crystallized from isooctane–EtOAc to give 2.47 g (88%) of 4,6-dipiperidino-2*H*-1,3,5-thiadiazin-2-one, mp 133–138°. Recrystallization from EtOH–H_2O and then heptane–EtOAc gave the pure material: mp 141–142°; ir ($CHCl_3$) 1650, 1523, 1440, 1410 cm^{-1}.

Anal. Calcd for $C_{13}H_{20}N_4OS$: C, 55.68; H, 7.19; N, 19.98; S, 11.44. Found: C, 56.01; H, 7.15; N, 20.17; S, 11.20.

4,6-Bis(1-pyrrolidinyl)-2*H*-1,3,5-thiadiazin-2-one was prepared by refluxing 3,5-bis(1-pyrrolidinyl)-1,2,4-dithiazolium bromide (3.23 g) and KNCO (0.86 g) in DMF (25 ml) for 1 hr. The DMF was stripped and the residue was extracted into MeOH. The MeOH extract was filtered and evaporated and the residue was extracted with hot EtOAc. Dilution of the EtOAc solution with hexane and chilling precipitated the product as a light tan solid (1.19 g, 40%, mp 133–137°). Recrystallization from EtOAc gave 0.80 g, mp 140–141°; ir ($CHCl_3$) 1650, 1530, 1410 cm^{-1}.

Anal. Calcd for $C_{11}H_{16}N_4OS$: C, 52.35; H, 6.39; N, 22.20. Found: C, 52.45; H, 6.21; N, 22.21.

Synthesis of 4 from 3-[*N*,*N*-(Dimethylamidino)]-1,1-dimethyl-2-thiourea[1] (5) and Carbonyldiimidazole.—A solution of **5** (258 mg) and 1,1-carbonyldiimidazole (240 mg) in toluene (12 ml) was refluxed for 4 hr, cooled, washed with H_2O, dried, and evaporated. The residue (40 mg, mp 124–129°) was recrystallized from CCl_4 to give pure **4**, mp 135–136°, shown by its infrared spectrum and by mixture melting point to be identical with that prepared from **1** and KNCO.

Reaction of 5-(Dimethylamino)-3-(methylimino)-3*H*-1,2,4-dithiazole Hydrobromide (6) with Potassium Cyanate.—A mixture of **6** (5.00 g) and KNCO (1.74 g) in DMF (50 ml) was refluxed under N_2 for 1 hr. After cooling to room temperature the mixture was filtered and the filtrate was stripped. The residue (in CH_2Cl_2) was added to a silica gel column. Elution with C_6H_6 gave 1 g of an unidentified yellow solid, mp 140–177°, that moved with the solvent front. The column was then eluted with $CHCl_3$–C_6H_6 and finally with $CHCl_3$. 6-(Dimethylamino)-4-(methylamino)-2*H*-1,3,5-thiadiazin-2-one (**7**) and 4-(dimethylamino)-6-(methylamino)-2*H*-1,3,5-thiadiazin-2-one (**18**) were eluted together over a series of fractions (as judged by nearly identical ir spectra of early and late fractions). The evaporated fractions were combined in hot CH_3CN; chilling the solution gave 0.80 g (22%) of a whilte solid, mp 185–195°. Several recrystallizations from EtOH and then CH_3CN gave pure **7**, mp 188–189°; ir (KBr) 1695, 1620, 1560, 1515, 1480, 985 cm^{-1}; nmr (DMSO-d_6) δ 3.11 (s, 6 H), 3.50 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 186 (100, molecular ion), 158 (22, M − CO), 113 (28), 88 (10), 84 (21), 83 (30). High-resolution analysis of the *m/e* 88 area showed two peaks with exact molecular weights 88.0100 and 88.0223 (calcd for $C_2H_4N_2S$ and C_3H_6NS, respectively, 88.0095 and 88.0221). The latter peak, absent in the spectrum of **8**, corresponds to $Me_2NC{=}S^+$ which could only have been derived from structure **7**.

Anal. Calcd for $C_6H_{10}N_4OS$: C, 38.69; H, 5.41; N, 30.08; S, 17.22. Found: C, 38.56; H, 5.29; N, 29.87; S, 17.42.

Crude **8** was obtained from the mother liquors of **7**; the analytical sample was obtained by repeated recrystallizations (three from EtOH, then two from CH_3CN), mp 218–220°; ir (KBr) 1665, 1610, 1510, 1430, 1260, 1110, 1020, 863 cm^{-1}; nmr (DMSO-d_6) δ 3.11 (s, 6 H) and 3.52 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 186 (100, molecular ion), 113 (34), 98 (14), 83 (11), 71 (10).

Anal. Calcd for $C_6H_{10}N_4OS$: C, 38.69; H, 5.41; N, 30.08; S, 17.22. Found: C, 38.92; H, 5.44; N, 30.33; S, 17.25.

Reaction of 3-(Dimethylamino)-5-phenyl-1,2,4-dithiazolium Perchlorate (9)[2] and KNCO.—A mixture of **9** (5.00 g) and KNCO (1.47 g) was heated for 0.5 hr in refluxing DMF (100 ml). The solution was cooled to room temperature, filtered, and stripped, and the residue was chromatographed on silica gel. 5-(Dimethylamino)-3-phenyl-1,2,4-thiadiazole (**13**) was quickly eluted with petroleum ether (bp 30–60°) and was obtained as a clear oil that solidified on standing (2.62 g, 83%). A portion was sublimed *in vacuo* and then recrystallized from MeOH–H_2O, mp 46°; ir ($CHCl_3$) 1540, 1410, 1340, 975, 885 cm^{-1}; nmr ($CDCl_3$) δ 3.25 (s, 6, Me_2N) 7.33–7.60 (m, 3, Ph), 7.84–8.17 (m, 2, Ph); mass spectrum (70 eV) *m/e* 205 (100, parent ion), 121 (12, $PhC{=}S^+$). The isomeric 3-(dimethylamino)-5-phenyl-1,2,4-thiadiazole has mp 89°.[2,6]

The same product was obtained by reacting **9** and KNCO in DMSO (100°, 45 min); the reaction mixture was partitioned between C_6H_6 and H_2O and **13** was obtained in 76% yield upon evaporation of the C_6H_6 solution.

Anal. Calcd for $C_{10}H_{11}N_3S$: C, 58.51; H, 5.40; N, 20.47. Found: C, 58.30; H, 5.35; N, 20.31.

Registry No.—**4**, 32251-48-2; **7**, 32251-49-3; **8**, 32304-28-2; **13**, 32251-50-6; 4,6-dipiperidino-2*H*-1,3,5-thiadiazin-2-one, 32251-51-7; 4,6-bis(1-pyrrolidinyl)-2*H*-1,3,5-thiadiazin-2-one, 32251-52-8.

Acknowledgment.—We thank Professor C. Storm of Howard University for the variable-temperature nmr spectra.

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Nuclear Magnetic Resonance Spectroscopy. Effect of *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine on the Schlenk Equilibrium of Ethylmagnesium Bromide[1]

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Contribution No. 4191 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

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The composition of Grignard reagents has been studied extensively by nuclear magnetic resonance spectroscopy and other physical techniques.[3] Recently Parris and Ashby,[4] using nmr spectroscopy, observed both dialkyl- and alkylmagnesium species in Grignard solutions from methyl and *tert*-butyl halides. Earlier Evans and coworkers[5] had observed diarylmagnesium and arylmagnesium halides by both fluorine and proton magnetic resonance. We wish to report the observation of diethylmagnesium and ethylmagnesium bromide in tetrahydrofuran solutions containing *N*,*N*,*N'*,*N'*-tetramethylethylenediamine.

The proton magnetic resonance spectrum of the Grignard reagent prepared from ethyl bromide and magnesium is a typical A_2X_3 type spectrum. The resonances of both the methyl, 1.11 ppm downfield from external tetramethylsilane, and methylene protons, 0.78 ppm upfield, are easily distinguished from those of the solvent. A small quantity of ethane is usually formed from trace amounts of moisture. Spectra obtained at temperatures down to −70° exhibited no change other than slight loss in resolution. Variable-temperature spectra of the methylene protons of 0.33 *M* ethylmagnesium bromide in tetrahydrofuran, which is 0.18 *M* in *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, are shown in Figure 1. Broadening of the resonance occurs when lowering the temperature and, at −50°, the methylene proton resonances appear as overlapping

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[1] Taken from the Ph.D. Dissertation of J. A. Magnuson, 1968. Supported by the National Science Foundation.

[2] National Defense Education Act Fellow, 1965–1967.

[3] For recent review articles, see the following and other volumes in series: (a) J. P. Oliver, *Advan. Organometal. Chem.*, **8**, 167 (1970); (b) D. Seyferth, *Organometal. Chem. Rev.*, *Sect. B*, **3**, 37 (1967); (c) B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966); (d) E. C. Ashby, *ibid.*, **5**, 225 (1969).

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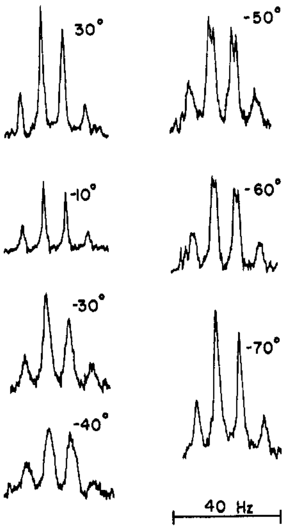


Figure 1.—The nmr spectra (60 MHz) of the $-CH_2Mg-$ protons in ethylmagnesium bromide in tetrahydrofuran and *N,N,N',N'*-tetramethylethylenediamine.

quartets. The $^3J_{HH}$ coupling constants of the species present, as indicated from the four central lines, are equal. The outer lines are unresolved because of lower intensity and resulting difficulty in obtaining good spectra. At still lower temperatures (down to $-70°$), the lines move closer together and coincide, presumably because of a differential chemical shift change with temperature.

No changes in the nmr spectra were found at low temperature for diethylmagnesium prepared from diethylmercury and magnesium in tetrahydrofuran when the diamine is present. Addition of magnesium bromide, prepared *in situ* from ethylene bromide and magnesium, did lead to a solution whose nmr spectra at low temperature consisted of two quartets. Dioxane precipitation of magnesium bromide from the Grignard reagent gave a solution which exhibited only one methylene quartet at low temperature in the presence of diamine.

Variable-temperature spectra taken of a sample to which diamine and then dioxane had been added were obtained within several hours of dioxane addition. Two clearly resolved quartets were obtained at $-40°$ for the methylene protons. After sitting for several months, presumably after all magnesium bromide had precipitated, only one quartet was observed. That the diamine reduces the rate of the dioxane precipitation was confirmed by measuring bromide concentration as a function of time by standard gravimetric silver precipitation.

In general, the equilibrium mixture of alkylmagnesium species can be obtained rapidly by several methods employing different starting materials. Figure 2 shows the 100-MHz spectrum ($-50°$) for the methylene protons for a mixture containing diamine, diethylmagnesium from diethylmercury, magnesium bromide from ethylene bromide and magnesium, and Grignard reagent from ethyl bromide and magnesium. All lines of both quartets are easily distinguished.

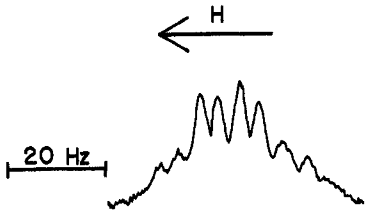
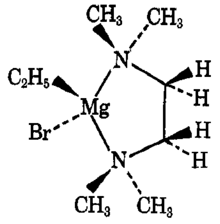


Figure 2.—The nmr spectrum (100 MHz) at $-50°$ of the $-CH_2Mg-$ protons in a sample of ethylmagnesium bromide, diethylmagnesium, and magnesium bromide in tetrahydrofuran and *N,N,N',N'*-tetramethylethylenediamine.

The quartets observed near $-50°$ are best attributed to methylene resonances of diethylmagnesium and ethylmagnesium bromide and support the existence of the Schlenk equilibrium[6] $(C_2H_5)_2Mg + MgBr_2 \rightleftharpoons 2\ C_2H_5MgBr$. House and coworkers[7] have demonstrated that *N,N,N',N'*-tetramethylethylenediamine can markedly affect rates of alkyl exchange of alkylarylmagnesium species. Fraenkel and coworkers[8] have found similar results for the diamine sparteine. Presumably exchange between alkylmagnesium species is slowed by the presence of complexes like **1**. A fourfold change in ratio of diamine to ethyl group from 0.5 to 2.0 has no apparent effect on the position of the equilibrium, as one might expect if one of the magnesium species were preferentially solvated. From the spectra obtained, the number of ethyl groups in both species is approximately equal, giving an equilibrium constant at $-50°$ of 4 for the Schlenk equilibrium as written above. This is similar to the 5.09 reported by Smith and Becker[9] from thermometric studies.



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All magnesium species may be solvated by the diamine in Grignard reagent solutions. The diamine appears to confer solubility on all species, unlike the result reported for Grignard reagents of 3-chloronortricyclene.[10] In particular, the solubility of magnesium bromide in tetrahydrofuran is increased markedly by the diamine. The nmr spectrum of the diamine changes with temperature in the presence of alkylmagnesium species or magnesium halide. The changes vary with Grignard reagent and concentration. Interpretation is not simple since spectra of several species, including very complicated spectra from species such as **1**, may contribute. The nmr spectra do indicate that tight solvent complexes exist, and these are reducing the rate of alkyl exchange allowing observation of the different species of the Schlenk equilibrium.

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(6) Careful studies by others have shown this Grignard reagent to be monomeric in tetrahydrofuran: (a) E. C. Ashby and F. Walker, *J. Organometal. Chem.*, **7**, 17 (1967); (b) E. C. Ashby and W. E. Becker, *J. Amer. Chem. Soc.*, **85**, 118 (1963); F. W. Walker and E. C. Ashby, *ibid.*, **91**, 3845 (1969).

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Experimental Section

Proton magnetic resonance spectra were obtained with a Varian HA-100 nmr spectrometer or with a Varian A-56/60A spectrometer equipped with a Varian C-1024 time-averaging computer. The probe on the A-56/60A spectrometer carried a dewar-jacketed probe insert which could maintain stable temperatures as low as −100°, so that low-temperature, time-averaged spectra could be obtained with no great difficulties.

The starting halides were commercial products and used as received. Tetrahydrofuran (Matheson Coleman and Bell) was distilled from lithium aluminum hydride and stored over Linde 13X molecular sieves. Solvent was never stored for more than 3 days. *N,N,N',N'*-tetramethylethylenediamine (Matheson Coleman and Bell) was dried over potassium hydroxide and then distilled from sodium immediately before adding to Grignard reagents. Magnesium was in the form of shavings ground from blocks of triply sublimed magnesium.[11] Dioxane (Eastman) was distilled from lithium aluminum hydride before use.

The various alkylmagnesium reagents were prepared directly in sealed nmr tubes. After centrifugation of solids to one end, careful decantation of the liquid to the other end of the tube provided a clear sample suitable for nmr spectroscopy.

Registry No.—*N,N,N',N'*-Tetramethylethylenediamine, 110-18-9; ethylmagnesium bromide, 925-90-6; diethylmagnesium, 557-18-6; magnesium bromide, 7789-48-2.

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[11] We thank Dow Chemical Co. for the gift of magnesium.

A Convenient Route to Aromatic α Diketimines and α Diketones

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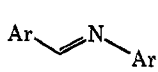
In a preliminary report[1] we have described a simple cyanide ion catalyzed oxidative dimerization of some aromatic aldimines **1** to α diketimines **3**.[2] This paper gives details of these experiments and additional examples delineating to some extent the scope and limitations of this method. Further, the smooth acid hydrolysis of α diketimines **3** constitutes a convenient route to α diketones **4**. Since the appearance of our communication another report of the cyanide ion catalyzed dimerization of aromatic Schiff bases has appeared.[3]



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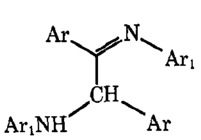

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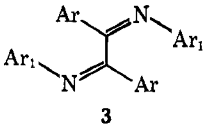

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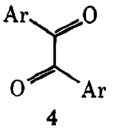

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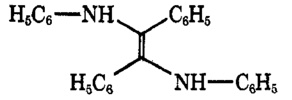
Although the benzoin condensation[4] is usually carried out in alcoholic solvents, we decided to investigate the reaction of aromatic aldimines **1** with cyanide ion in dimethyl sulfoxide (DMSO) in the hope that the initially formed anilinoimines **2**, a formal benzoin type condensation product of **1**, would suffer *in situ* oxidation by DMSO to yield directly diketimines **3**. We were gratified to find that the reaction of a 0.66 *M* solution of *N*-benzylideneaniline (**1a**) in dry DMSO with an equivalent amount of sodium cyanide at 20° afforded benzildianil (**3a**) in 65% yield. A recent note[3] describes the formation of dianilinostilbene (**5**) in dimethylformamide (DMF) when the reaction is run under nitrogen. Apparently under our conditions the initial product (**5** or **2a**) undergoes aerial oxidation to diketimine **3a**. We also find that the oxidative dimerization of **1** to **3** proceeds as well or better in DMF. The role of DMSO in this reaction is therefore only as a solvent (and not additionally as an oxidizing agent).

The data for the reaction carried out with 0.6–0.7 *M* solutions of **1** is presented in Table I. A small amount of anilide **6** was usually a by-product of reactions run in DMSO. The ratio of α diketimines **3** to anilide **6** was sensitive to both concentrations of azomethine **1** and to temperature (see Table I). The best results were obtained by running the reaction in dilute solution using DMF as solvent.



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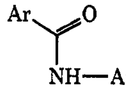

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That the cyanide ion acts as a specific catalyst in the oxidative dimerization **1** to **3** is shown by the observations that transformation of **1a** to **3a** proceeds to completion with as little as 0.1 molar equiv of cyanide ion, and **1a** in DMSO or DMF was unchanged either alone or in the presence of sodium hydroxide. The possibility of the reaction proceeding *via* prior hydrolytic cleavage of **1a** to benzaldehyde and aniline is dismissed, since the reaction of benzaldehyde, aniline, and cyanide ion in DMSO gives only benzoin.

Inspection of Table I shows that this method for the synthesis of α diketimines **3** is fairly general and the substituents in Ar and Ar$_1$ can vary considerably. The reaction is apparently limited to aromatic aldimines. However, diketimines were not obtained from *p*-dimethylaminobenzylideneaniline (**1m**), *p*-hydroxybenzylideneaniline (**1n**), *p*-nitrobenzylideneaniline (**1p**), *o*-methoxybenzylideneaniline (**1q**), or benzylidenecyclohexylamine (**1r**); the benzoin condensation also fails with the aromatic aldehydes of **1m**, **1n**, or **1p**.

The mechanism of this reaction appears to resemble that of the benzoin condensation;[5] a possible route is presented in Scheme I.

Experimental Section

General.—Melting points were taken on a Thomas–Hoover melting point apparatus and are uncorrected. Analyses were

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