Results and Discussion. – The general route for the synthesis of nonsymmetrically substituted mixed aryl-aryl′-, aryl-benzyl-, and alkyl-aryl viologens is depicted in *Scheme 1*, *Route I* and *II*. Double activation of 4,4′-bipyridine *via N,N′*-bis(2,4-dinitrophenyl)-4,4′-bipyridinium (*Route 0* in *Scheme 1*, corresponding to the traditional route for symmetrically substituted arylviologens) is not suitable, because the conversion of bis(2,4-dinitrophenyl)bipyridinium with a stoichiometric amount of a benzenamine derivative yielded always mixtures in our hands. However, the introduction of nonsymmetry is possible by *Route I* and *II via* mono(2,4-dinitrophenyl)bipyridinium **1**, a compound described earlier by *Hünig* [17]. Thus, all the syntheses described in the following start from the key intermediate **1**. According to *Route II*, this compound is first alkylated or benzylated at the free N-atom and then treated with benzenamine derivative. Alternatively, **1** is benzenamine-exchanged according to *Route I* and then either alkylated/benzylated (*Route Ib*) or phenylated and benzenamine-exchanged (*Route Ia*). The latter route opens a way to nonsymmetric diaryl-substituted viologens.

Nonsymmetric Diaryl Viologens via Route Ia. Using the key intermediate mono-(2,4-dinitrophenyl)bipyridinium **1** as a common starting material, we prepared the monoarylbipyridinium salts **2**–**10** (*Scheme 2*). The exchange of the 2,4-dinitroaniline moiety by the corresponding aromatic amines occurred smoothly under standard conditions (aq. EtOH at 80°, 24 h) in 52–88% yield, except for the preparation of **4** and **5** with 4-aminobenzoic acid and 4-aminobenzenesulfonic acid in which case a stoichiometric amount of Et_3N was used to prevent protonation of the aromatic-amine moiety. For the preparation of nonsymmetric diarylviologens **14**–**20**, we tried the traditional reagent 2,4-dinitrophenyl chloride, but only minor yields (*ca.* 20–30%) were obtained. The same unsatisfactory yields were observed with the corresponding fluorides and bromides, but using 2,4-dinitrophenyl 4-methylbenzenesulfonate, we found acceptable yields in the range of 30–60% [18][19]. Purification of the products was crucial and most easily performed by counter-ion-induced precipitation, making use of the fact that the dicationic viologens are H_2O-soluble and insoluble in organic solvents in the presence of halide counterions, but insoluble in H_2O and soluble in certain organic solvents as hexafluorophosphates. The exchange of the dinitrophenyl substituent was then achieved with a series of aromatic amines yielding the products **21**–**26** in yields of 50–80%.

Nonsymmetric Aryl-benzylviologens via Route Ib. In two exemplary reactions, we prepared compounds **11** and **12**, *i.e.*, asymmetrically aryl-benzyl-substituted viologens in yields of 50–70%. The synthetic route diverges from *Route Ia* after introduction of the first aryl group. The nucleophilicity of the second N-atom in **9** and **10** is sufficient for the complete conversion with benzyl bromides. The same *Route Ib* is probably also applicable to the synthesis of mixed alkyl-aryl-viologens; however, this class of compounds were prepared according to *Route II* in this work.

Nonsymmetric Alkyl-arylviologens via Route II. This route was followed mainly for the preparation of aryl-(phosphonoalkyl)viologens which were synthesized because of their excellent coordinating abilities towards mesoporous TiO_2 electrodes [13]. The synthesis started with the key intermediate. The monocationic bipyridinium salt reacted smoothly with diethyl (1-bromoethyl)phosphonate. After exchange of the 2,4-dinitrophenyl group by a series of *p*-substituted anilines in aq. EtOH, followed by hydrolysis in 50% HCl/EtOH, **28**–**34** were obtained. The synthesis is exemplified