

ANODIC MIXED COUPLING OF OLEFINS ¹⁾

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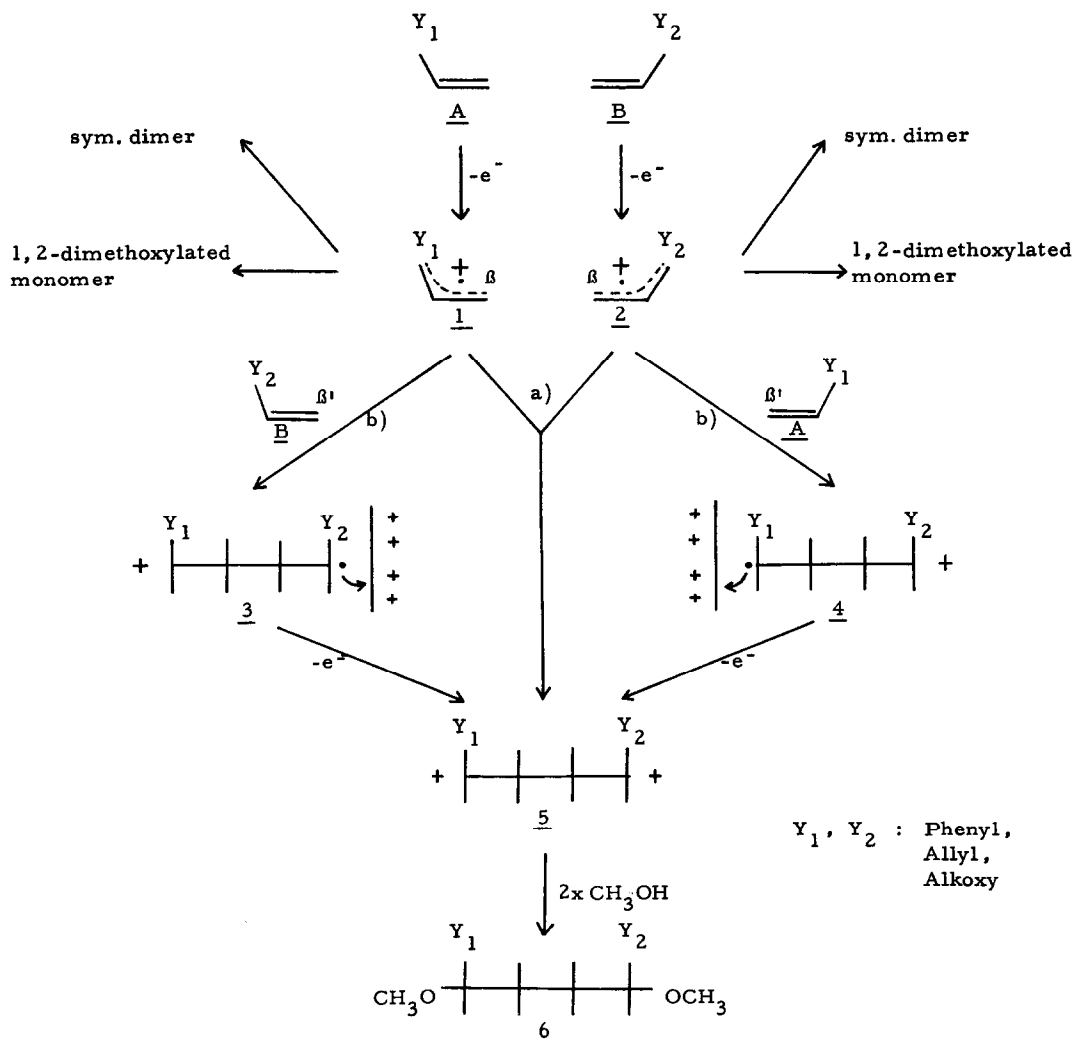
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Arylolefins ^{2, 3)}, butadiene ^{2, 4)} and enolethers ^{2, 5)} can be dimerized anodically. We have now obtained mixed coupling products on coelectrolysis of two different olefins together with symmetrical dimers and 1,2-dimethoxylated monomers. For that purpose olefin mixtures were electrolyzed at current densities of 12.5 to 25.0 mA/cm², anode potentials of +0.8 to +1.6 V (versus Ag/AgCl) and temperatures between -15° and -30° C in a flow cell without diaphragm in methanol-sodiumiodide or -sodiumperchlorate as solvent supporting electrolyte between graphite electrodes. The yields of mixed coupling products are given below :

Nr.	Olefin A	Olefin B	Mixed Dimer ^{a)}	Yield	
				% ^{b)}	% ^{c)}
1	Styrene (0.09 M) ^{d)}	Vinylethyl- ether (0.62 M)	1,4-Dimethoxy-4-ethoxy- 1-phenylbutane	30	55
2	Styrene (0.026 M) (0.085 M) ^{e)}	Butadiene (0.63 M)	1,4-Dimethoxy- 1-phenyl-5-hexene trans-1,6-Dimethoxy 1-phenyl-4-hexene	22	
3	α -Methyl- styrene (0.15 M)	Vinylethyl- ether (0.54 M)	1,4-Dimethoxy-1-ethoxy- 4-phenylpentane	32	
4	α -Ethoxy- styrene (0.17 M)	Vinylethyl- ether (0.62 M)	1,1,4-Trimethoxy-4- ethoxy-1-phenylbutane 1,1,4,4-Tetramethoxy- 1,4-diphenylbutane ^{f)}	17	45 54

a) symmetrical dimers were isolated in 7% to 21% current yield; those reported earlier²⁾ are omitted from the table; all products were characterized by IR- and NMR-spectra and elemental analysis of the compound or a derivative; b) current yield; c) yield based on consumption of olefin A; d) moles in 200 ml electrolyte; e) steadily added during electrolysis; f) symmetrical dimer.

The products may be rationalized as follows:



1 e-oxidation of the olefins A and B yields the radical cations 1 and 2 as first intermediates. These couple to symmetrical or unsymmetrical (5) dications (path a) and /or form symmetrical or unsymmetrical (3,4) 1,4-radical-cations by electrophilic addition to the same or the co-olefin (path b). 1 e-oxidation of the radical site in 3,4 yields 5, which solvolyzes to product 6. Both pathways lead to tail-tail dimers. Dimerization (path a) is favored at the positions of highest free valence: the β -carbon of 1 or 2. Electrophilic addition (path b) occurs predominantly at the sites of highest charge density and lowest atom-localization-energy: the β - and β' -positions in 1, 2 and A, B. The ratio of mixed to symmetrical dimer appears to be dependent on a set of yet unknown parameters: e. g., relative oxidation potentials of the olefins, relative olefinconcentrations at the electrode-electrolyte interface, which are determined by adsorption and relative olefin-monomer reactivities towards electrophilic addition. Without such data at hand current yields were optimized by proper empirical change of the olefin mixtures in two examples. In Nr. 1 the current yield was raised from 20% to 30%, in Nr. 2 from 8% to 22% in three runs. The yields based on consumption of the minor component are generally good.

Mixed coupling considerably broadens the synthetic applications of anodic olefin dimerizations. E. g., by use of enoethers as one component, the carbonylmethyl-group can be introduced into olefins to afford aldehydes (Nr. 1, 3) or unsymmetrical 1,4-dicarbonylcompounds (Nr. 4); with butadiene as the co-olefin, addition of the C_4H_6 -unit to double bonds is possible (Nr. 2).

We are currently exploring the preparative scope of these unsymmetrical couplings in greater detail.

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