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Preliminary communication

Interaction of organometallic reagents with certain aliphatic diazo compounds

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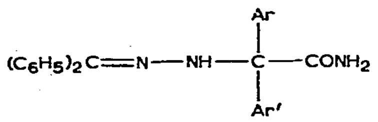
With two exceptions, the reactions of organometallic reagents with aliphatic diazo compounds to afford hydrazones appear to be limited to four unsubstituted Grignard reagents and five diazo compounds[1]. For example, phenylmagnesium bromide has been coupled with diphenyldiazomethane in ethyl ether to give the phenylhydrazone of benzophenone in 70% yield[2] (eq. 1). The two non-Grignard organometallics which have similarly been converted to hydrazones are sodiotriphenylmethane[3] and n-butyllithium[4]. Of course, neither of these reagents contained functional groups and, as above, the condensations were carried out in ether only.

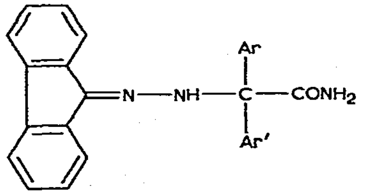
$$(C_6H_5)_2CN_2 + C_6H_5MgBr \xrightarrow{\text{ether}} \xrightarrow{\text{acid}} (C_6H_5)_2C{=}N{-}NHC_6H_5 \qquad (1)$$

We now wish to report that the scope of such condensation reactions is much larger than previously realized. This has been ascertained simply by taking advantage of the known synthesis of a wide variety of functionally substituted non-Grignard organometallic reagents prepared by metalations in liquid ammonia or in tetrahydrofuran (THF)/hexane. Straight-forward addition of various aliphatic diazo compounds to such nucleophilic metallic reactants then cleanly provides a wealth of new hydrazones in fair to excellent yields.

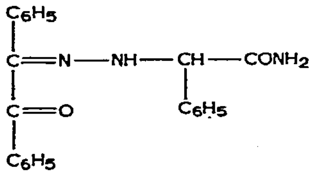
Some of the preliminary results of this study are listed in Table 1. This table shows that disodiodiphenylacetamide couples with diphenyldiazomethane and with 9-diazofluorene in liquid ammonia to afford hydrazones I and II in yields of 73% and 43%, respectively. The related dilithiodiphenylacetamide likewise couples with 9-diazofluorene in THF to give II in 46–50% yields; in this latter case, the temperature of the reaction mixtures seems not to be critical. Similarly, disodiophenylacetamide combines with diphenyldiazomethane and 9-diazofluorene in ammonia to afford hydrazones III and IV in yields of 88% and 56%, respectively. This same dianion couples with azibenzil at the terminal nitrogen atom giving hydrazone V, but in only 20% yield. Also, 4-sodiomethylpyridine condenses with diphenyldiazomethane in ammonia to afford VI in 41% yield.



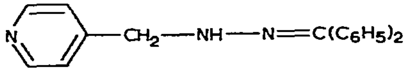
(I) Ar = Ar′ = C_6H_5
(III) Ar = C_6H_5, Ar′ = H



(II) Ar = Ar′ = C_6H_5
(IV) Ar = C_6H_5, Ar′ = H



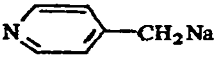
(V)



(VI)

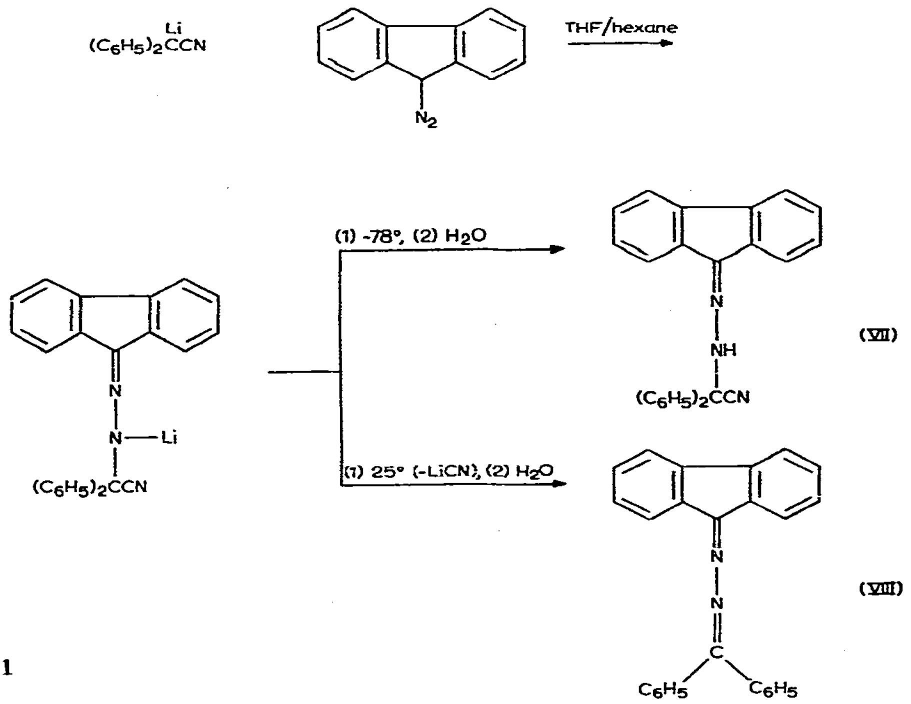
TABLE 1

PREPARATION OF HYDRAZONES FROM ORGANOMETALLIC REAGENTS AND ALIPHATIC DIAZO COMPOUNDS

Organometallic	Diazo compound	Solvent	Hydrazone	Yield (%)
$(C_6H_5)_2CNaCONHNa$	diphenyldiazomethane	NH_3	I	73
$(C_6H_5)_2CNaCONHNa$	9-diazofluorene	NH_3	II	43
$(C_6H_5)_2CLiCONHLi$	9-diazofluorene	THF (25°)	II	46
$(C_6H_5)_2CLiCONHLi$	9-diazofluorene	THF (−78°)	II	50
$C_6H_5CHNaCONHNa$	diphenyldiazomethane	NH_3	III	88
$C_6H_5CHNaCONHNa$	9-diazofluorene	NH_3	IV	56
$C_6H_5CHNaCONHNa$	azibenzil	NH_3	V	20
	diphenyldiazomethane	NH_3	VI	41
$(C_6H_5)_2CLiCN$	9-diazofluorene	THF (−78°)	VII	90 (crude)
$(C_6H_5)_2CLiCN$	9-diazofluorene	THF (25°)	–	

The last entry in Table 1, the condensation of lithiodiphenylacetonitrile with 9-diazofluorene, deserves special mention. Thus, when this reaction is performed at −78° in THF/hexane, the expected hydrazone VII is obtained in 90% yield. On the other hand, when this reaction is performed at 25°, an unexpected elimination of lithium cyanide is realized giving rise to the mixed azine VIII in 97% yield (Scheme 1). Although the synthetic utility of this latter reaction and related ones remains to be assessed, this elimination is, nevertheless, an interesting one. Such a loss of cyanide ion is reminescent of a similar result observed in the interaction of monoalkali or of 1,1-dialkali salts of phenylacetonitrile with azobenzene to give a cyanoenamine[5].

Each of the hydrazones described above is a new compound which should be capable of being reduced and hydrolyzed to new highly substituted hydrazines. The



SCHEME 1

structures of these hydrazones were supported by correct elemental analyses and by IR spectroscopy; the presence of N–H absorptions in the latter ruled out isomeric azo compounds which were initially possible.

Studies are currently underway to truely assess the generality of the above condensations which, synthetically, should be limited only by the ease of preparing the necessary diazo compounds. Incidentally, it has been established that diphenyldiazomethane can be prepared *in situ* in liquid ammonia itself by oxidizing potassiobenzophenone hydrazone with potassium permanganate (eq. 2).

$$(C_6H_5)_2C{=}NNHK + KMnO_4 \xrightarrow{NH_3} (C_6H_5)_2CN_2 \qquad (2)$$

ACKNOWLEDGEMENT

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