

ANODIC ADDITION OF GRIGNARD-REAGENTS TO OLEFINS¹⁾

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The combination of a redox-process with a chemical reaction offers new perspectives for constructing organic syntheses. The scope of conventional synthesis is often limited by the fact that a) a specific reagent can be used only for a single reaction type, e. g., anions can be applied in nucleophilic but not in radical or electrophilic reactions, and b) a reagent and a substrate of equal polar reactivity, e. g., a nucleophile and an electron-rich olefin, normally cannot be joined. With a redox-process preceding the chemical reaction it should be possible to change the reactivity of a reagent while retaining its structure, which would lift these limitations. E. g., anions could be utilized not only in nucleophilic, but by prior 1e- or 2e-oxidation also in radical or electrophilic reactions; two electrophiles might be joined reductively via radicals or a nucleophile as intermediates.

Electrolysis seems best suited to exploit these possibilities. The electrode is simultaneously a selective and a universal redox-reagent applicable for both mildest and most vigorous redox reactions. Electrode materials such as platinum or graphite are chemically nearly inert, thus suppressing unwanted side reactions. Parallel reactions subsequent to electron transfer can be controlled via current density²⁾, electrode potential³⁾ or composition of the electrical double layer at the interface⁴⁾.

We have made synthetic use of combining a redox process with a chemical reaction in anodic coupling of olefins⁵⁾ and in anodic addition of anions to olefins⁶⁾. In order to extend the preparative scope of anodic addition from stable anions to reactive anionic precursors with conjugate acids in the pK_A -range 20-45, we thought the use of metalorganic reagents might be profitable. Here the carbanion reactivity is reduced due to a partial homopolar bond between carbon and metal, thus suppressing unwanted anionic side reactions with the solvent or functional groups in the substrate. Grignard-reagents seemed convenient: they can be prepared quickly and in high yields; experimental experience on anodic coupling is available⁷⁾; they supply a very broad variety of alkyl- and aryl-groups for anodic addition.

Usually solutions (250 ml) of Grignard-reagent (0,2 Mol), the corresponding alkylbromide (0,2 Mol), lithium-perchlorate (0,1 Mol) and olefin in diethylether were electrolyzed

between platinum-, graphite- or copper electrodes at current densities of 10 mA/cm^2 in a flow cell without diaphragm until 0,1 to 0,15 F had been consumed. Alkylbromide was added to dissolve the magnesium deposits at the cathode, there by preventing the electrodes from bridging and causing short circuits. In this way a constant concentration of Grignard-reagent was also maintained which allowed constant current electrolysis without potentiostatic control. The adducts obtained are tabulated below :

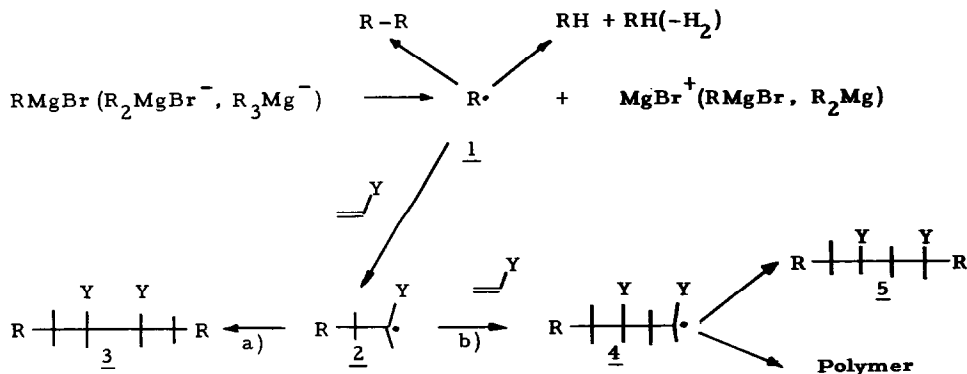
Nr.	R-Mg-Br R-	Olefin	Electrode	Product ^{a)}	Yield ^{b)}
1.	n-Butyl	Styrene(0, 7) ^{c)}	Pt	6, 8-Diphenyldodecane 6, 7-Diphenyldodecane	10% 5%
2.	n-Butyl	Styrene(2, 0)	Pt	Polymer (2500) ^{d)}	2, 6 g/Ah
3.	n-Butyl	Styrene(0, 7)	Cu	6, 7-Diphenyldodecane	29%
4.	tert. Butyl	Styrene(0, 7)	Cu	4, 5-Diphenyl-2, 2, 7, 7-tetra- methyloctane	14%
5.	n-Butyl	Butadiene (2, 0)	Cu	6, 7-Divinyl-dodecane 6-Vinyl-8-tetradecene 6, 10-Hexadecadiene 6-Dodecene	3% 15% 15% 7%
6.	n-Hexyl	Butadiene(2, 0)	Cu	8-Vinyl-10-octadecaene 8, 12-Eikosadiene 8-Hexadecene	8% 11% 6%
7.	Phenyl	Vinylethylether (4, 2)	Pt	Polymer (1040)	11g/Ah

a) all new compounds are characterized by C, H-analysis, IR-, NMR- and mass-spectra ;

b) current yield ; c) molarity ; d) average molecular weight .

The formation of the products is rationalized as follows :

The species RMgBr , R_2MgBr^- or R_3Mg^- are oxidized anodically to yield alkyl-radicals (1) ⁸⁾. These dimerize ⁷⁾, disproportionate ⁷⁾ or add to styrene or butadiene to form substituted benzyl - or allyl-radicals (2) .



Dimerization of 2 (path a) affords 3. The isomeric C 16- and C 20-dienes (Nr. 5, 6) are formed by 1, 1' -, 1, 3' - and 3, 3' -coupling of the allylradical 2. According to the product ratio, coupling in the 1-position occurs 5 to 11 times faster than in the 3-position. With higher concentrations of readily polymerizable olefins (e. g., styrene, vinylethylether) formation of 3 is suppressed and polymerization is initiated (path b)(Nr. 2, 7). Coupling of the oligomer 4 with 1 yields head-to-tail-dimers (5) (Nr. 1). From the product ratio at different electrodes the following preliminary conclusions can be drawn: polymerization is favored at pyrolytic graphite; at platinum the dimers 3 and 5 are formed non-specifically in low yields; at copper exclusively additive dimers 3 are obtained in moderate to fair yields, which indicates that possibly copper-alkyls are functioning as intermediates in the electrode process⁹⁾. The effect of transition-metal coated electrodes is under investigation.

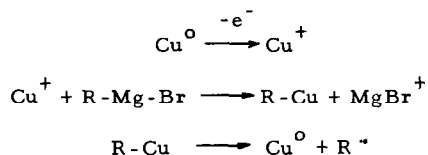
Thus the anodic addition of Grignard reagents to olefins affords at copper-electrodes a specific, one-step synthesis of complex hydrocarbons from four subunits. These can be selected from a broad variety of olefins and Grignard reagents. By proper variation of current density and olefin concentration possibly controlled telomerization to yield telomers with distinct chain length can be achieved.

We are currently attempting to extend the preparative scope of this addition by applying other Grignard reagents and metalorganic compounds.

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- 9) An indirect electrolysis is conceivable :



Reacting CuBr with n-Butyl-magnesiumbromide in the presence of styrene

K. Ziegler, E. Eimers, W. Hechelhammer and H. Wilms, Liebigs Ann. Chem. 567, 43 (1950), obtained the additive dimer 6,7-diphenyldodecane in low yield .