A Reversible Anionic Rearrangement Involving C→N and N→C Migration of an Ethoxycarbonyl Group

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Summary A reversible 1,2-anionic rearrangement of an ethoxycarbonyl group is described and shown to be dependent on the nature of the counter-ion.

Some time ago, we reported[1,2] that the *C*-ethoxycarbonyl monoanion (**1**; M = Na), derived from the reaction of the dianion (**2**) with ethyl chloroformate at −78 °C, rearranged at higher temperatures to the *N*-ethoxycarbonyl isomeric anion (**3**; M = Na). We have now established that the two isomeric anions are in equilibrium and conditions are delineated whereby the rearrangement can be reversed.

The rearrangement of (**1**) to (**3**) was observed to be slower in diethyl ether than in tetrahydrofuran, and with lithium as a counter-ion the rearrangement did not occur. Such observations are in accord with other 1,2-rearrangements of anions.[3] However, in view of the inability to obtain (**3**) with lithium as a counter-ion, we prepared it by proton removal from (**4**) using n-butyl-lithium as a base and diethyl ether as a solvent. The product of this reaction proved to be the monoanion (**1**) since protonation of the anionic product gave (**5**) and reaction with benzaldehyde gave (**6**). The isomeric anion (**3**) with benzaldehyde forms (**7**).†

With tetrahydrofuran as a solvent and lithium as the counter-ion, an equilibrium mixture of (**1**) and (**3**) was obtained. Thus, treatment of either (**4**) or (**5**) with n-butyl-lithium at −78 °C produced (**3**) and (**1**) respectively. No rearrangement of these anions occurred in 1 h at −78 °C. However, within 1 h at 20 °C, the same product composi-

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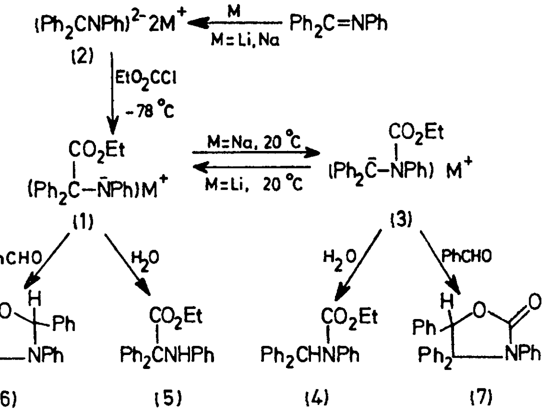
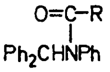
† Satisfactory analytical and spectral data were obtained for these compounds.

tion‡ (after protonation) of 12—15% of (**4**) and 88—85% of (**5**) from (**1**) or (**3**) indicated that an equilibrium composition of the anionic pair (**3**) and (**1**) had been obtained. This equilibrium composition remained unchanged for 10 h but was followed by a slow decomposition to produce $Ph_2C{=}NPh$, $Ph_2CHNHPh$, and (**4**) after 52 h. Treatment of the mixture at this point with D_2O led to no deuterium incorporation§ into (**4**), although the anion (**3**) can be efficiently deuteriated or alkylated[1] if freshly prepared. Protonation of the anion (**3**) by reaction with the solvent or by inter- or intra-molecular proton abstraction from the ethoxycarbonyl group¶ must have occurred during this long reaction time.




$$\begin{array}{c} O{=}C{-}R \\ | \\ Ph_2CHNPh \end{array}$$

(**8**)

It is suggested that the C → N migration of the EtO_2C (M = Na) is a result of the delocalized nature of the Ph_2C^- anion portion of (**3**) rendering it more stable than (**1**). With lithium as the counter-ion, the strong Lewis acidity of the lithium cation results in a close association between it and the amine anionic portion of (**1**) which reverses the relative thermodynamic stability of (**1**) and (**3**). Supporting this view is the fact that, although in diethyl ether complete N → C migration of the EtO_2C group occurs, the rearrange- is completely reversed on addition of *NNN′N′*-tetramethylethylenediamine (an efficient solvating agent for lithium[4]) and only (**4**) is isolated on protonation.

Attempts have been made to rearrange *N*-acyl derivatives such as (**8**; R = cyclopropyl, or *p*-tolyl) using n-butyllithium and ether, but only starting material was recovered. It appears that alkoxycarbonyl groups have inherently high migratory aptitudes since the $ClCH_2CH_2O_2C$ group is observed to migrate in a manner similar to the $MeCH_2O_2C$ group. Our earlier suggestion[1] of a three-membered cyclic intermediate in the rearrangement accommodates this observation. Electron-donating alkyl groups would reduce the electrophilicity of the migrating carbon and hence decrease its tendency to isomerise.**

While $EtCO_2$ groups have been observed to migrate in anions,[5] we believe this to be the first observation that such rearrangements may be reversed under appropriate reaction conditions.

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‡ Analysis was by g.l.c. using a 10 ft by 1/8 in column packed with 3% SE-52 on Varaport at 200 °C. Identity of the products was confirmed by comparison of retention times with those of authentic samples and also by isolation of the products by preparative t.l.c. on silica gel.

§ Addition of D_2O before anion (**3**) was completely protonated gave mixtures of non-deuteriated and deuteriated (**4**). Assuming that the anionic equilibrium is maintained, the amount of deuteriated (**4**) as determined by mass spectrometry permitted a calculation of the equilibrium amount of (**1**) and hence of (**5**) in the final product mixture. These calculations agreed with the analytical results.

¶ We thank a referee for this suggestion which explains the formation of $Ph_2CHNHPh$ by concomitant loss of carbon dioxide and ethylene.

** We thank a referee for pointing this out.

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[4] A. W. Langer, Jr., *Trans. New York Acad. Sci.*, 1965, **27**, 741.
[5] R. M. Acheson, *Accounts Chem. Res.*, 1971, **4**, 177.