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The Isomerization of Triphenylmethyl Isocyanide: Evidence for a Cationic Chain Mechanism in Polar Solvents**

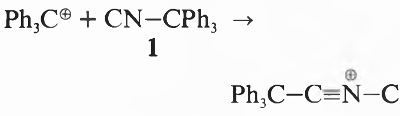
Michael Meier and Christoph Rüchardt*

Abstract: Triphenylmethyl isocyanide (**1**) isomerizes to triphenylmethyl cyanide (**2**) in non-polar solvents at 200–250 °C by a sigmatropic 1,2-rearrangement. To account for the high rate of rearrangement in polar solvents (e.g. acetonitrile) at 60–80 °C, a cationic chain mechanism is proposed in contrast to the ion pair return mechanism discussed in the literature.

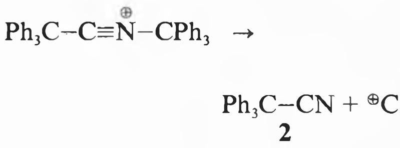
The free enthalpy of activation $\Delta G^{\neq}(250\,°C) = 38 \pm 2$ kcal·mol^{-1} for the isomerization of aliphatic isocyanides to the corresponding cyanides in the gas phase[1] or in non-polar solvents is remarkably independent of structure variation[2,3]. The mechanism involved is a sigmatropic 1,2-migration via a three-membered hypervalent transition state[3,4], which was independently proposed by ab-initio calculations[5]. We found that even the isomerization of triphenylmethyl isocyanide **1** in *n*-hexadecane follows this reactivity pattern (see Table 1).

This is in contrast to the observation, by *Austad* and *Songstad*[6], of a fast isomerization of the isocyanide **1** in acetonitrile at room temperature. We have therefore reinvestigated this reaction in acetonitrile[7] ($E_{T(30)} = 46.0$)[8] as well as in toluene (see Table 1) and in 1,2-dichlorobenzene ($E_{T(30)} = 38.1$)[8]. The yield of triphenylmethyl cyanide **2** was 95–100% in all solvents. **1** isomerized in 1,2-dichlorobenzene at 126.8 °C ($k_1 = 1.61 \cdot 10^{-3}$ s^{-1}) and in dry acetonitrile[7] at 81.5 °C ($k_1 = 2.15 \cdot 10^{-5}$ s^{-1}) with convenient rates, but slower than reported previously[6,7]. The strong influence of the solvent polarity on the rate is clearly evident from the different temperatures at which the isomerization occurs in solvents of varying polarity ($E_{T(30)}$)[8] and from a comparison of the activation parameters in Table 1.

The observation[6] of a positive salt effect by $LiClO_4$ and a strong negative salt effect by tetraphenylarsonium azide, cyanide, iodide or chloride at concentrations as low as 10^{-6}–10^{-5} M in 0.01 M acetonitrile solutions of **1** has led the previous investigators to suggest a complex ion pair return mechanism[6]. A cationic chain mechanism (a) and (b), initiated by acid catalysis[9] or by spontanous ionization of **1**



$$Ph_3C^{\oplus} + \underset{\mathbf{1}}{CN{-}CPh_3} \rightarrow Ph_3C{-}C{\equiv}\overset{\oplus}{N}{-}CPh_3 \qquad \text{(a)}$$



$$Ph_3C{-}C{\equiv}\overset{\oplus}{N}{-}CPh_3 \rightarrow \underset{\mathbf{2}}{Ph_3C{-}CN} + {}^{\oplus}CPh_3 \qquad \text{(b)}$$

which is similar to the Lewis acid catalyzed cyano-transfer reactions mentioned in the recent literature[9], seemed to us to be a more appropriate interpretation. In particular the extremely strong negative salt effect and the complete inhibition of the isomerization at concentrations of 10^{-3} mol/L of the same tetraphenylarsonium salts can be explained in this way. The trapping of minute concentrations of trityl

Table 1. Activation parameters of the isomerization of triphenylmethyl isocyanide **1** in *n*-hexadecane ($c_0 = 0.004$ M) and toluene ($c_0 = 0.05$ M)[a].

solvent	$\Delta G^{\neq}$ (250 °C)	$\Delta H^{\neq} \pm$ SE[b]	$\Delta S^{\neq} \pm$ SE[b]	ΔT[c]	$E_{T(30)}$[8]
	[kcal·mol^{-1}]		[e.u.]	[°C]	
n-hexadecane	38.1	36.5 ± 1.0	−3.1 ± 2.1	193–242	32.3
toluene	36.6	29.1 ± 0.2	−14.2 ± 0.4	164–235	33.8

[a] Rates measured by IR[3]; [b] SE = statistical error; [c] ΔT = temperature range of rate measurements (≥ four kinetic experiments).

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* *Correspondence:* Prof. Dr. C. Rüchardt
Institut für Organische Chemie und Biochemie
Universität Freiburg
Albertstrasse 21, D–7800 Freiburg i. Br.
(Bundesrepublik Deutschland)

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cations, which are required for propagating the chain, by nucleophilic anions suffices to interrupt the reaction.

This proposal is supported by the observation that the rate of isomerization of **1** in toluene increases with increasing concentrations of **1** (see Table 2). At higher concentrations of **1**, the participation of the ionic chain (a)–(b) is favoured because of its higher reaction order. In agreement with this assumption, addition of 7 mole equivalents of the polar solvent ethanol in experiment 3 of Table 2 leads to an almost threefold rate decrease which is probably due to trapping of the chain carrying trityl cations. For an ion pair return mechanism, addition of ethanol should have resulted in an enhanced rate of the disappearance of **1**. By addition of ethanol in higher concentrations the formation of triphenylmethyl cyanide is proportionally suppressed and triphenylmethyl ethyl ether is found as a product instead (see Table 3).

Table 2. Isomerization of **1** in toluene at 198.8 °C.

conc. of **1** [mol/L]	0.053	0.429	0.429[a]
$10^4 k_1$ [s^{-1}]	2.53	33.11	12.99

[a] 6.8 mol equivalent ethanol added.

Table 3. Products of the thermal reaction of **1** in the presence of ethanol.

solvent c_0 (**1**)[a]	c_0 (ethanol)[a]	T[°C] t[h][b]	RCN [%]	ROC_2H_5 [%]
toluene 0.053	0.89	200 10	86.5	12.6
toluene 0.429	2.94	200 2	84.2	7.6
acetonitrile 0.035	0.13	120 4	16.4	85.1

[a] mol/L; [b] reaction time in hours.

In conclusion there are, apparently, three mechanisms available for the isonitrile-nitrile rearrangement to occur in general. Besides the sigmatropic path[1–4] and a free radical chain[10], the ionic chain mechanism is viewed as a new alternative.

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