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Five authentic diradicals fail to initiate vinyl polymerization

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Summary
Authentic diradicals, generated from either bicyclic azo compounds and from a bicyclopentane derivative, fail to initiate the polymerization of styrene or acrylonitrile.

Introduction

A diradical polymerization, in which both chain ends would be active, would not only be interesting from a theoretical point of view, but could offer economic advantages such as faster polymerization rates and higher molecular weights.

Our earlier work on Bond Forming Initiation in the reaction of *p*-methoxystyrene with dimethyl cyanofumarate has given evidence for a polar diradical initiation and propagation mechanism.(1) This system is not useful for initiating the polymerization of a third monomer, because the initiating olefins are swept out of the reaction mixture due to copolymerization. To avoid this problem, we have also studied initiation of polymerization by the cleavage of a heavily substituted and stabilized cyclopropane.(2) However, more data would be desirable.

In this work, we shall examine several possible routes to diradicals, using the latest information provided by organic chemistry. Diradicals will be generated from bicyclic azo compounds and from a bicyclopentane derivative, and their ability to initiate diradical polymerizations will be investigated.

Background

Thermolysis of Bicyclic Azo Compounds.

1,4-Diphenyl-2,3-diazabicyclo[2.2.1]heptane **1** was synthesized by a multistep procedure by two groups of investigators.(3)(4) Thermolysis or photolysis gave the intermediate cyclopentane-1,3-diyl, which closed to 1,3-diphenylbicyclo[2.1.0]pentane or was trapped with oxygen.(5)(6)

Huenig (7) and Adam (8) demonstrated a much more direct synthesis of molecules of this class, such as **2** and **3**. Again thermolysis or photolysis readily gave the cyclopentane-1,3-diradicals. Adam et al. have performed extensive studies monitoring the lifetimes of the diradicals formed from the various substituted azo compounds.(9) To date, however, these have not been tested yet as potential initiators of diradical vinyl polymerizations.

A related much-studied 1,3-diradical system is the 2-methylene-1,3-diyl system, also known as trimethylenemethanes. The parent unsubstituted TMM merely cyclizes to

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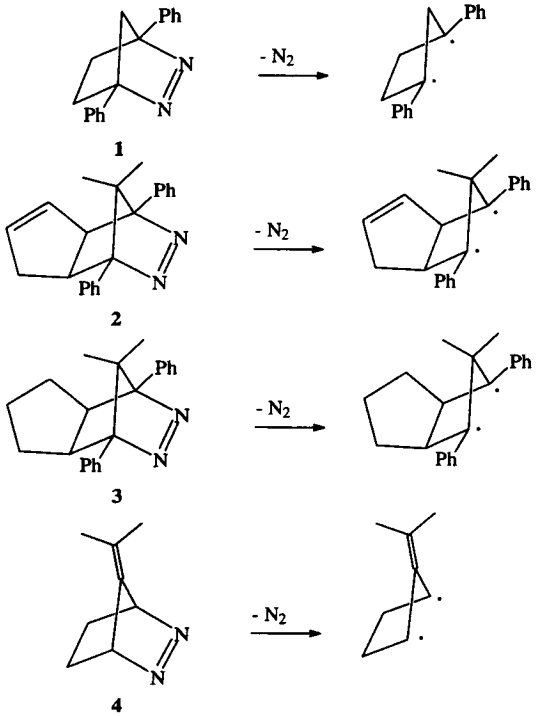

Figure 1 Azo Compounds as Precursors for Diradicals

methylenecyclopropene.(10) Berson et al. synthesized 7-isopropylidene-2,3-diazabicyclo-[2.2.1]hept-2-ene, **4**, an azo compound possessing an exo isopropylidene unit, by a multistep procedure.(11) Thermolysis of this compound in solution yields the substituted TMM-type diradical 2-isopropylidenecyclopentane-1,3-diyl, which does not cyclize but dimerizes. When the diazo compound is heated to 80 °C in a solution containing an olefin, this triplet 1,3-diradical intermediate could be trapped by vinyl monomers as cycloadducts.(12)(13) Electron-poor olefins gave highest yields, but even styrene reacted in this manner. Therefore the dimethyl trimethylene-methane is to be regarded as an electron-rich diradical intermediate. Accordingly it was reasonable to expect that carrying out the azo decompositions in bulk monomers, particularly electrophilic acrylonitrile, would be promising.

Bicyclo[2.1.0]pentane-1-carbonitrile

In earlier work, Gassman and This Laboratory have investigated the chemistry of bicyclo[2.1.0]pentanes.(14)(15) The central bond has been reported to be the most strained single bond known.(16) Gassman proposed diradical intermediates in the cycloaddition reactions of the parent bicyclo[2.1.0]pentane with olefins.(14) Such a strained bicyclic molecule seemed to be a good case to study as potential diradical initiating species. We preferred to introduce a cyano group to the bicyclo[2.1.0]-pentane to confer acceptor character to complement the donor monomer styrene. The advantage of this molecule is that it does not homo- or copolymerize with vinyl monomers under free radical initiation.(15)

Experimental Section

Instrumentation. ^{1}H NMR (200 MHz) and ^{13}C (50.3 MHz) spectra were recorded on a Varian Gemini 200 NMR Spectrometer. IR spectra were recorded on a Nicolet Impact 400D infrared spectrometer. Elemental Analysis were performed by Desert Analytics, Tucson, AZ. Mass spectra were obtained by direct insertion probe at the University of Arizona Department of Chemistry Mass Spectrometry Facility on a Hewlett-Packard 5988A apparatus with an RTE-6 data system at a source temperature of 200 °C.

Materials. 3-Cyanopentanone was prepared according to literature procedure.(17) Sodium borohydride, tosyl chloride, and pyridine were all from Aldrich Chemical Co. and used as received.

1,4-Diphenyl-2,3-diazabicyclo[2.2.1]heptane **1** was synthesized according to Coms and Dougherty (3), the bicyclic azo compounds (1a, 4a, 4aα, 7aα)-4,4a,7,7a-tetrahydro-8,8-dimethyl-1,4-diphenyl-1,4-dimethano-1*H*-cyclopenta[*d*]pyridazine **2** and (1a, 4a, 4aα, 7aα)-4,4a,5,6,7,7a-hexahydro-8,8-dimethyl-1,4-diphenyl-1,4-dimethano-1*H*-cyclopenta[*d*]pyridazine **3** were synthesized according to Huenig (7) and Adam.(8) 7-Isopropylidene-2,3-diaza-bicyclo[2.2.1]hept-2-ene **4** was synthesized according to Berson.(11)

3-Hydroxycyclopentanecarbonitrile. A solution containing 3-cyanocyclopentanone (4.72 g, 43.3 mmol) and ethanol (200mL) was placed into a 500 mL round bottom flask. $NaBH_4$ (1.64 g, 43.3 mmol) was added slowly to the solution and a reflux condenser was attached to the flask. The reaction mixture was refluxed for 30 min and then allowed to cool to room temperature. The mixture was diluted with ether (300 mL) and the organic layer was washed with water (2 x 100 mL) and brine (100 mL), and then dried over $MgSO_4$. The solution was filtered and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography (3 x 3 cm) on alumina with ethyl acetate as the eluent yielding a clear oil (3.51 g, 73%). ^{1}H NMR ($CDCl_3$) 4.30-4.57 (m, 1 H, CH-OH), 2.7-3.1 (m, 1 H, CH-CN), 1.60-2.35 (m, 7 H, 3 CH_2 and OH). ^{13}C NMR ($CDCl_3$) δ 123.1 (CN), 71.7 (CHOH), 392. (CHCN), 34.3 (CH_2), 28.3 (CH_2), 25.1 (CH_2), 25.1 (CH_2). IR (CH_2Cl_2) $\nu_{C\equiv N}$ 2246 cm^{-1}; Anal. Calcd for C_6H_9NO: C, 64.86; H, 8.11; N, 12.61. Found: C, 64.57; H, 8.00; N, 12.39.

3-Tosyloxycyclopentanecarbonitrile. To a solution containing 3-hydoxycyclopentane-carbonitrile (3.51 g, 31.6 mmol) in pyridine (15 mL) was added tosyl chloride (7.23 g , 37.9 mmol). The mixture was stirred overnight. The solution was diluted with 200 mL of ether and stirred for 30 minutes. The resulting solution was filtered through celite, 50 mL of cold dilute HCl was added to the ether solution and the mixture was stirred for 2 h. The ether solution was decanted and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield a slightly yellow colored oil (5.87 g, 70 %). ^{1}H NMR ($CDCl_3$) 7.81 (d, 2 H, aromatic CH), 7.32 (d, 2 H, aromatic CH), 5.00 (m, 1 H, CH-CN), 2.44 (s, 3 H, CH_3), 1.75-2.36 (m, 6 H, 3 CH_2). ^{13}C NMR ($CDCl_3$) δ 144.9 (aromatic C), 129.7 (aromatic CH), 127.4 (aromatic CH), 121.7 (CN), 82.4 (CH-OTs), 36.9 (CH-CN), 32.6 (CH_2), 28.5 (CH_2), 25.5 (CH_2), 21.3 (CH_3). IR (CH_2Cl_2) $\nu_{C\equiv N}$ 2246 cm^{-1}; Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.84; H, 5.69; N, 5.30. Found: C, 58.66; H, 5.46; N, 5.15.

Bicyclo[2.1.0]pentane-1-carbonitrile. The tosylate (7.93 g, 30 mmol) was placed in a 500 mL round bottom flask, which was evacuated and back filled with nitrogen. The tosylate was then dissolved in 300 mL THF. The resulting solution was placed in an ice bath and cooled to 0°C. To this solution was added dropwise 35.88 mL (36 mmol) of the 1M in THF sodium bistrimethylsilylamide solution. The solution immediately darkens upon addition of all of the base. This solution was stirred while in an ice bath for 30 min. The solution was allowed to warm to room temperature. Ammonium chloride (0.2 equivalents) was added and allowed to stir for 30 min. The resulting solution was filtered through celite and the solvent was removed under reduced pressure. The product was purified by distillation under reduced pressure (48-50° at 1 mm Hg) to yield pure product. (73% yield)

Polymerization Reactions. The polymerization reactions were run under a variety of conditions. For all polymerization reactions, the samples were prepared by freeze pump thaw method (2-3 cycles). Polymerization reactions using styrene or acrylonitrile as the monomer were carried out in the absence of inhibitor with 0.3 % initiator.

GC-MS Analysis: The residues from the attempted polymerizations were evaporated, dissolved in methanol and analyzed by gas chromatography / mass spectrometry using a Finnigan SSQ700, SN TS00417, quadrupole GC/MS system in EI, NH_3-PCl and NH_3-NCl modes.

The polymerization mixtures using the azo compounds **2** and **3** with acrylonitrile were examined. For azo compound **2** the only peak was due to 3,3-dimethyl-2,4-diphenyl-bicyclo[3.3.0]octa-1,7-diene, or an isomer. The other peaks amounted to less than 1 %. For the reaction with azo compound **3** and acrylonitrile, the only peak was identified as 3,3-dimethyl-2,4-diphenyl-bicyclo[3.3.0]octene, or an isomer.

The polymerization mixture of the attempted initiation of styrene polymerization with bicyclo[2.1.0]pentane-1-carbonitrile **5** was also analyzed. The two main peaks were cyclopentene-1-carbonitrile and 1-cyano-3-phenyl-bicyclo[2.2.1]heptane, and two isomers of the latter.

Results

Bicyclic Azo Compounds

Azo compound **1** was synthesized according to Coms and Dougherty.(3) Styrene was polymerized in the presence of potential diradical initiator **1**. In each case, the tube containing the initiator plus styrene was compared to a blank tube of pure styrene to see how the initiated polymerization reaction compared to that of the thermal polymerization of styrene. The polymerizations were run at temperatures ranging from 70 to 120 °C for 20 to 8.5 hours, respectively. In most cases the polymer yields for runs containing **1** were slightly lower than the corresponding blank runs, for example at 100 °C after 15 hours, 35.0 % of polystyrene was obtained for the blank run, while 27.1 % was isolated for the run containing **1**. We conclude that addition of the bicyclic compound **1** does not affect the polymerization reaction.

Other studies were conducted to see if compound **1** might affect the polymerization of acrylonitrile. At 100 °C after 16 hours, a blank run did not produce any polyacrylonitrile, while a run containing azo compound **1** led to 12.3 % or polystyrene. While acrylonitrile does polymerize, the extent to which such a reaction takes place is far less than that caused by a conventional monoradical initiator, such as AIBN (>98 % yield under the same conditions).

Two more readily accessible cyclopentane-1,3-diyl precursors were synthesized according to Adam and coworkers.(8) Both the unsaturated compound **2** and the dihydro form **3** were tested as initiators. The rate constants for thermolysis of these bicyclic azo compounds have been previously reported in the literature.(18) From these data, it was known that temperatures of at least 110°C would be required for an adequate rate of radical generation. At this temperature, styrene spontaneously homopolymerizes rather rapidly, (19) so our work was restricted to acrylonitrile. Di-t-butyl peroxide was used as a reference initiator. At 110 °C, a blank polymerization run (16 h) did not yield any polymer, neither did runs containing either azo compound **2** or **3**. A reference run using di-t-butyl peroxide under the same conditions led to polyacrylonitrile in 39 % yield. We conclude that the bicyclic azo compounds **2** or **3** are totally ineffective in initiating the free radical polymerization of acrylonitrile.

Since these results suggest that no initiation is taking place, the fate of the corresponding diyls was investigated by isolating the small molecule products from the acrylonitrile reactions and examining them by GC/MS. GC/MS analysis of reaction mixtures with either azo derivative **2** or **3** shows that the major product is loss of nitrogen followed by ring closure. In the case of azo compound **2**, the main decomposition product was 3,3-dimethyl-2,4-diphenyl-bicyclo[3.3.0]octa-1,7-diene, while for azo compound **3** it was 3,3-dimethyl-2,4-diphenyl-bicyclo[3.3.0]octene. These results suggest that, even though 1,3-diyls are formed, ring closure is much faster than radical propagation, even in the presence of excess monomer.

Bicyclic azo compound, 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene **4**, which possesses an exo double bond, was synthesized according to Berson.(11) Polymerization studies of bulk styrene were conducted at a variety of temperatures ranging from 80 to 100 °C with reaction times ranging from 22 to 12 hours, respectively. The runs containing azo compound **4** yielded exactly the same results as runs without, for example at 90 °C after 17 hours reaction time, 25.7 % yield of polystyrene was isolated from a blank run, while 26.0 % yield was obtained from a run containing **4**. In addition we determined the molecular weights of the polymers obtained in these runs. Again the presence of azo compound **4** had no effect. (For the blank run: M_w 638,000, M_n 485,000; for the run containing **4**: M_w 584,000, M_n 473,000) The polymerization of acrylonitrile was also investigated in the presence of **4**: at 100 °C after 23 hours, the yield was 0 % for the blank run, while the run containing **4** produced a trace of polyacrylonitrile.

Bicyclo[2.1.0]pentane-1-carbonitrile 5

This compound had been synthesized earlier by Hall via a multistep synthesis.(15) A much shorter synthesis was worked out, starting from commercially available 2-cyclopentenone. 3-Cyanocyclopentanone was synthesized according to a literature procedure.(17) The reduction of the ketone followed by conversion to the corresponding tosylate affords the bicyclopentane precursor. The final ring closure was also greatly improved over the former synthetic procedure by use of THF-soluble sodium bistrimethylsilylamide, instead of the insoluble sodium amide.

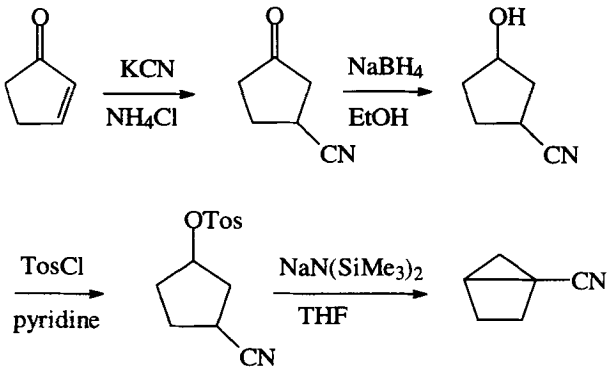

Figure 2: Synthesis of bicyclo[2.1.0]pentane-1-carbonitrile

Bicyclo[2.1.0]pentane-1-carbonitrile was then studied as a potential diradical initiator for a variety of vinyl monomers. Blank runs of styrene polymerization and runs containing **5** were investigated at temperatures ranging form 80 to 100 °C (reaction time 2 hours). No initiation due to the presence of **5** was observed: for example at 90 °C, a blank run produced 2.4 % yield of polystyrene (M_n 245,000), while a run containing **5** yielded 1.2 % of polystyrene (M_n 289,000). In an effort to determine if the donor and acceptor character of respectively the olefin and the initiator are important, similar polymerizations were conducted with 4-methylstyrene as the monomer. The polymerizations of 4-methylstyrene with **5** as the potential initiator showed that once again no initiation is occurring.

GC/MS analysis of the styrene polymerization reaction mixture using **5** as potential initiator shows formation of the rearranged product, namely cylopentene-1-carbonitrile, and the cycloadduct of the bicyclopentane with one molecule of styrene, namely 1-cyano-3-phenyl-bicyclo[2.2.1]heptane.

Discussion

The results of our investigation into the initiation of diradical polymerization are disappointing at best. We selected the most thoroughly characterized authentic diradicals we

could find in the current organic chemistry literature. Nevertheless, in only one case was a small extent of initiation attributable to these initiators, namely in the case of azo compound **1** with acrylonitrile. Only a small amount of polymer was obtained from the TMM diradical. Comparison with deliberately added monofunctional peroxide showed that the peroxide was far superior.

The cyclopentane 1,3-diyls preferred to close to the corresponding bicyclopentanes as indicated by GC-MS analysis. Their reaction ring closure was too rapid for them to react even with bulk vinyl monomer. Consistently, as yet neither cycloadducts nor polymers have been reported in the literature from the decomposition of these azo compounds in the presence of vinyl monomers.

Bicyclo[2.1.0]pentane-1-carbonitrile was hoped to undergo bond forming initiation to form an extended diradical. With styrene, a 1:1 cycloadduct, but no polymer, formed.

What is the explanation for this failure? It appears that the generated known authentic confirmed 1,3-diradicals either immediately cyclize, or add one molecule of vinyl compound and then cyclize. The proximity of the two radical centers gives ring closure too quickly (cage effect). The question arises why we were able to achieve diradical polymerization in the reaction of *p*-methoxystyrene with dimethyl cyanofumarate. The answer may be that the polar character of the latter stabilizes it by resonance, according to the concept of Huisgen (20), permitting it to last long enough to add further monomer molecules. However there must be only a rather narrow range of polar substitution capable to stabilize the diradical and to initiate free radical polymerization. If the donor and acceptor character becomes too great, the diradical intermediate acts predominantly as a zwitterion, and no radical polymerization will be observed.

At present no authentic, satisfactory diradical initiator for vinyl polymerizations has been found. Our work suggests that some polar stabilization of putative diradicals may be required for them to last long enough to initiate vinyl polymerizations.

Acknowledgments

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