crystallized product, which was identical with the spectrum of the crude product, had peaks at τ 6.20 (singlet, 3 H), 2.71 (singlet, 10 H), 3.18 (doublet, 2 H, J = 9 cps), 2.0 (doublet, 2 H, J = 9 cps). The ir spectrum showed dominant peaks at 1675, 1585, 1260, 1154, 815, 740, and 692 cm^{-1}.

Kinetics. The general procedure followed for the kinetic runs is patterned after that of Grob.[19] For reaction vessels at temperatures below 130°, thick-walled Pyrex test tubes were used. For higher temperatures, specially made heavier walled Pyrex tubes were used. Prior to use, all tubes were washed with dilute hydrochloric acid, dilute sodium bicarbonate, thoroughly washed with tap water and distilled water and dried in the oven. Except for runs to test reaction-rate dependence upon concentration, all runs were 0.00833 M in the reactant iodide. DMF was chosen as solvent rather than ethanol because of the much greater solubility of the vinyl iodides in it. Preliminary kinetic runs in DMF with only small amounts of water present showed very slow reaction rates. Thus, it was advantageous to increase the per cent water as much as possible without rendering the compound insoluble. Consequently the following apparently awkward method of filling the tubes was employed. Sufficient compound to make a 0.01 M solution was weighed into the appropriate volumetric. Enough water was added to make the solution 16% aqueous on the basis of the volume with freshly distilled DMF. At this concentration of water, the compounds were still soluble in the solvent system. However, preliminary runs on such solutions still showed inconveniently slow rates. Thus the final method chosen was to place 5 ml of the above-described solutions into each tube along with 1 ml of water making the concentration of the compound 0.0833 M and the solution 29.6% aqueous.

A thermostated oil bath was used which exhibited temperature variations of less than ±1° at 190° and ±0.3° at lower temperatures around 100°. In a given run, all tubes were immersed in the oil bath simultaneously. One tube was removed after 1 min and taken as $t = 0$. Tubes were then removed at appropriate times and quenched in ice–water. After cooling, the reaction mixture was quantitatively transferred into a beaker with more DMF and six drops of 2 N nitric acid was added. The iodide ion concentration was determined by potentiometric titration with 0.01 N silver nitrate solution. A calomel electrode was used as reference electrode with a silver wire as the indicator electrode. All runs were repeated at least once. Rates were calculated according to the equation 2.303 $\log [a/(a - x)] = k$, where a refers to the extent of reaction and was determined from the potentiometric titrations and x refers to the initial concentration of the reactant iodide. For compound IIIa the value of x as determined from the infinity points showed excellent agreement with the initial concentration as calculated from the weighed amount of sample. The value of x for the remaining compounds was determined from weighed amounts of sample only. Attempts to determine infinity points for these less reactive compounds at the long times and high temperatures required led to several explosions of the sealed tubes. It was observed for some long reaction time tubes that a gas had formed, evidently from secondary reactions, and the amount of iodide was about 85% of theoretical. The rate constants were calculated over that portion of the reaction for which first-order kinetics were seen to be valid. For all but compound IIIa, first-order rates could be observed for several half-lives. Sample data are in Table IV.

Table IV. Solvolysis of 0.0083 M 1-Anisyl-2,2-diphenyliodoethylene at 114.0°

Time, min	0.010 N AgNO_3, ml	10^5k, sec^{-1}
0	0.050	
10	0.686	98.5
30	1.545	85.9
45	2.049	84.3
60	2.537	83.0
90	3.110	76.5

Formation of 1,1-Dianions of Hydrazones by Certain Bases. N,N-Dialkylation with Halides. Decomposition to Form Hydrocarbons[1]

Edwin M. Kaiser, Fred E. Henoch, and Charles R. Hauser

Contribution from the Departments of Chemistry, Duke University, Durham, North Carolina 27706, and the University of Missouri, Columbia, Missouri 65201.

Received August 12, 1968

Abstract: Hydrazones of ketones or aldehydes were converted by 2 equiv of potassium amide in liquid ammonia to 1,1-dipotassio salts, which were dialkylated with halides to form N,N-dialkyl derivatives. Dipotassiobenzophenone hydrazone was allowed to react with 1 equiv of benzyl chloride to form exclusively the mono-N-benzyl derivative, whereas the monopotassio salt of benzophenone hydrazone afforded a mixture of the mono- and di-N-benzyl derivatives. These methods appear preferable to the common type of condensation of ketones or aldehydes with the appropriate mono- or dialkylhydrazines. The dipotassiohydrazones decomposed, evolving nitrogen, on replacing the liquid ammonia with tetrahydrofuran or hexane to form corresponding hydrocarbons. The mechanism evidently involves the intermediate formation of the dipotassio salts of the hydrocarbons. The reaction is related to the Wolff–Kishner reduction, which presumably involves intermediate formation of monoanions of hydrazones and hydrocarbons. Hydrazones were converted by 2 equiv of n-butyllithium in tetrahydrofuran–hexane to 1,1-dilithio salts, which were dialkylated or decomposed to form N,N-dialkylhydrazones or hydrocarbons, respectively.

Several active hydrogen compounds have previously been converted to 1,1-dianions by means of bases. Thus, phenylacetonitrile,[2] acetomesitylene,[2] and benzyl phenyl sulfone[3] have been converted to **1**, **2**, and **3**, respectively, by means of n-butyllithium, and benzamide

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(1) Supported at Duke University by the Office of Army Research (Durham) and at Duke University and at the University of Missouri by the Petroleum Research Fund, administered by the American Chemical Society.

(2) E. M. Kaiser and C. R. Hauser, *J. Am. Chem. Soc.*, **88**, 2348 (1966).

(3) E. M. Kaiser and C. R. Hauser, *Tetrahedron Letters*, 3341 (1967).

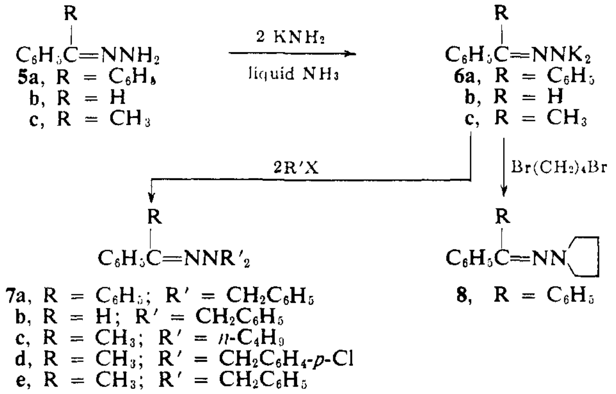
has been converted to **4** by this reagent[4] and by lithium aluminum hydride.[5]

$$\underset{\mathbf{1}}{C_6H_5CLi_2CN} \quad \underset{\mathbf{2}}{Li_2CHCOMes} \quad \underset{\mathbf{3}}{C_6H_5CLi_2SO_2C_6H_5} \quad \underset{\mathbf{4}}{C_6H_5CONLi_2}$$

In the present investigation, certain ketone and aldehyde hydrazones were converted to 1,1-dianions by means of potassium amide and *n*-butyllithium. These dianions are of interest, not only because they can be N,N-dialkylated or N-monoalkylated, but also because they undergo decomposition to form hydrocarbons, a type of reaction that is related to the well-known Wolff-Kishner reduction of monoanions of hydrazones.[6]

Results on N,N-Dialkylations. Hydrazones **5a-c** were converted by 2 equiv of potassium amide in liquid ammonia to 1,1-dipotassio salts **6a-c**, which were dialkylated with 2 equiv of appropriate halides to form N,N-dialkyl derivatives **7a-e**, respectively. Also, dipotassio salt **6a** was cyclized with 1,4-dibromobutane to give **8** (Scheme I).

Scheme I



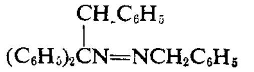
With the exception of **7e**, the N,N-dialkyl derivatives were readily isolated in the essentially pure condition in yields of 47-63%. Their structures were supported by analysis and absorption spectra. Besides characteristic infrared spectra, the nmr spectra of **7a,b** showed singlets for their four N-benzylic protons, and that of **7d** exhibited two sharp singlets for its benzyl and methyl protons. The nmr spectrum of **7c** showed a well-defined NCH_2 triplet integrating perfectly for 4.0 protons, and also other expected peaks (see Experimental Section).

The N,N-dialkyl derivative **7e** was difficult to isolate, and the crude product was hydrolyzed with acid to form acetophenone and 1,1-dibenzylhydrazine (eq 1).

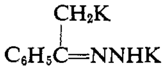
$$\mathbf{7e} \xrightarrow{20\%\ HCl} C_6H_5COCH_3 + H_2NN(CH_2C_6H_5)_2 \qquad (1)$$

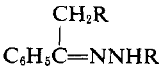
Although a resonance form of the 1,1-dianions of the dipotassiohydrazones would have a negative charge on carbon such as that in the dipotassio salt of benzophenone hydrazone represented as **9**, no C-alkylation along with N-alkylation appeared to occur. Thus, none of **10** was isolated in the reaction with benzyl chloride.


$$(C_6H_5)_2\overset{K}{C}N{=}NK$$
9

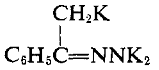

$$(C_6H_5)_2\overset{CH_2C_6H_5}{C}N{=}NCH_2C_6H_5$$
10

Interestingly, the secondary ionization of the intermediate monopotassio salt of acetophenone hydrazone involved the second hydrogen on nitrogen to form **6c**, not a methyl hydrogen to give **11**. Thus, the dialkylation products were **7c-e**, not those of type **12**.


$$C_6H_5\overset{CH_2K}{C}{=}NNHK$$
11


$$C_6H_5\overset{CH_2R}{C}{=}NNHR$$
12

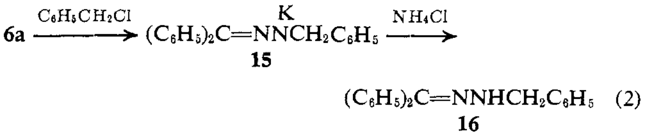
An attempt was made to effect tertiary ionization of a methyl hydrogen of dipotassio salt **5c** with an extra equivalent of potassium amide to form salt **13**, but treatment of the reaction mixture with 3 equiv of benzyl chloride failed to afford tribenzyl derivative **14** or any carbon derivative. Instead, dibenzyl derivative **6e** and stilbene were obtained; this hydrocarbon arose through self-condensation of the halide by the extra equivalent of alkali amide.[7]


$$C_6H_5\overset{CH_2K}{C}{=}NNK_2$$
13


$$C_6H_5\overset{CH_2CH_2C_6H_5}{C}{=}NN(CH_2C_6H_5)_2$$
14

Also, benzophenone hydrazone **5a** was converted by 2 equiv of *n*-butyllithium in tetrahydrofuran (THF)-hexane to the corresponding 1,1-dilithio salt, which was benzylated to form **7a** in 23% yield.

Results on N-Monoalkylation. Although both steps of the dibenzylation of dipotassiohydrazone **5a** appeared to be complete within 30 min, the first step might be expected to occur much more rapidly than the second because of 1,1-dianion should be much more nucleophilic than the resulting monoanion of the monoalkyl derivative. It therefore seemed possible to prepare a monoalkyl derivative uncontaminated with an appreciable amount of the dialkyl derivative. This was verified. Thus, treatment of dipotassiohydrazone **6a** with 1 equiv (or slightly less) of benzyl chloride afforded essentially pure monobenzyl derivative **16** in 52% yield; the monopotassio salt **15** was presumably present in the reaction mixture before neutralization (eq 2). Even the crude reaction product was indicated by tlc to contain none of the dibenzyl derivative **7e**.


$$\mathbf{6a} \xrightarrow{C_6H_5CH_2Cl} \underset{\mathbf{15}}{(C_6H_5)_2C{=}N\overset{K}{N}CH_2C_6H_5} \xrightarrow{NH_4Cl} \underset{\mathbf{16}}{(C_6H_5)_2C{=}NNHCH_2C_6H_5} \qquad (2)$$

It might appear that the monoanion of a hydrazone, such as monoanion **17** of benzophenone hydrazone, could be monoalkylated satisfactorily. However, treatment of **17** with 1 equiv of benzyl chloride afforded a mixture of the mono- and dibenzyl derivatives, **16** and **7a**, respectively, which were difficult to separate. Evidently, some of monobenzyl derivative **16** was converted by monopotassiohydrazone **17** to monopotassio derivative **15**, which underwent further benzylation (Scheme II).

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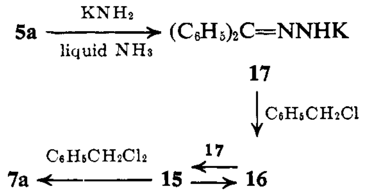
[4] E. M. Kaiser, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, **32**, 3640 (1967).

[5] M. S. Newman and T. Fukunaga, *J. Am. Chem. Soc.*, **82**, 693 (1960).

[6] See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 159.

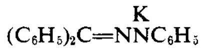
[7] See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Broadhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

Scheme II



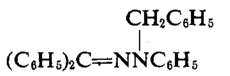
$$\begin{tikzcd}[column sep=large]
 & \mathbf{5a} \arrow[r, "KNH_2", "\text{liquid NH}_3"'] & (C_6H_5)_2C{=}NNHK & \\
 & & \mathbf{17} \arrow[d, "C_6H_5CH_2Cl"] & \\
\mathbf{7a} & & \mathbf{15} \arrow[ll, "C_6H_5CH_2Cl_2"'] \arrow[r, shift right] & \mathbf{16} \arrow[l, shift right, "\mathbf{17}"']
\end{tikzcd}$$

Such an equilibration accompanied by further alkylation has previously been observed on treatment of sodiophenylacetonitrile with 1 equiv of benzyl chloride.[8] Benzophenone phenylhydrazone has been monobenzylated satisfactorily through potassio salt **18** to form **19**, but this product is incapable of undergoing further benzylation.[9]



$(C_6H_5)_2C{=}N\overset{K}{N}C_6H_5$

18



$(C_6H_5)_2C{=}N\overset{\overset{CH_2C_6H_5}{|}}{N}C_6H_5$

19

Results on Decomposition. Although the dipotassiohydrazones were stable in liquid ammonia, they evolved nitrogen when the liquid ammonia was replaced with THF, and the resulting suspension refluxed, to form corresponding hydrocarbons. Thus, dipotassio salts **6a,b** were converted to diphenylmethane and toluene (**20a,b**) in yields of 80 and 81%, respectively (eq 3).

$$\mathbf{6a,b} \xrightarrow[+\text{THF}]{-NH_3} \xrightarrow[+\text{acid}]{-N_2} C_6H_5CH_2R \tag{3}$$

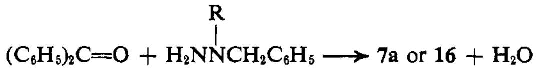
$$\mathbf{20a},\ R = C_6H_5$$
$$\mathbf{b},\ R = H$$

Similarly, the hydrazone of fluorenone was converted to fluorene in 80% yield. However, dipotassiohydrazone **6c** afforded ethylbenzene in only 5% yield under similar conditions.

Likewise, benzophenone hydrazone (**5a**) and fluorenone hydrazone were converted by 2 equiv of *n*-butyllithium in THF–hexane to dilithio salts, which underwent decomposition at room temperature or higher to form diphenylmethane and fluorene in yields of 56 and 45%, respectively. However, benzaldehyde and acetophenone hydrazones failed to yield appreciable amounts of the corresponding hydrocarbons under similar conditions.

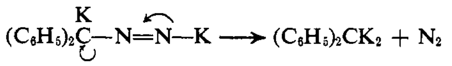
It should be mentioned that, whereas dipotassiohydrazone **6a** decomposed readily in refluxing THF, the corresponding monopotassiohydrazone **17** (see Scheme II) failed to decompose under similar conditions, and 89% of the original hydrazone was recovered. Although monoanions of hydrazones undergo decomposition to form hydrocarbons in the Wolff–Kishner reduction,[6] much higher temperatures and longer reaction periods have generally been employed.[10] However, such reductions have been effected even at room temperature in dimethyl sulfoxide.[11]

Discussion of Results. The N,N-dialkylations described above not only furnish evidence for formation of 1,1-dianions of the hydrazones, but they also illustrate a convenient and, presumably, quite general method for the synthesis of N,N-dialkylhydrazones where the two alkyl groups are the same. Also, the monoalkylation of a dipotassiohydrazone is convenient, and further alkylation with a different halide to form a mixed N,N-dialkylhydrazone appears feasible. These methods, especially that involving the dialkylation, seem preferable at the present time to the common type of condensation of a ketone or aldehyde with a di- or monoalkylhydrazine as illustrated by eq 4 (where R is benzyl or hydrogen), since such hydrazines appear not readily available or are rather expensive. Actually the 1,1-dibenzylhydrazine that was employed in this investigation in an independent synthesis of dibenzyl derivative **7a** was obtained by hydrolysis of dibenzyl derivative **7c** (see eq 1). Moreover, condensations of benzophenone with dibenzylhydrazine and monobenzylhydrazine (eq 4) were realized satisfactorily only by employing an excess of these hydrazines and/or relatively long reaction periods (see Experimental Section).



$$(C_6H_5)_2C{=}O + H_2N\overset{\overset{R}{|}}{N}CH_2C_6H_5 \longrightarrow \mathbf{7a}\text{ or }\mathbf{16} + H_2O \tag{4}$$

The decomposition of the 1,1-dianions of hydrazones to form hydrocarbons is of particular interest since the mechanism evidently involves the intermediate formation of a 1,1-dicarbanion of the hydrocarbon such as that in dipotassio salt **21**; this salt would arise from dipotassiohydrazone **6a** through a β elimination which may be illustrated with resonance form **9** (eq 5). This mechanism is analogous to that proposed for the Wolff–Kishner decomposition of hydrazones to form monocarbanions of hydrocarbons.[6]



$$(C_6H_5)_2\overset{K}{C}{-}N{=}N{-}K \longrightarrow (C_6H_5)_2CK_2 + N_2 \tag{5}$$

9 **21**

Although deuteration of the THF suspension of the reaction product after nitrogen was evolved from the dipotassiohydrazone afforded diphenylmethane containing only 0.9 methylene deuterium atom per molecule (by nmr), similar deuteration of a hexane suspension obtained on replacing the liquid ammonia with this solvent produced diphenylmethane having 1.54 methylene deuterium atoms per molecule. Similarly, deuteration of THF and hexane suspensions of the reaction product obtained from decomposition of dilithiobenzophenone hydrazone (prepared with *n*-butyllithium) afforded diphenylmethane containing 1.12 and 1.36 methylene deuterium atoms per molecule, respectively.

These results in hexane support the mechanism shown in eq 5; thus, 54% of the dipotassiodiphenylmethide (**21**) was evidently present at the time of deuteration. Apparently, when the decompositions were effected in THF, the dipotassio salt **21** or the corresponding dilithiohydrocarbon abstracted a proton from the solvent to form the monoalkalidiphenylmethide. Such abstractions of protons from THF by certain strongly basic organoalkali compounds have been reported.[12] An alternate mechanism would involve simultaneous abstraction of the proton and evolution of the nitrogen; this concerted mechanism would permit elimination of the monocarbanion of the hydrocarbon rather than that of the more strongly basic dicarbanion.

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[8] W. G. Kenyon, E. M. Kaiser, and C. R. Hauser, *J. Org. Chem.*, **30**, 4135 (1965).

[9] W. G. Kenyon and C. R. Hauser, *ibid.*, **30**, 292 (1965).

[10] See D. Todd, *Org. Reactions*, **4**, 387 (1948).

[11] D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

[12] For example, see H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957); R. Waack and M. A. Doran, *ibid.*, **32**, 3395 (1967).

There was a possibility that some deuterium had entered the *ortho* or *para* positions of the aromatic rings since, because of repulsion between the two negative charges on the diphenylmethide dicarbanion, these positions might have functioned as basic centers for abstraction of deuterium from the deuterium oxide. However, little if any deuterium appeared to be present on the rings of the diphenylmethane obtained, since a redetermination of the deuterium content of the 1.54-D sample employing toluene as a standard showed 1.58 methylene deuterium atoms per molecule; in this determination, the 10:2 ratio of the aromatic protons to methylene protons, which was used as the basis for the 1.54 D value, was not involved. Incidentally, a mathematical calculation has indicated that the 1.54 D value would have been a minimum for the methylene deuterium had some deuterium entered the ring.

Experimental Section[13]

Dialkylations of Benzophenone Hydrazone (5a). A. With Benzyl Chloride. To a stirred suspension of 0.05 mol of potassium amide in 300 ml of commercial anhydrous liquid ammonia,[14] prepared from 1.95 g (0.05 g-atom) of potassium, was added in portions 4.9 g (0.025 mol) of solid benzophenone hydrazone (**5a**). After 1 hr, the resulting brown-green mixture was assumed to contain 0.025 mol of dipotassio salt **6a**. The mixture was then treated, during 5 min, with a solution of 6.3 g (0.05 mol) of benzyl chloride in 20 ml of anhydrous ether. After 1.5 hr, the yellow reaction mixture was neutralized with 10 g of solid ammonium chloride, and the ammonia was evaporated (steam bath). The residue was taken up into ether and water, and the ethereal layer was combined with two ethereal extracts of the aqueous layer. The extracts were dried ($MgSO_4$) and concentrated to afford a yellow oil, which was dissolved in hot hexane. Upon cooling, the solution afforded 6.1 g (65%) of N,N-dibenzylbenzophenone hydrazone (**7a**), mp 68–70 and 74.5–75.5° after recrystallization from methanol; ir (KBr) 3065 (Ar-H), 2870 (aliphatic C-H), and 1340 cm^{-1} (C-N); nmr[15] 230 (s, 4.0, N-CH_2) and 435.5 (m, 20.0, ArH).

Anal. Calcd for $C_{27}H_{24}N_2$: C, 86.13; H, 6.43; N, 7.44. Found: C, 85.69; H, 6.37; N, 7.62.

Also, a solution of 0.025 mol of benzophenone hydrazone (**5a**) in 200 ml of THF[16] was added, during 3 hr, to a mixture of 55 ml (0.0875 mol) of 1.6 *M* *n*-butyllithium in hexane[17] and 55 ml of THF[16] at −80° to form a yellow solution which, after stirring for 15 min more, was assumed to contain 0.025 mol of dilithiobenzophenone hydrazone. To the stirred, cold solution was added 12.7 g (0.1 mol) of benzyl chloride in 50 ml of THF[16] and the solution refluxed for 20 hr. The reaction mixture was decomposed with 100 ml of 3 *N* hydrochloric acid, and the layers were separated. The aqueous layer, after being washed with ether, was neutralized with sodium carbonate. The resulting mixture was extracted with ether, and the ethereal extracts were worked up to give 2.12 g (23%) of the dibenzyl derivative **7a**, mp and mmp 74–75°.

B. With 1,4-Dibromobutane. To a stirred suspension of 0.025 mol of dipotassio salt **6a** (see above) in liquid ammonia was added a solution of 5.4 g (0.025 mol) of 1,4-dibromobutane in 20 ml of ether and the reaction mixture worked up after 1.5 hr essentially as described above under A to give 2.94 g (47%) of N-pyrrolidylbenzophenone imine (**8**), mp 40–42° after recrystallization from methanol; ir (mull) 3050 (Ar–H) and 770 and 730 cm^{-1} (aromatic); nmr 117.5 (m, 4.0, CH_2), 202 (m, 4.0, N–CH_2), and 479 (m, 10.0, Ar–H).

Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.60; H, 7.20; N, 11.20. Found: C, 81.71; H, 7.33; N, 10.99.

Dibenzylation of Benzaldehyde Hydrazone (5b). To a stirred suspension of 0.05 mol of potassium amide in 300 ml of liquid ammonia was added, during 2 min, a solution of 3.0 g (0.025 mol) of benzaldehyde hydrazone (**5b**) in 20 ml of ether. After 30 min, the resulting dark green solution was treated, during 10 min, with a solution of 6.3 g (0.05 mol) of benzyl chloride in 20 ml of ether. The resulting dark orange suspension was neutralized with ammonium chloride 1.5 hr later and worked up as described above for the dibenzylation of dipotassio salt **6a** to give, after recrystallization from 95% ethanol, 4.65 g (62%) of N,N-dibenzylbenzaldehyde hydrazone (**7b**), mp 78.5–80°; ir (KBr) 3020 (Ar—H), 2935 (aliphatic (C—H), 2820 (CHO), 1620 (C═N), and 1315 and 1345 cm^{-1} (C—N); nmr 267 (s, 4.0, N—CH_2), 439.5 (m, 14.9, Ar—H), and 564 (s, 1.0, aldehydic H).

Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 84.09; H, 6.67; N, 9.38.

The liquor obtained on filtration of the crude product afforded benzaldehyde, isolated as its 2,4-dinitrophenylhydrazone (0.5 g, 9%), mp and mmp 236–237°.

Dialkylation of Acetophenone Hydrazone (5c). A. With *n*-Butyl Bromide. A dark yellow-green solution of 0.025 mol of dipotassio salt **6c**, prepared from 3.35 g (0.025 mol) of acetophenone hydrazone (**5c**) and 0.05 mol of potassium amide in liquid ammonia, was treated with 6.85 g (0.05 mol) of *n*-butyl bromide in ether and the resulting bright orange suspension worked up essentially as described above for the dibenzylation of dipotassio salt **6b**. The residue obtained on evaporation of the ethereal solution of the product was distilled to give 2.95 g (48%) of N,N-di-*n*-butylacetophenone hydrazone (**7c**), bp 125–127° (0.3 mm); ir (neat) 3022 (Ar—H), 2840–2970 (aliphatic C—H), 1640 (C═N), 1290 cm^{-1} (C—N); nmr 71.5 (m, 13.8, -$CH_2CH_2CH_3$), 136 (s, 3.0, CH_3), 163 (t, 3.9, N—CH_2), and 450 (m, 5.0, Ar—H).

Anal. Calcd for $C_{16}H_{26}N_2$: C, 77.99; H, 10.64; N, 11.37. Found: C, 78.23; H, 10.59; N, 11.40.

B. With *p*-Chlorobenzyl Chloride. A solution of 0.04 mol of dipotassio salt **6c**, prepared from 0.04 mol of hydrazone **5c** and 0.08 mol of potassium amide in liquid ammonia, was treated with 12.88 g (0.08 mol) of *p*-chlorobenzyl chloride in 20 ml of ether, and the reaction mixture worked up as described for the dibenzylation of dipotassio salt **6a** to give 9.4 g (62%) of N,N-di-*p*-chlorobenzylacetophenone hydrazone (**7e**), mp 66–67° after recrystallization from methanol; ir (KBr) 3033 (Ar—H), 2860–2972 (aliphatic C—H), 1620 (C═N), 1310 cm^{-1} (C—N); nmr 125 (s, 3.0, CH_3), 231 (s, 4.0, N—CH_2), and 436 (m, 13.0, Ar—H).

Anal. Calcd for $C_{22}H_{20}N_2Cl_2$: C, 69.00; H, 5.26; N, 7.32. Found: C, 68.71; H, 5.31; N, 7.44.

C. With Benzyl Chloride. A solution of 0.04 mol of dipotassio salt **6c** was prepared and treated with 0.08 mol of benzyl chloride in ether as described under B to give 9.4 g of an oily solid which failed to crystallize on cooling or on attempted recrystallization from ethanol. The crude product (recovered from the ethanolic solution) was refluxed with 40 ml of 20% hydrochloric acid for 3 hr. After cooling, the reaction mixture was poured onto 100 g of crushed ice. The resulting slurry was extracted three times with ether and the extracts combined. The solution was dried ($MgSO_4$) and the solvent removed to afford 3.55 g of acetophenone, isolated as its 2,4-dinitrophenylhydrazone (8.88 g, 74%), mp and mmp 248–249°.

The acidic, aqueous solution remaining after the ethereal extraction was made basic with aqueous ammonia, and the resulting mixture was extracted three times with ether. The combined ethereal extracts were dried ($MgSO_4$) and saturated with dry hydrogen chloride gas to precipitate 6.0 g (56%) of 1,1-dibenzylhydrazine hydrochloride, mp 197–198° (lit.[18] mp 199–201°).

Attempted Preparation of Tripotassioacetophenone Hydrazone (13). To a stirred suspension of 0.12 mol of potassium amide in 300 ml of liquid ammonia,[14] was added a solution of 5.56 g (0.04 mol) of acetophenone hydrazone (**5c**) in 20 ml of ether After 30 min, the dark green solution was treated with a solution of 14.83 g (0.12 mol) of benzyl chloride in 30 ml of ether; a purple color appeared immediately. After 1.5 hr, the suspension was worked up

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(13) Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on Perkin-Elmer spectrophotometers Models 137 and 237 using potassium bromide disks [illegible] solids and sodium chloride plates for liquids. Nmr spectra were determined on a Varian Associates A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal standard. Vapor phase chromatography was performed on an F & M Model 500 gas chromatograph. Analyses were performed by Paul Demoen, Janssen Pharmaceutical Research Laboratories, Beerse, Belgium, and M–H–W Laboratories, Garden City, Mich. The hydrazones **5a–c** were prepared in excellent yields by the method of G. P. Newkome and D. C. Fishel, *J. Org. Chem.*, **31**, 677 (1966).

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

(15) In the nmr descriptions, s = singlet, t = triplet, m = multiplet, and b = broad; all values are reported as cycles per second (cps) values.

(16) Freshly distilled from lithium aluminum hydride.

(17) Obtained from the Foote Mineral Co., Exton, Pa.

(18) H. H. Fox, J. T. Gibas, and A. Motchane, *J. Org. Chem.*, **21**, 349 (1956).

as described above under C The residue obtained on evaporation of the ethereal solution of the product was filtered to afford 1.2 g (33%) of stilbene, mp and mmp 123–124°. Vpc analysis of the filtrate showed the presence of additional stilbene which was not isolated. The filtrate was refluxed with 50 ml of 20% hydrochloric acid for 3 hr and worked up as described above to give 2.92 g of acetophenone, identified as its 2,4-dinitrophenylhydrazone (7.29 g, 61%), mp and mmp 248–249°, and 4.3 g (44%) of 1,1-dibenzylhydrazine hydrochloride, mp and mmp[11] 197–198°.

Monobenzylation of Dipotassiobenzophenone Hydrazone (6a). To a stirred suspension of 0.025 mol of dipotassio salt **6a** (prepared as described above), was added, during 5 min, a solution of 3.15 g (0.025 mol) of benzyl chloride in 20 ml of ether. After 1.5 hr the resulting suspension was neutralized and worked up as above to give a light yellow solid which was shown by tlc to contain only two components. Fractional crystallization from ethanol–hexane afforded 1.2 g (24%) of the starting hydrazone, mp 98°, mmp 97–98°, and 3.64 g (52%) of N-benzylbenzophenone hydrazone (**16**), mp 80–81° (lit.[19] mp 80.8–81.2°); ir (KBr) 3320 (N—H), 3075 (Ar—H), and 1620 cm^{-1} (C=N).

Monobenzylation of Monopotassiobenzophenone Hydrazone (15). To a stirred suspension of 0.02 mol of potassium amide in 300 ml of liquid ammonia[14] was added 3.92 g (0.02 mol) of benzophenone hydrazone followed, after 30 min, by a solution of 2.53 g (0.02 mol) of benzyl chloride in 25 ml of ether, added during 3 min. After 2 hr, the reaction mixture was neutralized and worked up to give a crude yellow solid. Tlc showed the presence of three components. Fractional crystallization from ethanol gave 1.18 g (30%) of the starting hydrazone **5a**. Repeated fractional crystallizations of the filtrate from hexane–benzene–acetonitrile afforded only small quantities of essentially pure monobenzyl derivative **16**, mp and mmp 80–81°, and pure dibenzyl derivative **7a**, mp 74–75°, mmp 74–75.5°. These isolated products **16** and **7a** showed infrared spectra identical with those of authentic samples.

Condensations of Benzophenone with Hydrazines. In Table I are summarized the yields of hydrazones obtained in these condensations under various conditions. The details of these reactions are described below.

Table I. Yields of Mono- and Dibenzylhydrazones from Condensations of Benzophenone with Mono- and Dibenzylhydrazines under Various Conditions

R | $C_6H_5CH_2NNH_2$	Hydrazine: benzophenone	Time, hr	Product	Yield, %
R = $C_6H_5CH_2$	1:1	2	**6a**	24
$C_6H_5CH_2$	4:1	2	**6a**	38
$C_6H_5CH_2$	4:1	12	**6a**	76
$C_6H_5CH_2$	4:1	24	**6a**	76
H	1:1	2	**16**	28
H	4:1	2	**16**	42
H	4:1	12	**16**	66
H	4:1	24	**16**	74

A. With 1,1-Dibenzylhydrazine. A mixture of 0.46 g (0.0025 mol) of benzophenone, 0.62 g (0.0025 mol) or 2.49 g (0.01 mol) of 1,1-dibenzylhydrazine hydrochloride (see Table I), and 1.0 g (0.0125 mol) of sodium acetate in 20 ml of absolute ethanol was refluxed for the appropriate length of time. Upon cooling, the resulting clear yellow solution was shaken with ether and water. The layers were separated, and the ethereal layer was combined with several ethereal extracts of the aqueous layer. After drying ($MgSO_4$) and concentrating, the residual oily solid was collected and recrystallized from methanol to give **7a**, mp 74–75°, undepressed on admixture with a sample of **7a** obtained above by dibenzylation of dipotassio salt **6a**.

B. With Benzylhydrazine. A mixture of 0.91 g (0.005 mol) of benzophenone, 0.97 g (0.005 mol) or 3.9 g (0.02 mol) of benzylhydrazine hydrochloride[20] (see Table I), and 1.8 g (0.022 mol) of sodium acetate in 20 ml of absolute ethanol was refluxed for the appropriate time. Upon cooling, the resulting solution was worked up as described above under A to afford **16**, mp 80°, mmp 80–81°.

Decompositions of Dipotassiohydrazones to Form Hydrocarbons. A. Decomposition of Dipotassiobenzophenone Hydrazone (6a). Dipotassio salt **6a** (0.025 mol) was prepared from benzophenone hydrazone and potassium amide in 200 ml of liquid ammonia as described above. After 1 hr, the ammonia was evaporated under a a nitrogen atmosphere as 200 ml of THF[16] was added. The resulting brown-orange mixture was refluxed for 1 hr and then stirred with 100 ml of cold 3 N hydrochloric acid. The layers were separated, and the organic layer was combined with four ethereal extracts of the aqueous layer. The solution was dried ($MgSO_4$) and concentrated. Distillation of the residue afforded 3.36 g (80%) of diphenylmethane, bp 122–123° (10 mm) (lit.[21] bp 120° (10 mm)).

When benzophenone hydrazone (**5a**) was treated with only 1 equiv of potassium amide in liquid ammonia and the ammonia replaced by THF,[16] followed by refluxing for 1 hr, 4.35 g (89%) of hydrazone **5a** was recovered, mp and mmp 94–96°.

B. Decomposition of Other Dipotassiohydrazones. Similarly, the dipotassio salts of benzaldehyde hydrazone (**6b**) and fluorenone hydrazone were converted to toluene, bp 110° (lit.[22] bp 110.6°), and fluorene, mp and mmp 114–115°, in yields of 81 and 80%, respectively.

Similar treatment of dipotassioacetophenone hydrazone (**6c**) afforded ethyl benzene (identified by vpc) in only 5% yield; 2.18 g (65%) of acetophenone hydrazone (**5c**) was recovered.

Decomposition of Dilithiohydrazones to Form Hydrocarbons. Dilithiobenzophenone hydrazone was prepared at −8° from 0.02 mol of hydrazone **5a** in 200 ml of THF[16] and 0.05 mol of n-butyllithium[17] in hexane essentially as described above, and the solution warmed to room temperature during 1.5 hr. The green reaction mixture was neutralized with hydrochloric acid and worked up to give 1.88 g (56%) of diphenylmethane, bp[21] 89–90° (3 mm).

Similar results were obtained when the reduction of **5a** was carried-out in refluxing THF for 1 hr affording 1.37 g (33%) of diphenylmethane.

Also, fluorenone hydrazone was converted to its dilithio salt, which was decomposed at room temperature to give fluorene, mp and mmp 115–116° (recrystallized from benzene) in 45% yield.

Likewise, treatment of benzaldehyde hydrazone afforded toluene and benzaldehyde azine, mp 90° (lit.[23] mp 93°), in yields of 5 and 56%, respectively.

Similar treatment of acetophenone hydrazone produced acetophenone azine, mp 122–123° (lit.[24] mp 124°), in 38% yield; 36% of the starting hydrazone was recovered.

Deuteration of Decomposition Product of Dialkalibenzophenone Hydrazones. A. In THF. Dipotassiohydrazone **6a** (0.025 mol) was prepared in liquid ammonia and decomposed in THF[16] by refluxing for 1 hr as described above. Excess deuterium oxide was then added, and the resulting mixture worked up to give 3.2 g (75%) of diphenylmethane, bp[21] 100–101° (3.5 mm), which contained 0.9 α-deuterium atom per molecule (by nmr).

Similarly, dilithiobenzophenone hydrazone (0.025 mol) was prepared in THF–hexane by means of n-butyllithium[17] and decomposed at room temperature as described above. Excess deuterium oxide was then added, and the resulting mixture worked up to afford 2.75 g (66%) of diphenylmethane, bp[21] 89–90° (3 mm) having 1.12 α-deuterium atoms per molecule (by nmr).

B. In Hexane. Dipotassiohydrazone **6a** (0.025 mol) was prepared in liquid ammonia as described above, and the liquid ammonia then evaporated at 0° under nitrogen as an equal volume of hexane was added. The resulting orange-brown mixture was refluxed for 30 min, and then treated with excess deuterium oxide. The reaction mixture was worked up to give 2.33 g (56%) of diphenylmethane having 1.54 α-deuterium atoms per molecule.

In another experiment, the ammonia was replaced by hexane under nitrogen at about 25–30°. After refluxing the mixture for 1 hr, excess deuterium oxide was added to give 2.73 g (66%) of diphenylmethane having 1.24 α-deuterium atoms per molecule (by nmr). Apparently, a portion of dipotassiodiphenylmethane (**21**) produced at 25–30° reacted with ammonia before all of the latter had been removed.

Similarly, dilithiobenzophenone hydrazone (0.025 mol) was prepared in hexane as described above and refluxed for 1 hr. Subsequent deuteration and work-up gave 2.14 g (47%) of diphenylmethane having 1.36 α-deuterium atoms per molecule (by nmr).

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(19) G. H. Coleman, H. Gilman, C. E. Adams, and P. E. Pratt, *J. Org. Chem.*, 3, 99 (1938).

(20) Obtained from the Aldrich Chemical Co.

(21) G. Harris, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965, p 1235.

(22) Reference 21, p 3068.

(23) Reference 21, p 373.

(24) Reference 21, p 12.