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Reaction of Nitrosodurene with Grignard Reagents

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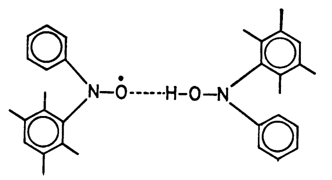
Synopsis. Nitrosodurene was allowed to react with alkyl- and arylmagnesium halides and the reaction was followed by ESR. The spectrum of nitrosodurene anion radical was observed, the stability sequence of alkyl duryl nitroxides being discussed on the basis of the coupling constants of α-hydrogen atoms of alkyl groups.

Study on the reaction of nitrosobenzenes with Grignard reagents started early,[1,2] the formation of diphenyl nitroxide radical on the reaction with phenylmagnesium bromide (PhMgBr) being studied precisely by ESR, but no resolvable spectrum was obtained on the reaction with methyl- and ethylmagnesium bromide (MeMgBr and EtMgBr) even at lower temperatures.[3] On the other hand, the development of spin-trapping studies[4] shed light on nitrosodurene as an especially useful spin-trap because of its stability and also the simple ESR spectra of the corresponding nitroxide radicals.[5] We wish to report the results obtained on the Grignard reaction of nitrosodurene.

The reaction was carried out in tetrahydrofuran (THF). Since the solubility of nitrosodurene dimer in ordinary solvents is very low, the substrate had to be added as a suspension in THF. When the suspension was added to an equimolar solution of PhMgBr at 0 °C, almost all of the solid nitrosodurene remained undissolved. The reaction started when the mixture was warmed up to about 30 °C, the solid dissolving gradually giving reddish brown coloration. Dark brown crystalline needles (**1**) were obtained by quenching the reaction mixture with saturated aqueous NH_4Cl followed by extraction with diethyl ether and removal of the solvent: mp 96—98 °C after recrystallization from petroleum benzine. A dilute solution of **1** in THF gave an ESR spectrum consisting of a set of coupling constants agreeing with that of phenyl duryl nitroxide: $a_N=9.93$ G, $a_{o,p\text{-H}}=2.76$ G and $a_{m\text{-H}}=0.90$ G. However, the magnetic susceptibility measurement gave only a 51% free spin, and the IR spectrum showed a broad and strong ν_{OH} absorption band at 3240 cm^{-1}. Thus the crystalline product **1** was suggested to be a hydrogen-bonded dimeric nitroxide-hydroxylamine complex. This was confirmed by conversion of **1** into deep red "free" nitroxide (crude, mp 116—123 °C, 88% free spin) by oxidation with Ag_2O in anhydrous diethyl ether.[6]

The coupling constants obtained directly from the reaction mixture with *p*-fluoro- and *p*-methoxyphenylmagnesium bromides are given in Table 1. The spin coupling with the *p*-hydrogen atom of the duryl group is usually unresolvable. However, it was resolved in the case of *p*-methoxyphenyl duryl nitroxide. The radical concentration of this nitroxide increased much faster than that of the *p*-fluoro derivative, indicating that the electron-donating substituent facilitates the reaction.



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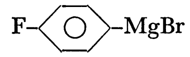
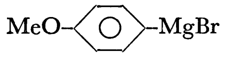
In the reaction with alkyl Grignard reagents, easily analyzable ESR spectra were obtained at room temperature. The results are summarized in Table 2. Since the nitroxyl oxygen atom coordinates to the ^+MgBr species present in our reaction system, all the a_N values are smaller than those obtained in the cases of "free" nitroxides obtained photolytically.[5] The a_N value (9.93 G) of the molecular complex **1**, in which the nitroxyl oxygen atom coordinates to the hydrogen atom, is also smaller than that obtained previously (10.11 G[5]).

When an equimolar MeMgBr was allowed to react with nitrosodurene, the ESR-spectrum obtained at the initial stage of the reaction consisted of a broad triplet signal due to the nitrogen atom ($a_N=12.69$ G), the spectrum changing rapidly into a set of weak signals of methyl duryl nitroxide.[5] When six molar equivalents of MeMgBr were used, the signals disappeared much faster. Three molar equivalents proved to give the strongest signals of the nitroxide, which disappeared in *ca.* 1 h. The triplet signal observed at the initial stage of the reaction could be ascribed to the anion radical of nitrosodurene formed as the result of electron-transfer from the Grignard reagent.[7] A similar phenomenon was observed in the reaction with isopropylmagnesium bromide. A set of broad quintet was observed at the initial stage the spectrum changing rapidly into a set of doublets of triplet assignable to isopropyl duryl nitroxide. Since a quintet (1: 2: 3: 2: 1) signal is observable when a free spin is delocalized on two equivalent nitrogen atoms,[8] the quintet could be assigned to the dimeric anion radical illustrated below. The appreciably small a_N value (9.6 G) is compatible with the proposed structure **2**.

The correlation of the order of the value of $a_{\alpha\text{-H}}$

Table 1. Coupling constants of aryl duryl nitroxides formed on the reaction with ArMgBr

ArMgBr	a_N	a_F	$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{p'\text{-H}}$
	10.19	6.57	2.78	0.92	—
	10.44	—	2.78	0.83	0.42

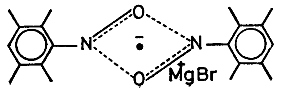


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Table 2. Coupling constants of alkyl duryl nitroxides formed in the reaction with RMgX

RMgX	a_N	$a_{\alpha-H}$	Order of radical concn[a)]	a_N of "free" nitroxides[5)]
CH_3MgBr	13.60	12.08	3	13.70
$PhCH_2MgCl$	13.58	7.92	2	13.61
$(CH_3)_2CHMgBr$	13.58	6.69	1	13.72

a) One indicates the highest concentration observed.

with that of radical concentration (Table 2) is of interest. The largest $a_{\alpha-H}$ value for methyl duryl nitroxide is responsible for its instability due to decomposition probably involving hydrogen-abstraction. The medium $a_{\alpha-H}$ value for benzyl duryl nitroxide is unambiguously due to the spin-delocalization on the phenyl group giving fair stability to the nitroxide. The smallest $a_{\alpha-H}$ value for isopropyl duryl nitroxide seems to be due to the steric effect of the two α-methyl groups. Since the degree of spin-distribution on these methyl groups should be very low, the small $a_{\alpha-H}$ value can be understood by considering the direction of the orbital of free spin on the nitrogen atom to be not parallel with that of the C_α–H_α bond. The low value is in line with the great stability of the radical.

Nitrosodurene was found to be a useful spin-trap also in the reaction with Grignard reagents. The hindered nitrosobenzene made it possible to observe easily analyzable spectra of nitroxides as well as the initially formed anion radical. A similar steric hindrance effect was discussed in detail.[7)]

Experimental

Materials. Nitrosodurene was prepared by the method of Smith and Taylor[9)] through mercuriation of durene followed by nitrosation: mp 160 °C. For the Grignard reaction tetrahydrofuran was dried over sodium wire, distilled, and stored on sodium wire. For ESR measurements it was dried by sodium hydride, frozen, degassed repeatedly, and distilled in a solvent reservoir on a vacuum line containing Na–K alloy. *p*-Fluorobromobenzene was prepared from fluorobenzene[10)] (Daikin Industrial Co.). Commercial halogen compounds were used (reagent grade). Half molar stock solutions of Grignard reagents in THF were prepared and stored under, N_2.

Procedures for Measurements. The apparatus used for the measurements was constructed according to the method reported by Maruyama.[3)] Nitrosodurene (0.0136 g, 0.25 mmol) was weighed and introduced into a reaction vessel, 5 ml of THF being distilled into it from a solvent reservoir using vacuum line. Only a small portion of nitrosodurene went into the solution with weak green coloration. When the two reactants were mixed by breaking the seal, the color of the resultant mixture turned yellow or orange due to the formation of nitroxide radical accompanied by the dissolution of the solid nitrosodurene dimer. In order to obtain hyperfine structures, a small part of the reaction mixture transferred into the measurement cell was diluted by distilling the solvent from the reaction vessel.

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