An Anomaly Resolved: Corrected Structure of the Cycloadducts Accompanying the Spontaneous Copolymerization of Styrene and Vinylidene Cyanide

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Introduction

Over the years, we have studied the spontaneous polymerizations and cycloadditions undergone by electron donor olefins with electron acceptor olefins.[1−4] We have identified the tetramethylene zwitterion-biradical as the key intermediate in both of these reactions (Scheme 1). For pairs of strong electron donor and strong acceptor olefins, the tetramethylene would be zwitterionic in nature and capable of initiating cationic homopolymerization of the donor olefin. With less extreme pairs, the tetramethylene would be biradical in nature, and as such initiate free radical copolymerization of both olefins. This postulate has allowed us to correlate a vast amount of data from the organic and polymer literature.

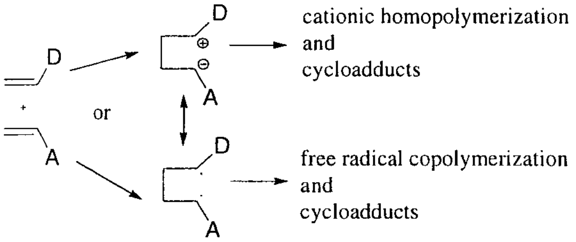
We noted a possible discrepancy in the literature, which is the subject of the present manuscript. Stille and Chung[5] carried out an extensive investigation of the reactions of various electron-rich olefins, such as vinyl ethers, with the very electron-poor vinylidene cyanide. In many cases cyclobutanes or cyclohexanes were obtained along with the homopolymer of the donor olefin. These assigned structures are readily interpretable in terms of a zwitterionic tetramethylene intermediate.

The case of styrene with vinylidene cyanide, however, was different.[6] Here along with alternating 1:1 copolymer, Stille and Chung obtained white crystals. Based on the 60 MHz NMR, they assigned the structure as 1,1,3,3-tetracyano-4-phenylcyclohexane, **1**. This structure would imply a zwitterionic tetramethylene, as shown in Scheme 2, in which case they should have obtained homopolymer of either or both of the participating olefins. A biradical initiating tetramethylene intermediate is implied by the actual formation of alternating 1:1 copolymer. So, here is a real anomaly. In the case of a biradical intermediate, the putative cyclohexane should have structure **2**, based on polar effects in free radical reactions. At first glance the NMR spectra reported by Stille and Chung might be compatible with structure **2** as well. It was the purpose of this investigation to repeat the experiments of Stille and Chung, and to analyze the structure of accompanying cycloadducts by modern NMR and other spectroscopic methods.

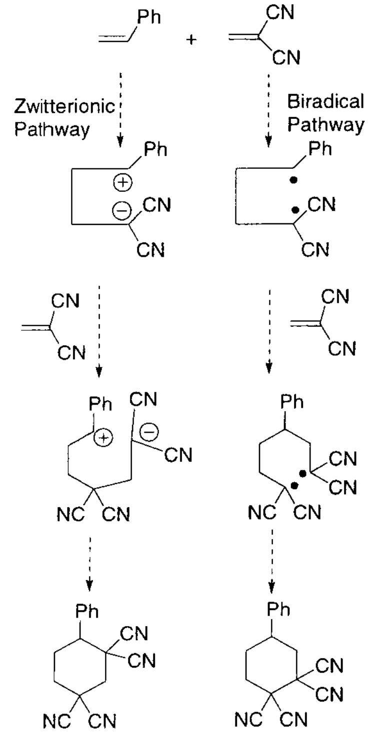
Experimental Section

Instrumentation and Materials. NMR spectra were recorded at ambient temperature on a 600 MHz Varian NMR in $CDCl_3$. IR spectra were obtained on a Nicolet Impact 410 infrared spectrometer. Mass spectrometry low resolution data (EI) were recorded on a HP 5988A GC/MS system and fast atom bombardment (FAB) on a JEOL HX 110A sector instrument.

Scheme 1



Scheme 2



Synthesis of Vinylidene Cyanide and Reaction with Styrene. Diacetylcyanide (1,1-dicyanoethyl acetate, 1.77 g, 12.8 mmol) was slowly distilled under reduced pressure into a pyrolysis column set at 650 °C and packed with quartz chips. The vinylidene cyanide (pyrolysis product) was directly collected into a stirring solution of styrene (1 g, 10 mmol) in toluene (75 mL) containing one drop of methanesulfonic acid or trifluoroacetic acid at −70 °C.[7] Special precautions have to be taken to deal with the extreme instability of vinylidene cyanide: the outlet tube of the pyrolysis column has to be flared at the bottom, and the distance between the hot column and the cold trap has to be minimal. After 2 h, all the diacetylcyanide had distilled, and the reaction mixture containing vinylidene cyanide and styrene in toluene was removed from the assembly and sealed under nitrogen. The reaction mixture at −70 °C was connected to vacuum and degassed. The vacuum was then disconnected; the flask was removed from the acetone bath and stirred for 3 days at room temperature. The mixture was filtered, and the solid polymer isolated. The solid polymeric residue (300 mg) was analyzed by ^{13}C NMR.

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Table 1. HMBC and HSQC Correlations for Isomer 3

carbon	proton two-bond coupling	proton three-bond coupling	proton one-bond coupling
C-1 (35.4)	H-2, H-2′	H-8, H-3, H-3′	quaternary
C-2 (29.7)	H-3, H-3′	H-4	H-2 (2.69) H-2′ (2.90)
C-3 (22.1)	H-2, H-2′, H-4		H-3 (2.38) H-3′ (2.38)
C-4 (42.3)	H-3, H-3′	H-2, H-2′, H-12	H-4 (3.69)
C-5 (131.3)		H-4, H-7	H-5 (7.79)
C-6 (131.3)		H-8	H-6 (7.62)
C-7 (130.8)		H-5	H-7 (7.62)
C-8 (130.1)		H-6	H-8 (7.84)
C-9 (129.0)		H-2′, H-4, H-7	quaternary
C-10 (132.9)	H-4	H-3, H-3′, H-6, H-8	quaternary
C-11 (37.0)	H-4, H-12	H-3, H-3′	quaternary
C-12 (23.30)		H-4	H-12 (1.96)
C-13 (117.3)		H-4, H-12	CN
C-14 (116.5)		H-4, H-12	CN
C-15 (116.6)		H-2, H-2′	CN
C-16 (116.6)		H-2, H-2′	CN

[a] Solvent CD$_3$CN with TMS as internal standard. Values in parentheses = δ values in ppm.

Table 2. HMBC and HSQC Correlations for Isomer 4

carbon	proton two-bond coupling	proton three-bond coupling	HSQC one-bond coupling
C-1 (35.8)		H-8	quaternary
C-2 (29.70)	H-3′		H-2 (2.62) H-2′ (2.62)
C-3 (22.4)			H-3 (2.03) H-3′ (2.22)
C-4 (34.2)	H-3′, H-11		H-4 (3.23)
C-5 (130.9)		H-7	H-5 (7.42)
C-6 (131.3)		H-8	H-6 (7.52)
C-7 (129.1)		H-5	H-7 (7.46)
C-8 (129.1)		H-6	H-8 (7.72)
C-9 (127.7)		H-5	quaternary
C-10 (132.8)		H-8	quaternary
C-11 (36.0)		H-3′	H-11 (2.31) H-11′ (2.50)
C-12 (21.5)			H-12 (4.24)
C-13 (114.0)	H-12	H-11, H-11′	CN
C-14 (114.0)	H-12	H-11, H-11′	CN
C-15 (116.7)		H-2	CN
C-16 (116.7)		H-2	CN

[a] Solvent CD$_3$CN with TMS as internal standard. Values in parentheses = δ values in ppm.

Alternating copolymer of styrene and vinylidene cyanide: IR, 2246, 3430 cm^{-1}; ^{13}C NMR in DMSO-d_6, 138.5, 138.3, 129, 115.14, 113.9, 113.5, 108.5, 43.3, 42.8, 40.5, 34.4, 34.0, and 33.2 ppm.

The filtrate was washed with 5% aqueous sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed under reduced pressure to give an oily mixture. Purification by column chromatography using silica gel and 60:40 ethyl acetate: hexanes as eluent gave 14 mg of a mixture of two cycloadducts.

MS data for both isomers: *m/e* 261 ($M + 1$), 293 ($-$HCN), 154 [base peak, $-$HCN $-$ CH$_2$=C(CN)$_2$]. NMR data: 1,1-dicyano-4-(1′,1′-dicyanoethyl)-1*H*,2*H*,3*H*,4*H*-tetralin (isomer **3**), ^{1}H NMR (600 MHZ, CD$_3$CN), δ 1.96 (12-H, s), 2.38 (3-H, 3′-H, m), 2.69 (2-H, m), 2.90 (2-H, ddd, $J = 4, 10, 14$ Hz), 3.69 (4-H, t, $J = 5.5$.Hz), 7.79 (5-H, m), 7.62 (6-H, 7-H, m), 7.84 (8-H, m) ppm; 1,1-dicyano-4-(2′,2′-dicyanoethyl)-1*H*,2*H*,3*H*,4*H*-tetralin (isomer **4**), ^{1}H NMR (600 MHZ, CD$_3$CN), δ 2.03 (H-3, m), 2.22 (H-3′, m), 2.31 (H-11, ddd, $J = 6, 10,14$ Hz), 2.50 (H-11′, ddd, $J = 4, 9, 14$), 2.62 (2-H, 2′-H, m), 3.23 (4-H, m), 4.24 (H-12, dd, $J = 5, 6, 9$), 7.42 (H-5, m), 7.46 (H-7, m), 7.52 (H-7, m), 7.72 (H-8, m) ppm. The ^{13}C, ^{1}H correlations (HMBC and HSQC) for the cycloadducts are summarized in Tables 1 and 2.

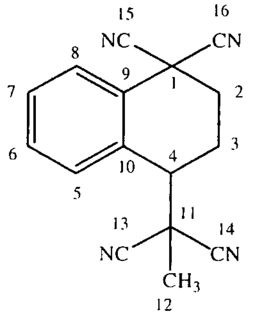
Results and Discussion

Stille and Chung[5,6] prepared vinylidene cyanide from 1,1,3,3-tetracyanopropane, which in turn came from malononitrile and formaldehyde. Its thermolysis gives a mixture of vinylidene cyanide and malononitrile, which is difficult to separate. Previously Gilbert et al. had successfully used 1,1-dicyanoethyl acetate (diacetyl cyanide) to prepare vinylidene cyanide.[8] 1,1-Dicyanoethyl acetate is now commercially available and its pyrolysis yields a readily separable mixture of vinylidene cyanide and acetic acid. The latter is beneficial in stabilizing against adventitious anionic homopolymerization and can be left in place for free radical copolymerizations. The presence of acid allows for accurate observation of the free radical behavior of labile monomers, a method pioneered by Otsu.[9] By using the setup described in the Experimental Section, vinylidene cyanide could be rather easily synthesized in the lab, and the unstable monomer was mixed with styrene in a toluene solution as soon as it was formed.

Following Stille and Chung, the spontaneous reaction was allowed to proceed at room temperature for 3 days, at which point the products were separated. A large amount of polymer was isolated, which was confirmed to be the alternating copolymer by ^{13}C NMR. Two cycloadducts were then purified using column chromatography.

Spectroscopic analysis led to the conclusion that these cycloadducts were not the proposed 2:1 cyclohexanes **1** or **2**. Mass spectroscopic analysis indicated that both cycloadducts had an $M + 1$ peak at 261, which did indeed correspond to an adduct composed of one styrene and two vinylidene cyanide moieties. Analysis by NMR using HMBC and HSQC of the mixture of the two cycloadducts identified them as being structures **3** and **4**, namely 1,1-dicyano-4-(1′,1′-dicyanoethyl)-1*H*,2*H*,3*H*,4*H*-tetralin and 1,1-dicyano-4-(2′,2′-dicyanoethyl)-1*H*,2*H*,3*H*,4*H*-tetralin. The detailed data of these NMR analyses are summarized in Tables 1 and 2.

The occurrence of adducts similar to **3** and **4** is not unusual in these donor/acceptor olefin systems. We isolated similar adducts in the reactions of styrene and acrylonitrile in the presence of zinc chloride.[10] As a matter of fact, Gilbert et al. proposed structure **4** in their 1956 publication based on elemental analysis and the fact that alkaline potassium permanganate oxidation led to phthalic acid.[8] Many other cases can be cited, such as the reaction of styrene with maleic anhydride or *N*-phenyltriazolinedione.[11] Interestingly, these [4 + 2]-ene reactions are usually accompanied by double



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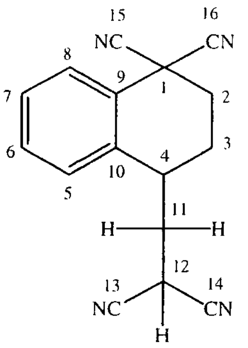

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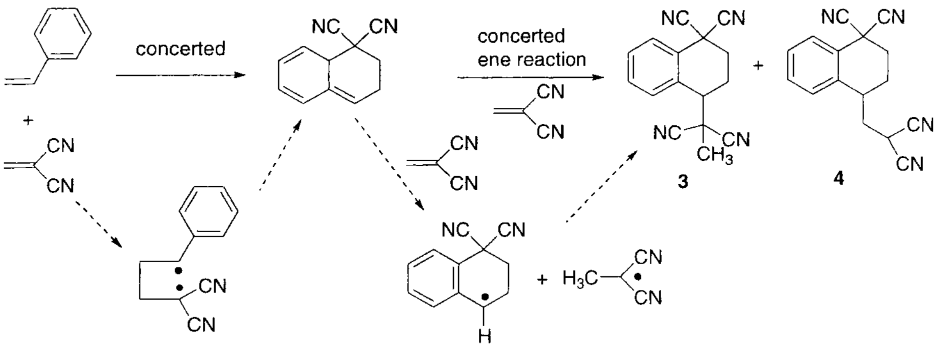
Scheme 3



Diels–Alder reactions, but in the present case the latter products were not detected. These reactions have been reviewed two decades ago by Wagner-Jauregg[12] and are fairly common.

How do these adducts form? The proposed mechanisms are shown in Scheme 3. The first reaction involves a Diels–Alder reaction of styrene with vinylidene cyanide, leading to a tetralin derivative, 1,1-dicyano-1*H*,2*H*,3*H*,9*H*-tetralin. This reaction is generally concerted, but a minor contribution from a biradical intermediate is a possibility in view of the accompanying free radical copolymerization. The second reaction is an ene reaction with a second molecule of vinylidene cyanide. This reaction again could proceed via a concerted mechanism, or via two free radicals in a molecular assisted homolysis (MAH), as first proposed by Mayo in the spontaneous homopolymerization of styrene.[13] The MAH mechanism would preferentially lead to isomer **3**, while the regiochemistry of the concerted reaction would be difficult to predict.

The reaction of vinylidene cyanide with styrene in this study was conducted in the presence of acid to stabilize the monomer and inhibit anionic homopolymerization. No products resulting from reaction of the putative zwitterion with the acid were isolated.

Conclusions. The original purpose of this study was to investigate the structure of the cycloadduct accompanying the spontaneous copolymerization of styrene and vinylidene cyanide. A mixture of two isomers of a 2:1 cycloadduct was isolated. A detailed NMR analysis showed that these adducts were formed by consecutive Diels–Alder/ene reactions. These reactions proceed via a concerted mechanism. A diradical tetramethylene initiates the free radical copolymerization of the two monomers, and no zwitterionic intermediate has to be postulated.

These results remove a literature anomaly inconsistent with our tetramethylene hypothesis. This is the third time we have detected literature errors by following our tetramethylene theory. The correct course of the reaction of vinyl ethers with nitroethylene[13] and of styrenes with electrophilic olefins[15] was arrived at using this hypothesis. At present we are unaware of other literature data inconsistent with our concept.

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(7) Comment: Not all vinylidene cyanide was trapped in the cold toluene solution, and some was found in the subsequent traps. This explains the rather low total yield.

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