

The geometry of the hydrogen bonds appears from Table 3. This bonding scheme is in accordance with the proposal in the X-ray work with the exception, that the existence of the bifurcated hydrogen bond from H_I was not foreseen. The O—H distances seem to be rather short, especially the O_{II} — H_{III} distance (0.85 Å). The deviation from the normal value 0.97 Å in water molecules is probably not significant. The absence of correction for thermal motion is most likely the reason for the difference. In $FeSiF_6 \cdot 6H_2O$ (Hamilton⁶) the calculated correction to be added to the smallest O—H distance is 0.07 Å using the "riding motion" method.

The lone pair coordination of the water molecules is of the type D (Chidambaram *et al.*⁷), in which the bisector of the lone pairs of the oxygen atom points towards the bivalent ion Mn^{2+} ; the groups $Mn-OH_2$ are planar.

Recently El Saffar⁸ has calculated the coordinates of the hydrogen atoms in β - $RbMnCl_3 \cdot 2H_2O$ using Baur's least electrostatic energy method.⁹ His results are in good agreement with the corresponding coordinates from this neutron study.

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Nitriles from Vilsmeier-Haack Formylations of Primary Nitro Compounds

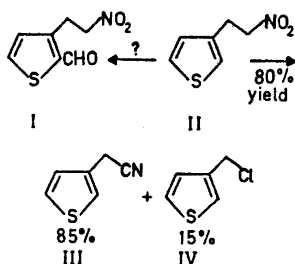
JAN SKRAMSTAD

*Division of Organic Chemistry,
University of Lund, Chemical Center,
Box 740, S-220 07 Lund 7, Sweden*

In connection with work on 5-nitro-4H-cyclopenta[b]thiophene,¹ the thiophene derivative I was a key intermediate, available from 2,3-dibromothiophene in six steps.¹ In search for an easier route to I, Vilsmeier formylation of β -(3-thienyl)nitroethane (II) was considered worth trying. Formylations according to Vilsmeier-Haack have found extensive use in the thiophene series.²⁻⁴ Thus, 3-methylthiophene (which is closely related to II) has been formylated in 62 % yield to give a mixture of 2- and 5-formyl-3-methylthiophene in the relative proportion 85:15.⁵ Although substrates with nitro groups at aromatic positions have been reported to undergo normal Vilsmeier-Haack formylations,^{6,7} reports on the application of this method to compounds with aliphatic nitro groups have, to the author's knowledge, not appeared.

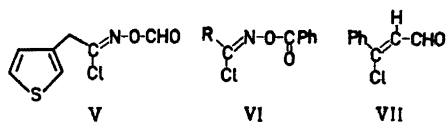
Compound II was prepared by reduction of β -(3-thienyl)nitroethylene⁸ with sodium borohydride in 70 % yield. The formylating reagent was prepared at 10–20°C from phosphorus oxychloride and *N,N*-dimethylformamide, 1 and 2 equivalents, respectively. To this mixture 1 equivalent of II was added with cooling. After a few minutes, the temperature was gradually increased. At about 105°C an exothermic reaction set in with evolution of hydrochloric acid. When the gas evolution had subsided, the reaction mixture was cooled and poured onto aqueous sodium acetate. After normal work-up *via* extraction with ether, an oil was isolated. Analysis (IR, NMR and GLC/MS) showed that this product was a mixture of about 85 % 3-thienyl cyanide (III) and 15 % 3-thienylchloride (IV) produced in a total yield of about 80 %. An analogous result was obtained when the same reaction was carried out with β -phenylnitroethane. In this case benzyl cyanide was the main product (identified by IR and GLC through comparison with an authentic sample). Interestingly enough, the reaction failed when

applied to β -(2-thienyl)nitroethane (prepared from β -(2-thienyl)nitroethylene⁸ by sodium borohydride reduction). In this case only resinous material resulted.

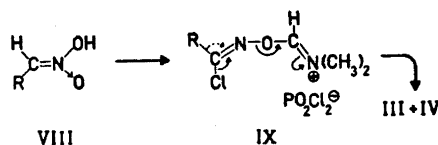


While exact mechanistic details of the reaction must remain speculative at this moment, certain observations have been made which are suggestive of the overall pathway.

When the reaction with II was interrupted at 80–85°C (before the evolution of gas had started) and the reaction mixture poured onto sodium acetate, the formate of 3-thienyl hydroxamic acid chloride (V) was obtained. This structure was evident from IR-, NMR-, and GLC/MS-analysis. Similar compounds (VI) are known to result from the reaction between primary nitroalkanes and benzoyl chloride with tertiary amines as catalysts.^{9,10} Another analogy is the reaction between the Vilsmeier-Haack reagent and phenylacetylene. In this case the net result is (after hydrolysis) addition of the elements of formyl chloride to the triple bond to give VII.



The following pathway for this new nitrile synthesis is suggested: (1) The nitro compound tautomerises to same extent to the corresponding nitronic acid (VIII) by the action of the excess dimethylformamide present; (2) The Vilsmeier-Haack reagent¹¹ adds to VIII to give a species which gains stability by elimination of water, resulting in the intermediate IX. Hydrolysis of IX gives the observed formate V; (3) The last step is probably a thermal decomposition of IX to give the nitrile and dimethylformamide by the electron shifts indicated.



The eliminated chloronium ion may react with water (from the elimination in step 2) to form hydrochloric acid and oxygen. The fact that even 3-thienyl chloride (IV) was formed in this reaction, is taken as further support of step 3. Instead of elimination of chloronium ion, 3-thienyl cation may be the leaving group, producing IV by reaction with chloride. Here we may also have a ready explanation for the failure of this reaction when applied to β -(2-thienyl)nitroethane. The 2-thienyl cation is a better leaving group than the 3-thienyl cation (due to more effective delocalisation of charge). The formation of any 2-thienyl chloride would probably only lead to polymers at this high temperature because of the reactivity of this compound.¹³

This new reaction may be of preparative significance as it is probably the first example of conversion of primary nitro compounds to nitriles in a single operation without the use of extreme conditions ($\text{H}_2/300^\circ\text{C}$).¹⁴ It should, however, be mentioned that salts of primary nitroalkanes give nitriles when treated with diethyl phosphorochloridite.¹⁵

Experimental. β -(3-Thienyl)nitroethane (II).

To a freshly prepared solution of 5.0 g (0.13 mol) of sodium borohydride in 200 ml of water, 10.0 g (0.065 mol) of β -(3-thienyl)nitroethylene⁸ was added with vigorous stirring. After stirring for one hour at room temperature (some cooling was necessary to maintain this temperature), the reaction mixture was filtered. The colourless filtrate was acidified with aqueous acetic acid and the liberated nitro compound isolated by extraction with ether, washing with sodium bicarbonate solution and drying (MgSO_4). This gave 7.0 g (69%) of the title compound. IR (neat): 1550 (s) and 1375 (s) cm^{-1} (NO_2 -vibrations). NMR (CDCl_3): τ = 2.6–3.2 ppm (3H, m, thiophene hydrogens); τ = 5.47 ppm (2H, t, α - CH_2); τ = 6.73 ppm (2H, t, β - CH_2). $J_{45} = 4.9$ c/s, $J_{25} = 3.0$ c/s, $J_{24} = 1.4$ c/s, $J_{\text{CH}_2-\text{CH}_3} = 7.0$ c/s.

β -(2-Thienyl)nitroethane. Starting from β -(2-thienyl)nitroethylene,⁸ the same procedure as above gave a 60% yield of the title compound. IR (neat): 1555 (s) and 1385 (s) cm^{-1} (NO_2). NMR (CDCl_3): τ = 2.7–3.3 ppm (3H, m, thio-

phene hydrogens); $\tau=5.45$ ppm (2H,t, α -CH₂); $\tau=6.54$ ppm (2H,t, β -CH₂). $J_{45}=4.6$ c/s, $J_{34}=3.4$ c/s, $J_{35}=1.8$ c/s, $J_{\text{CH}-\text{CH}_2}=7.0$ c/s.

Vilsmeier reaction with β -(3-thienyl)nitroethane (II). When this reaction was carried out as described in the previous section of this communication, with a reaction temperature of 105–110°C for about half an hour, an oil was isolated in about 80 % yield. IR (neat): 2250 cm⁻¹ (CN) and 1415 cm⁻¹. NMR (CDCl₃): 3-thienyl cyanide: $\tau=2.6$ –3.1 ppm (3H,m,thiophene hydrogens); $\tau=6.35$ ppm (2H,d,CH₂). $J_{45}=4.7$ c/s, $J_{35}=2.9$ c/s, $J_{34}=1.7$ c/s, $J_{\text{CH}_2-\text{C}}=1.0$ c/s. GLC/MS: (*m/e*, %): 3-thienyl chloride (15 %): 134, 6 %; 132, 15 % (M⁺); 97, 100 % (M⁺-Cl). 3-Thienyl cyanide (85 %): 123, 92 % (M⁺); 122, 100 % (M⁺-H); 97, 25 % (M⁺-CN); 96, 61 % (M⁺-HCN, or 122-CN).

Vilsmeier reaction with β -(2-thienyl)nitroethane. When this reaction was carried out in the same way as for the 3-isomer, the usual exothermic reaction occurred at about 95°C. However, no definite product could be isolated after the usual work-up. Mostly ether-insoluble material resulted.

Vilsmeier reaction with β -phenylnitroethane. In this case a quite analogous result to that found in the case of β -(3-thienyl)nitroethane was obtained. An exothermic reaction occurred at about 105–110°C. The product was benzyl cyanide, isolated in about 90 % yield. The IR and GLC analyses proved it to be identical with an authentic sample.

3-Thienylhydroxamic acid chloride formate (V). When the temperature in the reaction between β -(3-thienyl)nitroethane (II) and the Vilsmeier reagent was not allowed to exceed 85°C and the reaction mixture after treatment with aqueous sodium acetate was worked up in the usual way, the title compound was the main product. GLC/MS analysis also showed the presence of 3-thienyl cyanide, starting material and some unidentified components with much longer retention times. A distillation gave a fraction mainly composed of the title compound (b.p. 75°C/0.02 mm Hg). IR (neat): 1765 (s) cm⁻¹ (formate carbonyl), 1620 (m) cm⁻¹ (C=N), 1065 (s) cm⁻¹ (C-O). NMR (CDCl₃): $\tau=1.50$ ppm (1H,s,-OCHO); $\tau=2.4$ –3.2 ppm (3H,m,thiophene hydrogens); $\tau=6.10$ ppm (2H,s,CH₂). GLC/MS: (*m/e*, %): 205, 8 %; 203, 18 % (M⁺); 160, 7 %; 158, 21 %

(M⁺-OCHO); 133, 10 %; 131, 24 % (rearrangement); 123, 83 % (M⁺-OCHOCl); 122, 100 % (M⁺-OCHO-HCl); 97, 70 %; 96, 55 %.

The IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer type 257, the NMR spectra on a Varian A60 (with TMS as an internal standard). The GLC/MS analyses were obtained with an LKB 9000 with an ionisation energy of 70 eV and a gas chromatographic inlet system.

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