JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 7
1983

Nucleophilic Attack on Chloro(phenyl)ethyne by Azide Ion

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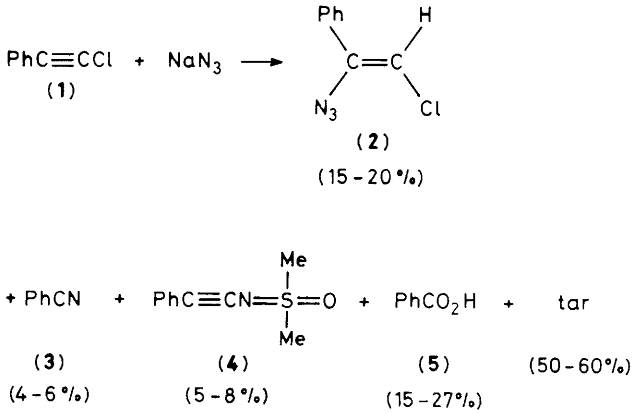
The reaction of chloro(phenyl)ethyne (**1**) with sodium azide in dimethyl sulphoxide gave the nucleophilic addition product (*Z*)-α-azido-β-chlorostyrene; phenylethynylnitrene (**7**) was trapped by the solvent to give *N*-(phenylethynyl)-*S*,*S*-dimethylsulphoximine (**4**), indicating the prior formation of the hitherto unknown substitution product azido(phenyl)ethyne (**6**).

Conceptually the simplest synthetic route to the thus far 'elusive' azidoacetylenes would involve the nucleophilic substitution of halogenoacetylenes[1,2] with azide ion, but the attempted synthesis of azido(phenyl)ethyne (**6**) from sodium azide and iodo- or bromo-(phenyl)ethyne failed.[3] We have now studied the reaction of azide ion with chloro(phenyl)ethyne (**1**).

In a typical run, equimolar (0.09 mol) amounts of (**1**) and dry sodium azide were stirred in anhydrous dimethyl sulphoxide (DMSO; 250 ml) at 25 °C for 3 days. After work-up with ice–water and benzene, the crude mixture was chromatographed on alumina with 200 ml portions of eluants in the order: hexane, ether, benzene, and benzene–methanol (1 : 1).

From the hexane eluate was isolated (*Z*)-α-azido-β-chlorostyrene (**2**) as pale yellow needles (20.2%): m.p. 36—37 °C; *m/z* 179 and 181 (3 : 1, $M^{\cdot+}$), 151 and 153 ($M^{\cdot+} - N_2$), 116 ($C_8H_6N^{\cdot+}$), and 103 ($C_7H_6N^{\cdot+}$); ^1H n.m.r. (CCl_4) δ 5.84 (s, 1H, =CH) and 7.39 (m, 5H, Ph); i.r. (KBr) 2110 (N_3) and 1605 (C=C) cm^{-1}. On hydrogenolysis (1 atm H_2; Pt black; ethanol; 25 °C), (**2**) decomposed into acetophenone and ammonium chloride. Benzonitrile (**3**) (3.5%) was isolated from the ether eluate.



Scheme 1. Conditions: DMSO; 25 °C; 1 h to 9 days.

The benzene–methanol eluate contained only a single product, *N*-(phenylethynyl)-*S*,*S*-dimethylsulphoximine (**4**). When left in a refrigerator after complete removal of the eluant, (**4**) crystallized as colourless plates (1.5%): m.p. 103—104 °C;‡ *m/z* 193 (98%, $M^{\cdot+}$), 115 (90, $C_8H_5N^{\cdot+}$), 78 (49, $C_2H_6OS^{\cdot+}$), 77 (39, $C_6H_5^{\cdot+}$), 63 (100, $C_2H_6SH^{\cdot+}$), and 62 (99, $C_2H_6S^{\cdot+}$); ^1H n.m.r. ($CDCl_3$) δ 3.50 (s, 6H, Me) and 7.33 (m, 5H, Ph); i.r. 2152 (C≡C), 1199 (S=O), and 1152 (S=N) cm^{-1}.

Approximately 50% of (**1**) had been converted into an intractable tar. In addition, benzoic acid (**5**) was isolated (12%) on acidifying the water layer left after the initial workup.

Analyses (n.m.r. and h.p.l.c.) of the reaction mixture sampled at intervals revealed that the product distribution remained almost constant regardless of the extent of consumption of (**1**) (Scheme 1).

Even though the putative primary substitution product, azido(phenyl)ethyne (**6**), was not found at any stage of the reaction, the formation of (**4**) appears to be most easily rationalized in terms of the prior formation of (**6**), which readily decomposed to give the nitrene (**7**) (Scheme 2). The

$$\begin{tikzcd}
 & \mathrm{PhC{\equiv}CCl} + \mathrm{N_3^-} \arrow[r] & {[\mathrm{PhC{\equiv}CN_3}]} \\
 & & \mathbf{(6)} \arrow[d, "-\mathrm{N_2}"] \\
\mathbf{(4)} & & {[\mathrm{PhC{\equiv}C\ddot{N}}]} \arrow[ll, "\mathrm{DMSO}"'] \\
 & & \mathbf{(7)}
\end{tikzcd}$$

Scheme 2

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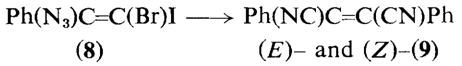
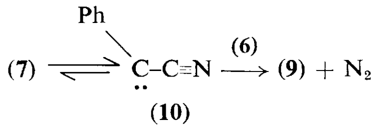
‡ Satisfactory elemental analyses were obtained.



$$\underset{(\mathbf{8})}{Ph(N_3)C{=}C(Br)I} \longrightarrow \underset{(E)\text{- and }(Z)\text{-}(\mathbf{9})}{Ph(NC)C{=}C(CN)Ph}$$

Scheme 3. Conditions: heat; Al_2O_3, Mg, or Zn.



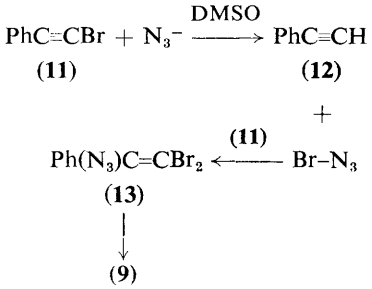
Scheme 4

trapping of a nitrene by a sulphoxide leading to the corresponding sulphoximine is a well known reaction.[4,5] The azide (**6**) was considered by Boyer and Selvarajan to be the probable key intermediate in the transformation of the azidodihalogenostyrene (**8**) to the dicyanostilbenes (**9**)[6] (Scheme 3).[6] If the nitrene (**7**) were involved in the formation of (**9**), (**7**) would need to act as its fluxional isomer, the carbene (**10**) (Scheme 4). However, except for (**9**), nothing diagnostic of (**7**) or (**10**) was found among the products. Hassner and Isbister were not able to capture (**10**) in a similar system with added diphenylethyne,[7] which had been shown to trap efficiently (**10**) generated from phenyldiazoacetonitrile.[8] Hence the nitrene–carbene route leading to (**9**) is unlikely.

That the fluxional isomerism, (**7**) ⇌ (**10**), is incompatible with the use of DMSO as solvent arises from the observations of Isomura and Taniguchi on a closely related system: bromo(phenyl)ethyne (**11**) reacted with sodium azide in DMSO at 25 °C and gave (*E*)-(**9**) (5—10%) and phenylethyne (**12**) (18—20%) in addition to (**3**), (**5**), and α-azido-β-bromostyrene, but the sulphoximine (**4**) was not detected. α-Azido-β,β-dibromostyrene (**13**) was found initially, and then disappeared.[9] In our reaction of (**1**), in contrast, (**9**) and (**12**) were not found. Hence we presume that (**4**) and (**9**) were derived from different precursors, for, if the nitrene (**7**) had been formed prior to (**9**) then some of (**7**) would have been trapped by DMSO to form (**4**) in Isomura's system, while some (**9**) should have been formed in ours. Since (**12**) was another major product in the reaction of (**11**), we propose the mechanism in Scheme 5.

The systems of Boyer, Hassner, and Isomura involved the α-azido-β-dihalogenostyrenes (**8**) or (**13**). The routes from them to (**9**) seem to bypass (**7**), and alternatives have to be considered.

The formation of (**2**) and α-azido-β-bromostyrene, respectively, from (**1**) and (**11**), indicates that the attack at C-2 is a major competing process in the azide reactions as it is in other nucleophilic reactions with halogeno(aryl)acetylenes.[1]



Scheme 5

Neither (**2**) nor α-azido-β-bromostyrene was transformed into (**4**) or (**9**) under the conditions employed.

We are not yet able to rationalize the formation of (**3**) and (**5**); (**2**) does not spontaneously give rise to (**3**) at room temperature, nor is the nitrile (**3**) hydrolysed to (**5**) under our work-up conditions.

In conclusion, the marked contrast between the reactions of azide ions with (**1**) and (**11**) suggest that (**1**) undergoes nucleophilic substitution at C-1 to give (**6**), which eventually gives (**4**) *via* the nitrene (**7**), whereas the preferred sites of attack in (**11**) are the bromine and C-2.

We thank Professor H. Taniguchi and Dr. K. Isomura of Kyushu University for disclosing their unpublished results and for stimulating discussions.

Received, 30th November 1982; Com. 1377

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