Formation of α-Nitro-acetylenes by the Coupling Reactions of Lithium Acetylides with 2-Chloro-2-nitropropane or 2,2-Dinitropropane

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Summary Reaction of lithium acetylides with 2-chloro-2-nitropropane or 2,2-dinitropropane gives high yields of the nitroacetylenes, which in acidic solution undergo hydration and elimination of nitrous acid to yield αβ-unsaturated ketones.

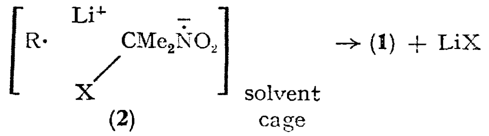
WE have observed that the lithium salts of 1-alkynes in tetrahydrofuran (THF) or dimethoxyethane (DME) give substitution products with the tertiary halide 2-chloro-2-nitropropane. Even more surprising is the observation that substitution also occurs readily with 2,2-dinitropropane [equation (1)].

$$RC\equiv CLi + XCMe_2NO_2 \xrightarrow{THF} \underset{(1)}{RC\equiv CCMe_2NO_2} + LiX \qquad (1)$$

$$X = Cl \text{ or } NO_2, \qquad R = \text{n-alkyl}$$

The yield of (**1**) varies according to the alkyl group R, the leaving group X, and the reaction conditions employed, as follows: R = Me, X = Cl at 30 °C for 39 h, 20% yield; R = Et, X = Cl at 30 °C for 44 h, 47% yield; R = Pr^n, X = Cl at 32 °C for 28 h, 53% yield; R = Pr^n, X = NO_2 at 30 °C for 48 h, 52% yield; R = Bu^n, X = Cl at 55 °C for 5 h, 46% yield; R = Bu^n, X = NO_2 at 55 °C for 5 h, 24% yield; R = n-C_5H_{11}, X = Cl at 25 °C for 48 h, 53% yield; and R = n-C_6H_{13}, X = Cl at 55 °C for 5 h, 21% yield.

Under the reaction conditions employed t-butyl chloride failed to give any substitution. Moreover, in Me_2SO potassium acetylides and 2-chloro-2-nitropropane failed to yield (**1**). It thus appears that reaction (1) is not a standard nucleophilic substitution. Substitution by a free radical chain process has been previously reported for the reactions of 2-substituted-2-nitropropanes with a variety of carbanions.[1] However, this process ($S_{RN}1$)[2] is excluded by the observations that the coupling reaction (1) is neither promoted by irradiation nor retarded by the presence of 5 mol % of di-t-butyl nitroxide or *p*-dinitrobenzene, efficient inhibitors for other $S_{RN}1$ processes. We conclude that substitution probably occurs by a bimolecular process involving electron transfer *via* an intermediate similar to (**2**). The lithium cation apparently hinders the nucleophilic



(**2**)

attack of the acetylide anion upon the substituent X (chloride or nitro) to yield the 1-nitro-1-methylethyl anion (the preferred reaction course in Me_2SO or when sodium is the counter ion in ethereal solvents).† Even with lithium as the counter ion the coupling reaction (1) does not compete with this nucleophilic attack when the substituent X is bromine or the cyano group.‡

The nitro acetylenes (**1**) are hydrated regioselectively to yield β-nitro ketones which readily eliminate the elements of nitrous acid [reaction (2)]. Thus, (**1**) with R = n-propyl, n-butyl, or n-pentyl, is converted into 2-methyl-4-oxohept-2-ene, -oct-2-ene, or -non-2-ene in yields of *ca.* 60% by treatment with aqueous mercury(II) sulphate–sulphuric acid for 5 h at 80 °C.

$$\begin{tikzcd} \mathrm{R{-}C{\equiv}CCMe_2NO_2} \arrow[r, "\mathrm{HgSO_4}", "\mathrm{H_2O,H_2SO_4}"'] & {[\mathrm{RC(:O)CH_2CMe_2NO_2}]} \arrow[d, "\mathrm{H_3O^+}"] \\ & \mathrm{RC(:O)CH{=}CMe_2} \end{tikzcd} \qquad (2)$$

$R = Pr^n, Bu^n, \text{ or } n\text{–}C_5H_{11}$

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† Low yields of (**1**) have also been observed in the reaction of 2-chloro-2-nitropropane with $Bu^nC{\equiv}CMgBr$ in THF.

‡ Hex-1-ynyl-lithium and 2-cyano-2-nitropropane in THF give hept-2-ynenitrile in >50% yield.

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