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CONDUCTIVE MATERIALS BASED ON DELOCALIZED CARBANIONS
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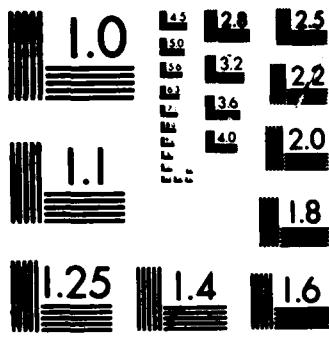
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Conductive Materials Based On Delocalized Carbanions

by

Lawrence F. Hancock and Bernard Gordon III

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Penn State University
Polymer Science Section
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<p>Studies on the perparation of organic conductors based on delocalized carbanions are presented. The synthesis of sodium and potassium diphenylmethyl anions and potassium α, α'-diphenylxlylenyl dianion. The anions were characterized by gas chromatographic analysis of protonated quench products. Preliminary DC conductivity measurements indciate a conductivity of 5×10^{-18}/cm for sodium diphenylmethyl anion. The synthesis of polyethers containing the diphenylmethyl structural unit are described.</p>			
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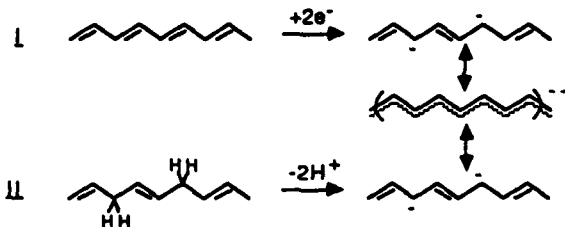
CONDUCTIVE MATERIALS BASED ON DELOCALIZED CARBANIONS

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INTRODUCTION

Organic materials which possess metal-like conductivity have long been of interest to chemists. Since 1977, when it was demonstrated that polyacetylene on treatment with a variety of electron donors or acceptors could be transformed from a semiconductor to a metal-like conductor¹, interest in polymeric conductors has flourished. Within this deluge a plethora of other polymers have been shown to be capable of metal-like conductivity upon similar treatment.

Chemically, the transformation of a semiconductive, fully conjugated polymer (such as polyacetylene) to a metal-like conductor is believed to be a simple electronic oxidation or reduction reaction.² The reductive process is shown schematically in Reaction I for polyacetylene and an electron donor as the dopant. The resulting electrically conductive material is apparently based on an extended delocalized carbanionic structural unit. Our research is based on an alternative chemistry to an equivalent delocalized carbanionic structure, as shown in reaction II.

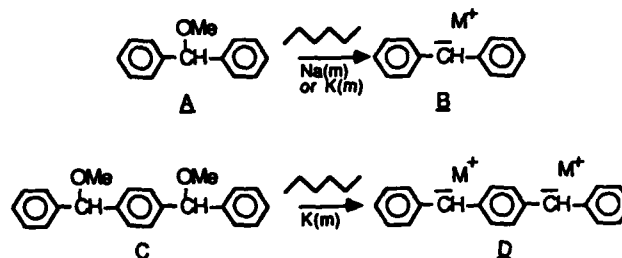


Proton abstraction from relatively acidic doubly allylic and/or benzylic methylene units is facile. The utility of strong base chemistry for the preparation of electrically conductive materials was first demonstrated through the synthesis of poly(*p*-phenylene pentadienylene) and its "doping" with *n*-BuLi.³ Tolbert et al. have also demonstrated proton abstraction doping for the preparation of doped polyacetylene.⁴

In this work we would like to present further studies on the utility of proton abstraction doping for the preparation of organic conductors, concentrating on the synthesis and properties of low molecular weight conductive anions.

EXPERIMENTAL

Synthetic schemes for the preparation of delocalized anions used in this study are outlined below.



Synthesis of Diphenylmethoxymethane (A)

Diphenylmethoxymethane was prepared through a facile two step procedure. First benzophenone was reduced with NaBH₄ to benzhydrol. Methylation was accomplished with a Williamson reaction using DMSO as the solvent, KOH as the base and MeI.⁵ (Characterization of A: bp 117-119°C @ 2mmHg, ¹H NMR δ 7.2, 10H; δ 5.1, 1H; and δ 3.2, 3H)

Synthesis of K/Na Diphenylmethyl Anion (B)

Diphenylmethoxymethane was dissolved in hexane (0.2M); to this mixture a minimum of 5eq of the appropriate metal was added. The reaction was then stirred under an inert atmosphere for 2-4 days. The anions were formed as a fine suspension in the inert solvent. These were isolated via centrifugation and subsequently washed at least 2X with hexane. The anions were then dried to a fine powder on a high vacuum line.

Synthesis of α,α' -diphenyl- α,α' -dimethoxy-*p*-xylene (C)

Compound C was prepared in a two-step reaction procedure. Initially, 2.2 equivalents of phenyl lithium was added to a THF solution of terephthalaldehyde. The bis alkoxide formed by addition to the carbonyl moieties was then methylated in situ with dimethylsulfate to form compound C (mp 78-80°C; ¹H NMR δ 7.3, 14H; δ 5.15, 2H; and δ 3.3, 6H).

Synthesis of K α,α' -diphenyl-*p*-xylenyl dianion (D)

Compound D was prepared directly by the ether cleavage reaction shown above. In excess of 5 equivalents of potassium metal was added to a 0.01M solution of C in dry cyclohexane. The mixture was stirred at RT for 2 days at which time the potassium dianion was isolated and washed with fresh cyclohexane through successive centrifugation and decantation.

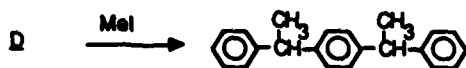
DISCUSSION

The aim of these studies is to lay the groundwork for the development of polymeric conductors based on delocalized anions. Preparation of chemically pure anions and characterization of their electrical properties are pivotal to the development of such a material. The ether cleavage reaction, described in the experimental, provides a convenient route for the preparation of chemically pure delocalized anions. Isolation of the anions is facilitated by precipitation from the hydrocarbon solvent; which are then easily dried under vacuum to a fine powder.

Chemical purity of the anions was determined by both their reactivity (methylation with MeI) and through direct analysis of the quenched anion using capillary gas chromatography. Methylation of both the Na and K diphenylmethyl anions provided 1,1-diphenylethane.



Similarly, methylation of K α,α' -diphenylxylynyl dianion yielded α,α' -diphenyl- α,α' -dimethylxylylene.

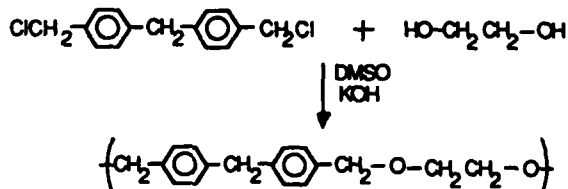


Capillary GC analysis was performed on quenched samples of the Na and K diphenylmethyl anions. Samples of the anions were dissolved in THF, quenched with *t*-BuOH, then neutralized. The samples were analysed on a Hewlett-Packard 5880 capillary gas chromatograph using a 12 meter methyl silicone column. No peaks were detected other than the expected signals for the solvents (*t*BuOH and THF) and diphenylmethane.

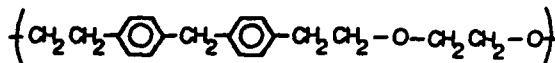
Initial studies on the electrical properties of the anions have been made by 2pt and 4pt DC conductivity measurements. Measurements have been performed using a Kiethly 617 electrometer, Kiethly 124 current source and a Kiethly 197 multimeter. In most cases measurements have been performed on pre-pressed pellets of the anions (samples were routinely pressed for 10-20mins at 10,000Kg/m² in a stainless steel KBr pellet press).

Results obtained for the Na diphenylmethyl anion tested in a linear 4pt geometry showed a conductivity of 5×10^{-1} S/cm. However, at this point the affect of a minute amount of residual Na metal has not been discerned. The K diphenylmethyl anion exhibited a more complex behavior. Prepressed pellets of the anion were very resistive ($>G\Omega$). However under a pressure of 2,000Kg/m² resistivities as low as 10-15K Ω have been noted. A more detailed evaluation of this behavior is being undertaken.

Preparation of polymer supported delocalized anions is proceeding concurrently with our studies of isolated anions. A Williamson ether condensation polymerization has been utilized for the preparation of a polyether possessing a diphenylmethyl structural unit (shown below).



Structural confirmation of the polyether was obtained from ¹H NMR. Gel permeation chromatography of the material indicated a polystyrene equivalent molecular weight of 2000amu. Treatment of a THF solution of the above polyether with *n*-BuLi yielded a deep blue solution, apparently indicating anion formation. However, the color began to dissipate within 5mins, presumably due to cleavage of the labile benzyl ether linkage. Our current synthetic target is compound E, which should eliminate this concern.



E

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