

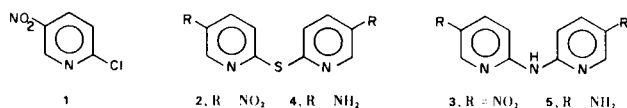
Coupling Reaction of the Anion of 2-Methyl-5-nitropyridine

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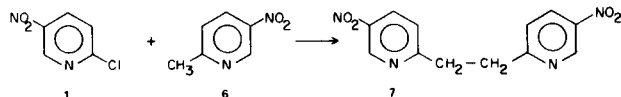
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It is well known that 2-halopyridines undergo very facile displacement reactions with various nucleophiles. This reactivity is generally enhanced by the introduction of an electron withdrawing group at the three or five position. 2-Chloro-5-nitropyridine (**1**) is an excellent example of a system which supports such activity, and a number of dinitrobipyridyl compounds such as 5,5'-dinitro-2,2'-bipyridyl sulfide (**2**) (1) and 5,5'-dinitro-2,2'-bipyridylamine (**3**) (2) have been synthesized from **1** utilizing this general displacement reaction.



Recently, our attention has been directed toward the preparation of various diamino compounds containing bipyridyl units as potential monomers for polyimide synthesis. In an earlier paper (3), we described the synthesis of several diaminobipyridyl compounds including **4** and **5**. These two compounds were obtained from the condensation of **1** and either sodium sulfide or 5-nitro-2-aminopyridine following by chemical reduction of the nitro functions. However, our attempts to prepare 5,5'-dinitro-2,2'-bipyridylmethane by a similar condensation of **1** with 2-methyl-5-nitropyridine (**6**) were unsuccessful and the only product which could be isolated was 5,5'-dinitro-2,2'-bipyridylethane (**7**). This unexpected result has prompted us to examine this particular reaction further.

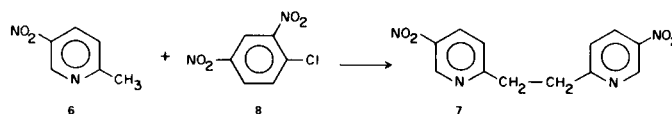


The reaction of **1** and **6** in dry toluene with potassium *t*-butoxide gave **7** in 16% yield, but no evidence of either 5,5'-dinitro-2,2'-bipyridylmethane or 5,5'-dinitro-2,2'-bipyridine could be found. When this same reaction was carried out under nitrogen, the yield of **7** was increased to 30%. The relatively low yield of **7** in both cases might be attributed to some involvement or interaction of the pyridyl nitro group with the reactive organometallic compounds (4).

Edwards and Teague (5) have described the air oxidation of 2-picolyllithium, which gave rise to 2-pyridylmethanol and a radical coupling product; 1,2-bipyridylmethane. Similarly, the air oxidation of phenyllithium has been reported to give the corresponding biphenyl as a coupling product (6).

We have observed however, that treatment of **6** with potassium *t*-butoxide in dry toluene, in an air atmosphere but without **1**, results only in the decomposition of **6**. No identifiable products could be isolated from the reaction mixture under these conditions. In view of these results, it seemed most likely that **7** was not arising *via* the simple air oxidation of the anion of **6**.

The formation of **7** would appear then to be directly associated with but not ultimately involved with the 2-chloro-5-nitropyridine (**1**), since the desired dinitrobipyridylmethane was never observed in the product work-up. The role of the chloronitro compound was further tested by examining the introduction of other similarly substituted aromatic species in place of **1**. Of the compounds which were evaluated (Table I) 1-chloro-2,4-dinitrobenzene **8** was found to give the best yield of **7**. Furthermore, when the reaction was run under nitrogen, the dinitrobipyridylethane **7** could be isolated in 40% yield. *m*-Dinitrobenzene and *p*-chloronitrobenzene were also tried, however, only the former compound was effective in producing **7**, but only then in very poor yield.



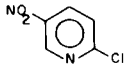
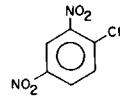
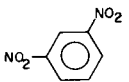
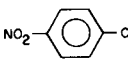
The reaction of **1** and **6** was also attempted in dry ether with phenyllithium under nitrogen. It proceeded almost homogeneously, however, both **1** and **6** were recovered (74% recovery each) after heating for six hours and only a tarry material was obtained, from which no identifiable compounds could be isolated.

Kornblum and co-workers (7,8) have suggested that the displacement reaction of *p*-nitrocumyl chloride or α -*p*-dinitrocumene by anions proceeds by radical anion mechanisms. The coupling reactions of 2-halo-2-nitropropanes (9) or 4-isopropylpyridine (10) were also interpreted as

proceeding by radical anion mechanism.

It seems then very likely that the formation of **7** would involve a radical anion process in which the electron transfer from the anion is followed by the radical coupling reaction. Our view or interpretation is supported by the

TABLE I

Electron Acceptor	Condition	Yield, %	Recovery, % Electron Acceptor 6	
none	air	0	-	0
	air	16	34	33
	N ₂	30	13	18
	air	18	44	36
	N ₂	40	13	31
	air	3	53	45
	air	0	73	7

following observations: (I) the better electron acceptor appeared to give the better yields of **7**; (II) better yields of the bipyridylethane were obtained under a nitrogen atmosphere.

EXPERIMENTAL

The following procedures were all carried out under a stream of nitrogen. Dry toluene (30 ml.) was heated at reflux for 10 minutes to remove the residual air. To the cooled toluene was added 1.0 g. (0.00725 mole) of 2-methyl-5-nitropyridine (**6**). The solution was then cooled in an ice bath and when the precipitate began to appear, 1.14 g. (0.0102 mole, 1.4 mole equivalent) of potassium *t*-butoxide was added. The mixture turned dark green and after stirring at 0° for 5 minutes, 1.15 g. (0.00725 mole) of 2-chloro-5-nitropyridine (**1**) was added. The mixture was stirred at room temperature for 10 minutes and then heated at reflux for 10 hours. The resulting dark mixture (heterogeneous) was filtered and the solid was extracted with benzene by Soxhlet extraction for two days. The combined filtrate and extract were evaporated under reduced pressure to give a brown solid, which

was found to be a mixture of the starting materials and the product by nmr spectrum.

The starting materials were removed by sublimation at 60° and 1 mm Hg. The sublimed white crystalline material weighed 0.33 g. and its nmr spectrum showed it to be a mixture of 0.18 g. (18% recovery) of 2-methyl-5-nitropyridine and 0.15 g. (13% recovery) of 2-chloro-5-nitropyridine. The brown sublimation residue (0.70 g.) was recrystallized from benzene and petroleum ether to give 0.30 g. (30%) of 5,5'-dinitro-2,2'-bipyridylethane (**7**) as a light brown crystalline solid, m.p. 195-212°. Three more recrystallizations gave very pale tan flakes, m.p. 207-210°; ν max (potassium bromide) 1600, 1570, 1510 cm⁻¹; nmr (DMSO-d₆): δ 3.47 (s, 4), 7.35 [d (J = 9 Hz), 2], 8.37 [dd (J = 9, 2.7 Hz), 2], 9.36 [d (J = 2.7 Hz), 2].

Anal. Calcd. for C₁₂H₁₀N₄O₄: C, 52.56; H, 3.68; N, 20.43. Found: C, 52.54; H, 3.51; N, 20.37.

Acknowledgements.

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- (11) Melting points are uncorrected and were obtained on either a Mel-Temp or Thomas Hoover melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Nuclear Magnetic Resonance spectra were recorded on a Varian Model T-60 spectrometer with tetramethylsilane as the internal standard.