

at 30° for 3 days. The ether layer was decanted off from a dark colored sludge which was washed with ether and water and then triturated with alcohol to give a solid. The ether decantate was washed successively with 2 *N* HCl, water, aqueous NaHCO<sub>3</sub> and water, and dried and evaporated. The residue became crystalline with alcohol. The combined solids (1.5 g) were shaken with cold chloroform to give an insoluble part, which was crystallized from hot chloroform to give the disulfone **7** (0.5 g), mp 215° dec (lit.<sup>13</sup> mp 212°) (*Anal.* Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: C, 54.19; H, 4.55. Found: C, 54.43; H, 4.55; N, 0). The chloroform soluble fraction was concentrated and an intermediate fraction separated. The mother liquor was evaporated and the residue crystallized from acetone to give **8** (0.6 g), mp 187–188° (*Anal.* Calcd for C<sub>26</sub>H<sub>27</sub>NS<sub>2</sub>: C, 74.80; H, 6.52; N, 3.36; S, 15.33. Found: C, 75.09; H, 6.73; N, 3.37; S, 14.67).

**Reaction of Fischer's Base with *p*-Toluenesulfonyl Chloride.**—A solution of **1** (3.4 g) and triethylamine (4.5 g) in 50 ml of dry ether was mixed at 0° with a solution of *p*-toluenesulfonyl chloride in carbon tetrachloride (prepared from 5 g of *p*-toluenethiol and chlorine in nitrogen atmosphere). After being left overnight, the mixture was filtered and washed with ether and water. The crystalline precipitate was recrystallized from acetone to give **8** (2.8 g): mp 185–186° identical with the previous preparation (*Anal.* Calcd for C<sub>26</sub>H<sub>27</sub>NS<sub>2</sub>: C, 74.80; H, 6.52; N, 3.36. Found: C, 75.08; H, 6.62; N, 3.57).

**Registry No.**—**1**, 118-12-7; **2**, 26212-68-0; **3**, 26212-69-1; **3** picrate, 26212-70-4; **6**, 26212-71-5; **6** hydrochloride, 26212-55-5; **8**, 26212-56-6.

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## Synthesis and Properties of *N*-Ethyneylcarbazole and Poly-*N*-ethyneylcarbazole<sup>1</sup>

YOSHIYUKI OKAMOTO\* AND SAMAR K. KUNDU

Research Division, Department of Chemical Engineering,  
School of Engineering and Science, New York University,  
University Heights, New York, New York 10453

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Recently much attention has been focused on the electronic properties of organic solids and in particular on those exhibiting photoconductive behavior.<sup>2–4</sup> Although numerous organic compounds have been shown to have photoconductive properties, one of the most significant is poly-*N*-vinylcarbazole.<sup>5</sup> In this polymer, carbazole moieties are pendant to a polymer chain containing carbon-carbon single bonds. No conjugation exists in this main chain.

Currently available experimental data show that, in conjugated chain structures, large numbers of electrons cause a decrease of the excitation energy of the  $\pi$  electrons resulting in a compound that shows electrical

conductive properties. It was therefore thought that the conjugate form ( $\text{R} > \text{C} = \text{C} < \text{H}$ )<sub>*n*</sub>, where R is carbazole, might possess enhanced electrical conduction. Thus, a study of the polymer might shed additional light on the relationship between chemical structure and electronic properties. Such conjugated polymers appeared to be most easily prepared by polymerization of acetylenic compounds.<sup>6,7</sup> Therefore, we wish to report the preparation and properties of *N*-ethyneylcarbazole<sup>8</sup> and its polymers.

The most attractive method for the synthesis of **3** appeared to be by conversion of the commercially available *N*-vinylcarbazole to the  $\alpha,\beta$ -dihalo derivative followed by dehydrohalogenation. Although the preparation of *N*-( $\alpha,\beta$ -dibromoethyl)carbazole was reported,<sup>9</sup> we were unable to repeat the synthesis even at low temperature and under basic conditions, *e.g.*, by pyridinium hydrobromide perbromide.<sup>10</sup>

An alternate route for the preparation of **3** is from *N*-acetylcarbazole by successive treatment with phosphorus pentachloride and then with potassium hydroxide or sodium amide in liquid ammonia.<sup>7</sup> Accordingly, when *N*-acetylcarbazole (**1**) was reacted with phosphorus pentachloride in refluxing benzene or toluene, *N*-( $\alpha,\beta$ -dichloroethyl)carbazole (**2**) was obtained. Dechlorination of **2** with zinc dust,<sup>11</sup> *e.g.*, moist zinc dust in tetrahydrofuran or isopropyl ether, failed. In each case, starting material was recovered. When **2** was refluxed with moist zinc dust in *n*-butyl ether, *N*-( $\beta$ -chloroethyl)carbazole was obtained. If **2** was treated with ethanolic potassium hydroxide, nucleophilic substitution by ethoxide occurred instead of dehydrochlorination.

The synthesis of **3** was finally achieved by treatment of **2** with sodium amide in liquid ammonia and then decomposition with ammonium chloride. The structure of **3** was established by elemental analysis and ir, pmr, and mass spectra. The ir spectrum of **3** showed a typical triple bond absorption at 2145 cm<sup>-1</sup> and acetylenic hydrogen absorption at 3330 cm<sup>-1</sup>. Its pmr spectrum showed the characteristic singlet due to acetylenic proton at  $\tau$  6.82.<sup>12</sup> The presence of a terminal acetylenic group was also confirmed by the formation of silver, copper, and mercury acetylides.<sup>13</sup>

When **3** was allowed to stand at room temperature, it became dark. It was thermally polymerized in toluene, cyclohexane, or without solvent at 100–120° in the absence of a catalyst in sealed tubes under vacuum. These polymers (**4**) were dark brown, soluble in solvents such as benzene, chloroform, and tetrahydrofuran, and insoluble in methanol and ethanol. The ir spectra showed the absence of acetylenic absorption and the presence of intense carbon-carbon double bond absorp-

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\* To whom correspondence should be addressed.

(1) This work was supported in part by the Air Force Cambridge Research Laboratory, Contract F 19-(628)-69-C-0154.

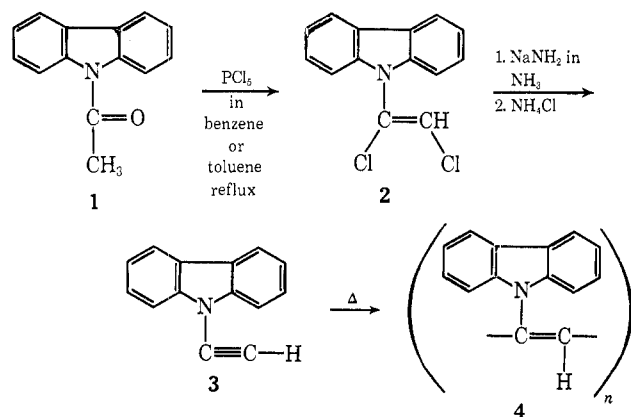
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tions at 1621 and 1614  $\text{cm}^{-1}$ . The molecular weight of the polymer obtained from toluene is 1530 ( $n = \sim 8$ ) and those from cyclohexane or without solvent are 1960 ( $n = \sim 10$ ). For comparison purpose, poly-*N*-vinylcarbazole was also synthesized *via* the polymerization of purified *N*-vinylcarbazole.



Electrical measurements were performed in a sandwich type cell. The cell consisted of 0.02–0.03 cm thick compressed pellets on two transparent quartz plates (20  $\times$  25 mm) coated with tin oxide. Dc voltage (200 V) from a Keithley high voltage supply (Model 241) was applied to the sample and the dark and photocurrents were measured by a Keithley electrometer (Model 610 B). The results are summarized in Table I.

TABLE I  
ELECTRONICAL PROPERTIES OF POLY-*N*-VINYL- AND  
POLY-*N*-ETHYNYLCARBAZOLE<sup>a</sup>

	Dark current ( $I_d$ )	Photocurrent ( $I_p$ ) <sup>b</sup>	$I_p/I_d$	Dark resistivity, ohm cm
Poly- <i>N</i> -vinyl- carbazole <sup>c</sup>	$6.3 \times 10^{-13}$	$6.5 \times 10^{-12}$	10	$1.0 \times 10^{18}$
Poly- <i>N</i> - ethynyl- carbazole <sup>d</sup>	$1.1 \times 10^{-9}$	$1.1 \times 10^{-9}$	1	$9.6 \times 10^{12}$

<sup>a</sup> These data were obtained at ambient temperature. <sup>b</sup> 100-W tungsten light. <sup>c</sup> The resistivity of poly-*N*-vinylcarbazole has been reported as  $1.9 \times 10^{16}$   $\Omega$  cm at room temperature. This measurement was made on film containing a vapor-deposited aluminium electrode; cf. Y. Hayashi, M. Kuroda, T. Imura, and A. Inami, *Polym. Chem. Jap.*, **21**, 577 (1964). <sup>d</sup> All the poly-*N*-ethynylcarbazoles prepared showed almost identical conductivities.

Although the molecular weights of the various poly-*N*-ethynylcarbazole obtained are relatively low, the conductivity of the polymer was found to be  $10^3$  times larger than that of poly-*N*-vinylcarbazole. However, photoconductivity could not be detected for the poly-*N*-ethynylcarbazole.

#### Experimental Section

**Reaction of *N*-Acetylcarbazole with Phosphorus Pentachloride.**—A mixture of 209 g (1 mol) of **1** and 436.8 g (2.1 mol) of phosphorus pentachloride in 1500 ml of dried toluene or benzene was heated until the evolution of hydrochloric acid gas ceased ( $\sim 24$  hr). The reaction mixture was cooled in an ice bath and then poured slowly over crushed ice. The organic layer was separated and washed twice with cold water. The organic solution was dried over anhydrous magnesium sulfate and then concentrated under reduced pressure to yield a red viscous residue. This was dissolved in 2 l. of hot methanol and heated with active charcoal.

It was then kept in an ice box overnight to give 130 g (49.6%) of **2**: mp 55°; ir ( $\text{CCl}_4$ ) 3062, 1615, 878, 800  $\text{cm}^{-1}$ ; pmr ( $\text{CDCl}_3$ )  $\tau$  2.12–2.47 (m, 2 H), 2.60–3.15 (m, 6 H), 3.67 ppm (s, 1 H,  $=\text{CH}$ ); mass spectrum  $m/e$  261 ( $\text{M}^+$ ) 226, 191. *Anal.* Calcd for  $\text{C}_{14}\text{H}_9\text{NCl}_2$ : C, 64.12; H, 3.43; N, 5.34; Cl, 27.10. Found: C, 64.33; H, 3.46; N, 5.45; Cl, 27.33. From the mother liquor after separation of **2**, carbazole (30%) was isolated.

**Reaction of *N*-( $\alpha,\beta$ -Dichloroethenyl)carbazole (**2**) with Zinc.**—A solution of 2.62 g (0.01 mol) of **2** in 150 ml of *n*-butyl ether containing a few drops of water was heated with 6.53 g (0.1 mol) of zinc dust for 70 hr. The reaction mixture was cooled and zinc dust was filtered off, and the filtrate was evaporated under vacuum after drying over anhydrous magnesium sulfate. The residue was recrystallized from methanol to afford 1.30 g (57%) of  $\beta$ -chloro-*N*-ethenylcarbazole: mp 102°; ir ( $\text{CCl}_4$ ) 1630, 1615  $\text{cm}^{-1}$ ; pmr ( $\text{CDCl}_3$ )  $\tau$  2.08–2.35 (m, 2 H), 2.68–3.05 (m, 6 H), 2.90 (d, 1 H,  $J = 12.5$  Hz), 3.70 ppm (d, 1 H,  $J = 12.5$  Hz); mass spectrum  $m/e$  227 ( $\text{M}^+$ ) 191, 165, 140. *Anal.* Calcd for  $\text{C}_{14}\text{H}_{10}\text{NCl}$ : C, 73.84; H, 4.39; N, 6.16; Cl, 15.60; mol wt, 227.5. Found: C, 73.74; H, 4.29; N, 6.06; Cl, 15.55; mol wt, 227 (in  $\text{CCl}_4$ ).

**Reaction of *N*-( $\alpha,\beta$ -Dichloroethenyl)carbazole (**2**) with Ethanolic Potassium Hydroxide.**—A solution of 2.62 g (0.01 mol) of **2** in 100 ml of 30% ethanolic potassium hydroxide was refluxed under nitrogen atmosphere for 72 hr. The reaction mixture was then cooled and poured over crushed ice. The white solid that separated was filtered, washed with water, and recrystallized from aqueous ethanol to give 2.0 g of the ethoxy substituted compound: mp 102°; ir ( $\text{CHCl}_3$ ) 1662, 1640, 1620 ( $\text{C}=\text{C}$ ), 1280, 1048  $\text{cm}^{-1}$  ( $-\text{OC}_2\text{H}_5$ ); pmr ( $\text{CDCl}_3$ )  $\tau$  1.92–2.20 (m, 2 H), 2.30–2.95 (m, 6 H), 4.34 (s, 1 H  $=\text{CH}$ ), 6.50 (q, 2 H,  $-\text{CH}_2\text{CH}_3$ ), 8.85 ppm (t, 3 H,  $-\text{CH}_2\text{CH}_3$ ); mass spectrum  $m/e$  271 ( $\text{M}^+$ ) 256, 243, 214, 192, 167, 140. *Anal.* Calcd for  $\text{C}_{16}\text{H}_{14}\text{NOCl}$ : C, 70.72; H, 5.15; N, 5.15; Cl, 13.08. Found: C, 70.62; H, 5.41; N, 5.11; Cl, 12.88.

**Preparation of *N*-Ethynylcarbazole (**3**).**—A solution of 89 g (0.34 mol) of **2** in 400 ml of dry ether was added dropwise during a period of 1 hr with vigorous stirring to a liquid ammonia solution of sodium amide, prepared from 40 g of sodium. The reaction mixture was left overnight to evaporate the ammonia. The dark colored residue was diluted with 500 ml of ether and treated with excess solid ammonium chloride. It was then poured in 500 ml of cold water and extracted with ether. The ether layer was washed with water and then dried over anhydrous magnesium sulfate. After the ether was evaporated, the viscous residue was treated with 200 ml of petroleum ether. Evaporation of the petroleum ether extract afforded 20 g (30.7%) of crude **3**. Purification was further achieved by repetition of the above procedure and then recrystallized from aqueous methanol, after treatment with activated charcoal, as shining white crystals: mp 58°; ir ( $\text{CCl}_4$ ) 3300 ( $\text{C}\equiv\text{C}-\text{H}$ ), 2145  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ ); pmr ( $\text{CDCl}_3$ )  $\tau$  2.10–3.10 (m, 8 H), 6.82 ppm (s, 1 H,  $\text{C}\equiv\text{C}-\text{H}$ ); mass spectrum  $m/e$  191 ( $\text{M}^+$ ) 163. *Anal.* Calcd for  $\text{C}_{14}\text{H}_9\text{N}$ : C, 88.00; H, 4.71; N, 7.33. Found: C, 87.92; H, 4.72; N, 7.47.

**Polymerization of *N*-Ethynylcarbazole.**—One gram of **3** dissolved in 10 ml of toluene, cyclohexane, or without solvent was heated at 100–120° in an oil bath in a sealed tube under vacuum. The reaction time varied from 25 to 35 hr. The solid produced was dissolved in excess toluene and then petroleum ether was added to precipitate the polymer. Purification of the polymer was achieved by repeating the above procedure. In the ir spectrum ( $\text{CCl}_4$ ), these polymers showed the absence of bands at 3300 ( $\text{C}\equiv\text{C}-\text{H}$ ) and 2145  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ ), but intense bands at 1621 and 1614  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ) appeared. The polymers were soluble in benzene, toluene, carbon tetrachloride, chloroform, tetrahydrofuran, and dioxane, but insoluble in acetonitrile, acetone, ethanol, and petroleum ether, mp 220–250°.<sup>14</sup>

**Polymerization of *N*-Vinylcarbazole.**<sup>14</sup>—*N*-vinylcarbazole obtained from the Borden Chemical Co. was purified by recrystallization from methanol and was then polymerized by heating at 100–110° for 20–25 hr in a sealed tube under vacuum. The polymer was purified by the reprecipitation from methylene chloride solution by adding methanol, mp 60–70°.

**Registry No.**—**2**, 26210-95-7; **2** (O-Et substituted product), 26157-61-9; **3**, 26157-62-0; **3** (polymer),

(14) The molecular weights of polymers were determined using Micro-lab osmometer by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

26142-41-6;  $\beta$ -chloro-*N*-ethenylcarbazole, 23787-95-3; 4 (polymer), 25067-59-8.

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### Chloromethyltriethylammonium Chloride. A Serendipitous Preparation

DAVID A. WRIGHT AND CLAUS A. WULFF\*

Department of Chemistry, The University of Vermont,  
Burlington, Vermont 05401

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In a cryogenic study of the thermodynamics of hydrogen bond formation in the previously described adduct<sup>1</sup> of triethylamine (TEA) and methylene chloride (MC), we encountered an unexpected reaction at room temperature that yielded chloromethyltriethylammonium chloride (1). This salt crystallized in analytically pure form from a solution of the components containing excess amine. The nmr spectrum [ $\delta$  (CDCl<sub>3</sub>) 1.50 (t, 9,  $J$  = 8 Hz), 3.72 (q, 6,  $J$  = 8 Hz), and 5.68 ppm (s, 2)] was consistent for structure 1.

The analogous reaction of triethylphosphine and MC was described over 100 years ago.<sup>2</sup> An alkylation product from MC and a tertiary amine has apparently not been isolated, although formation of polymers from diamines and methylene chloride at 40° has been observed.<sup>3</sup>

#### Experimental Section

**Materials.**—The Eastman TEA was distilled three times from a slurry with KOH and the Baker MC was triply distilled from CaCl<sub>2</sub> in a dry N<sub>2</sub> atmosphere. The minimal purities of these reagents, as determined by subsequent fractional fusion, were: TEA, 99.9%; MC, 99.8%.

**Product.**—Compound 1 was formed in ca. 1% yield by allowing a TEA-rich mixture of the two reagents to stand undisturbed, at room temperature, for three days. It was noted that product formation was inhibited at lower temperatures, and we were unable to prepare it at -80°. The compound crystallized in fine white needles. X-ray powder photographs indicated a noncubic structure. The  $d$  spacings corresponding to the three most prominent lines were 3.62 Å, 3.33 Å, and 5.47 Å. The compound melted at 186°.

**Anal.** Calcd for [C<sub>7</sub>H<sub>17</sub>NCl]<sup>+</sup>Cl<sup>-</sup>: C, 45.1; H, 9.12; N, 7.5; replaceable Cl, 19.0. Found: C, 44.8; H, 9.5; N, 7.2; replaceable Cl, 18.7.

**Registry No.**—1, 26157-53-9.

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\* To whom correspondence should be addressed.

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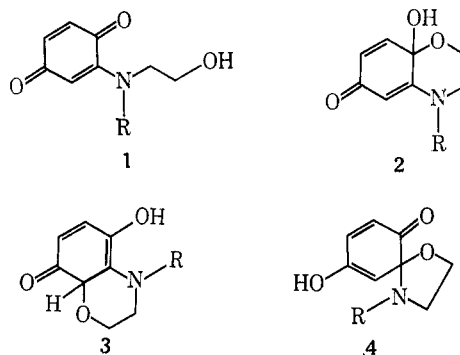
### König's Adducts of *N*-Alkyl(aryl)aminoethanols and Quinones. 3,4-Dihydro-4-alkyl(aryl)-8a-hydroxy-2*H*-1,4-benzoxazin-6(8*aH*)-ones

KENNETH D. McMURTREY AND G. DOYLE DAVES, JR.\*

Oregon Graduate Center, Portland, Oregon 97225

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König<sup>1-3</sup> discovered that adducts of *p*-benzoquinones and 2-alkyl(aryl)aminoethanols (1) are in equilibrium with a second, usually predominant species which (a) is nearly colorless in crystalline form and in nonpolar solvents, (b) is soluble in base, and (c) exhibits a double polarographic reduction curve<sup>3-6</sup> very different from those exhibited by quinones.<sup>7</sup> Three structures (2-4) can be considered for the bicyclic form of the adduct. We have studied some aspects of the chemistry of these interesting compounds and have established that the correct structure is 3,4-dihydro-4-alkyl(aryl)-8a-hydroxy-2*H*-1,4-benzoxazin-6(8*aH*)-one (2).



Previous workers<sup>1-6,8,9</sup> have focused on the thermochromic, solvatochromic, and unusual electrochemical properties of the quinone-aminoethanol adducts. Surprisingly, no detailed study of the structure of the adducts has been reported. Structure 3 has been considered and discarded<sup>9</sup> since the adducts, formed under equilibrating conditions, exhibit properties (*e.g.*, ABX systems in the aromatic/olefinic region of the nmr spectra) inconsistent with their formulation as the thermodynamically more stable hydroquinone tautomer of 3.<sup>10</sup> Berg and coworkers<sup>8</sup> suggested the correct structure (2) for the adducts; however, they appear not to have con-

\* To whom correspondence should be addressed.

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