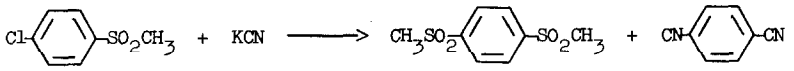
Tetrahedron Letters No.8, pp. 759-760, 1967. Pergamon Press Ltd. Printed in Great Britain.

A novel reaction involving methanesulphinate ion

P. ten Haken

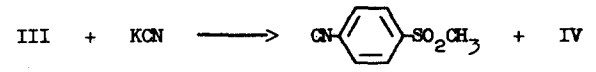
(Received 15 December 1966)

1-Chloro-4-(methylsulphonyl)benzene (I) and cuprous cyanide failed to react and give the desired 1-cyano-4-(methylsulphonyl)benzene (II) when refluxed for 24 hours in dimethylformamide. However, when equimolar amounts of (I) and potassium cyanide were allowed to react in boiling dimethyl sulphoxide (DMSO) for 30 minutes, a 1:1 mixture of 1,4-bis(methylsulphonyl)benzene (III) and terephthalonitrile (IV) was obtained in about 80% yield, but none of the anticipated 1-cyano-4-(methylsulphonyl)benzene (II).



I III IV

(I) was recovered quantitatively after heating for 30 minutes in DMSO, excluding the possibility of solvent participation in this reaction. As was expected, no change occurred when (II)[1] was heated alone in DMSO, indicating that the observed reaction was not due to a thermal disproportionation. Repetition of this experiment with the inclusion of one molar equivalent of potassium cyanide afforded terephthalonitrile (IV) in 70% yield of recrystallised product. A qualitatively similar result was obtained when (III) was treated under the same conditions : (II) and (IV) were obtained in yields (recrystallised) respectively of 15% and 20%, uncorrected for about 40% of starting material (III) recovered.



II

The formation of (II) and (IV) may be interpreted by :

1. Reaction of the chloro-sulphone with cyanide ion to give the cyano-sulphone;
2. Reaction of the cyano-sulphone with cyanide ion to give the dicyanide and methanesulphinate ion;
3. Reaction of methanesulphinate ion with the chloro-sulphone to give the disulphone.

The formation of (III) by a reaction involving methanesulphinat ion not generated from a metal sulphinate is believed to be the first time such a reaction has been recognised.

References

1. J. Chem. Soc., 1946, 767