methyl-1-nitro-2-thiopseudourea. An analytically pure sample, mp 162 (lit.[10] mp 160.6–161°),[11] was obtained after several recrystallizations from ethanol.

Methylguanidinium Bromide.—Equimolecular quantities of aqueous methylamine (40%) and 2-benzyl-2-thiopseudourea hydrobromide were refluxed with 50 ml of H_2O for 2.5 hr. The mixture was cooled to 10° and extracted three times with 100-ml portions of ether to remove the benzyl mercaptan. The aqueous phase was evaporated to dryness and the white solid was recrystallized from absolute ethanol–ethyl acetate (mp 143–144°). *Anal.* Calcd for $C_2H_8N_3Br$: C, 21.42; H, 5.95; N, 25.00. Found: C, 21.82; H, 5.93; N, 24.47.

1,3-Dimethylguanidinium Bromide.—Equimolecular quantities of aqueous methylamine (40%) and 2-benzyl-1-methyl-2-thiopseudourea hydrobromide gave impure 1,3-dimethylguanidinium bromide, mp 138–139°. Several recrystallizations from ethanol–ethyl acetate gave an analytically pure sample, mp 144–145° (lit.[12] mp 144°).

(10) L. Fishbein and J. A. Gallaghan, *J. Am. Chem. Soc.*, **76**, 1877 (1954).
(11) All melting points were taken on a micro Kofler hot stage.
(12) J. O. Mold, J. M. Ladino, and E. J. Schantz, *J. Am. Chem. Soc.*, **75**, 6321 (1953).

1,2,3-Trimethylguanidinium Bromide.—The reaction of aqueous methylamine (40%) with 2-benzyl-1,3-dimethyl-2-thiopseudourea hydrobromide gave crude 1,2,3-trimethylguanidinium bromide, mp 342–346°. An analytical sample (mp 350°) was obtained by four recrystallizations from absolute ethanol–ethyl acetate. *Anal.* Calcd for $C_4H_{12}N_3Br$: C, 26.37; H, 6.59; N, 23.08. Found: C, 26.33; H, 6.45; N, 22.80.

Nuclear Magnetic Resonance Mesurements.—The measurements were made with a Varian DP-60 spectrometer equipped with a superstabilizer and a Varian high-speed recorder. The separation of doublet peaks was measured (with a precision of ±0.05 cps) by placing side bands of the doublet 20 cps on both sides of the doublet. The side-band frequency was measured with a Hewlett-Packard Model 522-B electronic frequency counter. Temperature was kept constant to within ±0.2° by the use of a Leeds and Northrup Azar II recorder controller. The temperature was varied with dry nitrogen gas and the use of a Varian 4340 variable-temperature nmr probe assembly and a Model V-4331-THR spinning sample dewar probe insert.

Kinetic *vs.* Thermodynamic Control in Addition Reactions of Dialkaliphenylacetamides with Benzophenone in Liquid Ammonia[1]
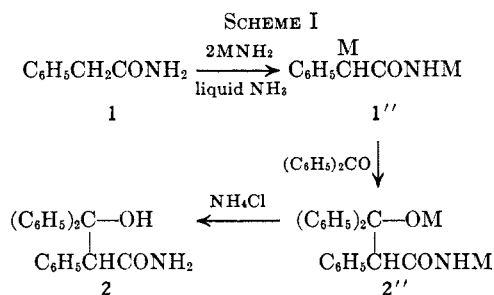
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Disodio-, dipotassio-, and dilithiophenylacetamides underwent addition reactions with benzophenone to form, on inverse neutralization after a relatively short period, the corresponding adduct in good yields. However, only starting materials were recovered after longer periods. Evidently, the initial addition reaction is kinetically controlled, and this is followed by a thermodynamically controlled addition reaction between the alkali amide and the ketone present in equilibrium. The relative ease of the latter reaction as the metallic cation is varied decreased in the order K > Na > Li. Theoretical and synthetic aspects are considered.

Recently,[2] dipotassiophenylacetamide (1″, M = K) was reported not to undergo an addition reaction with benzophenone to form adduct 2 (Scheme I), and dilithiophenylacetamide (1″, M = Li) was found to do so in only 7% yield even though the reaction mixtures were neutralized inversely.[3] This seemed

SCHEME I

$$C_6H_5CH_2CONH_2 \xrightarrow[\text{liquid NH}_3]{\text{2MNH}_2} \overset{M}{C_6H_5CHCONHM}$$

1　　　　　　　1″

$(C_6H_5)_2CO \downarrow$

$$(C_6H_5)_2C\text{—OH} \xleftarrow{NH_4Cl} (C_6H_5)_2C\text{—OM}$$
$$C_6H_5CHCONH_2 \qquad\qquad C_6H_5CHCONHM$$
2　　　　　　　　　　　2″

rather surprising since, not only had these dialkali salts 1″ been shown to undergo satisfactorily other types of condensations, *e.g.*, alkylation,[4] benzoylation,[2] and conjugate addition,[5] but the related disodio- or

dilithiophenylacetate[6] and dipotassiobenzoylacetone[7] had been observed to exhibit carbonyl addition reactions with benzophenone in good yields under similar conditions.

We have now obtained adduct 2 in good yields from dialkali salts 1″ (M = Na, K, and Li) and benzophenone (Scheme I) by inverse neutralization of the reaction mixtures after relatively short periods; after more common condensation periods, only starting materials were recovered. In Table I are summarized the yields of adduct 2 and of recovered benzophenone obtained on adding the ketone to the dialkali salt 1″ during 5 min, and neutralizing the reaction mixture after an appropriate further condensation period. Phenylacetamide was recovered along with the ketone but its isolation was generally not attempted.

Table I shows that disodiophenylacetamide (1″, M = Na), which was studied the most thoroughly, afforded adduct 2 in 53% yield on inverse neutralization after 1 min (beyond the 5-min ketone-addition period), whereas none of 2 was isolated after 10–15 min (expt 1–3). When 2.2 molecular equiv of sodium amide was employed in the preparation of disodio salt 1″ instead of the required 2 equiv (see Scheme I), adduct 2 was obtained in yields of 64–86% on inverse neutralization after 1–15 min but none was isolated after 30 min (expt 4–8). In these experiments with

(1) (a) Supported by the Army Research Office (Durham) and by the National Science Foundation; (b) a preliminary report appeared as a communication, *Chem. Ind.* (London), 1299 (1965).
(2) S. D. Work, D. R. Bryant, and C. R. Hauser, *J. Org. Chem.*, **29**, 722 (1964).
(3) This method of neutralization, which involves pouring the reaction mixture into excess ammonium chloride, was employed to minimize possible reversion of this aldol-type condensation during work-up.
(4) R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, **26**, 3696 (1961).
(5) R. B. Meyer and C. R. Hauser, *ibid.*, **26**, 3187 (1961).
(6) P. J. Hamrick, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **82**, 1957 (1960).
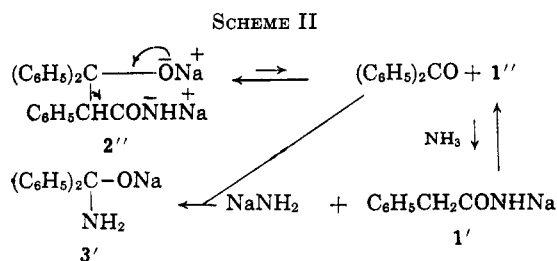(7) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **26**, 1716 (1961).

TABLE I

YIELDS OF ADDUCT **2** AND RECOVERED KETONE FROM BENZOPHENONE AND DIALKALIPHENYLACETAMIDES **1″** IN LIQUID AMMONIA UNDER VARIOUS CONDITIONS

Expt no.	M in dialkali salt 1″	Equiv of MNH$_2$ used for 1″^{a}	Condn period, min^b	Neutraliza- tion method	Yield of 2, %	Ketone recov- ery, %
1	Na	2.0	1^c	Inverse	53	40
2	Na	2.0	10^d	Inverse	0	96
3	Na	2.0	15^d	Inverse	0^e	80
4	Na	2.2	1^c	Inverse	64	25
5	Na	2.2	5^c	Inverse	83 (86)^f	17
6	Na	2.2	10^c	Inverse	75	10
7	Na	2.2	15^c	Inverse	71	10
8	Na	2.2	30^d	Inverse	0	98
9	Na	2.0	1^c	Direct^g	2	91
10	Na	2.0	1^c	Direct^h	43	38
11	Na	2.2	1^c	Direct^g	3	91
12	Na	2.2	5^c	Direct^g	0	87
13	Na	2.2	5^c	Direct^h	35	60
14	Na	3.0	10^c	Inverse	51	41
15	K	2.2	0	Inverse	33	44
16	K	2.2	0	Inverse^i	38	47
17	K	2.2	30 sec	Inverse	78	19
18	K	2.2	1	Inverse	40	52
19	K	2.2	5–10	Inverse	0	92
20	Li	2.0	15	Inverse	60	32
21	Li	2.0	60	Inverse	0	94
22	Li	2.2	60	Inverse	51	37

^{a} Molecular equivalents of alkali amide used in the preparation of dialkali salt **1″** from one of phenylacetamide (**1**); 0.05 mole each of **1** and benzophenone were generally employed. ^{b} Condensation time of **1″** with benzophenone after the ketone had been added during 5 min. ^{c} A heavy precipitate was present. ^{d} A light precipitate was present. ^{e} Only one run out of six gave some of **2**. ^{f} The amount of benzophenone used was 0.06 mole; see footnote a. ^{g} The ammonium chloride was added to the reaction mixture during 2 min. ^{h} The ammonium chloride was added very rapidly (vigorous reaction). ^{i} More ethyl ether (200 ml) was used than usual; see footnote a.
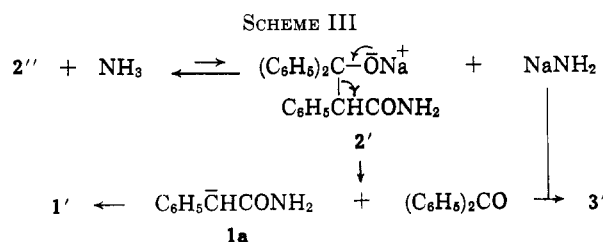
and without the 10% excess of sodium amide, **2** was obtained when the reaction mixture contained a heavy precipitate but not when it contained only a light precipitate (see footnotes c and d in Table I). Addition of ammonium chloride to the reaction mixture (direct neutralization) afforded less or none of **2** under otherwise similar conditions (expt 9–13). In these reactions the percentage recovery of benzophenone increased as the yield of **2** decreased (see Table I).

These results may be rationalized by a kinetically controlled addition reaction of disodio salt **1″** with the ketone (see Scheme I), and a thermodynamically controlled addition reaction of sodium amide with the ketone present in equilibrium; the latter control would require regeneration of the sodium amide and ketone, which may involve reversions of initial reactions (Scheme II).

SCHEME II

$$(C_6H_5)_2C\!\!-\!\!ONa \quad \longleftarrow \quad (C_6H_5)_2CO + 1″$$
$$\underset{|}{C_6H_5CHCONHNa}$$
$$\mathbf{2″}$$

$$(C_6H_5)_2C\!-\!ONa$$
$$\underset{|}{NH_2} \quad \longleftarrow \quad NaNH_2 + C_6H_5CH_2CONHNa$$
$$\mathbf{3'} \qquad\qquad\qquad \mathbf{1'}$$

$$NH_3 \downarrow \uparrow$$

Evidently, the initial addition reaction was essentially complete as soon as the ketone was added since the brown-green color of disodio salt **1″** was then discharged and a heavy white precipitate of disodio adduct **2″** produced (see Scheme I). The subsequent conversion of **2″** to the sodium amide adduct of the ketone (**3'**) and monosodiophenylacetamide (**1'**) was accompanied by a change of this heavy precipitate to a much lighter one[8] (see Scheme II). That the latter precipitate consisted partly of **3'** was demonstrated by filtration of the unneutralized reaction mixture and hydrolysis of the solid to afford benzophenone;[9] also, **3'** was identified by cleavage to form benzamide (Haller–Bauer reaction).

Another possible course for the conversion of disodio adduct **2″** to **3'** and **1'** would involve equilibration of **2″** with ammonia and cleavage of the resulting monosodio adduct **2'** (Scheme III).

SCHEME III

$$\mathbf{2″} + NH_3 \;\rightleftharpoons\; (C_6H_5)_2C\!-\!ONa^+ \;+\; NaNH_2$$
$$\underset{|}{C_6H_5CHCONH_2}$$
$$\mathbf{2'}$$
$$\downarrow$$
$$\mathbf{1'} \;\leftarrow\; \underset{\mathbf{1a}}{C_6H_5\bar{C}HCONH_2} \;+\; (C_6H_5)_2CO \;\rightarrow\; \mathbf{3'}$$

Indeed, if sufficient monosodio adduct **2'** were present in the equilibrium, this course might be expected to predominate since the cleavage of **2'** would involve β elimination of a monoanion (**1a**, in Scheme III), whereas that of **2″** would involve β elimination of a dianion (**1″**, in Scheme II). Moreover, in contrast to the cleavage of **2″**, that of **2'** should be irreversible, since the eliminated monoanion **1a** would be converted immediately to the more stable monoanion **1'** (see Scheme III).

The increase in the yield of adduct **2** and the retardation of the conversion of disodio adduct **2″** to **3'** and **1'** by the presence of 10 mole % of sodium amide (see Table I) may be ascribed to shifts in appropriate equilibria involving the alkali amide (see Schemes I–III). Interestingly, even when 100 mole % of sodium amide was present, the yield of adduct **2** was 51%, which is about equal to that (53%) with no excess and two-thirds that (75%) with 10% excess of the alkali amide under somewhat similar conditions (compare expt 1 and 6 with expt 14, Table I). This indicates (but does not establish because of unknown relative solubilities) that disodio salt **1″** is more nucleophilic than sodium amide.

The driving force in the condensation of dianion **1″** with benzophenone appears ascribable mainly to formation of a weaker base which would be dianion **2″** (see Scheme I), since the liberated adduct **2** undergoes cleavage in the presence of a catalytic amount of sodium amide (see next section). Precipitation of the salt or chelation of the metallic cation is evidently not

(8) Similar precipitates were obtained in blank experiments in which benzophenone and phenylacetamide were each added to 1 molecular equiv of sodium amide in liquid ammonia, though a smaller amount of solid was produced in the latter case.

(9) No appreciable amount of the ketone was obtained in a blank experiment in which the reaction mixture containing the initial heavy precipitate was treated similarly.

the controlling factor for the condensation, since dipotassio salt 1″ undergoes the analogous addition reaction without appreciable precipitation and chelation in this case should be relatively minor (see below).

The subsequent conversion of dianion 2″ to monoanions 3′ and 1′ occurs in spite of formation of a lighter precipitate apparently because the addition reaction of sodium amide with benzophenone is less reversible than that of disodio salt 1″ with the ketone; presumably the monoanions would be more weakly basic than dianion 2″.
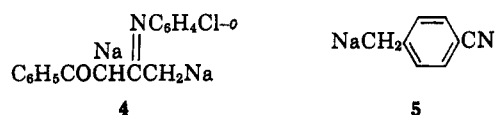
Table I further shows that dipotassio- and dilithiophenylacetamides (1″, M = K and Li, respectively) similarly undergo addition reactions with benzophenone (see Scheme I), but that the resulting dipotassio adduct 2″ is relatively less stable and the resulting dilithio adduct 2″ is relatively more stable than disodio adduct 2″. Thus, dipotassio salt 1″ afforded adduct 2 in 78% yield on inverse neutralization after 30 sec (beyond the 5-min ketone-addition period), whereas none of 2 was isolated after 5 min even though a 10% excess of potassium amide was present (expt 17 and 19, Table I); the yield of 2 from disodio salt 1″ after a comparable 5-min period was 83% (expt 5, Table I). Dilithio salt 1″ afforded adduct 2 in 60% yield after 15 min but none after 1 hr in the absence of excess lithium amide (expt 20 and 21, Table I); none of 2 was obtained from disodio salt 1″ after even 15 min under otherwise similar conditions (expt 3). As in the experiments with disodio salt 1″, the percentage recovery of the ketone increased as the yield of adduct 2 decreased; presumably, the ketone was present in the unneutralized reaction mixture as its potassium amide or lithium amide adduct, like 3′, though this was not established.

These results indicate that the relative ease of conversion of the dialkali adduct 2″ to the corresponding monoalkali adduct of the ketone and monoalkaliphenylacetamide decreases as the metallic cation is varied in the order K > Na > Li, which is the expected decreasing order for the extent of coordination (chelation) of the metallic cation in the dialkali adduct 2″.
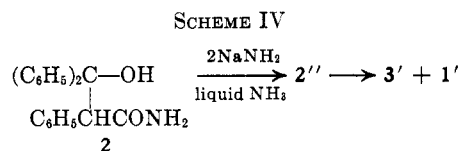
For synthesis of adduct 2, the disodio salt 1″ is recommended, since not only did it afford the best yield (see Table I), but it is more convenient to employ. The reaction with dipotassio salt 1″ has to be stopped too soon for satisfactory reproducibility, and the formation of the dilithio salt 1″ from 1 and lithium amide appears relatively sluggish.

Although these are the first recognized examples of a kinetic vs. thermodynamic control in a carbonyl addition reaction of a carbanion to a ketone or aldehyde in liquid ammonia, the thermodynamic control might operate in certain of the known reactions of this type[10] after a much longer period. More significantly, this knowledge[1b] has already been instrumental in the success of two recently observed addition reactions of disodio salt 4[11] and monosodio salt 5[12] with benzophenone, with which reaction periods of only 5 min
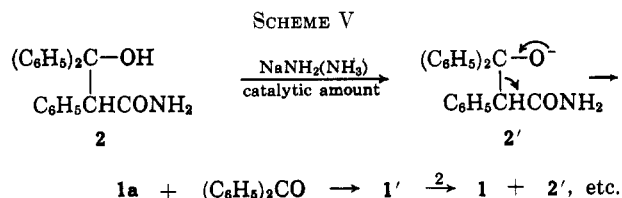
appeared to be required for satisfactory yields of the corresponding adduct. The success of other reactions may likewise be dependent on application of such knowledge.

$$\underset{\substack{\text{Na} \;||\\ C_6H_5COCHCCH_2Na \\ \textbf{4}}}{\overset{NC_6H_4Cl\text{-}o}{}} \qquad \underset{\textbf{5}}{NaCH_2\langle\!\!\!\bigcirc\!\!\!\rangle CN}$$

Cleavage of Adduct 2 by Sodium Amide.—First, adduct 2 was cleaved by means of 2 molecular equiv of sodium amide in liquid ammonia, which, after an initial twofold acid–base reaction, would simulate the conversion of disodio adduct 2″ to 3′ and 1′ as represented in Schemes II and III. Thus, solid 2 was added to the reagent to form, initially, a heavy precipitate of disodio adduct 2″, which was soon converted to a much lighter one of 3′ and 1′ (Scheme IV). Filtration of the reaction mixture and hydrolysis of the solid afforded benzophenone.

<div align="center">

Scheme IV

$$\underset{\substack{|\\ C_6H_5\overset{|}{C}HCONH_2 \\ \textbf{2}}}{(C_6H_5)_2C{-}OH} \xrightarrow[\text{liquid NH}_3]{2NaNH_2} 2'' \longrightarrow 3' + 1'$$

</div>

Next, adduct 2 was cleaved by means of a catalytic amount of the base, which is one of the common ways for effecting such a reverse aldol condensation.[13] Thus, solid 2 was added to about 15 mole % sodium amide in liquid ammonia to afford benzophenone and phenylacetamide; presumably, only 15 mole % 2 was converted initially to monoanion 2′ which underwent cleavage, more of 2′ being produced in the last step where neutral adduct 2 serves as an acid (Scheme V).

<div align="center">

Scheme V

$$\underset{\substack{|\\ C_6H_5\overset{|}{C}HCONH_2 \\ \textbf{2}}}{(C_6H_5)_2C{-}OH} \xrightarrow[\text{catalytic amount}]{NaNH_2(NH_3)} \underset{\substack{|\\ C_6H_5\overset{|}{C}HCONH_2 \\ \textbf{2}'}}{(C_6H_5)_2C\overset{\frown}{-}O^-} \longrightarrow$$

$$\mathbf{1a} \; + \; (C_6H_5)_2CO \; \longrightarrow \; 1' \xrightarrow{2} 1 \; + \; 2', \text{ etc.}$$

</div>

Incidentally, the relatively low yields of adduct 2 obtained from disodio salt 1″ and benzophenone when the reaction mixture was neutralized directly (see Table I) was probably due to at least some catalytic cleavage of 2.

Whereas the driving force in the cleavage of 2 by 2 equiv of the reagent appears to be associated with the conversion of 2″ to the presumably more weakly basic anions 3′ and 1′ (see above), that in the cleavage by a catalytic amount of reagent must be the formation of thermodynamically more stable neutral products; i.e., benzophenone and phenylacetamide are more stable than carbinol amide 2.

(10) For two such reactions of dianions, see ref 6 and 7, and for two of monoanions, see P. J. Hamrick, Jr., and C. R. Hauser, J. Am. Chem. Soc., 81, 2096 (1959), and W. R. Dunnavant and C. R. Hauser, J. Org. Chem., 25, 1693 (1960).

(11) S. Boatman and C. R. Hauser, ibid., in press.

(12) F. H. Rash, S. Boatman, and C. R. Hauser, Chem. Ind. (London), submitted for publication.

(13) See P. J. Hamrick, Jr., and C. R. Hauser, J. Am. Chem. Soc., 81, 3144 (1959).

Experimental Section[14]

Addition Reactions of Dialkaliphenylacetamides.—In Table I are summarized the yields of adduct 2 and of recovered benzophenone obtained with three dialkaliphenylacetamides and this ketone under various conditions. The details are given below.

A. Reactions of Disodiophenylacetamide (1″, M = Na).—To a stirred suspension of 0.1 or 0.11 mole of sodium amide in 300 ml of commercial, anhydrous liquid ammonia[15] was added 6.75 g (0.05 mole) of solid phenylacetamide (1). After 30 min, the resulting brown-green, light suspension was assumed to contain 0.05 mole of disodiophenylacetamide (1″). To the stirred suspension of disodio salt 1″ or of 1″ plus the 10% excess of sodium amide was added, during 5 min, a solution of 9.1 g (0.05 mole) of benzophenone in 50 ml of anhydrous ether to discharge the color of 1″ and produce a heavy white precipitate, which gradually changed to a much lighter one. In some experiments, the reaction mixture containing the heavy precipitate was poured into a suspension (magnetically stirred) of 15 g of ammonium chloride in 200 ml of liquid ammonia in a 2-l. flask, and the original flask was washed with two 100-ml portions of ether; these washings were added to the neutralized mixture. The ammonia was allowed to evaporate and the remaining ethereal suspension was shaken with 100 ml of 3 N hydrochloric acid. The resulting solid was collected in a funnel (suction), washed with water followed by ether, and recrystallized from absolute ethanol to afford adduct 2, mp 202–203°, undepressed on admixture with an authentic sample.[2] The layers from the original filtrate were separated, and the aqueous layer was extracted with four 50-ml portions of ether. After drying over magnesium sulfate, the solvent was removed to afford recovered benzophenone (Table I), mp and mmp 48–49°.

In some other experiments, the reaction mixture was not worked up until the light precipitate had formed. In these cases neutralization and subsequent hydrolysis afforded no solid residue; removal of the ether gave only recovered benzophenone.

In still other experiments, the reaction mixture containing the heavy precipitate was neutralized directly by addition of 15 g of solid ammonium chloride through a powder funnel (caution). After the ammonia had evaporated, the residues were worked up as above.

B. Reactions of Dipotassiophenylacetamide (1″, M = K).—To a stirred solution of 0.11 mole of potassium amide in 300 ml of anhydrous liquid ammonia was added 6.75 g (0.05 mole) of solid phenylacetamide (1). After 30 min, the resulting brown solution was treated during 5 min with a solution of 9.1 g (0.05 mole) of benzophenone in 50 ml of anhydrous ether; neither a change of color nor a precipitate were observed. After an appropriate time, the reaction mixture was inversely neutralized and worked up as described above for disodiophenylacetamide.

C. Reactions of Dilithiophenylacetamide (1″, M = Li).—To a stirred suspension of 0.1 or 0.11 mole of lithium amide in 300 ml of anhydrous liquid ammonia was added 6.75 g (0.05 mole) of solid phenylacetamide (1). After 60 min, the resulting pale green suspension was treated, during 5 min, with a solution

(14) Melting points were taken on a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer spectrometer Model 137 or 237 with potassium bromide disks or Nujol mulls.

(15) See C. R. Hauser, F. W. Swamer, and J. T. Adams, Org. Reactions, 8, 122 (1954).

of 9.1 g (0.05 mole) of benzophenone in 50 ml of anhydrous ether. Although the green color was intensified, no appreciable precipitate was observed. After an appropriate time, the reaction mixture was inversely neutralized and worked up as described above for disodiophenylacetamide.

Detection of the Sodium Amide Adduct of Benzophenone (3′).—To a stirred suspension of 0.05 mole of disodio salt 1″ in 300 ml of anhydrous liquid ammonia, was added during 5 min, 0.05 mole of benzophenone in 50 ml of anhydrous ether. After 30 min, the gray reaction mixture, which contained a light precipitate, was filtered under nitrogen through a Büchner funnel fitted with an asbestos filter. The gray solid on the funnel was washed thoroughly with 200 ml of liquid ammonia, followed by 200 ml of anhydrous ether, and then treated with 100 ml of water (ammonia evolved) followed by 100 ml of 3 N hydrochloric acid. The layers were separated. The ethereal layer (with which was combined three ethereal extracts of the aqueous layer) was dried over magnesium sulfate, and the solvent was removed to afford 7.16 g (79%) of benzophenone, mp and mmp 46–48°. Excess ammonium chloride was added to the original filtrate, and the ammonia was evaporated. The crude product was hydrolyzed and worked up as above to give 1.25 g (14%) more of this ketone, mp and mmp 46–48°.

In a blank experiment, a solution of 9.1 g (0.05 mole) of benzophenone in 50 ml of anhydrous ether was added, during 5 min, to a suspension of 0.05 mole of sodium amide in 300 ml of anhydrous liquid ammonia. After 30 min, the gray suspension was filtered and worked up as above to yield 7.2 g (79%) of benzophenone, mp and mmp 47–48°. Work-up of the filtrate and subsequent treatment with methanolic 2,4-dinitrophenylhydrazine afforded 1.8 g (10%) of the corresponding hydrazone of benzophenone, mp 241.5–242.5°, mmp 241–242.5°.

In another experiment, 0.05 mole of disodiophenylacetamide was allowed to react with 0.05 mole of benzophenone in 300 ml of anhydrous liquid ammonia for 30 min. The ammonia was then replaced by 250 ml of anhydrous toluene, and the suspension was refluxed for 18 hr. When it cooled, 100 ml of water was added, and the two layers were separated. The organic layer was dried (magnesium sulfate), and the toluene was then removed to afford benzamide, mp and mmp 127–128°, after recrystallization from water.

Cleavage of Adduct 2 by Means of Sodium Amide in Liquid Ammonia. A. Stoichiometric.—Solid adduct 2 (15.85 g, 0.05 mole) was added over 2 min to a suspension of 0.11 mole of sodium amide in 300 ml of anhydrous liquid ammonia. After 30 min, the suspension was filtered under suction and the gray solid was washed thoroughly with liquid ammonia and ether. Hydrolysis of the solid with water, then 3 N hydrochloric acid, afforded 5.77 g (63%) of benzophenone, mp and mmp 48–49°. Treatment of the filtrate as described above for the sodium amide adduct of benzophenone yielded 2.9 g (30%) more of the ketone, mp and mmp 48–49°.

B. Catalytic.—This reaction was performed essentially as described above for the stoichiometric reversion except that adduct 2 was added to 0.01 mole of sodium amide. After 30 min, the suspension was filtered under suction and the gray solid was washed thoroughly with liquid ammonia and ether. In contrast to the above experiments, no solid remained on the Büchner funnel. Excess ammonium chloride was added to the filtrate and the ammonia was evaporated. The usual work-up gave 4.34 g (65%) of phenylacetamide, mp and mmp 158–159°, and 9.01 g (99%) of benzophenone, mp and mmp 48–49°.