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Carlons: Organic Oligomers from Condensation of Carbon Dinucleophiles with Difunctional Derivatives of Carboxylic Acids[1]

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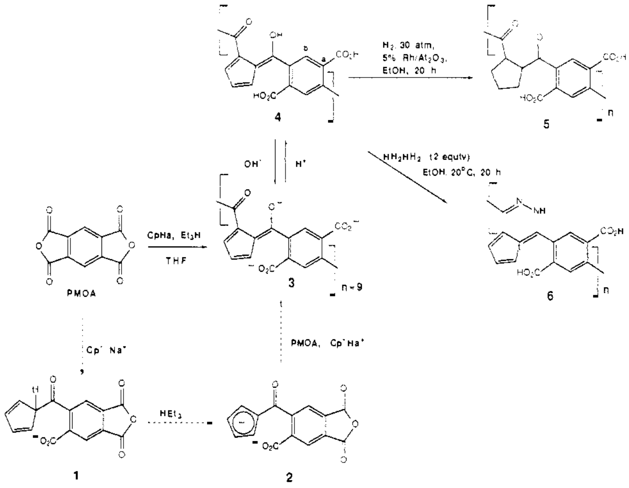
A substantial fraction of the polymers used in large scale are synthesized by reaction of nitrogen- or oxygen-containing dinucleophiles (diamines or diols) with dicarboxylic acids or derivatives of them (anhydrides, acid halides, esters, isocyanates).[2] Here we report reactions of *carbon*-centered dinucleophiles (both latent dinucleophiles such as cyclopentadienide anion, indenyl anion and analogues, and actual dinucleophiles such as bisacetylides) with the same classes of difunctional carbonyl compounds that lead to oligomers. Because these oligomers are carbon analogues of nylons—that is, they are condensation oligomers having carbon–carbon rather than carbon–nitrogen bonds joining the monomer units—we call them "carlons" as a class. Scheme I illustrates a representative reaction, with use of cyclopentadienide (Cp^-) and pyromellitic dianhydride (PMDA).[3-7]

Initial reaction of CpNa and PMDA probably yields **1** as a transitory intermediate.[3-7] Deprotonation of **1** or an isomer by triethylamine generates **2**, which reacts in turn with another anhydride moiety. We have not determined the regiochemistry of the second addition of a nucleophile to PMDA: we write the product having para carboxylate groups on the basis of ^{13}C NMR spectroscopic data,[8] but the meta isomer is probably also present. Oligomer **4** can be isolated in protonated form as a dark orange-brown solid in nearly quantitative yield by treating the reaction mixture with HCl.[9] The form of **4** having CO_2H groups is soluble in THF, ethyl acetate, alcohols, and other organic solvents but insoluble in water at pH 7; **4** readily dissolves in water at pH > 8 as a polyanion **3**.[10] Because the molecular weights of the materials prepared so far have been low, the solutions are not viscous.

Scheme I. A Sequence of Reactions Used To Prepare Carlon 4 and To Form Derivatives of It



We have surveyed a number of reactants for formation of carlons: as nucleophiles, cyclopentadienylsodium, indenylsodium, 1,3-(diethynyllithium)benzene (**7**), and 1,9-decadiynyllithium (**8**); and as electrophiles, PMDA, 3,3′,4,4′-benzophenone tetracarboxylic anhydride (BTDA), terephthaloyl chloride (**9**), adipoyl chloride (**10**), diethyl carbonate (**11**), and toluene 2,4-diisocyanate (TDI). We have not examined all of the possible combinations of these reactants, but we have successfully obtained soluble oligomers from Cp^- with PMDA, BTDA, **9**, **10**, and **11**, from Ind^- with PMDA and BTDA, and from **7** or **8** with PMDA. Preliminary evidence indicates that Ind^- gives 1,3-disubstituted fulvenes[11] and that acetylenic ketones are an important functionality present in the products of reaction of **7** and **8** with anhydrides.[12] Reactions of CpNa with **11** in THF in the presence of NEt_3 produced brown oligomers that were insoluble in organic solvents but dissolved in water at pH 9.

These materials have attractive physical properties. Most are soluble in water and/or common organic solvents and should, as a result, be easily processed. The oligomers from Cp^- and PMDA or benzophenone tetracarboxylic dianhydride (BTDA), for example, formed clear, dark yellow solutions in THF and could be cast into thin films and pulled into fibers from these solutions. The oligomer from indenylsodium and PMDA formed a yellow solution in water at pH 8 but reversibly changed to an intense green at pH 10. Heating solution-cast thin films of **4** in air at 300 °C produced tough, dark, clear materials that were no longer soluble in THF or other organic solvents. DSC and TGA indicated that **4** lost water in successive stages but retained 50% of its mass on heating to 800 °C in argon.

The array of functionality present in many of these oligomers offers obvious opportunities for further modification. Thus, for example, **4** is readily hydrogenated, probably with formation of **5**.[13] Treatment of **4** with hydrazine gives another new material with a composition we propose to be **6**, based on analogy with reactions of simpler molecules.[4,14]

Polymers that incorporate a high proportion of aromatic units into their backbone (polyimides, PEEK, poly(phenylsulfide),

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[2] Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, 1981.

[3] Reactions of CpNa with carboxylic acid chlorides give high yields of 1,2-disubstituted fulvene enols.[4-7]

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[8] The ^{13}C NMR spectrum of **4** (pH 9) shows signals at δ 176.7, 156.2, 138.3, 137.9, 136.8, 133.1, 128.9, 127.5, 127.4, 126.8, 136.4, 126.1. The two strong signals at δ 138.3 and 126.1 are tentatively assigned to carbons a and b, respectively (Scheme I).

[9] In a typical synthesis, sublimed 1,2,4,5-benzene tetracarboxylic anhydride (pyromellitic dianhydride, PMDA) (2.7 g, 12 mmol) dissolved in 100 mL of THF was treated with triethylamine (2 mL, 15 mmol, distilled from calcium hydride) and cooled to 0 °C. Cyclopentadienylsodium (CpNa, 2.15 M in THF, 5.8 mL, 12 mmol) was added over 0.5 h. After overnight stirring and warming to ambient temperature, the dark brown solution was added to 300 mL of 0.25 M aqueous HCl and stirred until the oligomer agglomerated. The aqueous solution was decanted, and the oligomer was dissolved in THF and dried over sodium sulfate. Residual THF was removed by rotary evaporation. The oligomer was ground to a fine powder, washed with 500 mL of water in 100-mL portions, and dried over P_2O_5 at 110 °C ($<10^{-2}$ Torr). This procedure yielded 2.8 g (87%) of dark brown granular solid. Anal. Calcd for $C_{15}H_8O_6$: C, 63.39; H, 2.84. Found: C, 63.55; H, 2.69. Gel permeation chromatography (THF, room temperature) was not successful because the oligomer gelled in the column. Size exclusion chromatography (Springborn Testing Institute; THF, room temperature, polystyrene reference) of a methylated sample (prepared by reaction of **3** with diazomethane in diethyl ether at 0 °C) showed major peaks at 2610 (DP = 9), 586 (DP = 2), and 285 (DP = 1). Individual peaks at intermediate values of retention time due to other oligomers were not resolved.

[10] The pK_a of 6-hydroxy-2-formylfulvene is 4.5 and that of 6-hydroxy-2,4-diformylfulvene is 1.8: Hafner, K.; Koenig, C.; Dreuder, M.; Ploss, G.; Schulz, G.; Sturm, E.; Voepel, K. H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 123–134.

[11] The anion regenerated after the initial reaction of indenylsodium with the anhydride is expected to be most nucleophilic at the 3 position, see: Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillan: New York, 1981; pp 1036–1037.

[12] The material obtained from 1,3-(diethynyllithium)benzene (**7**) and PMDA had IR 2200, 2220, 1690–1720 cm^{-1}; that from 1,9-decadiynyllithium (**8**) and PMDA had IR 2190, 1680–1720 cm^{-1}.

[13] A 0.5-g sample of **4** dissolved in 50 mL of 5:1 ethyl alcohol/glacial acetic acid was treated with 20 mg of 5% Rh on alumina, pressurized to 30 atm with H_2, and stirred magnetically at room temperature for 20 h. ^{13}C NMR signals (20 °C, D_2O, pH 9) tentatively assigned to the cyclopentadiene segment at δ 136.8, 128.9, 126.8, and 126.4 disappeared on hydrogenation and were replaced by signals at δ 27.9, 30.2, and 44.6 (cyclopentyl).

[14] UV spectroscopy of a very dilute aqueous solution of **5** showed a strong absorbance at 208 nm; see: Anderson, A. G., Jr.; Fowkey, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 924–927.

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poly(phenylcarbonate)) often show useful combinations of high thermal stability and strength but may be difficult to form and process.[15] Polymers having all-carbon backbones usually have high hydrolytic stability. The structures of the carlons can be tailored to impart both stability and processability. They are easily formed from readily available precursors and their residual functionality provides the basis for post-synthetic modification and for cross-linking. At present, the reactions described here provide linear oligomers having molecular weights most suitable for use as prepolymers in thermosets and related materials, and a significant improvement in per-step yield will be required to achieve high mw linear polymers. Efforts to achieve this improvement are in progress.

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(15) *Polyimides: Synthesis, Characterization, and Applications*; Mittal, K., Ed.; Plenum Press: New York and London, 1984; Volume 1.

Insertion Reactions of Chromium-Carbene Complexes with Organic Nitriles and a Diastereoselective Alkylation of a Resulting Imino-Carbene Complex

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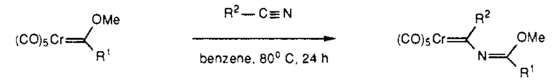
The reaction of Fischer carbene complexes of the group 6 metals with acetylenes has become a reaction of demonstrated importance in synthetic organic chemistry.[2] The reaction of the phenyl complex **1** with alkynes produces naphthol complexes where the newly formed benzene ring incorporates the acetylene in the C-2 and C-3 positions of the naphthalene ring. The study of the reactions of heteroatom-stabilized carbene complexes with other triply bonded functional groups has been limited to the carbon-nitrogen triple bond of cyanamides,[3] cyanates,[4] and thiocyanates[4] which react rapidly to give insertion products of the type **3** rather than heteroaromatic products as might be anticipated from their reaction with acetylenes. Nonetheless, the imino complexes **3** are potentially useful reagents for organic synthesis although at the present time the range of complexes that are available is rather limited. We wish to report that organonitriles undergo facile insertion into the metal-carbon bond of heteroatom-stabilized Fischer carbene complexes, the first observation of a reversible insertion of a nitrile, and the first stereoselective reaction of an imino complex in which the stereodifferentiation is a consequence of a chiral center arising from the allenic nature of the C–N–C linkage in these complexes.

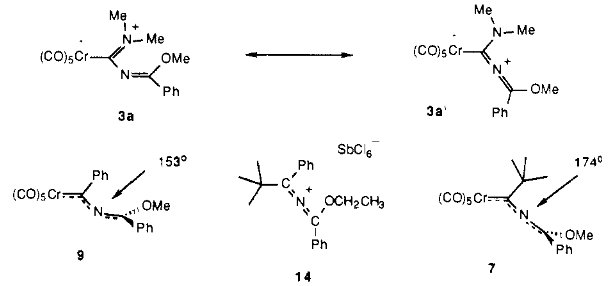
Table I. Insertions of Organonitriles into Complexes **1** and **12**[a]

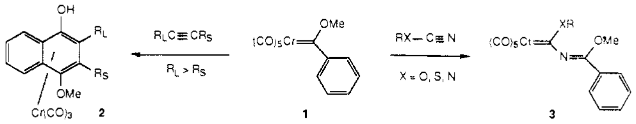


R^1	R^2	insertion product	% yield	% recov of starting complex	tot mass balance
		Starting Complex **1**			
Ph	Me	**4**	36 (54[b])	38	74
	n-Pr	**5**	51	31	82
	i-Pr	**6**	73	9	82
	t-Bu	**7**	31 (53[c])	34	65
	CH_2Ph	**8**	72	7	79
	Ph	**9**	85	0	85
	p-$MeOC_6H_4$	**10**	93[d]	0	93
	2-furyl	**11**	92	0	92
		Starting Complex **12**			
Me	Ph	**13**	68[e]	–	–

[a] Unless otherwise specified all reactions were carried out at 0.13 M in **1** or **12** in benzene with 14 equiv of nitrile at 80 °C for 24 h under an argon atmosphere. [b] 10 equiv of nitrile, 5 days. [c] 5 equiv of nitrile, 5 days. [d] 2.4 equiv of nitrile, 4 days. [e] 3 equiv of nitrile, 38 h.

Scheme I





A variety of imino complexes can be made in moderate to excellent yields from both aliphatic and aryl nitriles. The typical procedure indicated in Table I involves heating the (pentacarbonyl)chromium-carbene complex with excess nitrile in benzene at 80 °C for 24 h. In the case of acetonitrile and 2,2-dimethylpropiononitrile slightly better yields can be obtained with longer reactions times. Successful insertion reactions include those with aryl- and alkyl-substituted carbene complexes. The mass balance of these reactions is quite good, and in none of these reactions could we isolate and identify any compound derived from an annulation reaction of the type observed with acetylenes. Imino complexes bearing a carbon substituent on the carbene carbon (R^2) have been reported as products in a few unrelated reactions,[7] but the insertion of organic nitriles into heteroatom-stabilized complexes has not been previously reported. A recent account[8] describes the insertion reactions of organonitriles into a nonstabilized complex (diphenyl), and it has been reported that the reaction of this same complex takes a different course with silyl nitriles.[9b]

The solid-state structures of a few complexes derived from the insertions of cyanamides,[3a,c] cyanates,[7a] and thiocyanates[4] have

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