Tetrahedron Letters No.12, pp. 729-731, 1965. Pergamon Press Ltd.
Printed in Great Britain.

CYANOGEN BROMIDE AS AN ACYLATING AGENT.

B.S.Thyagarajan and K.Rajagopalan.

Department of Organic Chemistry, University of Madras, Madras - 25, India.

(Received 2 February 1965)

We wish to report a novel acylating action utilizing cyanogen bromide and the sodium salts of organic acids as reactants.

In the course of a study of brominative decarboxylation of pyridone- and quinolizone carboxylic acids (1,2), by the action of bromine in refluxing acetic acid, we desired to explore the possibility of effecting cyanative decarboxylation by means of cyanogen bromide. In the event, although quantitative evolution of CO_2 was observed, the products were found to be only the starting acids (3). However, when the action of CNBr was tried on the sodium salts of salicylic acid or p-hydroxybenzoic acid in refluxing acetic acid, quantitative release of CO_2 was again observed but the products isolated after removal of acetic acid and sodium bromide were found to be different. They were devoid of bromine or nitrogen. Their infrared spectra revealed the presence of an extra carbonyl while elemental analyses showed the addition of an acetyl group. Further confirmation was at hand from the NMR spectra which clearly showed the presence of the $CO.CH_3$ group. Comparison with authentic specimens of acetylsalicylic acid and p-acetoxybenzoic acid showed complete identity in mixed melting point and infrared spectra. In so far as we know, THIS IS THE FIRST REPORT OF CYANOGEN BROMIDE FUNCTIONING AS AN ACYLATING AGENT UNDER THE EXPERIMENTAL CONDITIONS REPORTED.

Cyanogen bromide has been utilized as a brominating agent and a cyanating agent (4,5). Reports are also available in the literature wherein the sodium salts of carboxylic acids are converted into the corresponding NITRILES by cyanogen bromide under pyrolytic conditions (300°) (6,7). Our observations are unique in utilizing CNBr as an acylating agent.

By carrying out the reaction between the sodium salt of p-hydroxybenzoic acid and CNBr in the presence of other acids like propionic, butyric and isobutyric acids, we have obtained the corresponding acyl derivatives in good yields. The products were identified by comparison with authentic specimens. In every case the reaction was extremely fast and facile, the reaction being complete within fifteen minutes as indicated by the quantitative evolution of CO_2 within this time.

Further work is in progress to determine the mechanistic details of this acylation reaction like the source of the CO_2 and the nature of the acylating intermediate. We are also exploring the general applicability of CNBr as an acylating agent.

Acknowledgements:

Our grateful thanks are due to the Government of India for the award of a fellowship to K.R. and to Dr.P.S.Landis, Socony Mobil Research Laboratory, Paulsboro, New Jersey, U.S.A. for ready assistance with infrared and N.M.R. spectra.

REFERENCES

1. B.S.Thyagarajan and P.V.Gopalakrishnan, Tetrahedron, in press.
2. B.S.Thyagarajan and K.Rajagopalan, unpublished results.
3. The products in the case of the pyridone- and quinolizone carboxylic acids

could well have been the corresponding acetoxy derivatives which are known to be unstable, thus accounting for the recovery of the starting acids.

4. W.Steinkopf, H.Augestad-Jensen, and D.Donat, *Annalen* **430** 78 - 112 (1923)

5. A.H.Klopp and G.F.Wright, *J.Org.Chem.* **4** 142-149 (1939)

6. D.E.Douglas, Jean Eccles and A.E.Almond, *Can.J.Chem.* **31** 1127 (1953)

7. D.E.Douglas and A.M.Burditt, *Can.J.Chem.* **36** 1256 (1958).