A Novel Nucleophilic Substitution of 1,2,2-Tricyano-vinylbenzene by the Grignard Reagent

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The reactions of tricyanovinyl compounds with nucleophilic reagents generally result in the replacement of the 1-cyano group.[1] The present report is concerned with a semi-quantitative comparison of the reactivity between 1- and 2-cyano groups of 1,2,2-tricyanovinylbenzene (I).

This compound[1] and methylmagnesium iodide (1 : 3 molar ratio) were allowed to react in boiling ethyl ether for 3 hr ; after the usual work-up, a mush was obtained. The mush was fractionated into four components, A, B, C and D, and a tarry material by chromatography on alumina (solvent: benzene-cyclohexane), distillation, and preparative vapor-phase chromatography (QF-1,1 m). Components A and B were identified as 1-methyl-2,2-dicyanovinylbenzene (II)[2] and 1-cyano-2,2-dimethylvinylbenzene (III)[3] respectively from the NMR and infrared spectra data as well as from mixed melting

1) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *J. Am. Chem. Soc.*, **80**, 2805 (1958).

2) J. Bastus, *Tetrahedron Letters*, **1963**, 955.

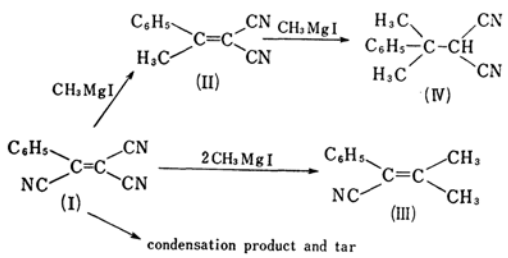
3) J. Jarrousse, *Compt rend.*, **244**, 2515 (1957).

point determinations with authentic samples.

Component C is a colorless oil, bp 96—98°C/3 mmHg, n_{25} : 1.5194; the results of the elementary analysis indicate the formula $C_{12}H_{12}N_2$ for it. (Found: C, 78.44; H, 6.65; 15.21%. Calcd: C, 78.23; H, 6.57; N, 15.21%) The NMR spectrum (in benzene) shows the presence of CH_3 (δ 1.10, singlet) and CH (δ 2.75, singlet). The ratio of the integrated signal strength is about six to one. This compound was also synthesised separately from compound II and methylmagnesium iodide under similar conditions. Thus component C may be concluded to be 1,1-dimethyl-2,2-dicyanoethylbenzene (IV).

Component D is composed of yellow crystals with a melting point of 173°C. The analytical data show that the formula is $C_{22}H_{16}N_4$. (Found: C, 78.70; H, 4.68; N. 16.62%, mol wt (Rast), 330. Calcd: C, 78.55; H, 4.79; N, 16.66%, mol wt, 336.4) The infrared spectrum of this compound showed peaks ascribable to the NH_2 and to the CN group, but no peak ascribable to the CH_3 group was detected; the results of the NMR spectrum confirmed this observation. The ultraviolet spectrum (λ_{max}=251 mμ, ε=~10000) indicates the presence of a conjugate ethylenic system. Although its exact structure is not known, component D seems to be a condensation product of 2 molecules of the starting material under the reducing conditions influenced by the presence of the Grignard reagent.

The whole reaction scheme may, therefore, be formulated as follows:



The relative yields of II, III, and IV were 50, 18, and 32%, and no 2-monomethyl compound was obtained.

From these results, it may be concluded that the Grignard reaction on 1,2,2-tricyanovinylbenzene results in the substitution reaction of cyano groups with the alkyl groups, and that the relative reactivity of the 1- to the 2-cyano group toward the Grignard reagent is about four to one.