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Vinylogous Nucleophilic Substitution: A Route to New Polymers

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ABSTRACT

The basic chemistry underlying the successful synthesis of poly-(enaminoesters) by vinylogous nucleophilic substitution is examined. It is concluded that a new mechanism must be operative. A Michael addition followed by elimination of a volatile fragment is proposed.

In preliminary work [1-3] it has been demonstrated that the reaction of bis-β-ketoesters with aromatic diamines can lead to novel polymer structures, poly(enaminoesters), which can be thermally cyclized to very thermally stable poly(quinolone) structures (Fig. 1). As the flexibility of the backbone increases, the solubility of the forming polymer is enhanced, and the attainable molecular weight increases. Using a flexible diamino siloxane, 1,3-bis-(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, a poly(enaminoester) of weight-average molecular weight of approximately 800,000 was obtained (Fig. 2) [3].

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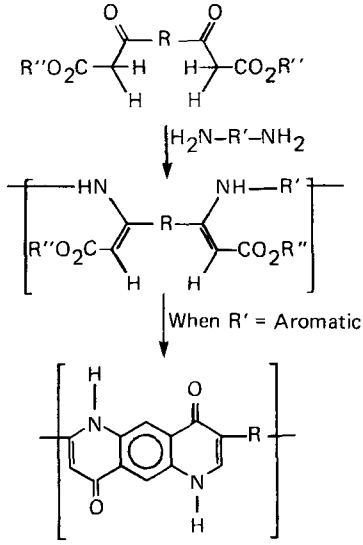

FIGURE 1.

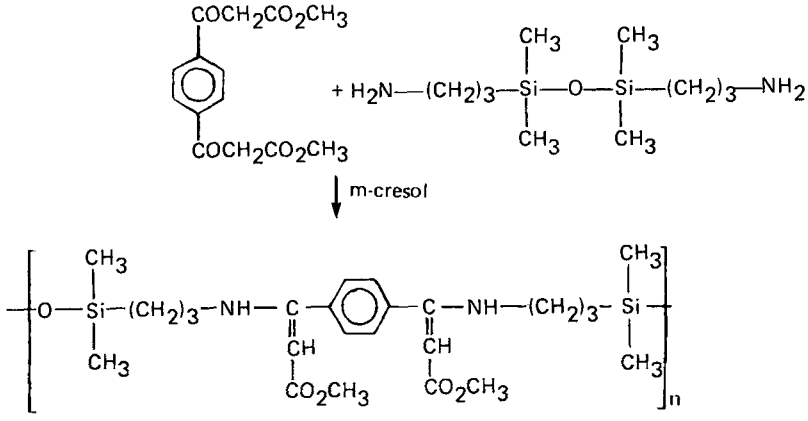

FIGURE 2.

Higashi, Tai, and Adachi [4] have developed a mechanistic scheme for the reaction of diethyl cyclohexa-1,4-diene-2,5-dicarboxylate with amines. They proposed a reaction pathway involving an intermediate salt composed of the amine and the completely enolized β-ketoesters (Fig. 3).

To test the requirement that β-ketoesters and amines react through

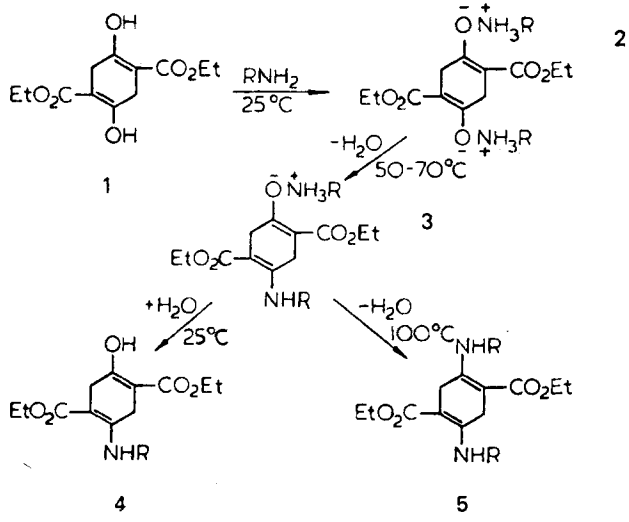

FIGURE 3.

the formation of salts, we treated diketodiester 1 with trimethylchlorosilane/triethylamine in toluene [5]. The silylated product, 1,4-bis-(trimethylsiloxy) cyclohexa-1,4-diene-2,5-dicarboxylate, was found to undergo polymerization with diamines (albeit to lower molecular weight than unsilylated material) despite the fact that salt formation of the type indicated in Fig. 3 cannot occur.

The possibility that transilylation reactions might complicate the interpretation of our results prompted us to investigate a different model system. If ethyl benzoylacetate is reacted with diazomethane, a mixture of Z and E enol ethers is formed (Fig. 4). If the mixture is treated with hexylamine at 25°C without added catalyst, only the Z-isomer reacts to form exclusively Z product. The progress of the reaction was followed by gas chromatography (Figs. 5-7).

Figure 5 shows a plot of concentration of reactants and product versus time over 48 h. This experiment dramatically illustrates that the E-isomer is not consumed under the reaction conditions. The Z-isomer follows second-order kinetics, as is shown in Fig. 6, with a rate constant of 1.37×10^{-6} $M^{-1}s^{-1}$. Figure 7 demonstrates that the E-isomer is essentially unreactive in the system.

CONCLUSION

It is apparent that salt formation is, under the conditions so far examined, a pathway competing with that which leads to polymer formation. It is more likely that the reaction to form poly(enaminoester)

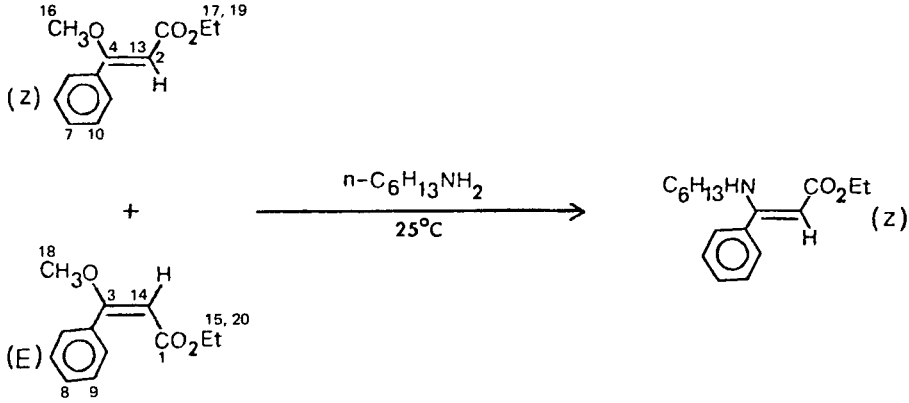

FIGURE 4.

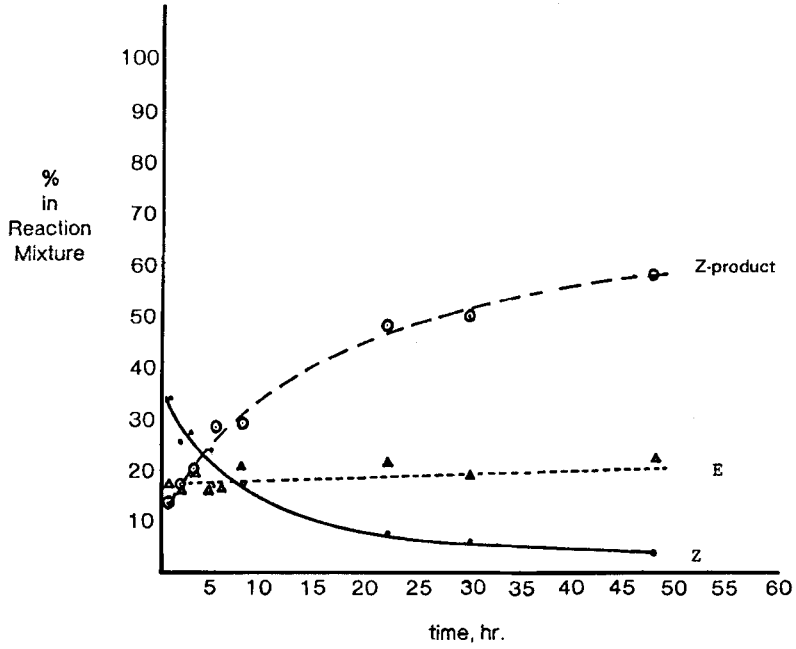

FIG. 5. Plot of concentration vs time for the reaction of ethyl β-methoxycinnamate with n-hexylamine at 25°C.

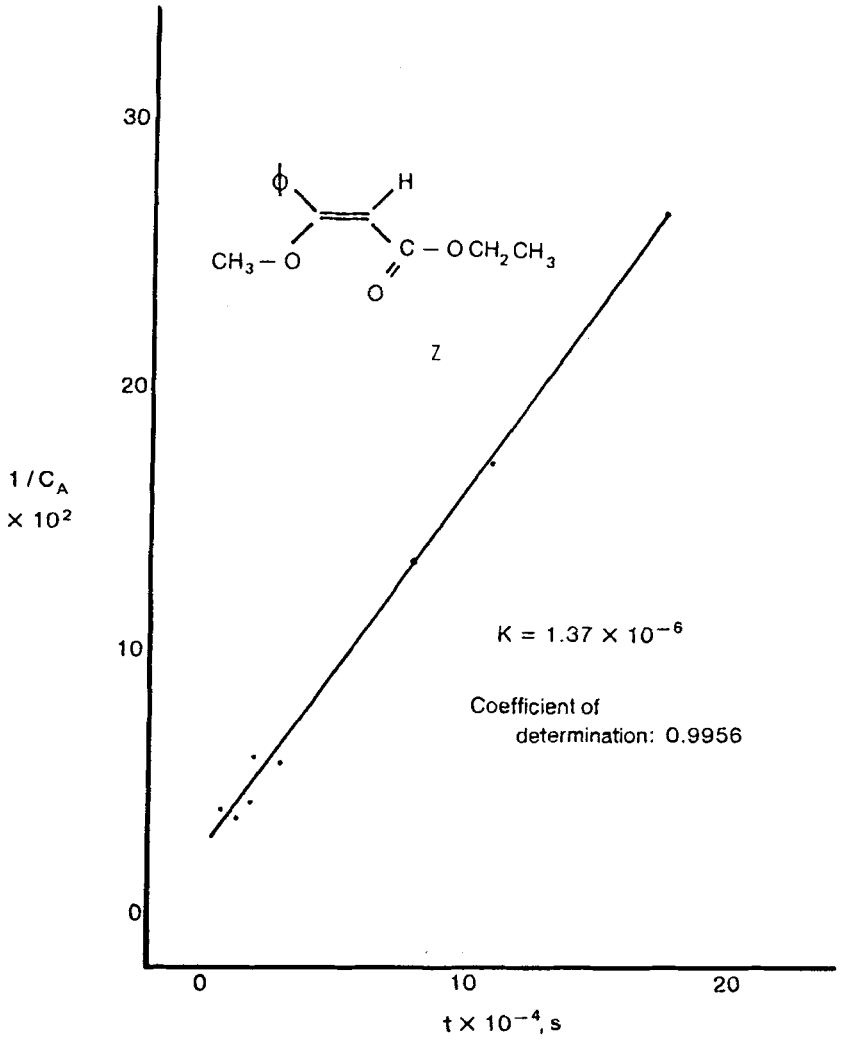

FIG. 6. Second-order kinetic plot of the reaction of Z-ethyl β-methoxycinnamate with n-hexylamine at room temperature (25°C).

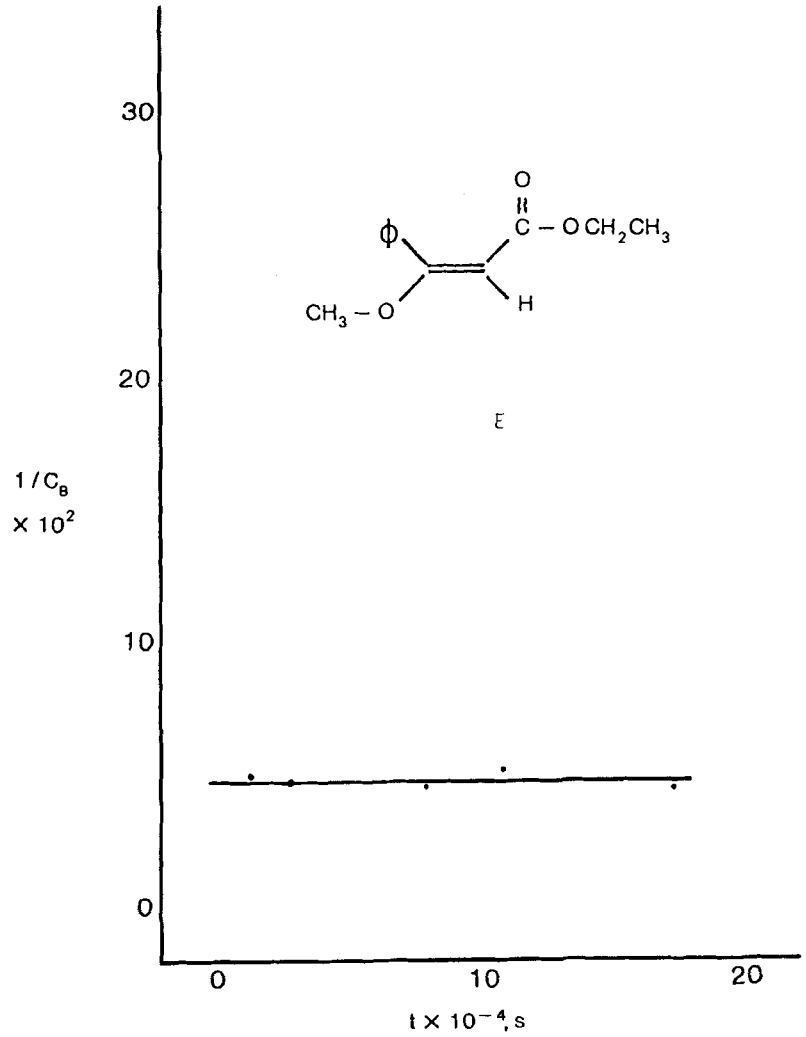

FIG. 7. Second-order kinetic plot of the reaction of E-ethyl β-methoxycinnamate with n-hexylamine at room temperature (25°C).

proceeds by a Michael-type addition reaction [6] followed by elimination of ROH (Fig. 8). Work on the mechanism of this polymerization is being continued in an effort to elucidate the limitations and utilities of vinylogous nucleophilic substitution as a route to new polymers.

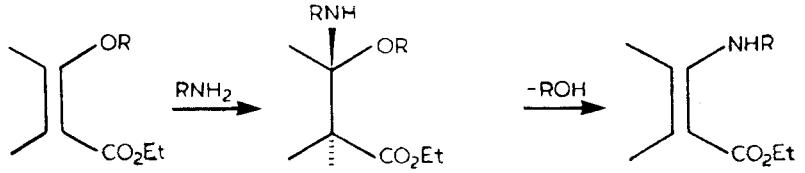

FIG. 8. Michael-type addition mechanism.

EXPERIMENTAL

All melting points are uncorrected and were determined in capillary tubes with a Hoover-Thomas Unimelt apparatus. Nuclear magnetic resonance (NMR) spectra were obtained on Varian T-60 and CFT-20 Spectrometers and are reported in δ units using tetramethylsilane as an internal standard. Infrared spectra (IR) were recorded on a Perkin-Elmer model 521 Spectrophotometer with the following band intensity notations being used: vs = very strong, s = strong, m = medium, and w = weak; for known compounds only characteristic bands are given. Ultraviolet spectra (UV) were recorded on a Cary 14 spectrophotometer. Mass spectra were taken on a CEC 21-104 mass spectrometer operating at 70 eV and are reported as m/e with relative intensity (percent of base peak) in parentheses. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Gas chromatography-mass spectral data (GC-mass spec) was obtained on a Varian MAT 111 instrument using an electron impact detector. A 10-ft glass column (2 mm i.d.) packed with OV-17 on 100-120 mesh Gas Chrom Q was used. The instrument was programmed from 30 to 300°C at 20°C/min using helium as the carrier gas. Thin-layer chromatography (TLC) analyses were obtained using 50 mm × 100 mm silica-gel-coated glass slides which were purchased from VWR Scientific, Rochester, New York. The developed TLC plates were visualized with a USVL25 Mineralight producing short and long wavelengths of ultraviolet light (Ultraviolet Products, San Gabriel, California).

Extractions were usually completed by a final washing with a saturated sodium chloride solution, drying over anhydrous magnesium sulfate, followed by filtration and evaporation of solvent under vacuum on a rotary evaporator at room temperature up to 100°C.

Z, E-Ethyl β-Methoxycinnamate

Ethyl benzoylacetate (19.1 g, 0.10 mol) was reacted with diazomethane in diethylether. Diazomethane was prepared in special glassware

with polished connections obtained from Aldrich Chemical Co. To the 1-L flask was added 16 g of KOH, 40 mL of water, 120 mL of 2-(2-ethoxyethoxy)ethanol, and 40 mL of diethylether. A dropping funnel was placed above the flask which was arranged for distillation into a receiver cooled in an ice bath. In the dropping funnel was placed a solution of 56.1 g (261.6 mmol) of N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) in 560 mL of diethylether (this amount will generate ~200 mmol of diazomethane). This solution was added dropwise to the KOH solution heated at 70°C in a water bath. Codistillation of diazomethane started immediately into a flask containing ethyl benzoylacetate in 100 mL of ether. The receiver was kept in an ice bath until an excess of diazomethane had been added. The pale yellow solution was warmed to room temperature and stirred overnight. Ether and excess diazomethane were evaporated under a stream of dry nitrogen while in a good fume hood. The residue (19 g) was fractionally distilled using a Nester Faust Adiabatic Teflon Spinning Band Distillation Apparatus, bp 120°C/1.8 torr (Ref. 7: 115-120°C/0.8 torr). 8.8 g (43%) of pure ethyl β-methoxycinnamate was obtained. Analysis by gas-liquid phase chromatography show the product to be a mixture of isomers (75% Z-isomer and 25% E-isomer): IR (film) 3060w, 2983m, 2940m, 2905w, 2845w, 1710s (ester C=O), 1620s (C=C), 1578m, 1493w, 1454s, 1368m, 1340m, 1270s (C–O), 1220w, 1156s (C–O), 1116s, 1090m, 1042m, 1030m, 780m, and 700m cm^{-1}; ^{1}H-NMR($CDCl_3$) δ_E, δ_Z, 1.13, 1.30, (s, 3H, $CH_2C\underline{H}_3$), 3.82, 3.90 (s, 3H, $OC\underline{H}_3$), 4.03, 4.22 (q, 2H, $OC\underline{H}_2CH_3$), 5.37, 5.65 (s, 1H, $C=C\underline{H}CO_2Et$) and 7.33-7.87 (m, 5H, Ar$\underline{H}$); ^{13}C-NMR($CDCl_3$) Z, E, 167.52, 170.18 (C=O), 164.02, 165.55 (C-3,4), 134.05, 134.27, (C-6,5), 129.25, 128.50 (C-7,8), 127.51, 127.78 (C-9,10), 126.37, 126.51 (C-11,12), 98.80, 91.49 (C-13,14), 58.38, 59.37 ($O\underline{C}H_2$), 58.55, 55.09 ($O\underline{C}H_3$), 13.29, and 13.08 ppm ($C\text{–}\underline{C}H_3$); mass spectrum m/e (relative intensity) 206 (M^+, 27), 205 (13), 161 (M^+–C_2H_5O, 100), 134 (21), 133 (28), 115 (17), 105 (30), 102 (20), 91 (22), 77 (36), 69 (15), 59 (21), 51 (18), 29 (21), 28 (21), and 15 (12).

Analysis: Calculated for $C_{12}H_{14}O_3$: C, 69.90; H, 6.80; O, 23.30. Found: C, 70.16; H, 6.84.

Z-Ethyl β-(Phenylamino)cinnamate

To a 100-mL three-necked flask equipped with a mechanical stirrer and condenser was added 4.8 g (25 mmol) of ethylbenzoyl acetate, 4.6 g (50 mmol) of aniline, 6.8 g of anhydrous $CaSO_4$, 1.0 mL of concentrated HCl, and 50 mL of ethanol. The mixture was stirred and refluxed. After 1.5 h, analysis by TLC on silica gel showed two spots when developed with methylene chloride: unreacted aniline (R_f = 0.32) and

the enaminoester (R_f = 0.69). The reaction mixture was cooled to room temperature, vacuum filtered to remove the $CaSO_4$, diluted to 400 mL with diethylether, and refiltered to remove precipitated aniline hydrochloride. The ether folution was then washed with water, dried ($MgSO_4$), and concentrated. The residue was dissolved in 100 mL of hexane and stirred for 4 h with 10 g of silica gel. Filtration and concentration of the solution gave 4.6 g (70%) of the product as a white solid: mp 70-72°C (Ref. 8: 71-72°C); IR (KBr) 324w (NH, broad), 1646s (C=O), 1608s (C=C), 1590s, 1582s, 1575s, 1503m, 1478m, 1448m, 1360m, 1280s (C–O), 1180s (C–O), 1155s, 1037m, 797m, 700m, 766m, 703m, and 688 cm^{-1}; UV λ_{max} (MeOH) 249 nm (ϵ13,452 and 323 (17,630)); ^{1}H-NMR($CDCl_3$) δ 1.26 (t, 3H, $CH_2\underline{CH_3}$), 4.23 (q, 2H, OCH_2CH_3), 5.06 (s, 1H, C=C$\underline{H}$$CO_2$Et), 6.58 (m, 10H, Ar$\underline{H}$), and 10.68 (s, 1H, N$\underline{H}$); ^{13}C-NMR($CDCl_3$) 170.13 (ester $\underline{C}$=O), 159.08 (C=), 140.41 (anilino C-1), 136.03 (C-1), 129.43 (C-4), 128.60 (C-2, C-6), 128.41 (C-3, C-5), 128.25 (anilino-C-3, C-5), 122.95 (anilino-C-4), 122.21 (anilino-C-2, C-6), 91.21 (HC=), 59.31 ($O\underline{C}H_2$), and 14.53 ppm (C–$\underline{C}H_3$); mass spectrum m/e (rel. intensity) 267 (M^+, 90), 238 (7), 222 (34), 194 (M^+–$C_3H_5O_2$, 99), 193 (M^+–$C_3H_6O_2$, 100), 180 (56), 165 (11), 104 (12), 77 (49), 51 (13), and 28 (10).

Analysis: Calculated for $C_{17}H_{17}O_2N$: C, 76.40; H, 6.37; N, 5.24; O, 11.99. Found: C, 76.19; H, 6.40; N, 5.32.

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