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Reaction of Triarylchloroallenes with Nucleophiles under Solvolytic Conditions

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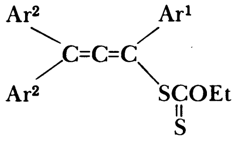
Synopsis. Solvolytic reactions of triarylchloroallenes in the presence of thiocyanate and *O*-ethyl dithiocarbonate anions gave the corresponding allenyl derivatives, while the reaction in the presence of cyanate anion afforded the corresponding propargyl derivative. These results are interpreted in terms of a steric factor of the nucleophiles.

Since allenyl cations were first suggested in solvolysis by Jacobs and Fenton,[1)] much work has been done about the chemistry of allenyl cations; especially Schiavelli and co-workers have revealed intervention of the allenyl cations in their detail mechanistic studies.[2)] One of the most interesting features is an ambident character of allenyl cations, which can provide allenyl and/or propargyl derivatives. However, most works on solvolysis of allenyl halides indicate that nucleophiles attack on the γ-position of the resulting allenyl cations unless bulky substituents are present on the γ-position.[3)]

On the other hand, we have studied photolysis of arylvinyl halides and disclosed that the photogenerated vinyl cations react with various nucleophiles to give substituted ethylenes and heterocyclic compounds.[4)] This successful vinylic substitution led us to examine the reaction of the extended unsaturated carbenium ions, allenyl cations. Here we report a high regioselectivity depending on nucleophiles in the reaction of triarylchloroallenes under solvolytic conditions.

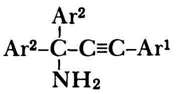
Results and Discussion

1,3,3-Triphenylchloroallene (**1a**) solvolyses under mild conditions: the half-life period $t_{1/2}$=1.0 h at 26.1 °C in 70:30 acetone water (v/v).[3)] The solvolysis was carried out in the presence of KSCN, KS_2COEt, and KNCO in a similar manner as conducted by Schiavelli and co-workers.[3)] In contrast to the reported results,[3)] solvolytic reaction of chloroallenes **1a**—**c** with potassium thiocyanate gave allenyl thiocyanates **2a**—**c** in high yields. In the IR spectra of **2a**—**c** were observed a sharp absorption of the thiocyanato group at 2150 cm^{-1} and a weak absorption of the allenyl bond at 1920—1930 cm^{-1}, but the latter was obscured by overlapping with aromatic ring absorptions. The strong evidence for the allenyl structure was obtained from the ^{13}C NMR spectra. The allenyl carbons of triphenylallenyl thiocyanate (**1a**) resonated at 207 ppm for the β carbon, and at 99 and 118 ppm for γ and α carbons, respectively.[5)] The carbon of thiocyanato group resonated at 110 ppm.[6)] Similar substitution at the α carbon observed in the presence of potassium *O*-ethyl dithiocarbonate as a nucleophile. Solvolytic reaction of chloroallenes **1a** and **1b** led to formation of the corresponding allenyl *O*-ethyl dithiocarbonates **3a** and **3b** in 73 and 57% yield, respectively.



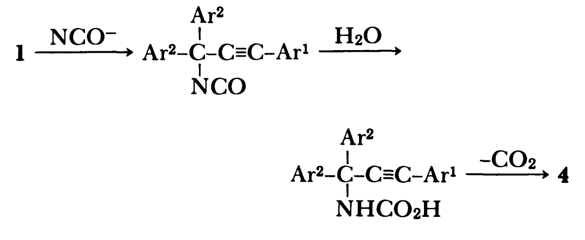
3a: 73%
3b: 57%

However, when potassium cyanate was used as a nucleophile, the cyanate anion attacked on the γ-position to give propargyl derivatives **4**. The IR spectrum of the crude product showed the absorpotion at 3340—2700 and 1700—1645 cm^{-1}, which were assignable to propargylcarbamic acids **5**. However, the compounds **5** could not be isolated because of their instability. Instead, propargyl amines **4** were isolated after treatment of the crude product with an alkaline solution.



$$Ar^2\text{-}\underset{NH_2}{\overset{Ar^2}{C}}\text{-}C{\equiv}C\text{-}Ar^1$$

4a: 45%
4b: 68%



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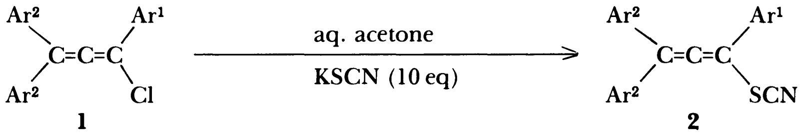
These results indicate that the reaction manner can be controlled by choice of nucleophiles. From the kinetic[3)] and theoretical[7)] studies, it is predicted that



1 **2**

a: $Ar^1=Ar^2=Ph$
b: $Ar^1=Ph$, $Ar^2=p\text{-}MeC_6H_4$
c: $Ar^1=n\text{-}Bu$, $Ar^2=Ph$

2a: 98%
2b: 88%
2c: 72%

nucleophiles react at the propargyl position of the allenyl cation. However, when the γ-position bears a sterically hindered substituent a nucleophile should attack on the allenyl position.[8] Such a steric factor may be operative for a bulky nucleophile. Among the nucleophiles used in this study, thiocyanate and *O*-ethyl dithiocarboate anions are greater in size than cyanate anion because sulfur atom has much larger van der Waals radius than nitrogen or oxygen atom does.[9] The larger nucleophile prefers to attack the allenyl position which has less steric congestion, while the smaller nucleophile prefers the propargyl position which is more reactive than the allenyl position.[3,7] Thus, a high regioselectivity of nucleophiles toward triarylallenyl cations can be explained in terms of the capacity and reactivity of the reacting position and the size of the nucleophiles.

Experimental

Chloroallene 1. Chloroallenes **1** were prepared according to the method prepared by Jacobs and Fenton,[1] from the corresponding propargyl alcohols.[1,3]

Solvolytic Reaction of Chloroallenes 1 in the Presence of Nucleophiles (KSCN, KS_2COEt, and KNCO). To a solution (100—200 ml) of 70:30 acetone-water (v/v) were added chloroallene **1** (1 mmol) and a nucleophile (10 mmol; KSCN, KS_2COEt, or KNCO) and the mixture was stirred for 12—48 h at 25 °C. The reaction mixture was poured into water and the products were extracted with ether. The organic layer was washed with water, saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. After evaporation of the ether, the products were separated by column chromatography on silica gel or alumina using ether-hexane eluent. In the case of potassium cyanate, the crude product obtained by extraction with ether was refluxed for 12 h in a solution of sodium hydroxide (5 mmol) in ethanol (20 ml), benzene (10 ml), and water (20 ml). The product was extracted with ether-benzene and separated by column chromatography on silica gel.

The products obtained are as follows. 1,3,3-Triphenylallenyl thiocyanate (**2a**): mp 115—116 °C (benzene-hexane); ^{1}H NMR ($CDCl_3$) δ=7.20—7.60 (m, ArH); ^{13}C NMR ($CDCl_3$) δ=98.60 (C-3), 110.06 (SCN), 118.01 (C-1), 126.72, 128.95, 129.13, 131.83, 134.12 (aromatic carbons), and 206.90 (C-2); IR (Nujol) 2150 (m, SCN) and 1920 cm^{-1} (m). Found: C, 80.74; H, 4.65; N, 4.20%. Calcd for $C_{22}H_{15}NS$: C, 81.20; H, 4.65; N, 4.30%. 3,3-Bis(*p*-methylphenyl)-1-phenylallenyl thiocyanate (**2b**): Mp 114—115 °C (benzene-hexane); ^{1}H NMR ($CDCl_3$) δ=2.37 (s, Me) and 7.05—7.63 (m, ArH); IR (Nujol) 2150 (m, SCN) and 1920 cm^{-1} (m). Found: C, 81.40; H, 5.41; N, 3.98%. Calcd for $C_{24}H_{19}NS$: C, 81.55; H, 5.42; N, 3.96%. 1-Butyl-3,3-diphenylallenyl thiocyanate (**2c**): Oil; ^{1}H NMR ($CDCl_3$) δ=0.80—2.73 (m, *n*-Bu) and 7.10—7.70 (m, ArH); IR (neat) 2150 (s, SCN) and 1930 cm^{-1} (m). Found: C, 78.55; H, 6.32; N, 4.62%. Calcd for $C_{20}H_{19}NS$: C, 78.65; H, 6.27; N, 4.59%. 1,3,3-Triphenylallenyl *O*-ethyl dithiocarbonate (**3a**): Oil; ^{1}H NMR ($CDCl_3$) δ=1.12 (t, *J*=7 Hz, Me), 4.47 (q, *J*=7 Hz, CH_2), and 6.75—7.70 (m, ArH); ^{13}C NMR ($CDCl_3$) δ=13.35 ($OCH_2\underline{C}H_3$), 70.12 ($O\underline{C}H_2CH_3$), 102.24 (C-3), 112.95 (C-1), 126.65, 128.06, 128.37, 128.72, 129.01, 129.66, 134.13, 134.77 (aromatic carbons), 211.01, and 211.31 (C-2 and C=S); IR (neat) 1930 (w), 1220, 1100, and 1030 cm^{-1} (S_2CO). 3,3-Bis(*p*-methylphenyl)-1-phenylallenyl *O*-ethyl dithiocarbonate (**3b**): Oil; ^{1}H NMR (CCl_4) δ= 1.12 (t, *J*=7 Hz, Me), 2.31 (s, Me), 4.44 (q, *J*=7 Hz, CH_2), and 6.55—7.62 (m, ArH); IR (neat) 1920 (m), 1230, 1115, and 1040 cm^{-1} (S_2CO). **3a** and **b** were not satisfied with their elemental analyses because of their instability. 3-Amino-1,3,3-triphenylpropyne (**4a**): mp 90—91 °C (EtOH-benzene); ^{1}H NMR ($CDCl_3$) δ=2.25 (s, NH_2) and 7.13—7.78 (m, ArH); ^{13}C NMR ($CDCl_3$) δ=59.06 (C-3), 85.12 (C-2). 95.18 (C-1), 123.24, 126.42, 127.30 128.36, 131.71, and 146.19 (aromatic carbons); IR (Nujol) 3370, 3300 (NH_2), and 2200 cm^{-1} (w, C≡C). Found: C, 88.69; H, 6.22; N, 4.92%. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94%. 3-Amino-3,3-bis(*p*-methylphenyl)-1-phenylpropyne (**4b**): Mp 101—103 °C (EtOH-benzene); ^{1}H NMR (CCl_4) δ=2.18 (s, NH_2), 2.29 (s, Me), and 6.99—7.64 (m, ArH); IR (Nujol) 3300 and 3350 cm^{-1} (NH_2). Found: C, 88.54; H, 6.58; N, 4.65%. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50%.

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