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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Fatica, Michael G. and Harwood, H. James(1978) 'Convenient Syntheses of Perdeuterioacrylonitrile and  $\beta,\beta$ -Dideuterioacrylonitrile', *Journal of Macromolecular Science, Part A*, 12: 8, 1099 – 1108

**To link to this Article: DOI:** 10.1080/00222337808063177

**URL:** <http://dx.doi.org/10.1080/00222337808063177>

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## Convenient Syntheses of Perdeuterioacrylonitrile and $\beta,\beta$ -Dideuterioacrylonitrile

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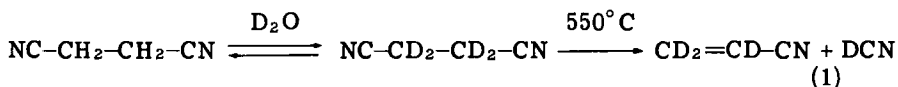
### ABSTRACT

Perdeuterioacrylonitrile can be prepared conveniently from succinonitrile in a two-step process. Succinonitrile is exchanged with  $D_2O$  to obtain perdeuteriosuccinonitrile, which is then pyrolyzed at  $\sim 550^\circ C$  to obtain perdeuterioacrylonitrile and DCN.  $CD_3CN$  and  $C_2D_5CN$  are by-products of this reaction. A chemical procedure for separating perdeuterioacrylonitrile from these materials was developed. This involved formation of the Diels-Alder adduct of cyclopentadiene with perdeuterioacrylonitrile, followed by pyrolysis of the purified adduct at  $\sim 330^\circ C$ . Cyclopentadiene was removed from the resulting pyrolyzate by reaction with maleic anhydride. Purified perdeuterioacrylonitrile exchanged with  $H_2O$  to yield  $\beta,\beta$ -dideuterioacrylonitrile in good yield and good isotopic purity.

Convenient syntheses of perdeuterioacrylonitrile (I) and  $\beta,\beta$ -dideuterioacrylonitrile (II) are needed to support studies on the microstructure of polymers and copolymers derived from acrylonitrile. The best procedure hitherto available for preparing perdeuterioacrylonitrile has involved partial deuteration of deuteriopropargylnitrile [ 1, 2]. We were reluctant to adopt this procedure

because of the limited stability of propargylnitrile, because Lindlar reductions are difficult to execute, and because several deuterated intermediates were required. Perdeuterioacrylonitrile has also been prepared in very small amounts by the addition of DCN to perdeuterioacetylene [3]. Minter and Gherghel [4] described a laboratory procedure for preparing acrylonitrile from HCN and acetylene, and it should be possible to use it to prepare I from DCN and DC≡CD. However, very careful control of the DCN/DC≡CD ratio employed in this preparation is necessary and an elaborate setup is required. LeCoustumer, Lautie, and Dizabo [5] have prepared β,β-dideuterioacrylonitrile from formaldehyde-d<sub>2</sub> by a Wittig reaction. Unfortunately, formaldehyde-d<sub>2</sub> is prepared by a tedious process and is expensive to purchase.

We wish to report a two-step procedure for preparing CD<sub>2</sub>=CDCN that is simple, inexpensive, convenient, and amenable to large-scale preparations. Our synthesis proceeds by the reactions (1).



Three patents issued in the 1940s claimed that acrylonitrile can be prepared in nearly quantitative yield by the pyrolysis of succinonitrile [6-8]. With the hope that perdeuterioacrylonitrile could be prepared by the reaction sequence outlined above, the exchange of succinonitrile with D<sub>2</sub>O and its pyrolysis behavior were investigated. Exchange of succinonitrile with D<sub>2</sub>O is very easily accomplished by refluxing a homogeneous solution of the nitrile (25 wt %) in D<sub>2</sub>O. Equilibrium is obtained in 1 hr provided that solid CaO is present. Removal of the solvent by distillation yields partially exchanged succinonitrile. Several exchanges afford perdeuteriosuccinonitrile of 99% isotopic purity, in nearly quantitative yield, provided that fresh CaO is used in each exchange step. The yield of perdeuteriosuccinonitrile is reduced by hydrolysis reactions, but this complication can be circumvented by using large excesses of D<sub>2</sub>O to reduce the number of exchanges required for a particular degree of isotopic purity.

The pyrolysis of succinonitrile was investigated extensively. Temperature (200-700°C), flow rate, carrier gas, and pyrolysis column packing (Molecular Sieve 3A, charcoal impregnated with KCN, stainless steel turnings, glass helices) were varied in an effort to obtain conditions favorable for the production of acrylonitrile. In all cases, acetonitrile and propionitrile were obtained in significant amounts in addition to acrylonitrile. These were identified by NMR and GC analyses of the pyrolyzate. Thus, Fig. 1 shows the NMR spectrum of a typical pyrolyzate. The presence of acetonitrile is indicated by the singlet at 1.95δ. Propionitrile is responsible for the

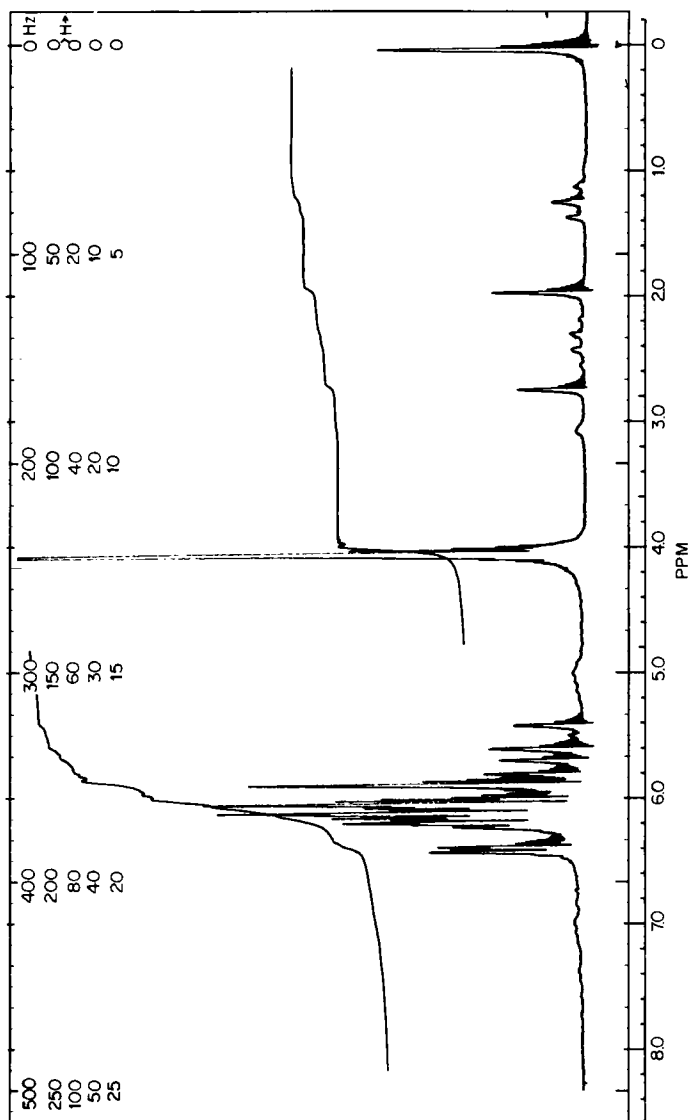
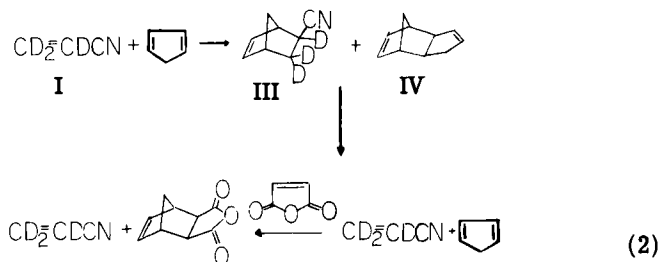


FIG. 1. 60 MHz PMR spectrum of product mixture (neat) obtained from the pyrolysis of succinonitrile at 550°C.

quartet centered at 2.3 $\delta$  and the triplet centered at 1.2 $\delta$ . HCN and unreacted succinonitrile are responsible for the singlets observed at 4.05 and 2.8 $\delta$ , respectively. Acetonitrile and propionitrile were formed when acrylonitrile was submitted to the pyrolysis conditions and it was found that the amounts of these by-products could be reduced by reducing the residence time of the pyrolysate in the pyrolysis chamber. Optimum conditions for the pyrolysis of succinonitrile led to a nearly quantitative yield of a pyrolyzate that contained 45.8 mole % acrylonitrile, 1.0 mole % succinonitrile, 1.6 mole % acetonitrile, 1.8 mole % propionitrile, and 49.8 mole % HCN. The conditions developed for pyrolysis of succinonitrile were then modified slightly for use in the pyrolysis of perdeuteriosuccinonitrile. Gas chromatography was used to monitor the pyrolysate composition in these studies and it was similar to that reported above.

Separation of acrylonitrile or perdeuterioacrylonitrile from the pyrolysis mixtures by distillation proved to be very difficult. Acetonitrile, HCN, and succinonitrile (or their deuterated analogs) could be removed partially by distillation, but it was not possible to separate acrylonitrile from propionitrile by this method. A sequence of Diels-Alder and retro-Diels-Alder reactions (2) was therefore used to purify perdeuterioacrylonitrile.



Treatment of the perdeuteriosuccinonitrile pyrolyzate with an excess of cyclopentadiene at 0°C resulted in the formation of a mixture of 2,3,3-trideuterio-5-norbornene-2-carbonitrile (III) and dicyclopentadiene (IV). This mixture was readily separated from DCN, CD<sub>3</sub>CN, CD<sub>3</sub>CD<sub>2</sub>CN, and NCCD<sub>2</sub>CD<sub>2</sub>CN by distillation. The mixture of cyclopentadiene adducts was pyrolyzed at ~330°C to regenerate cyclopentadiene and perdeuterioacrylonitrile. These were collected at -78°C and were treated with a solution of maleic anhydride in (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O at -78°C to enable the cyclopentadiene-(maleic anhydride) adduct to form. Pure CD<sub>2</sub>=CDCN was easily separated from the resulting mixture by distillation. It was necessary to remove cyclopentadiene by this method because cyclopentadiene

and  $\text{CD}_2=\text{CDCN}$  readily recombine when allowed to warm to room temperature together.

Starting with 10 g of succinonitrile, the operations outlined above yielded 3.6 g of pure  $\text{CD}_2=\text{CDCN}$ , corresponding to a 54% overall yield. For some studies, it may not be necessary to separate  $\text{CD}_3\text{CN}$  and  $\text{C}_2\text{D}_5\text{CN}$  completely from  $\text{CD}_2=\text{CDCN}$ , and the purification procedure can be avoided. In such cases, the yield of  $\text{CD}_2=\text{CDCN}$  is approximately 85-90%, starting with deuterated succinonitrile.

Leitch [9] has reported that  $\alpha$ -deuterioacrylonitrile can be prepared by exchanging acrylonitrile with  $\text{D}_2\text{O}$  in the presence of  $\text{CaO}$ . This procedure can also be used to prepare  $\beta,\beta$ -dideuterioacrylonitrile by exchanging perdeuterioacrylonitrile with  $\text{H}_2\text{O}$  in the presence of  $\text{CaO}$ . More so than is the case for the exchange of succinonitrile with  $\text{D}_2\text{O}$ , it is necessary that solid  $\text{CaO}$  (5%) be present in the reaction mixture and that fresh  $\text{CaO}$  be used for each exchange step. Pure  $\text{CD}_2=\text{CDCN}$  must be used for this reaction, because  $\text{CD}_3\text{CN}$  and  $\text{CD}_3\text{CD}_2\text{CN}$  are cyanoethylated by acrylonitrile- $\text{d}_3$  in alkaline media.  $\beta,\beta$ -Dideuterio- $\beta$ -hydroxypropionitrile, formed by cyanoethylation of water during the exchange reaction, is a byproduct of this reaction. However, it can be dehydrated to obtain an additional yield of  $\beta,\beta$ -dideuterioacrylonitrile by simply heating the concentrated reaction mixture at  $100^\circ\text{C}$  under vacuum [10].

In our hands, a 58% yield of  $\text{CD}_2=\text{CHCN}$  was obtained by a two-fold exchange of  $\text{CD}_2=\text{CDCN}$  with  $\text{H}_2\text{O}$ . Lindsay [10], working with larger quantities of acrylonitrile obtained a 90% yield of  $\alpha$ -deuterioacrylonitrile by this modification of Leitch's method.

Figure 2 shows the 300 MHz NMR spectrum of  $\beta,\beta$ -dideuterioacrylonitrile. The two doublets centered at  $\delta 6.07$  ( $J = \sim 11$  Hz, cis) and  $\delta 6.20$  ( $J = \sim 18$  Hz, trans) are due to the residual methylene protons. On the basis of this spectrum, the  $\text{CD}_2=\text{CDCN}$  is estimated to be 98% isotopically pure.

Figure 3 compares the 300 MHz pmr spectra of poly- $\beta,\beta$ -dideuterioacrylonitrile and polyacrylonitrile in  $\text{DMSO}-\text{d}_6$  at  $\sim 90^\circ$ . The spectrum of poly- $\beta,\beta$ -dideuterioacrylonitrile is practically devoid of methylene proton resonance at  $\sim 2.0$  ppm. The methine proton resonance pattern of this polymer is similar to that reported by Matsuzaki [11], indicating the resolution of pentad or higher resonances. This resonance pattern is very sensitive to temperature and will be discussed at length in a future publication.

## EXPERIMENTAL

### Perdeuteriosuccinonitrile

A mixture of succinonitrile (20.0 g, 0.25 mole),  $\text{D}_2\text{O}$  (20.0 ml), and  $\text{CaO}$  (0.3 g, 0.005 mole) was stirred vigorously at  $40^\circ\text{C}$  for 48 hr.

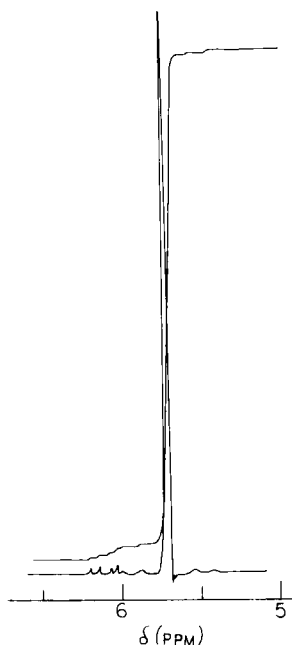


FIG. 2. 300 MHz PMR spectrum of  $\beta,\beta$ -dideuterioacrylonitrile in  $\text{CDCl}_3$  solution at room temperature.

The mixture was then evaporated nearly to dryness under reduced pressure, the bath temperature being kept below  $80^\circ\text{C}$ . The exchange was repeated five times, fresh  $\text{D}_2\text{O}$  and  $\text{CaO}$  being employed each time. The perdeuteriosuccinonitrile thus formed was purified by distillation to separate it from  $\beta$ -cyanopropionamide, mp  $93\text{--}94^\circ\text{C}$ , a higher boiling impurity that is formed during the repeated alkaline treatment. Berther reports a melting point of  $94^\circ\text{C}$  for  $\beta$ -cyanopropionamide [12].

Perdeuteriosuccinonitrile, bp  $90^\circ\text{C}/1$  Torr, solidifies to a clear waxy solid, mp  $46\text{--}49^\circ\text{C}$ . The isotopic purity of the product was determined by comparing the intensity of resonance observed at  $2.77\delta$  to that at  $1.95\delta$  in an NMR spectrum of a solution of the dinitrile and acetonitrile in  $\text{CDCl}_3$ . On this basis the isotopic purity was estimated to be 99%. Since purified perdeuteriosuccinonitrile does not readily undergo proton exchange with adventitious water, it can be stored in a stoppered flask placed in a desiccator without changing its isotopic purity. It is a good solvent for polyacrylonitrile and has considerable potential as an NMR solvent.

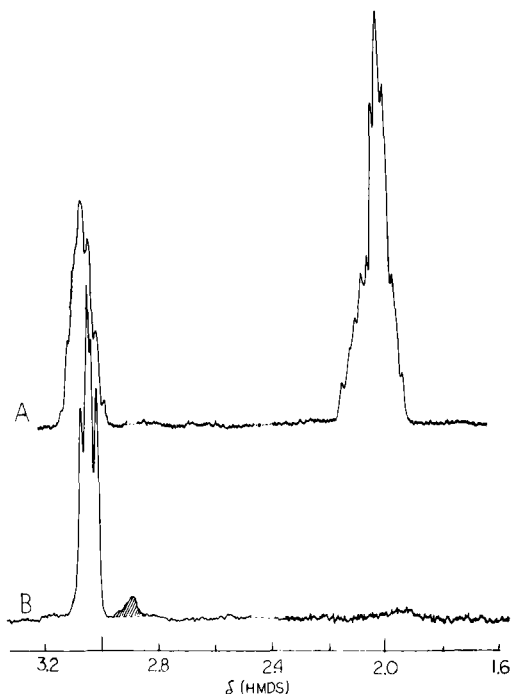


FIG. 3. 300 MHz PMR spectra of (A) polyacrylonitrile and (B) poly- $\beta,\beta$ -dideuterioacrylonitrile in  $\text{DMSO-d}_6$  solution at  $86^\circ\text{C}$ .

### Pyrolysis of Perdeuteriosuccinonitrile

Perdeuteriosuccinonitrile (9.90 g, 0.12 mole) was added dropwise (0.5 drops/sec) into a vertical stainless steel column ( $58 \times 1.25$  cm, i. d.) that was packed with 17 cm (21.0 g), of rod-type 3A Molecular Sieves and through which a stream of nitrogen passed at the rate of 2 ml/sec. The central portion of the tube, which contained the Molecular Sieves, was maintained at  $550^\circ\text{C}$ . The bottom of the pyrolysis column was connected directly to a trap that was maintained at  $-78^\circ\text{C}$ . Gases which were not collected by the trap were passed through saturated potassium hydroxide solution. The pyrolyzate (9.3 g) was a clear liquid that gradually darkened on warming to room temperature. It was analyzed by GC and found to be a mixture of unreacted succinonitrile- $\text{d}_4$ , acrylonitrile- $\text{d}_3$ , acetonitrile- $\text{d}_3$ , propionitrile- $\text{d}_5$ , and DCN. Fractional distillation



of this mixture yielded 7.2 g of a mixture of acrylonitrile- $d_3$  (57.0%), propionitrile- $d_3$  (2.1%), acetonitrile- $d_3$  (4.0%), and DCN (36.8%). To obtain pure acrylonitrile- $d_3$ , it was found best to submit the pyrolyzate to the procedure outlined below.

### Reaction of Perdeuteriosuccinonitrile Pyrolyzate with Cyclopentadiene

Pyrolyzate collected from the above procedure (9.3 g) was allowed to warm to room temperature and was then mixed with cyclopentadiene (8.73 g, 0.132 mole) that had been cooled to  $0^\circ\text{C}$ . The reaction was mildly exothermic and the mixture was stirred for 10 hr at room temperature and distilled to obtain 11.5 g (0.09 mole, 92% yield) of 2,3,3-trideuterio-5-norbornene-2-carbonitrile, bp  $55-60^\circ\text{C}/3$  Torr,  $n_D^{20}$  1.4867, NMR spectrum (neat):  $\delta$  6.0 (m,2H), 3.0 (m,2H), 1.25 (m,2H). The boiling point reported for 5-norbornene-2-carbonitrile is  $82-86^\circ\text{C}/10$  Torr;  $n_D^{20}$  1.4885 [13].

### Preparation of Perdeuterioacrylonitrile from 2,3,3-Trideuterio-5-norbornene-2-carbonitrile

2,3,3-Trideuterio-5-norbornene-2-carbonitrile (10.0 g, 0.08 mole) was dropped (0.5 drop/sec) into a  $1 \times 23$  cm vertical glass column through which nitrogen passed at the rate of 2 ml/sec. The central portion (10 cm) of the column was packed with glass helices and was maintained at  $310-330^\circ\text{C}$ . The pyrolyzate was collected in an Erlenmeyer flask that was connected to the bottom of the pyrolysis tube and was maintained at  $-78^\circ\text{C}$ . The pyrolysis product was mostly a mixture of acrylonitrile- $d_3$  and cyclopentadiene. Following the pyrolysis step, a solution of maleic anhydride (8.83 g, 0.09 mole) in bis[2-(2-methoxyethoxy) ethyl] ether (20 ml) was added to the pyrolyzate at  $-78^\circ\text{C}$ . The reaction was exothermic. The reaction mixture was then filtered to remove any solids present and distilled ( $60^\circ\text{C}$  bath, 200 – 20 Torr) to obtain pure (GC or NMR for protonated analog) perdeuterioacrylonitrile (3.62 g, 0.065 mole, 79% yield), bp  $40^\circ\text{C}/185$  Torr,  $n_D^{25}$  1.3861. The isotopic purity of the product (99%).

was estimated by comparing the intensities of the resonances observed at 5.6–6.8 $\delta$  and 3.75 $\delta$  in a spectrum of a mixture of the product and malononitrile in  $\text{CDCl}_3$ .

### Preparation of $\beta,\beta$ -Dideuterioacrylonitrile

Equal volumes of perdeuterioacrylonitrile (3.1 g, 0.55 mole) and a suspension of 5% calcium oxide in  $\text{D}_2\text{O}$  that contained 4-tert-butylpyrocatechol (2 mg) were refluxed with stirring for 5 hr. The nitrile

was distilled from the reaction mixture as its azeotrope with  $\text{H}_2\text{O}$ , bp  $30\text{--}35^\circ\text{C}/210$  Torr. After removing most of the remaining  $\text{H}_2\text{O}$  by distillation, the residue was heated to  $100^\circ\text{C}$  at 120 Torr with stirring for 3 hr to dehydrate the  $\beta,\beta$ -dideuterio- $\beta$ -hydroxypropionitrile which remained. This led to an additional quantity of  $\beta,\beta$ -dideuterioacrylonitrile. The combined nitrile samples were then exchanged once more with  $\text{H}_2\text{O}$ .  $\beta,\beta$ -Dideuterioacrylonitrile recovered from the azeotrope and the distillation residue was dried over  $\text{CaH}_2$  and distilled to obtain 1.8 g (58% yield) of the pure monomer, bp  $40^\circ\text{C}/185$  Torr.

The isotopic purity (98%) of this product was determined by comparing the intensities of resonances observed at 3.75 and 5.74 $\delta$  in the spectrum of a mixture of the product and malononitrile. In addition, comparison of the relative intensities of resonances observed at 5.73 (singlet), 6.07 (doublet) and 6.20  $\delta$  (doublet) in the spectrum of  $\beta,\beta$ -dideuterioacrylonitrile (Fig. 2) indicated the same level of isotopic purity.

### Polymerization of $\beta,\beta$ -Dideuterioacrylonitrile

A solution of  $\beta,\beta$ -dideuterioacrylonitrile (0.262 g), azobisisobutyronitrile (0.0005 g) and freshly distilled dimethyl sulfoxide (0.32 g), was heated at  $60^\circ\text{C}$  for 3 hr. The solution was then diluted with an additional ml of dimethyl sulfoxide, and the solution was poured into methanol. The polymer which precipitated was collected, reprecipitated from dimethyl sulfoxide into methanol and dried at  $50^\circ\text{C}$  in a vacuum oven for 48 hr.

NOTE ADDED IN PROOF: A procedure for preparing deuterated acrylonitriles from propiolamide has also been described recently [ 14 ].

### ACKNOWLEDGMENTS

The authors are indebted to Professor A. Guyot of Lyon University for helpful suggestions concerning the purification of perdeuterioacrylonitrile. The experimental assistance of Mr. Dan Sparks is also gratefully acknowledged. This work was supported by the National Science Foundation, Polymer Program, Grant DMR-75-19372.

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Accepted by editor May 15, 1978

Received for publication June 6, 1978