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On the polymerization of 1-substituted 2-azabutadienes

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Summary

Three 2-aza-1,3-butadienes carrying substituents at the 1-position have been synthesized by flash vacuum pyrolysis of precursor cyclopentadiene cycloadducts. 1-Phenyl-2-aza-1,3-butadiene led to low molecular weight polymer when exposed to anionic and radical initiators. 1-(2',4',6'-Trimethylphenyl)-2-aza-1,3-butadiene and 1-t-butyl-2-aza-1,3-butadiene were synthesized similarly, but they did not polymerize.

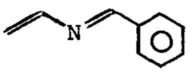
Introduction

In contrast to the extensive literature on the polymerization of C=C and C=O bonds, very little is known about the polymerization via the C=N bond. We have chosen aza-1,3-butadienes for study because the vinyl group often provides a handle for the polymerization of functional groups that would otherwise not polymerize.(1)

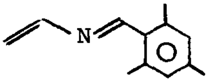
In a previous publication we described the synthesis and polymerization of a new class of monomer, namely 1-substituted 1-aza-1,3-butadienes.(2) These monomers polymerized successfully under anionic conditions if the substituent was aromatic. These monomers also polymerized with acidic initiators. Polymerization did not occur if donor substituents were used, regardless of initiator type.

We now extend this investigation of the polymerizability of C=N bonds to 1-substituted 2-aza-1,3-butadienes. These monomers also contain a vinyl group to facilitate polymerization, but the C=N bond is placed in the opposite sense from our previous study. Ripoll and coworkers have synthesized a number of 2-azabutadienes. They report adventitious polymerization, particularly in the presence of dienophiles.(3)

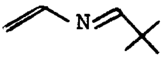
In this paper we describe the synthesis of three substituted 2-aza-1,3-butadienes, and a preliminary investigation of their polymerization.



1 1-Phenyl-2-aza-1,3-butadiene



2 1-(2',4',6'-Trimethylphenyl)-2-aza-1,3-butadiene



3 1-t-Butyl-2-aza-1,3-butadiene
(2,2-Dimethyl-4-aza-3,5-hexadiene)

Experimental

Methods - ^{1}H NMR spectra were taken on Varian EM 360 L and Bruker WM 250 spectrometers at 60 and 250 MHz, respectively. ^{13}C NMR spectra were obtained from the latter instrument at 62.9 MHz. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. Elemental analyses were performed by MicAnal, Tucson, Arizona

Source of Materials - Aldehydes and amines were purified by distillation. n-Butyllithium and t-butylmagnesium chloride were purchased from Aldrich as hexane and ether solutions, respectively. Acidic initiators, BF_3OEt_2, CF_3COOH and CF_3SO_3H, were distilled and diluted with dichloromethane. Toluene was refluxed over sodium and distilled. Dichloromethane was successively washed with sulfuric acid, water, Na_2CO_3(aq) and water, dried over $CaCl_2$, refluxed over CaH_2 and distilled.

Precursor synthesis - Precursors for monomers were synthesized from exo-5-norbornenylamine, prepared according to the procedure of Stille and Sannes (4), and the corresponding aldehydes under varying conditions depending on reactivity of the aldehydes.

N-Norborn-2-en-5-yl-benzylidenimine(4) - exo-5-Norborn-2-enylamine (11 g, 0.10 mole) and benzaldehyde (11.5 g, 0.11 mole) were refluxed in benzene for 3 hr to remove water azeotropically. The product solution was dried over NaOH, concentrated and distilled on a Kugelrohr apparatus. The imine solidified at -10°C. b.p. 84~86°C/0.05 mmHg. Yield 17.6 g (90%).
IR (neat): 3059, 2970, 2865, 1640 (C=N), 1491, 1450 (C=C), 1579, 1060, 753, 713, 693 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.18 (s), CH=N; 7.7 (m) and 7.3 (m), phenyl; 6.20 (dd, J=5.7, 29 Hz) and 6.05 (dd, J=5.7, 3.1 Hz), CH=CH; 3.26-3.30 (m, 1H), 2.88 (s, 1H), 2.68 (s, 1H), 2.09 (d, 1H) and 1.51~1.55 (m, 3H), norbornenyl residue. ^{13}C NMR ($CDCl_3$): 158.16 (d), CH=N; 136.34 (s), substituted phenyl; 134.11 (d) and 139.55 (d); CH=CH; 129.98 (d), 128.15 (d) and 127.73 (d), CH (phenyl); 70.24 (d), CH-N=, 50.30 (d) and 41.62 (d), CH; 45.74 (t), CH (bridge head); 34.97 (t), CH_2. Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.22; H, 7.76; N, 7.10

N-Norborn-2-en-5-yl-(2,4,6-trimethylphenyl)methylidenimine(5) - This imine was prepared in a similar manner as above in the presence of β-alanine. b.p. 100~110°C/0.05 mmHg, mp. 57.5~58.8°C. Yield 99%.
IR (KBr): 3057, 2975, 2867, 1634 (C=N), 1608, 859, 709 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.56 (s), CH=N; 6.82 (s), CH (phenyl); 6.12 (m), CH=CH; 2.37 (s), o-CH_3; 2.23 (s), p-CH_3; 1.3~3.4 (br. m), norbornenyl residue.
Anal. Calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.84; N, 5.85. Found: C, 85.14; H, 9.01; N, 5.78.

N-Norborn-2-en-5-yl-2,2-dimethylpropylidenimine(6) - The reaction was performed at room temperature in benzene. b.p. 52~55°C/0.2 mmHg. Yield 78%. IR (neat) : 3059, 2965, 2865, 1659 (C=N), 1367, 709 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.49 (s), CH=N; 6.03 (m), CH=CH; 3.03 (br, t), CH-N=; 1.2~2.9 (m), norbornenyl residue; 1.04 (s), $C(CH_3)_3$
Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.59; H, 11.06; N, 8.09.

Monomer Synthesis: The 2-aza-butadienes were prepared from the corresponding precursors by thermolysis under vacuum. Thermolysis was carried out at 580-600°C at 0.1~1.5 mmHg on a quartz tube (2 x 40 cm) packed with quartz fragments. Details of the procedure were described in a previous paper.(2)

1-Phenyl-2-aza-1,3-butadiene(1) - Thermolysis of 4 (9.06 g, 46 mmole) at 580°C and at 0.5~0.3 mmHg gave 5.05 g of 1. Yield 84%. b.p. 38~39°C/0.05 mmHg. IR (neat) : 3060, 2955, 2862, 1957, 1895, 1806, 1632 (C=N), 1592, 1571, 1149, 1311, 1160, 980, 896, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.07 (s), CH=N; 7.3 and 7.7 (m), phenyl; 6.62 (dd, J-9.0, 14.7 Hz), = CH; 5.72 (d, J=7.0) and 5.68 (d, J-14.7), CH_2=. ^{13}C NMR ($CDCl_3$) : 161.85 (d), CH=N; 148.27 (d), =CH1; 135.75 (s), substituted phenyl C; 131.09 (d), 128.59 (d) and 128.54 (d), phenyl CH, 114.07 (t) CH_2 = . Anal. Calcd for C_8H_9N : C, 82.41; H, 6.92; N, 10.68. Found: C, 82.44; H, 6.72; N, 10.65.

1-(2',4',6')-Trimethyliphenyl)-2-aza-1,3-butadiene(2) - Thermolysis of 5 gave 2 in 82% yield. b.p. 64.5-65°C/0.05 mmHg. Solid at 0°C.
IR (KBr) : 2961, 1640, 1605, 1460,1330, 860, 680 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.54 (s), CH=N; 6.94 (dd, J=22, 14.7 Hz), CH=; 6.82 (s), phenyl; 5.50 (d, J=14.7) and 5.02 (d, J=7.2), CH_2=; 2.43 (s), 0-CH_3; 2.23 (s), p-CH_3. ^{13}C NMR ($CDCl_3$) : 161.92 (d), CH=N; 149.16 (d), CH= 139.42 (s), 138.45 (s) and 129.87 (s), substituted phenyl C; 129.55 (d), phenyl CH; 112.88 (t), CH_2=; 20.94 (q), CH_3.
Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 82.92; H, 8.79; N, 7.95.

1-t-Butyl-2-aza-1,3-butadiene(3) - Thermolysis of 6 led to 3 in 70% yield. IR (neat): 3093, 3035, 2961, 1806, 1642, 1620 (C=N, C=C), 1477, 1362, 1218, 1151, 973, 887, 678 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ : 7.56 (s), CH=N; 6.75 (dd, J=24, 15.0 Hz), CH=; 5.32 (d, J=15.0) and 4.88 (d, J=7.4), CH_2=; 1.11 (s), $(CH_3)_3$. ^{13}C NMR ($CDCl_3$) : 173.95 (d), CH=N; 147.95 (d), CH=; 111.37 (t), CH_2=; 35.92 (s), $\underline{C}(CH_3)_3$; 26.52 (q), $(CH_3)_3$.
Anal. Calcd for $C_7H_{13}N$: C, 75.62; H, 11.78; N, 12.60. Found: C, 75.62; H, 12.04; N, 12.60.

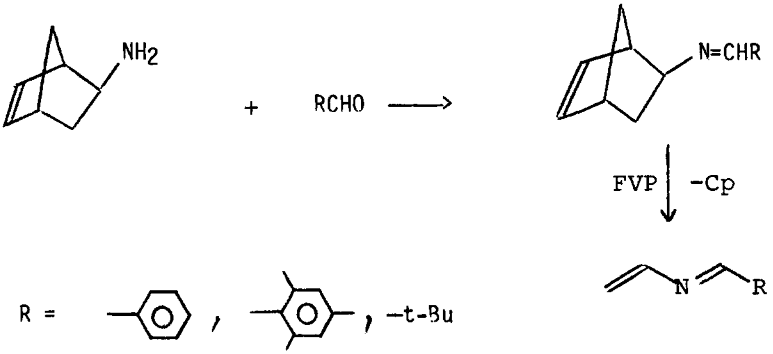
Polymerization of 1 - Solutions of monomer and initiator were placed in each side arm of a Y-shaped tube under nitrogen. After these solutions are brought to the desired temperature, they are mixed. The reaction mixture is precipitated in hexane after 20 hours, and the polymer was collected by filtration and dried.
NMR ($CDCl_3$) : Two very broad peaks at δ 2 and 4 ppm and a peak for the aromatic protons at 7.5 ppm.
IR (KBr) : 3058, 3026, 2922, 2854, 1659, 1492, 1452, 756, 699 cm^{-1}.
Anal. Calcd for C_8H_9N: C, 82.40; H, 6.92; N, 10.68. Found: C, 81.22; H, 6.93; N, 10.33.

Results and Discussion

Synthesis of Monomers

Flash vacuum pyrolysis (FVP) of their anthracene adduct precursors has recently been used by Ripoll and coworkers to synthesize a series of substituted 2-aza-1,3-butadienes.(3) Anthracene is formed as a side product, which leads to separation problems. In analogy with our 1-aza-1,3-butadiene synthesis, we use norbornene derivatives as precursors for the 2-azadienes, which upon pyrolysis should yield the desired product and cyclopentadiene.

The starting material is 5-amino-norborn-2-ene, prepared according to literature procedure.(4) The amine is reacted with the appropriate aldehyde, and the precursor is then pyrolyzed in a quartz column at about 600°C. The product is purified by distillation. High yields are obtained for 1, 2, and 3 (70-85%).



All spectra and chemical analyses were in agreement with the proposed structures.

Polymerization

Polymerization of all three 2-azabutadiene monomers was attempted using anionic initiators (butyllithium in toluene or tetrahydrofuran at 0° and at -78°C), cationic initiators (boron trifluoride etherate or trifluoroacetic acid in dichloromethane at -78°C and at -10°C) and a radical initiator (AIBN in toluene at 70°C). The results for monomer 1, 1-phenyl-2-aza-1,3-butadiene, are summarized in Table I. Anionic polymerization using butyllithium in toluene at 0° or in tetrahydrofuran at -78° and at 0°C led to high yields of a very low molecular weight polymer. Trifluoroacetic acid led to a low yield of low molecular weight polymer at -10°C in dichloromethane, as did AIBN at 70°C. The inherent viscosities of these polymers were below 0.1 dl/g (50 mg of polymer in 10 ml chloroform at 30°C). Monomer 2, 1-(2',4',6'-trimethylphenyl)-2-aza-1,3-butadiene, and monomer 3, 1-t-butyl-2-aza-1,3-butadiene, did not yield any polymer in any of the above conditions.

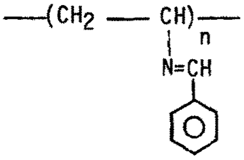
Poly- 1, obtained from anionic polymerization, is very low molecular weight (less than 5000). The infrared spectrum does not show any residual terminal vinyl groups, but does show a peak for C=N at about 1660 cm^{-1}. This indi-cates that the polymerization occurred in either a 4,3-fashion, leading to units with structure A, or in a 4,1-fashion, yielding units with structure B, or a mixture of both.

Table I : Polymerization of 1-Phenyl-2-aza-1,3-butadiene 1[a]

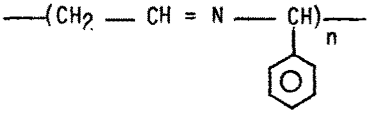
Initiator	Amount Initiator (mmole)	Solvent	Temp (°C)	Yield (%)	$\nu C=N$[b] (cm^{-1})
BuLi	0.10	Toluene	-78	trace	
BuLi	0.10	Toluene	0	87.3	1659
BuLi	0.10	THF	-78	94.3	1660
BuLi	0.10	THF	0	58.9	1659
tBuMgCl	0.10	Toluene	-78	0	
BF_3OEt_2	0.07	CH_2Cl_2	-78	0	
CF_3COOH	0.07	CH_2Cl_2	-10	10	
AIBN	0.05	Toluene	70	27	1642

[a] Conditions: Monomer 0.5 ml (3.65 mmole), solvent 5 mL (0.5 mL for radical polymerization). Time 24 hr.

[b] From infrared spectrum.



Structure A



Structure B

The peaks in the NMR spectrum are very broad, but correspond to structure B. No peak is observed for the proton in a pendant $—N=CH-C_6H_5$ unit, but this signal could be buried under the phenyl group. The ^{13}C spectrum of this polymer is very complex and indicates that polymer obtained in these conditions has a very complex structure.

Conclusion

In this preliminary investigation, we have established that 1-phenyl-2-aza-1,3-butadiene 1 does polymerize under anionic conditions, but the structure of the polymer is still unclear. The other two monomers 1-trimethyl-phenyl-2-azabutadiene 2 and 1-t-butyl-2-azabutadiene 3 did not polymerize. From this study we can conclude that 1-azabutadienes are much more efficient monomers than 2-azabutadienes.

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