rationalised solely on the basis of current hypotheses. Examples include the reaction of certain cage diketones which gave the corresponding amines with the concomitant carbinolamine ethers[4] and the so-called abnormal Leuckart reaction of benzophenone with diphenylurea and formic acid which gave the unexpected products o- and p- diphenylmethylanilines[5]. We now report the discovery of a rate-limiting C-H bond (of $HCONH_2$ or $HCOONH_4$) cleavage in the reaction of benzophenone with formamide. Thus, the mechanism of this reaction involves an initial reduction of the ketone to the alcohol and a subsequent alkylation of formamide by the latter. This formulation explains the formation of o- and p-diphenylmethylanilines, the cage carbinolamine ethers and some other 'abnormalities' observed in the Leuckart reaction.

Results and Discussion

As a consequence of the earlier reported isolation of benzhydrylalcohol in the Leuckart reaction[6], it was desirable to establish its mode of formation. Thus, benzophenone was heated with triethylammonium formate at 180-185°C during 42 h to give a 60 per cent yield of benzhydrylalcohol, unreacted benzophenone and an almost negligible yield of benzhydrylformamide. This result shows, unequivocally, the susceptibility of the carbonyl function to reduction and the primary formation of benzhydrylalcohol rather than benzhydrylformamide under Leuckart reaction conditions. However, involvement of the carbinolamine intermediate or its derived products may not now be excluded.

Since ketone ammonias are well known to form unstable addition compounds, an indirect method of detection of a possible adduct intermediate (i.e. carbinolamine) in this reaction was sought. Carbonyl reactions similar to the addition step of a hypothetical benzophenone-formamide product formation have been well documented and are known to be susceptible to substituent effects. Previously reported values of ρ for such reactions range from -1.49 to 2.33[7,8]. Consequently, the linear free energy relationship in the benzophenone-formamide reaction was investigated. Benzophenone mono substituted at the 4-position with methoxy, methyl, fluoro and chloro groups were synthesized by the Friedel-Crafts acylation of the appropriate benzenoid compounds[9]. The Leuckart reaction of the individual ketones was run using a mole ratio of ketone : formamide of 1 : 6 at 185°C for reaction periods of 1, 2, 3 and 4 h respectively. The products and unreacted ketones were isolated by preparative thin layer chromatography (PTLC, SiO_2, benzene) (Table 1) and characte-

rized (mp, IR, NMR, MS and combustion analyses). The table shows that both benzhydrylalcohol and benzhydrylether were formed in all of the reactions in confirmation of our earlier observation[6].

The specific rate constants for the reactions of the individual benzophenones with formamide were evaluated (under pseudo first order conditions) using the least squares method. Thus plotting of the $\log_{10}$ concentration of the unreacted ketone against reaction time gave linear curves from which the respective rate constants were determined. These were 0.67, 0.41, 0.55 and 0.62 h^{-1} for H, 4-MeO, 4-Me, 4-F and 4-Cl ketones respectively. Subsequently, the Hammet ρ value for the system was obtained by plotting the $\log_{10}$ k's against the Hammett's substituent constant, σ^{+*}[10]. (See Figures 1 and 2).

Table 1. Isolated Benzophenone and Product Yield[a] from the Leuckart Reaction of mono 4-substituted Benzophenone with Formamide during 4 h at 185°C.

Mono 4-substituted Benzophenones	Products			
	Benzhydryl-formamide (%)	Benzhydryl-alcohol (%)	Benzophenone (mg)	Benzhydryl-ether (mg)
H	44.2	2	48	3
Methoxy	21.9	3	128	9
Methyl	32.5	8	128	13
Fluoro	26.0	3	106	17
Chloro	43.7	4	42	18

a These yields are averages of three runs for each reaction period.

The rate constants show a linear logarithmic correlation with σ^+, with a ρ value of 0.21. Therefore this reaction is only slightly aided by electron withdrawal from the reaction centre and infers that neither an addition intermediate nor the reduction of the ketone to the alcohol is rate limiting in this system. However, it is known[11] that operation of a free radical mechanism (as postulated by Lukasiewicz) or cyclic transition state (as postulated by Noyce and Bachelor) exhibit very small ρ values as has been observed. But the addition of 1 mmol hydroquinone to a reaction mixture containing 6 mmol formamide with 1 mmol benzophenone did not decrease the yield of benzhydrylformamide.

On the basis of the observations it became necessary to investigate the deuterium isotope effect on the rate of the benzophenone-ammonium formate reaction. Thus the Leuckart reaction of benzophenone with C-H and C-D ammonium formate were run using a mole ratio of ketone : formate of 1 : 6 at 185°C

*Dickinson and Eaborn[10b] have suggested the use of σ^+ values to represent the approximate substituent effects (which include resonance interactions) in addition reactions to the carbonyl function in benzophenone.

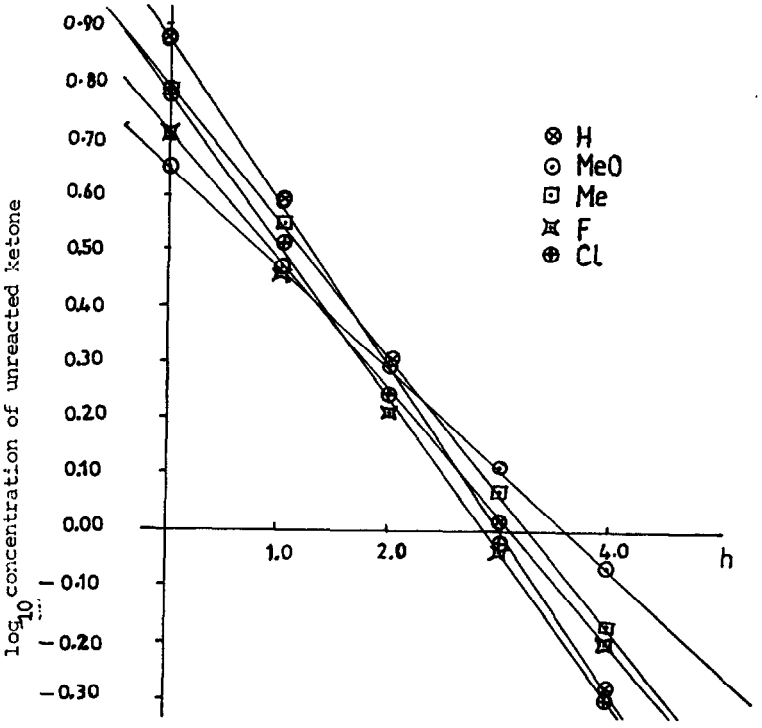


Fig. 1. Plot of $\log_{10}$ concentration of unreacted ketone against reaction time for the reactions of mono 4-substituted benzophenones with formamide during 1,2,3 and 4 h reaction periods, respectively, at 185°C.

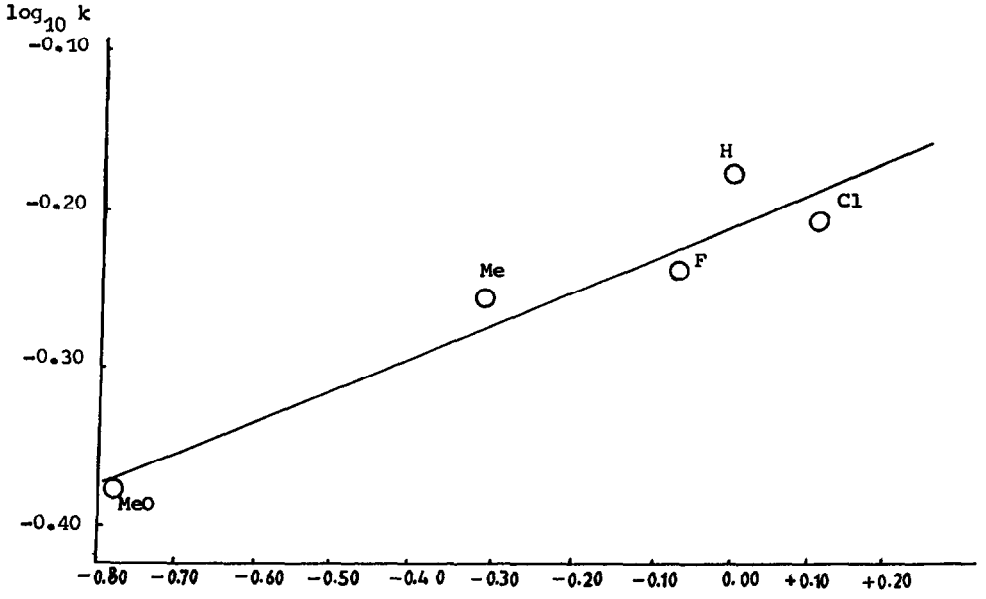


Fig. 2. Plot of $\log_{10} k$'s for Leuckart reaction of mono 4-substituted benzophenones against the corresponding substituent constants, σ^+.

during 1, 2, 3 and 4 h reaction periods respectively. The yields of benzhydrylformamide and unreacted benzophenone from these reactions are detailed in Table 2. The identity of the deuterated benzhydrylformamide was established on the basis of melting point, combustion analysis and spectrometric data (IR, NMR and MS). Notably, the ^{1}H NMR spectrum of d_2-benzhydrylformamide showed absence of both the formyl (H-C=O) and benzhydryl (Ph_2CH-) protons which occur at 8.20 and 6.30 ppm, respectively, in the spectrum of the undeuterated compound. Presence of benzhydryl D indicates translocation of the deuterium from C-D ammonium formate to the carbonyl carbon of benzophenone and thus the reductive function of ammonium formate during the reaction. Furthermore, the molecular ion peak, $M^{+\cdot}$, and $[M-1]^+$ ion, occur at m/z 213 and 212 respectively, having been shifted by two mass units higher than in the undeuterated compound.

The rate constants for the reaction of benzophenone with C-H and C-D ammonium formate were obtained by least squares plots of $\log_{10}$ concentration of unreacted ketone versus the reaction time. From these the rate constants obtained were 0.44 and 0.25 h^{-1} for C-H and C-D ammonium formate reactions, respectively. Consequently, the calculated kinetic isotope effect, $\frac{k_H}{k_D}$, from these values, is 1.80. This value compares favourably with those of 1.5-1.6 obtained by Rekasheva and Miklukhin[12] in the reaction of acetophenone and benzaldehyde with C-D ammonium formate which were shown to exhibit kinetic isotope effect similar to the Cannizzaro reaction.

Table 2. Recovered Benzophenone and Yields[a] of Benzhydrylformamide from the Leuckart Reaction of Benzophenone with C-H (A) and C-D (B) Ammonium Formate during 1, 2, 3 and 4 h reaction periods at 185°C.

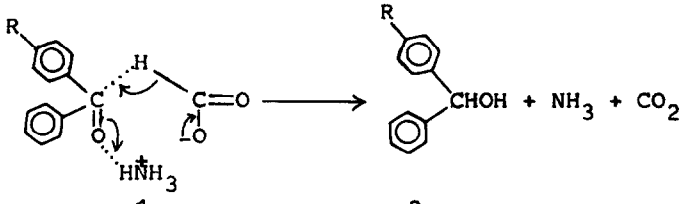
Reaction time (h)	Benzophenone (mg)		Benzhydrylformamide	
	A	B	A	B
1	114	174	65 mg 30.8%	12 mg 5.9%
2	94	165	95 mg 44.9%	15 mg 7.1%
3	34	155	175 mg 82.9%	20 mg 9.4%
4	30	149	192 mg 90.9%	24 mg 11.2%

a These yields are averages of three runs for each reaction period.

On the basis of these results, it appears that the rate limiting step in the Leuckart reaction involves a transfer of the C-H bound hydrogen (of formamide or ammonium formate) to benzophenone or the carbinolamine or its derived imine. H transfer to the carbonyl carbon of benzophenone may occur via a cyclic transition state (1) similar to the Meerwein-Ponndorf-Verley reduction of aldehydes and ketones. For the imine and carbinolamine, a rate limiting H transfer may involve a quasi-ring activated complex[2] (3) for the former and

the formate ester of the alcohol (5) for the latter. In both cases reduction occurs via transfer of the formate H to the benzhydryl carbon atom with concomitant loss of CO_2.

The case for a rate limiting formation or reduction of the carbinolamine (or its derived imine) appears not to be favoured by the discovery in this work that the reaction of triethylammonium formate with benzophenone under the Leuckart conditions gives a high yield of benzhydrylalcohol. This result indicates the primary formation of benzhydrylalcohol rather than the carbinolamine.



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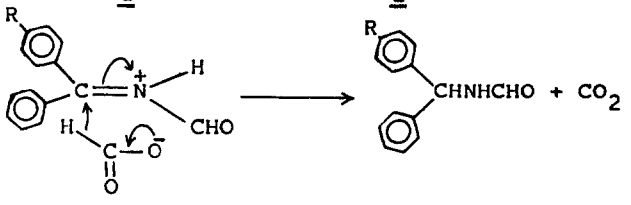

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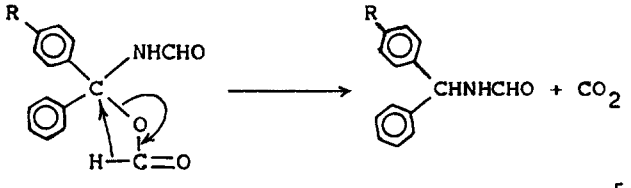
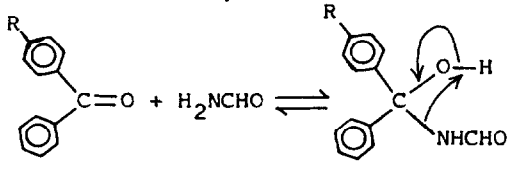


5 [R = H, MeO, Me, F, Cl]

Formation of the carbinolamine adduct may still occur in the benzophenone reaction but it has to be fast and reversible (scheme 2). In this case electron-withdrawing substituents will tend to favour the forward while electron-releasing substituents will tend to favour the reverse reaction. For a fast reversible reaction, as in the benzilic acid rearrangement in which formation



[R = H, MeO, Me, F, Cl]

Scheme 2

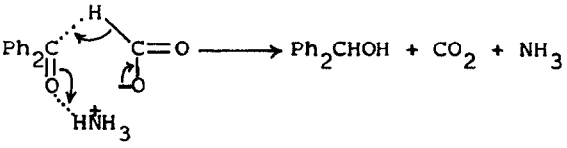
of an addition intermediate is fast and reversible[13], or in a situation where a steady state exists, the addition step will not be reflected in the $\log_{10}k$-

σ^+ correlation as has been observed.

The case for the intermediate formation of benzhydrylalcohol, via a rate limiting C-H bond cleavage, is strengthened by literature evidence. Firstly, olefinic bonds[14], nitriles[15], nitro[16] and imino[17] functions have been reduced under Leuckart reaction conditions. The variety of functional groups thus reduced would not suggest a selective reductive process. Invariably then, the carbonyl function does suffer reduction to the corresponding alcohol under the Leuckart reaction conditions. It is pertinent to remark that the Leuckart transformation along with reduction of a carbonyl function (to yield some carbinolamine ethers) were observed in the reactions of certain cage diketo compounds with formamide[5*]. Secondly, although it has been postulated that acid catalysis increases the polarisation of the carbonyl function thereby facilitating addition of the reagent, acid catalysis may also aid the formation of a carbonium ion from the carbonyl function derived alcohol. Accordingly, the weakly basic dialkylformamides, N-formylpiperidines and certain other tertiary amides which are resistant to the Leuckart transformation do readily react under catalysis with magnesium chloride or formic acid. Finally, when formamide is used with a dehydrating agent[17], hydrolysis of the former and thus reduction of the carbonyl function are inhibited. Consequently, there is a decrease in the yield of the formylamine.

In conclusion we state that the mechanism of the Leuckart readtion involving a carbinolamine or a ketimine intermediate, as proposed by Wallach, could not be validated by our findings. On the basis of facts available from this work, it is therefore proposed that in the benzophenone-formamide reaction the mechanism is as written below and could be used to explain certain 'abnormalities' observed in the Leuckart reaction:

step 1 : $HCONH_2 + H_2O \longrightarrow HCO\bar{O}\overset{+}{N}H_4$

step 2 : 

step 3 : $Ph_2\overset{+}{C}H \quad :NH_2CHO \longrightarrow Ph_2CHNHCHO + H^+$

Experimental Section

Elemental analyses were performed by the Microanalytical Laboratory, University of Illinois, Urbana, USA and Department of Chemistry, University of Edinburgh, UK. Mass spectra were determined on a Varian MAT CH-5 spectrometer at 70 eV and given in m/z (relative intensity, %). Infrared spectra were mea-

*Preliminary examination of the reaction mixtures derived from the Leuckart reaction of benzaldehyde and acetophenone have yielded alcohols invariably derived from the reduction of the carbonyl functions. These alcohols were converted to the Leuckart products in low yields.

sured with a Perkin-Elmer 251 Grating Infrared spectrometer in KBr and values expressed in reciprocal centimetres (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian T-60 NMR spectrometer in $CDCl_3$ or $CDCl_3$-DMSO with tetramethylsilane as an internal standard and stated in ppm. The J values were recorded in hertz. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected.

Reactions were carried out in the dark on a regulated sandbath and the components of the reaction mixtures isolated by preparative thin layer chromatography (using silica gel PF 254 previously washed with petroleum ether (40-60°C) and benzene. Final extraction from the gel was achieved with chloroform-methanol. The confidence level in PTLC isolation of the components of the various reaction mixtures is 98%.

The reagents used in these experiments were of analytical grade. The substituted benzophenones, triethylammonium formate, $DCOONH_4$ and $HCOONH_4$ were synthesized according to literature procedures.

Reaction of Benzophenone with Triethylammonium Formate

Benzophenone (1 mmol, 182 mg) with triethylammonium formate (30 mmol, 4.26 g) were placed in a round-bottom, quick-fit flask and refluxed on a sandbath at 185°C during 48 h. The reaction mixture was cooled to room temperature, treated successively with chloroform (10 mL) and water (5 mL), then the flask was stoppered and shaken vigorously for 10 min. The chloroform layer was run off, the aqueous layer successively extracted with chloroform (10 x 5 mL). The combined chloroform extract was dried over anhydrous Na_2SO_4, concentrated in vacuo and resolved by PTLC (benzene) to give a negligible amount of benzhydrylformamide and the following:

i) Benzhydrylalcohol: 111 mg (60%), mp 68°C, R_f=0.45
ii) Benzophenone: 19 mg, R_f=0.73
iii) Benzhydrylether: 19 mg, mp 106-7°C, R_f=0.83.

Reaction of Benzophenone with Formamide and Hydroquinone

Benzophenone (0.5 mmol, 90 mg), formamide (3 mmol, 0.12 mL) and hydroquinone (0.5 mmol, 60 mg) were placed in a round-bottom, quick-fit flask equipped with a water-cooled reflux condenser and heated under reflux at 185°C on a sandbath during 4 h. The usual work-up yielded 46 mg (43.6%) benzhydrylformamide and 35 mg benzophenone.

Reactions of mono 4-substituted Benzophenone with Formamide

The appropriate benzophenone (1 mmol) and formamide (6 mmol, 0.24 mL) were placed in four different 50 mL round-bottom quick-fit flasks equipped with water-cooled reflux condensers and heated simultaneously under reflux at 185°C on a sandbath during 1, 2, 3 and 4 h respectively. The reaction mixtures were worked-up as described for the reaction of benzophenone with triethylammonium formate to yield, in all cases, benzhydrylformamide, benzhydrylalcohol, benz-

hydrylether and the unreacted ketone.

a) Reaction of Benzophenone

Reaction time (h)	1	2	3	4
Products:				
Benzophenone (mg)	144	119	102	48
Benzhydrylalcohol (mg)	1	1	2	2
Benzhydrylformamide (mg)	6	21	48	93
(%)	2.8	10.0	22.7	44.1
Benzhydrylether (mg)	1	3	3	3

b) Reaction of 4-Methoxybenzophenone

Reaction time (h)	1	2	3	4
Products:				
4-Methoxybenzophenone (mg)	159	133	132	128
4-Methoxybenzhydrylalcohol (mg)	5	3	3	2
4-Methoxybenzhydrylformamide (mg)	9	14	31	53
(%)	3.7	5.8	12.9	22.0
4-Methoxybenzhydrylether (mg)	6	7	9	17

4-Methoxybenzhydrylformamide: mp 91-2°C, R_f=0.10; NMR 8.20 (s, 1H, -CHO), 7.28-6.78 (m, 10H, aromatic H), 6.26 (d, 1H, $Ph_2\underline{CH}$, J=9), 3.80 (s, 3H, $-OCH_3$) IR 3315 (s, N-H), 1667 (s, C=O), 1540-1520 (s, N-H); MS 241 ($M^{+\bullet}$, 100), 240 ($[M-1]^+$, 49), 197 (MeO-$Ph_2\overset{+}{C}H$, 26), 195 (8), 182 (13), 167 (6), 165 (24), 152 (20), 107 (3), 77 (38).

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.69; H, 6.22; N, 5.81.
Found: C, 74.63; H, 6.28; N, 5.80.

4-Methoxybenzhydrylalcohol (as oil): R_f=0.30; IR 3600-3200 (br, O-H), 1110 (s, C-O).

4-Methoxybenzhydrylether (as oil): R_f=0.86, n_D^{26}=1.602; IR 1298 (C-O).

c) Reaction of 4-Methylbenzophenone

Reaction time (h)	1	2	3	4
Products:				
4-Methylbenzophenone (mg)	152	148	137	128
4-Methylbenzhydrylalcohol (mg)	3	3	4	8
4-Methylbenzhydrylformamide (mg)	7	13	36	81
(%)	3.1	5.8	16.0	36.0
4-Methylbenzhydrylether (mg)	5	7	8	13

4-Methylbenzhydrylformamide: mp 96-8°C, R_f=0.13; NMR 8.14 (s, 1H, -CHO); 7.28 (s, 5H, aromatic H), 7.14 (s, 4H, aromatic H), 6.27 (d, 1H, $Ph_2\underline{CH}$, J=8), 2.28 (s, 3H, CH_3-); IR 3240-3180 (s, N-H), 1680-1640 (s, C=O), 1536 (s, N-H); MS 225 ($M^{+\bullet}$, 100), 224 ($[M-1]^+$, 53), 210 (31), 181 (Me-$Ph_2\overset{+}{C}H$, 13), 179 (19), 167 (5), 166 (22), 165 (73), 152 (7), 90 (8), 77 (34).

Anal. Cald for $C_{15}H_{15}NO$: C, 80.0; H, 6.67; N, 6.22.
Found: C, 79.94; H, 6.76; N, 6.26.

4-Methylbenzhydrylalcohol (as oil): R_f=0.43; IR 3500-3200 (br, O-H), 1080 (s, C-O).

4-Methylbenzhydrylether (as oil): R_f=0.96, n_D^{26}=1.602; IR 1300-1260 (unresolved, C-O).

d) Reaction of 4-Fluorobenzophenone

Reaction time (h)	1	2	3	4
Products:				
4-Fluorobenzophenone (mg)	143	139	110	106
4-Fluorobenzhydrylalcohol (mg)	1	2	3	6
4-Fluorobenzhydrylformamide (mg)	9	18	45	58
(%)	3.9	7.8	19.7	25.3
4-Fluorobenzhydrylether (mg)	9	10	13	17

4-Fluorobenzhydrylformamide: mp 101-2°C, R_f=0.12; NMR 8.24 (s, 1H, -CHO), 7.35-7.07 (m, 9H, aromatic H), 6.32 (d, 1H, $Ph_2\underline{C}H$, J=9); IR 3284 (s, N-H), 1665 (s, C=O), 1540-1520 (s, N-H); MS 229 ($M^{+\cdot}$, 100), 228 ($[M-1]^+$, 57), 210 (3), 185 (F-$Ph_2\overset{+}{C}H$, 16), 183 (73), 170 (6), 165 (15), 152 (12), 77 (25).

Anal. Calcd for $C_{14}H_{12}FNO$: C, 73.36; H, 5.24; F, 8.30; N, 6.11.
Found: C, 73.35; H, 5.52; F, 7.78; N, 5.95.

4-Fluorobenzhydrylalcohol (as oil): R_f=0.47; IR 3500-3200 (br, O-H), 1060 (s, C-O).

4-Fluorobenzhydrylether (as oil): R_f=0.96, n_D^{26}=1.586; IR 1296 (w, C-O).

e) Reaction of 4-Chlorobenzophenone

Reaction time (h)	1	2	3	4
Products:				
4-Chlorobenzophenone (mg)	144	132	120	40
4-Chlorobenzhydrylalcohol (mg)	3	3	4	6
4-Chlorobenzhydrylformamide (mg)	11	18	47	107
(%)	4.5	7.3	19.2	43.7
4-Chlorobenzhydrylether (mg)	4	5	11	18

4-Chlorobenzhydrylformamide: mp 122°C (litt. 124°C), R_f=0.15; NMR 8.25 (s, 1H -CHO), 7.28 (s, 8H, aromatic H), 6.59 (br, NH), 6.28 (d, 1H, $Ph_2\underline{C}H$, J=8); IR 3310-3200 (s, N-H), 1680-1660 (s, C=O), 1550-1500 (s, N-H); MS 245 ($M^{+\cdot}$, 91), 244 ($[M-1]^+$, 57), 210 (12), 201 (Cl-$Ph_2\overset{+}{C}H$, 11), 199 (5), 165 (100), 152 (5), 111 (9), 77 (4).

Anal. Calcd for $C_{14}H_{12}ClNO$: C, 68.43; H, 4.89; Cl, 14.46; N, 5.70.
Found: C, 68.38; H, 5.16; Cl, 14.88; N, 5.62.

4-Chlorobenzhydrylalcohol (as oil): R_f=0.43; IR 3600-3200 (br, O-H), 1085 (s, C-O).

4-Chlorobenzhydrylether (as oil): R_f=0.96, n_D^{26}=1.613; IR 1280 (s, C-O).

Preparation of d_2-Formic Acid, DCOOD.

Oxalic acid dihydrate (1 mol, 126.0 g) in a 500 mL round-bottom, quick-fit

flask was dehydrated at 110°C for 48 h then treated with 100 mL deuterium oxide, D_2O, under an atmosphere of dry nitrogen gas. Anhydrous benzene (sodium dried) was added and azeotropic distillation continued until the oxalic acid was thoroughly dehydrated. This was then pyrolyzed on a sandbath at 200-250°C under anhydrous conditions. About 8.0 mL (7.3 g) of a crude DCOOD containing some oxalic acid was collected. Redistillation of the crude product yielded 7.0 g (15%) d_2-formic acid (bp 97-8°C).

Reactions of Benzophenone with $DCOONH_4$ and $HCOONH_4$

Benzophenone (1 mmol, 182 mg) was reacted with $DCOONH_4$ (6 mmol, 384 mg) and $HCOONH_4$ (6 mmol, 378 mg) respectively under conditions as in the case of benzophenone/mono para-substituted benzophenones with formamide. The products yields and analytical data are given below.

a) Reaction of Benzophenone with $DCOONH_4$

Reaction time (h)	1	2	3	4
Products:				
Benzophenone (mg)	174	170	165	149
D-Benzhydrylalcohol (mg)	5	3	3	2
D_2-Benzhydrylformamide (mg)	12	15	20	24
(%)	5.9	7.1	9.4	11.2
D_2-Benzhydrylether (mg)	2	5	6	10

D_2-Benzhydrylformamide: mp 127-8°C, R_f=0.08; NMR 7.32 (s, 10H, aromatic H), 6.68 (br s, 1H, NH); IR 3200 (s, N-H), 1670-1630 (s, C=O), 1540-1530 (m, N-H) MS 213 ($M^{+\cdot}$, 100), 212 ($[M-1]^+$, 95), 168 ($Ph_2\overset{+}{C}D$, 8), 166 (54), 152 (7), 77 (43).

Anal. Calcd for $C_{14}H_{11}D_2NO$: C,78.87; H, 7.04; N, 6.57.
Found: C, 78.62; H, 6.16; N, 6.52.

D -Benzhydrylalcohol: R_f=0.45; IR 3500-3200 (br, OH), 1025 (s, C-O).

D_2-Benzhydrylether: R_f=0.83; IR 1270 (s, C-O).

b) Reaction of Benzophenone with $HCOONH_4$

Reaction time (h)	1	2	3	4
Products:				
Benzophenone (mg)	114	94	34	30
Benzhydrylalcohol (mg)	3	2	2	4
Benzhydrylformamide (mg)	65	95	175	192
(%)	30.8	45.0	82.9	91.0
Benzhydrylether (mg)	8	9	9	11

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