Tetrahedron Letters No.2, pp. 77-78, 1969. Pergamon Press. Printed in Great Britain.

THE AMINATION OF CARBANIONS

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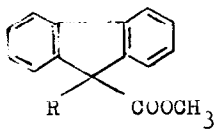
(Received in UK 4 November 1968; accepted for publication 3 December 1968)

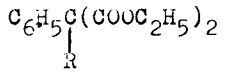
The direct displacement of a hydrogen by an amino group is known only in cases in which the hydrogen atom departs as a hydride ion (nucleophilic substitution by NH_2^-) (1). Amination in the opposite, more common case, in which the hydrogen departs as a proton (electrophilic substitution by NH_2^+) has not been reported yet. Such a reaction would be useful in the synthesis of various types of amines otherwise available only by multistep processes.

We have recently reported that the dinitrophenoxy group of O-(2,4-dinitrophenyl)hydroxylamine (I) (2) is easily displaced by nucleophilic reagents (3), thus (I) can serve as an amination reagent for nucleophiles. The reaction has now been applied to the amination of carbanions, yielding the corresponding amines directly in fair yields, as illustrated by the following examples:

(1)



(II)



(III)

(a, R = H. b, R = NH_2. c, R = $NHCOCH_3$)

A solution of 9-fluorenecarboxylic acid methyl ester (IIa) in benzene-methanol was treated with potassium methoxide and (I), stirred overnight and potassium dinitrophenolate was then removed by filtration. The hydrochloride of 9-amino-9-fluorenecarboxylic acid methyl ester (IIb) (m.p. 223-226°, 50%) precipitated upon passing dry HCl through the ethereal solution. Treatment with NaOH yielded the free amino ester (IIb) m.p. 113°. (Acetyl derivative (IIc) m.p. 239-240°).

A slightly different procedure was used for the amination of a series of diethyl malonates. For example, treatment of diethyl phenylmalonate (IIIa) in DMF with sodium hydride and then with (I) yielded diethyl α-amino-α-phenylmalonate (IIIb), b.p. 150-160°/7mm in 53% yield. (Acetyl derivative (IIIc) b.p. 180°/1mm, m.p. 75°).

Satisfactory elemental analyses were obtained for all new compounds. Spectral properties (I.R., N.M.R. and mass spectra) were in accord with the expected structures.

Studies on the application of the reaction to additional types of carbanion as well as other nucleophiles are in progress.

REFERENCES

1) The most known example is the α-amination of pyridine by sodamide (Chichbabin Reaction). Reviewed by M.T. Leffler, Organic Reactions 1 91 (1942).

2) T. Sheradsky, J. Heterocyclic Chem., 4, 413 (1968). The procedure described therein was much improved by using dinitrofluorobenzene instead of dinitrochlorobenzene.

3) T. Sheradsky, Tetrahedron Letters, 1909 (1968).