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STEREOCHEMISTRY OF PHENYLDIIMIDE ADDITION TO PHENYLACETYLENE

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Recent studies of the hydrazine oxidation product diimide (H-N=N-H) (1) have demonstrated a one-step cis-hydrogenation of carbon-carbon double and triple bonds. Aryldiimides, which are believed to be formed by the oxidation of arylhydrazines and by the ethanolysis of N-phenyl-N'-carbethoxydiimide and N-phenyl-N'-benzoyldiimide (2), decompose to radicals which arylate aromatics, attack solvent, initiate the polymerization of acrylonitrile, and add to the C=C bond of fumaric acid (2). Since diimide does not attack the aromatic ring it is reasonable to assume that phenyldiimide also does not, and that decomposition to phenyl radicals must precede aromatic phenylation. The addition to carbon-carbon multiple bonds is less straightforward; either a one-step cis-addition, or a decomposition to radicals followed by radical addition seems possible.

We have, therefore, examined a system (phenylacetylene) in which the two mechanisms would have different stereochemical consequences. A one-step cis-addition of phenyldiimide should yield trans-stilbene exclusively (no 1,1-diphenylethylene, the product of reverse addition is observed experimentally), whereas phenyl radical attack should give a mixture of cis- and trans- stilbene, with some steric preference for the former in the subsequent hydrogen atom addition or abstraction step by the 1,2-diphenylvinyl radical.

Treatment of 0.05 mole portions of phenylhydrazine and phenylacetylene with a 10% excess of silver oxide in ethanol at room temperature gave a 12% combined yield of stilbenes (estimated by capillary g.c.; yield isolated by preparative g.c., 7%), with a cis/trans ratio of about 4. Unchanged phenylacetylene, biphenyl, and benzene are also present. Under these conditions the reaction must involve largely or entirely a radical addition.

Other hydrazines and unsaturated compounds react under similar conditions. Phenylhydrazine and 1-octene with silver oxide in ethanol give a 5% yield (isolated) of 1-phenyloctane (about 2% of biphenyl is also obtained). The conditions used are almost certainly not the optimum ones. Small-scale experiments were carried out from which the products have been tentatively identified by comparison of capillary g.c. retention times with those of authentic samples of the products and the possible isomeric products of reverse addition: ethyl carbazate and 1-octene yield ethyl nonanoate; benzhydrazide and 1-octene (in ethanol) give nonanophenone, ethyl benzoate, and benzaldehyde; formylhydrazine and 1-octene give octane; and phenylhydrazine and ethyl acrylate give biphenyl, ethyl β-phenylpropionate, and ethyl α-phenylpropionate. All of these products are consistent with the formation of radicals and their subsequent reactions.

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