as pale yellow needles (0.36 g, 56%): mp 120-122°; ir (Nujol) 695, 770, 895, 1090 (ClO_4), 1350, 1560, 1620 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}ClN_2O_4$: N, 8.7; Cl, 11.0. Found: N, 8.7; Cl, 10.7.

Registry No.—**11a,** 274-55-5; **11b,** 31420-26-5; **11c,** 31420-27-6; **11d,** 31420-28-7; **11e,** 31420-29-8; **12a** (X = ClO_4), 31420-30-1; **12b** (X = ClO_4), 31420-31-2; **12c** (X = ClO_4), 31420-32-3; **13a** (X = ClO_4), 31489-80-2; **13b** (X = ClO_4), 31420-33-4; 1-acetonyl-3,6-dimethylpyridazinium bromide, 31420-34-5; 3,6-dimethyl-1-phenacylpyridazinium bromide, 31420-35-6.

Acknowledgment.—The author wishes to thank Drs. R. Buchan, D. H. Reid, G. Youngson, and M. B. Watson for encouragement and assistance in preparation of the manuscript, and also to record thanks to Mr. C. Scott, Mr. R. Webster, and Mrs. W. Kirk.

A Nuclear Magnetic Resonance Spectral Study of Some Organometallic Derivatives of Indoles[1]

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Received March 22, 1971

The nmr spectra of several alkali metal and Grignard derivatives of indole in THF indicate these species to be essentially ionic but not necessarily dissociated *N*-metal derivatives. The proton chemical shifts for the alkali metal salts are in the order Li > K > Na suggesting that the first of these is a solvent-separated ion pair and the last two are contact ion pairs. Mixtures of indole and the alkali metal derivatives undergo rapid exchange on the nmr time scale in all solvents studied while the Grignard reagent does so only in HMPT. The unique reactivity of indolylmagnesium halides is accommodated with these results by assuming extensive association of the magnesium and nitrogen atoms of these reagents in all solvents studied except HMPT.

The constitution and chemistry of Grignard reagents which react at a position different from that where an atom was displaced in their preparation have intrigued chemists for many years.[3-7] Heterocyclic representatives of these reagents include the pyrrolyl- and indolylmagnesium halides.[8] Recent investigations[1,9-12] have substantiated the earlier generalization[8] that these Grignard reagents react with electrophiles predominantly at carbon and not at nitrogen in contrast to the corresponding alkali metal derivatives.[13-16] An explanation of these reactions reasonably requires a knowledge of the structure of the reactive, or at least the predominant species present in solution. Heeding the assertion that structural problems of this type are "incapable of purely chemical solution,"[17] an investigation of the organometallic derivatives of several indoles by the nmr method so successfully applied to allylic systems[6] was undertaken.

Preliminary examination established that the indole[18] as well as pyrrole[19] Grignard reagents consist primarily of N-MgX species. A more detailed study became possible[20] only after the solvent[21] and concentration[21,22] dependence of the nmr spectra of indole had been examined. This paper will report the results of that study.

Results and Discussion

The nmr spectrum of indolylmagnesium bromide in THF (Figure 1) consists of three complex multiplets, relative areas 3:2:1, centered at τ 2.65, 3.25, and 3.65, respectively. Indolyllithium, -sodium, and -potassium have similar nmr spectra (Table I) differing only in the detailed fine structure of the multiplets.

The high field quartet ($J_{3,7}$ = 0.9, $J_{2,3}$ = 2.3 Hz) was assigned to the 3 proton because it is absent in the nmr spectrum of 3-methylindolylmagnesium bromide.[18]

The 2-proton resonance occurs as a sharp doublet ($J_{2,3}$ = 2.3 Hz) superimposed on the lowest field multiplet. This assignment is confirmed by the disappearance of the doublet and the decrease in the relative area of the multiplet from three to two in 2-methylindolylmagnesium bromide.[18]

The remaining two protons responsible for this low-field multiplet are those at the 4 and 7 positions while the broad peak centered at τ 3.25 arises from the 5 and 6 protons. These assignments were based on a comparison of chemical shifts with those of the same protons

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[2] To whom inquiries should be sent at Texas Christian University.

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[17] Reference 3, p 1154.

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TABLE I

CHEMICAL SHIFTS (τ ±0.02) OF 10% THF SOLUTIONS OF SOME INDOLE METAL DERIVATIVES

Compd	Registry no.	2 H	3 H	5 H	4 H		7 H	
Indole	120-72-9	2.89	3.62					
Indolyl MgBr	20356-50-7	2.65	3.65	3.25			2.3–2.7	
Indolyl Li	18344-49-5	2.65	3.73	3.35			2.3–2.7	
Indolyl Na	16982-67-5	2.52	3.63	3.29			2.3–2.7	
Indolyl K	31163-74-3	2.61	3.73	3.29			2.3–2.7	
2,5-Dimethylindole[a]	1196-79-8		4.02		3.23	2.85		2.94
2,5-Dimethylindolyl MgBr[a]	31163-76-5		4.05		3.45	2.94		2.67
2,5-Dimethylindolyl Li[a]	31163-77-6		4.15		3.60	3.02		2.96
2,5-Dimethylindolyl Na[a]	31163-78-7		4.02		3.41	2.87		2.78
2,5-Dimethylindolyl K[a]	31163-79-8		4.13		3.45	2.95		2.87
2,6-Dimethylindole[b]	5649-36-5		4.00	3.26		2.77		3.03
2,6-Dimethylindolyl MgBr[b]	31163-81-2		3.93	3.37		2.68		2.62

[a] $J_{4,6} \approx 1.5$, $J_{6,7} \approx 8.0$ Hz. [b] $J_{5,7} \approx 1.5$, $J_{4,5} \approx 8.0$ Hz.

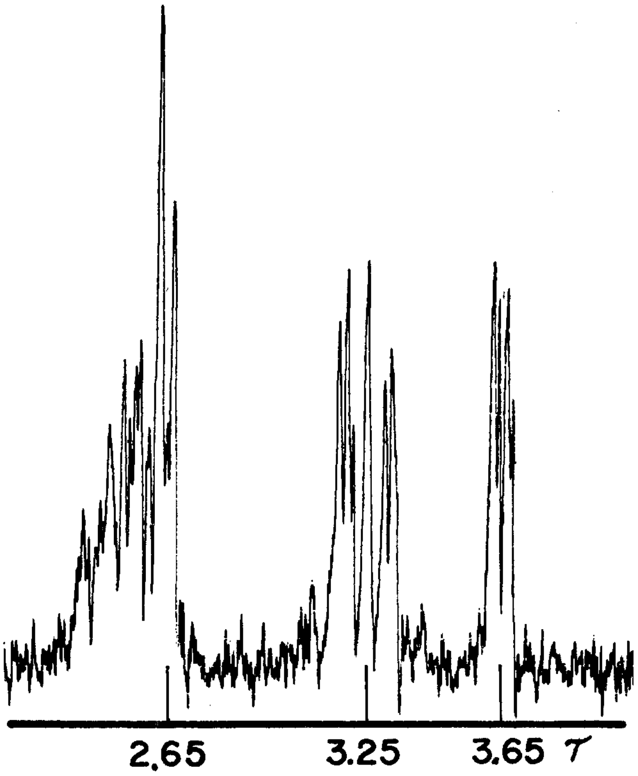
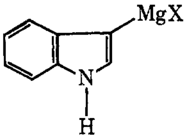


Figure 1.—Indolylmagnesium bromide in THF.

in the nmr spectra of 2,5- and 2,6-dimethylindolylmagnesium bromide (Table I) which in turn are available from first-order analysis of peak areas and splitting patterns.[1,21,23]



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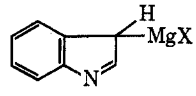
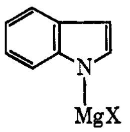


2

The improved and expanded data in Table I in no way alters our previous conclusion[18] that these indole Grignard reagents in THF contain no appreciable quantities of C-MgX species[26] such as **1** or **2**. The suggestion[18] that an N–MgX structure such as **3**, containing a covalent N–Mg bond, be excluded in favor of the largely ionic (but not necessarily dissociated) resonance hybrid **4** should be examined in more detail, however. This claim was based on the similarity of the nmr spectra of indolylmagnesium bromide and indolylsodium to each other and their difference from the nmr spectrum of indole itself[18,21] which contains an essentially covalent N–H bond.[27] The degree of ionic character of the bond to nitrogen would be expected to have pronounced effects on the π-charge density of the indole nucleus[1,28,29] and on its magnetic anisotropy due to the partial generation of a pyridine-like nonbonded electron pair on the nitrogen. Both the first[30,31] and the second[32,33] of these factors should lead to readily observable changes in the nmr spectrum of the indole residue. Therefore, since the nmr spectra of *all* the metal derivatives of indole studied (Table I) are more like one another than like the nmr spectrum of indole itself, and since the alkali metal derivatives are best described as being predominantly ionic,[27] our previous[18] exclusion of an essentially covalent species such as **3** as a possible representation of the indole Grignard reagent in THF seems justified.



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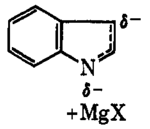

4

Further support for this hypothesis comes from the qualitative agreement between calculated and observed chemical shifts differences in the nmr spectra of indole and its metal derivatives. The calculations involve a combination of π-charge density[1] and point–anisotropy[25] approximations applied to a free anion model.

Naturally the indole portion of these derivatives is not actually a *free* anion. A detailed consideration of the data in Table I reveals that for a series of alkali metal salts the chemical shift of a particular proton con-

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[23] A recently reported[24] incorrect assignment of these protons is based on superficial charge-density arguments which have been shown to be inadequate in this series.[25]

[24] H. Nomura, S. Kato, and Y. Miyahara, *Nippon Kagaku Zasshi*, **90**, 1285 (1969).

[25] J. F. Sebastian, M. G. Reinecke, and H. W. Johnson, Jr., *J. Phys. Chem.*, **73**, 455 (1969).

[26] Reference 9, p 107 ff.

[27] Using the data on pp 93–98 of L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, the following per cent ionic bond character can be estimated: N–H, 19%; N–Mg, 55%; N–Li, 63%; N–Na, 67%; N–K, 70%.

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[31] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

[32] G. Fraenkel, D. G. Adams, and R. R. Dean, *J. Phys. Chem.*, **72**, 944 (1968).

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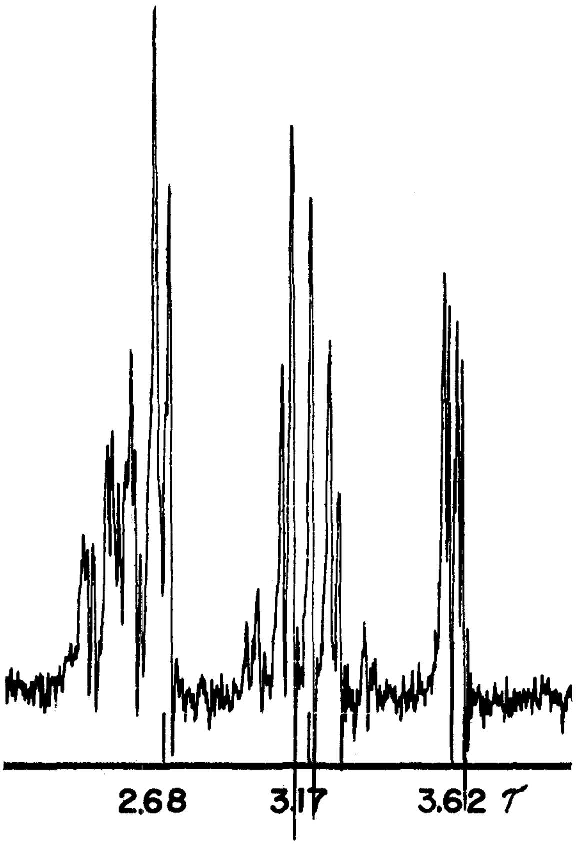
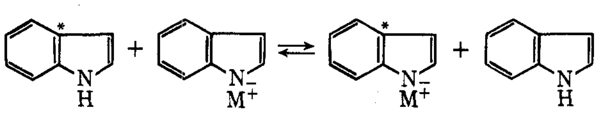


Figure 2.—Indole and indolylsodium (1:1) in THF.

sistently decreases in the order Li, K, Na. An identical phenomenon has been observed in the nmr spectra of alkali metal salts of fluorene[34] and 1,3-diphenylpropene[35] and has been interpreted in terms of two different kinds of associated ion pairs, "contact" (for Na and K) and "solvent separated" (for Li).[36] A similar interpretation therefore seems justified for the alkali metal salts of indole.

Unfortunately this observation is of little help in further elucidating the structure of the indole Grignard reagent since the chemical shifts of its protons do not display a consistent relation to those of the alkali metal salts. A comparison of the nmr spectra of mixtures of indole and various indole metal derivatives does lead to additional information, however. An equimolar mixture of indole and indolylsodium in THF gives a time-averaged spectrum (Figure 2) down to −30° indicating a rapid exchange between these species (eq 1). Similar results are obtained for the



(1)

lithium and potassium compounds and in other solvents such as dioxane, diethyl ether, 1,2-dimethoxyethane, and hexamethylphosphoric triamide (HMPT).

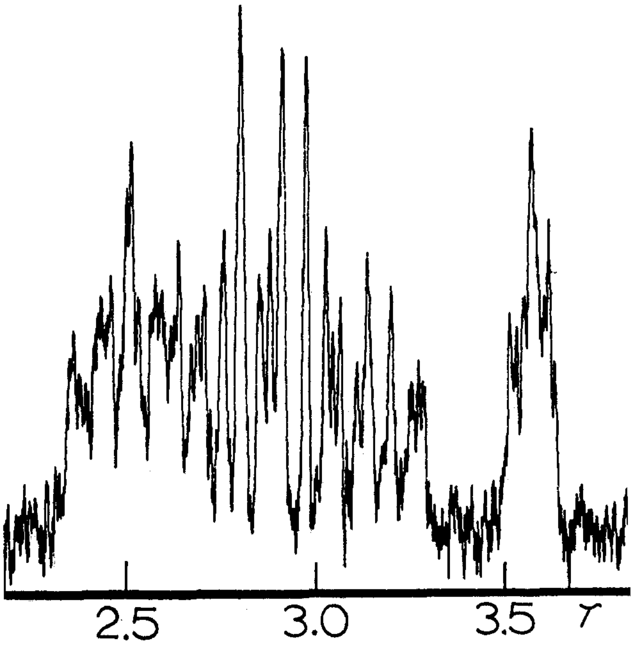


Figure 3.—Indole and indolylmagnesium bromide (1:1) in THF.

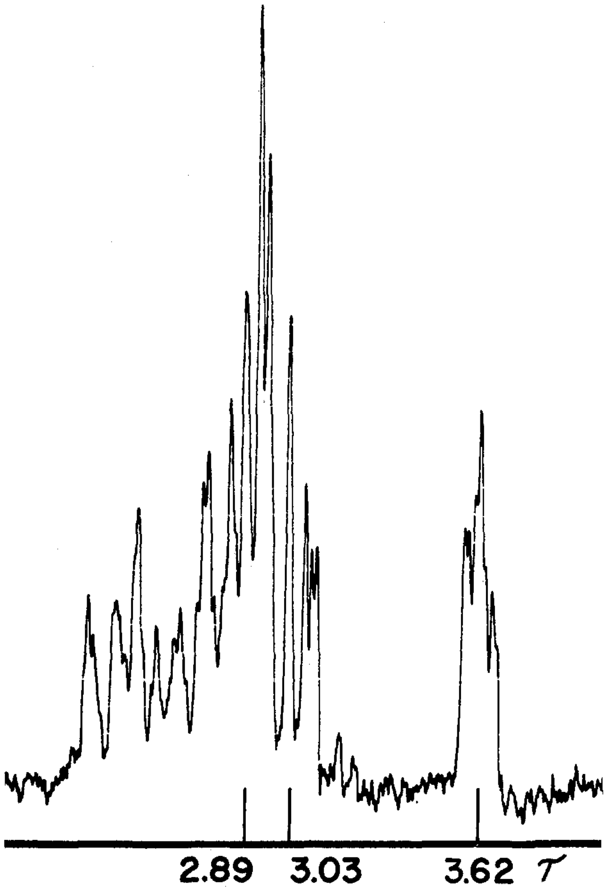


Figure 4.—Indole in THF.

By way of contrast even at 60° the nmr spectrum of a mixture of indole and indolylmagnesium bromide in THF (Figure 3) shows two distinct groups of signals attributable to the separate species (Figures 1 and 4) thereby indicating a relatively slow exchange (eq 1). The possibility that no exchange at all occurs is inconsistent with the frequent formation of polysubstitution products from indolylmagnesium halides.[9] Furthermore, with HMPT as the solvent, both the alkali

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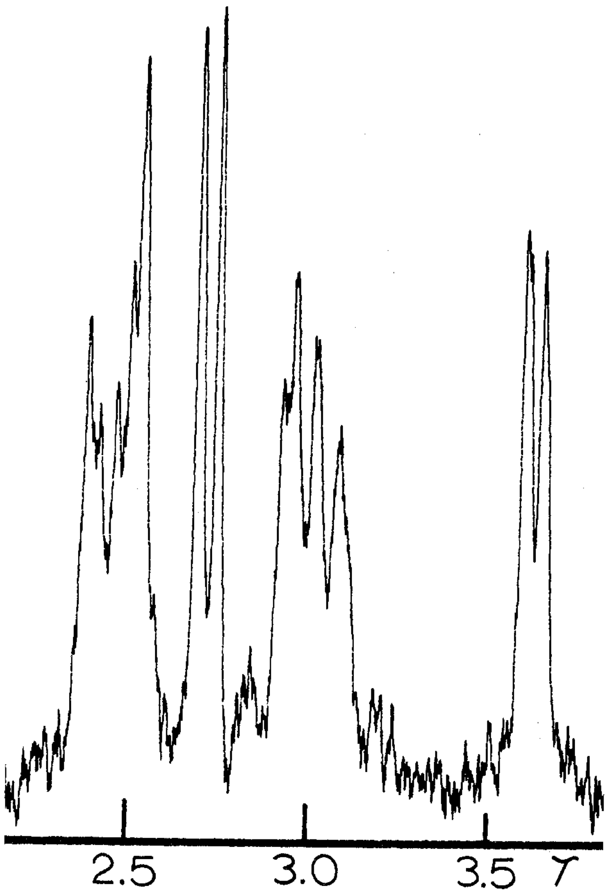

Figure 5.—Indole and indolylmagnesium bromide (1:1) in HMPT.

metal and the Grignard derivatives of indole display similar time-averaged nmr spectra (Figure 5) indicating a rapid rate of exchange (eq 1). In THF-HMPT mixed solvent systems the change from a "fast" to a "slow" exchange nmr spectrum occurs at 40 ± 10 vol % HMPT.

The similarity between the indole Grignard reagent in HMPT and the alkali metal salts of indole is not restricted to the nmr exchange behavior. Both isoamyl bromide[37] and methyl iodide[38] alkylate the indole Grignard reagent in HMPT exclusively on nitrogen, a result more typical of the alkali metal salts.

This ability of solvent to erase the distinction between the Grignard and alkali metal derivatives of indole further supports the idea that these species do not differ drastically in structure. For example, the above observations can be explained by assuming that in most solvents the magnesium atom of the indole Grignard reagent is tightly associated with the nitrogen atom thus blocking attack at that location by either indole or alkyl halide. In HMPT this association presumably is decreased,[39] at least to the extent found in the alkali metal salts, and exchange (eq 1) or N-alkylation therefore can proceed. A similar rationale has been used to explain the solvent and cation dependence of a variety of related ambident nucleophiles.[14,16,26,37]

In conclusion, it appears that the unusual reactivity of the indole Grignard reagent is due neither to the location of the metal atom (on N or C) nor to the degree of ionic character (polarity) of the N-metal bond, since both these factors are essentially the same in the alkali metal salts of indole. Rather, the unique feature of the indole Grignard reagent appears to be its greater extent of intramolecular association in all solvents studied except HMPT. Intermolecular aggregation as is observed in many simpler Grignard reagents[40] may also be involved. Determining the nature and extent of such association and aggregation will require additional physiochemical measurements.

Experimental Section

Equipment.—Nmr spectra of 2,6-dimethylindole and the 2,6-dimethylindole Grignard reagent were determined, at 25°, on a Varian Associates Model DP-60 high-resolution spectrometer operating at 56.4 MHz. Peak positions were measured by the audiofrequency side-band technique. Tetramethylsilane was used as an internal standard. Nmr spectra of all other indoles were taken, at 38 ± 2°, on a Varian Associates A-60 or A-60A spectrometer operating at 60 MHz. Chemical shifts were obtaind from precalibrated chart paper with the internal tetramethylsilane reference signal set at 0.00 ppm. A variable temperature probe regulated with a Varian V-6040 variable temperature controller was used for the temperature studies.

Chemicals.—Tetrahydrofuran was stored over potassium hydroxide and distilled immediately before use from lithium aluminum hydride. Dioxane, 1,2-dimethoxyethane, and diethyl ether were distilled from sodium. Hexamethylphosphoric triamide was dried over BaO powder, decanted, and distilled under a nitrogen atmosphere at 84° (2 mm) pressure. Magnesium, 99.99% pure, was purchased from A. D. Mackay, Inc., New York, N. Y. Methyllithium in diethyl ether was obtained from Alfa Inorganics, Inc., Beverly, Mass. The source and purity of the indoles has been described previously.[21]

Indole Salts. General Precautions.—Glassware was flamed prior to use and cooled with a stream of pure, dry nitrogen. A positive pressure of dry nitrogen was maintained over the reaction mixtures at all times.

Indolylmagnesium bromide was prepared as follows. To 1.2 g of magnesium (99.99%), in 15 ml of dry THF, was slowly added 5.2 g of ethyl bromide in 10 ml of THF, without cooling but with vigorous stirring. After the reaction was completed 5.0 g of indole in 30 ml of dry THF was added. The liberated ethane was measured in an inverted graduated cylinder filled with water. The theoretical amount of ethane was collected in all cases. The indole Grignard reagent was completely soluble in THF. Samples for nmr determinations were removed *via* a dry syringe and placed in a Varian precision bore nmr tube, which previously had been dried at 110° and cooled in a vacuum dessicator. The tubes were then sealed with a cork and molten wax.

For studies in HMPT a solution of the Grignard reagent, prepared as above except in diethyl ether, was diluted with twice its volume of HMPT and the mixture distilled at 30 mm until the temperature of the distillate reached 90°. The cooled amber-colored gelatinous mixture was diluted with an equal volume of HMPT for the nmr studies.

Indolyllithium was prepared by adding 5.0 g of indole in 15 ml of THF to a refluxing mixture of 0.35 g of lithium hydride in 45 ml of THF. The resulting mixture was refluxed for 10–15 hr. The indolyllithium thus formed appeared to be quite soluble. Preparation of indolyllithium in other solvents was carried out in essentially the same way except for HMPT. In this case 9 ml of a 2.2 *N* solution of methyllithium in diethyl ether was added slowly to a solution of 2.1 g of indole in HMPT and the ether removed by distillation at 90° (35 mm) as above.

Indolylsodium.—A solution of 5.0 g of indole in 20 ml of dry THF was added to a mixture of 1 g of sodium hydride in 40 ml of refluxing THF. The mixture was heated under reflux for another 30–60 min. Solutions of indolylsodium in other solvents were prepared in an analogous manner except that with HMPT the reaction was carried out at room temperature.

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(37) B. Cardillo, G. Casnati, and A. Pochini, *Chim. Ind.* (*Milan*), **49**, 172 (1967).

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Indolylpotassium.—A solution of 5.0 g of indole in 20 ml of THF was slowly added to 2 g of molten potassium in 40 ml of refluxing THF. The solution was refluxed for an additional 12 hr. With HMPT the reaction was complete in 30-60 min at room temperature.

Exchange Studies.—The indolyl metal derivative was prepared as above except that an excess of indole was utilized. The relative amounts of indole and its salt present in solution were determined by integrating the 3- and N-hydrogen resonances in the nmr.

Acknowledgment.—This research was supported by The Robert A. Welch Foundation, the T. C. U. Research Foundation, and a Lockheed Fellowship to J. F. S.

I. Ligand Transfer of Halides (Cl, Br, I) and Pseudohalides (SCN, N_3, CN) from Copper(II) to Alkyl Radicals

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Received March 25, 1971

The ligand transfer oxidation of alkyl radicals by a variety of copper(II) halides (X = Cl, Br, I) and copper(II) pseudohalides (X = SCN, N_3, CN) is described: $n\text{-C}_4\text{H}_9\cdot + \text{Cu}^{\text{II}}\text{X} \longrightarrow n\text{-C}_4\text{H}_9\text{X} + \text{Cu}^{\text{I}}$. Alkyl radicals are generated during the copper-catalyzed reaction of diacyl peroxides in the presence of $\text{Cu}^{\text{II}}\text{X}$. Initiation of the chain process by copper(I) depends on whether the copper(II) halide or pseudohalide undergoes disproportionation in solution. In the absence of disproportionation, the deliberate addition of catalytic amounts of copper(I) allows the catalytic process to be carried out at 0°, and deleterious side reactions involving nucleophilic attack on the peroxide by halide or pseudohalide are minimized. *n*-Butyl radicals formed under these conditions from valeryl peroxide are efficiently trapped by $\text{Cu}^{\text{II}}\text{X}$ to form *n*-butyl chloride, bromide, iodide, thiocyanate, azide, and cyanide in good yields. Other competing reactions of *n*-butyl radicals are not important under most conditions.

Oxidation–reduction reactions of free radicals constitute important steps in a number of organic reactions catalyzed by metal complexes.[1] The oxidation of alkyl radicals by metal complexes has been classified into two categories which have been described as electron transfer[1,2] and ligand transfer.[1,3] In the latter, the ligand X associated with the metal complex MX_n is transferred to the alkyl radical R· during the oxidation process (eq 1). The transfer of chlorine and bromine from

$$\text{R}\cdot + \text{M}^{+n}\text{X}_n \longrightarrow \text{RX} + \text{M}^{+n-1}\text{X}_{n-1} \qquad (1)$$

copper(II) complexes to *n*-butyl radicals was reported earlier.[3] The study of these elementary processes depends on a general, reliable, and unequivocal method of generating alkyl radicals.

The decomposition of diacyl peroxides are induced by a variety of copper(II) complexes and the stoichiometry can be deliberately altered. For example, the copper-catalyzed decomposition of valeryl peroxide in the presence of cupric chloride is given by eq 2. The

$$(n\text{-BuCO}_2)_2 + \text{Cl}^- \xrightarrow{\text{Cu}^{\text{II}}} n\text{-BuCl} + \text{CO}_2 + n\text{-BuCO}_2^- \qquad (2)$$ [4]

mechanism of reaction 2 includes a step involving the efficient ligand transfer (eq 5, X = Cl) of chlorine from copper(II) chloride to *n*-butyl radicals as shown by the radical chain process (eq 3-5).

$$(n\text{-BuCO}_2)_2 + \text{Cu}^{\text{I}} \longrightarrow n\text{-BuCO}_2\text{Cu}^{\text{II}} + n\text{-Bu}\cdot + \text{CO}_2 \qquad (3)$$ [5]

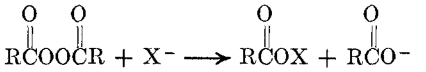
$$n\text{-BuCO}_2\text{Cu}^{\text{II}} + \text{X}^- \rightleftharpoons n\text{-BuCO}_2^- + \text{Cu}^{\text{II}}\text{X} \qquad (4)$$

$$n\text{-Bu}\cdot + \text{Cu}^{\text{II}}\text{X} \longrightarrow n\text{-BuX} + \text{Cu}^{\text{I}}\text{, etc.} \qquad (5)$$

In the earlier study[3] the reaction between valeryl peroxide and cupric chloride was carried out at 55° by using catalytic amounts of copper(II) chloride. The induction period was attributed to the formation of butyl radicals by the limiting homolysis (eq 6) of the peroxide, followed by the pro-

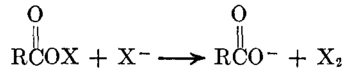
$$(n\text{-BuCO}_2)_2 \xrightarrow{\Delta} 2n\text{-Bu}\cdot + 2\text{CO}_2 \qquad (6)$$

duction of the copper(I) initiator (eq 5). There are two limitations to this procedure as a general method: (a) the competing heterolytic rearrangement of the peroxide[6] and (b) the nucleophilic attack on the peroxide by ionic chloride (eq 7, X = Cl).[7] The latter is



$$\text{RC(=O)OOC(=O)R} + \text{X}^- \longrightarrow \text{RC(=O)OX} + \text{RC(=O)O}^- \qquad (7)$$

particularly deleterious because the acyl hypochlorite



$$\text{RC(=O)OX} + \text{X}^- \longrightarrow \text{RC(=O)O}^- + \text{X}_2 \qquad (8)$$

and molecular chlorine formed as intermediates oxidize copper(I) and inhibit the chain process (eq 8).[3] Both side reactions increase in importance at higher temperatures.

In this report we wish to describe an improved method of generating alkyl radicals in high yields from diacyl peroxides at low temperatures. The efficient generation of alkyl radicals provides the opportunity to examine the ligand transfer of a variety of halogens (chlo-

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[3] J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965).

[4] In this and subsequent equations no attempt will be made to include all the coordination around copper or the charge on the ion unless pertinent to the discussion.

[5] The valeryloxy radical may be an intermediate in this step.

[6] F. D. Greene, H. S. Stein, C. C. Chu, and F. M. Vane, *J. Amer. Chem. Soc.*, **86**, 2081 (1964); S. Oae, T. Kashiwagi, and S. Kozuka, *Chem. Ind. (London)*, 1964 (1965); J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).

[7] J. K. Kochi, B. M. Graybill, and M. Kruz, *ibid.*, **86**, 5257 (1964); N. J. Bunce and D. D. Tanner, *ibid.*, **91**, 6096 (1969).