important to gain insight into polymerization processes which hamper the synthesis of molecular phosphorus suboxides. A comparative study of phosphorus suboxides and phosphorus subsulfide is underway.

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[1] H. Novottnick, R. Blachnik, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1966, and references therein.

[2] J. Pelouze, *Ann. Chim. Phys.* **1832**, *50*, 83.

[3] L. Andrews, R. Withnall, *J. Am. Chem. Soc.* **1988**, *110*, 5605.

[4] S. A. Jarret-Sprague, I. H. Hillier, I. R. Gould, *Chem. Phys.* **1990**, *140*, 27; L. Lohr, *J. Phys. Chem.* **1990**, *94*, 1807; L. Lohr, *J. Phys. Chem.* **1990**, *94*, 4832.

[5] For the simulated annealing procedure[14] we used the Monte Carlo method[15] combined with the PM3 approach.[16] Test calculations have shown that PM3 is able to predict reasonable estimates for the geometrical parameters also for P_4O_n isomers that possess unusual bonding.

[6] The DFT computations were performed with the B3LYP functional[17] in connection with an AO basis of double zeta plus (DZP) polarization quality.[18] The second step of our procedure is necessary because for phosphorus suboxides the PM3 method gives reasonable geometries but fails in the prediction of reliable heats of formation.

[7] For the refinement of the geometries an analytical gradient optimization were used. These computations were performed by employing the DFT approach described in reference [6]. Bond lengths obtained from second-order perturbation theory (second-order MBPT theory[19]) differ by less than 0.01 Å.

[8] To test the accuracy of the DFT approach we performed CCSD(T) computations in conjunction with the DZP AO basis for selected systems. In addition we checked the basis set dependency of the B3LYP functional. Both computations point to an error bar of about 3 $\text{kcal}\,\text{mol}^{-1}$ for the relative energies of the various isomers. Furthermore the DFT approach always predicted the same energetical ordering as the more sophisticated CCSD(T) method. In addition we found that the DFT calculations predict the correct energetical ordering for the isomers of P_4S_6 and P_4O_6.

[9] The explicit geometrical data can be obtained from the authors.

[10] M. Haeser, O. Treutler, *J. Chem. Phys.* **1995**, *102*, 3703.

[11] The energy difference between both isomers increases to about 8 $\text{kcal}\,\text{mol}^{-1}$ if the more sophisticated CCSD(T) method is employed. Using a more flexible AO basis (triple zeta quality plus two polarization functions) combined with the DFT approach gave an energy difference of about 6 $\text{kcal}\,\text{mol}^{-1}$.

[12] J. Clade, F. Frick, M. Jansen, *Adv. Inorg. Chem.* **1994**, *41*, 327.

[13] The heats of formation were obtained from the reaction energy of the reaction $P_4+\frac{n}{2}O_2\rightarrow P_4O_n$. All computations were performed on the level described above.[6] The influence of the nuclear motion and temperature effects were incorporated in the standard approach.[19]

[14] *Adaption of Simulated Annealing to Chemical Optimization Problems* (Ed.: J. H. Kalivas), Elsevier, **1995**.

[15] J. P. Valleau, S. G. Whittington in *Modern Theoretical Chemistry, Vol. 5* (Ed.: B. J. Berne), Plenum, New York, **1977**.

[16] J. J. P. Stewart, *QCPE Bull.* **1985**, *5*, 2823.

[17] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[18] H. Huzinaga, *Approximate Atomic Wave Functions, Vol. 1+2*, University of Alberta, **1971**; A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639.

[19] F. Jensen, *Introduction to Computational Chemistry*, Wiley, Chichester, **1999**; J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc., Pittsburgh, PA, **1993**.

Alkylating Polymers: Resin-Released Carbenium Ions as Versatile Reactive Intermediates in Polymer-Assisted Solution-Phase Synthesis**

Jörg Rademann,* Joachim Smerdka, Günther Jung, Philipp Grosche, and Dietmar Schmid

Dedicated to Professor Ivar Ugi
on the occasion of his 70th birthday

Although combinatorial chemistry was dominated by solid-phase synthesis during its first decade,[1, 2] the solution-phase synthesis remains to show indisputable advantages, for example, in respect to the versatility of reactions applicable and the accumulated knowledge of synthetic protocols. Ideally, a synthetic strategy should be able to combine these merits with the advantages of solid-phase synthesis protocols, such as the possibility to use reagents in high excess, to remove them by filtration, and to employ automated multiple synthesizers. This combination can be realized in polymer-assisted solution-phase (PASP) synthesis either by using scavenger resins or by the implementation of polymeric reagents.[3–5] Especially desirable is the substitution of chemicals which are highly toxic, explosive, or difficult to handle during preparation, reactions, work-up, waste disposal, and in large amounts. Many alkylating agents, such as diazoalkanes, sulfate esters, sulfonate esters, and alkyl halogens belong to this group of hazardous compounds.[6] Solid-supported sulfonate esters have been employed in alkylations of amines and thiols at elevated temperatures under basic conditions.[7]

Elemental nitrogen is an excellent leaving group in alkylations. Therefore we focused our efforts on introducing a novel concept of alkylating polymers based on the release of carbenium ions and nitrogen from precursors bound to insoluble polystyrene gels. The alkylating species are generated from solid-phase-bound 3-alkyl-1-aryltriazenes under acidic conditions and we demonstrate their use as very reactive, mild, and versatile alkylation reagents.[8] The chemistry and applications of triazenes have a long history dating back to the 19th century.[9, 10] Their alkyl derivatives are stable entities unless treated with acid.[11–14] They fragment into radicals when moderately heated,[15] under irradiation[15] or by one-electron oxidation.[16]

Electron-rich triazenes have higher reactivity,[17] and therefore *para*-alkoxy-substituted anilines were selected as efficient starting materials. Solid-supported triazenes have been

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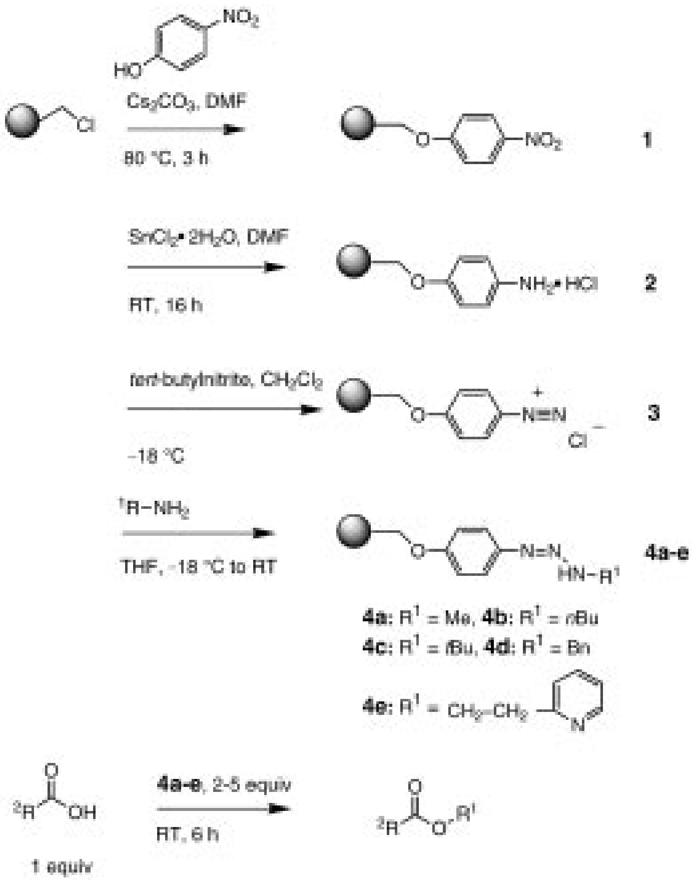
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

prepared by two research groups.[13, 14] We developed a modified procedure (Scheme 1) via the solid-phase bound nitroarene **1**, which was reduced to the polymeric ammonium hydrochloride **2**. The best results in the diazotation reaction were obtained by directly employing the ammonium hydrochloride salt **2** with *tert*-butylnitrite in CH_2Cl_2 at $-18\,°C$, no improvement was observed by adding further protic or Lewis acids. The diazonium salt **3** was treated with methylamine, *n*-butylamine, *tert*-butylamine, benzylamine, and 2-(2-aminoethyl)pyridine to furnish triazenes **4a**–**e**, respectively, which should be useful in the transfer of methyl-, *n*-butyl-, *tert*-butyl-, benzyl-, and 2-(2-pyridylethyl) cations, respectively. Triazene **4a** was obtained with a loading of 1.54 $mmol\,g^{-1}$ of reactive sites by starting from polystyrene containing 2.0 $mmol\,g^{-1}$ of chloromethyl groups. When the mass increase during the reaction sequence is taken into account this loading corresponds to an excellent conversion (94%) of chloromethyl groups into triazenes. Completion of the reaction steps could be monitored by following characteristic vibrational bands in the attenuated total reflection IR spectrum (FT-ATR-IR) directly from washed and dried resin samples. Products **4a**–**e** were stable at room temperature for at least several months when kept in the dark.



Scheme 1. Preparation of reactive polymers **4a**–**e** starting from the chloromethyl–polystyrene resin and employing the reaction sequence alkylation, reduction, diazotation, and nucleophilic addition of an amine. For details see the Experimental Section.

Various reactions of the novel polymeric reagents **4a**–**e** were then investigated. First esterifications were studied with acids representing a broad range of pK_a values, size, steric hindrance, as well as chemical lability and additional functionality. As the reaction requires acidic conditions and is initiated supposingly by protonation of the triazene moiety, the pK_a value is a possible determinant of the reaction. Furthermore, there is evidence pointing to carbenium ion intermediates either as ion pairs in the case of benzyl ions or through a concerted mechanism in the case of primary alkyl ions.[18]

Sterically demanding benzilic acid (**7**) was used to optimize the reaction conditions in respect to reagent excess and reaction time. Complete conversion (99%) of benzilic acid to the corresponding methyl ester was obtained with two equivalents of alkylating polymer **4a** after 6 h, while 96% conversion was obtained with resin **4b** (Figure 1). The polymer-supported reaction of **4a** (2 equiv) with *p*-nitrophenylacetic acid (**5**, 1 equiv, 2 $mg\,mL^{-1}$) in CH_2Cl_2 was analyzed after various reaction times by HPLC. A 53% conversion from the acid to the ester product was observed after 5 min; data analysis[19] indicated a second-order reaction as observed in homogeneous solution.[17]

The results of esterifications are summarized in Table 1. A diverse selection of acids was converted into highly pure ester products when treated with five equivalents of the alkylating polymers **4a**, **4b**, **4d**, and **4e** for 2–6 h. Typical yields for the conversion of 5 mg acid were in the range of 80%. In case of

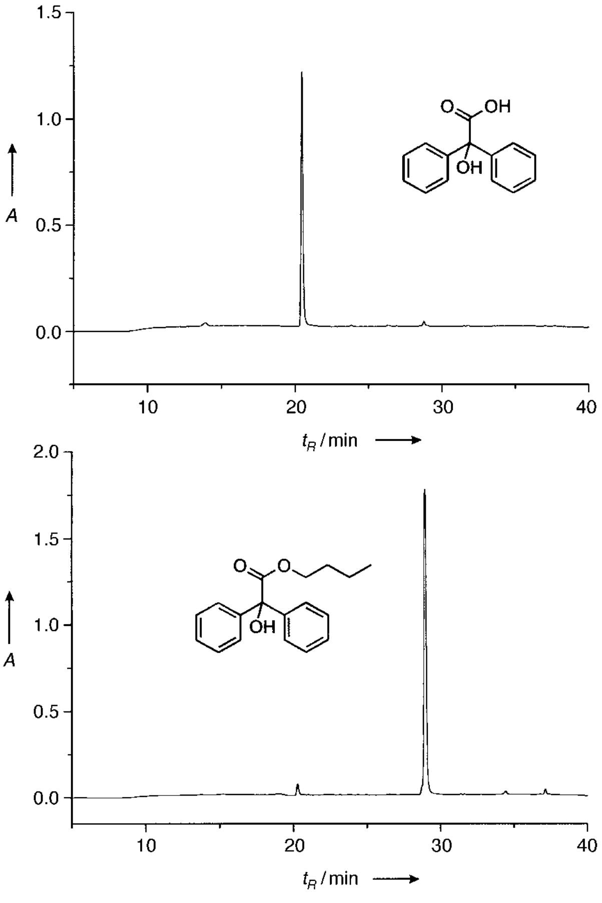
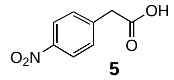
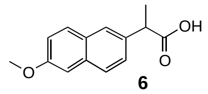
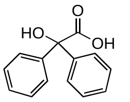
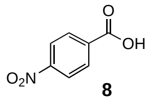
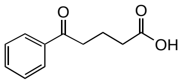
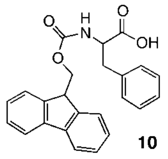
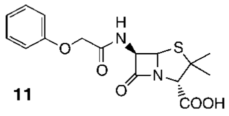
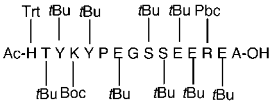
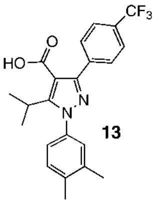
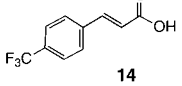


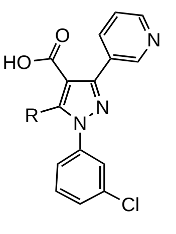
Figure 1. HPLC chromatogram of **7** (top) and after 6 h reaction with five equivalents of **4b** (bottom). The *n*-butyl ester was formed in a purity of 96% (see Table 1).

Table 1. Conversion of a diverse collection of various acids with the alkylating polymers **4a**, **b**, **d**, **e**. The purity was determined by HPLC with UV detection at 214 nm.

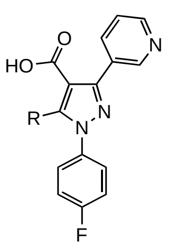
Entry	Acid	R^1 of **4**	Purity
1	 **5**	Me	96
2	**5**	*n*Bu	95
3	**5**	C_2H_4-C_5NH_4	92
4	 **6**	*n*Bu	91
5	**6**	C_2H_4-C_5NH_4	91
6	 **7**	Me	99
7	**7**	*n*Bu	96
8	**7**	C_2H_4-C_5NH_4	94
9	 **8**	Me	90
10	 **9**	Me	86
11	**9**	*n*Bu	87
12	 **10**	Me	96
13	 **11**	Me	92
14	 Trt tBu tBu tBu tBu Pbc Ac-HTYKYPEGSSEEREA-OH **12** tBu Boc tBu tBu tBu tBu	Me	82
15	 **13**	Bn	90
16	 **14**	Me	91

the esterification of acid **5** with resin **4b** NMR analysis was employed to prove the structure of the *n*-butyl ester; the NMR spectrum did not display any signals of an isobutyl ester by-product formed by rearrangement. In contrast, alkylation to the *tert*-butyl ester (**4c**) failed, though the generation of gaseous products indicated decomposition of the triazene moiety. Possibly, the intermediary *tert*-butyl cation reacts under proton abstraction to yield isobutene. The reagents tolerate the presence of non-acidic hydroxy groups (**7**, entries 6–8), enolizable carbonyl functions (**9**, entries 10 and 11), and nitrogen heterocycles with limited basicity such as in pyridine (pK_a 5.25) and pyrazole systems (**13**, entry 15). The reaction fails in the case of alkylic amines such as the unprotected amino acids. The conversion of acid-sensitive structures is exemplified with penicillin V (**11**, entry 13). Esterification of this especially labile structure failed under acidic and basic conditions as well as with diazomethane.[20] After conversion of the potassium salt of penicillin V into the free acid by employing ion-exchange resin Amberlyst 15 in dioxane/water, the ion exchanger was removed and the remaining solution was treated immediately with polymeric reagent **4a** to yield the respective penicillin ester. A pentadecapeptide bearing various acid-labile side protecting groups and having a mass of 2924.5 Da (**12**, entry 14) was investigated in the reaction with resin **4a** (5 equiv). After 6 h the starting peptide was consumed and the product was formed as analyzed by HPLC and ESI-MS. The etherification of alcohols was attempted without significant formation of product.[21]

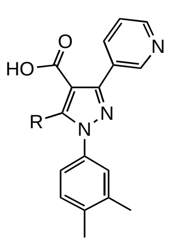
Finally, the conversion of a collection of druglike molecules was investigated, since this process might be useful for lead optimization in a medicinal chemistry program. An equimolar mixture of 20 pyrazolecarboxylic acids **15a–u**[22] was synthesized by a split-and-combine approach via solid-phase-bound β-dicarbonyl compounds that were cyclized regioselectively with various aldehydes and arylhydrazines. One portion of



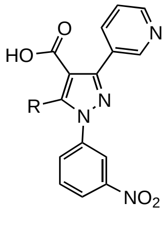
15a : R = Me
15b : R = Et
15c : R = *i*Pr
15d : R = Phe



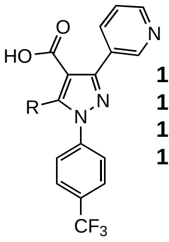
15e : R = Me
15f : R = Et
15g : R = *i*Pr
15h : R = Phe



15i : R = Me
15k : R = Et
15l : R = *i*Pr
15m: R = Phe



15n : R = Me
15o : R = Et
15p : R = *i*Pr
15q : R = Phe



15r : R = Me
15s : R = Et
15t : R = *i*Pr
15u : R = Phe

this mixture was treated with resin **4a** (5 equiv) for 6 h to yield the methyl esters of the pyrazolecarboxylic acids. Both the mixtures of acids and esters were analyzed by electrospray ionization Fourier transform ion cyclotron mass spectrometry (ESI-FT-ICR-MS) using both direct infusion measurements and coupling to micro-HPLC. All 20 pyrazolecarboxylic acids (**15a–u**) could be assigned in the starting mixture (Figure 2, top) as well as the corresponding 20 methyl esters (Figure 2, bottom) in the product mixture. Assignment was based on accurate mass determination with a relative mass error of less than 2.2 ppm.

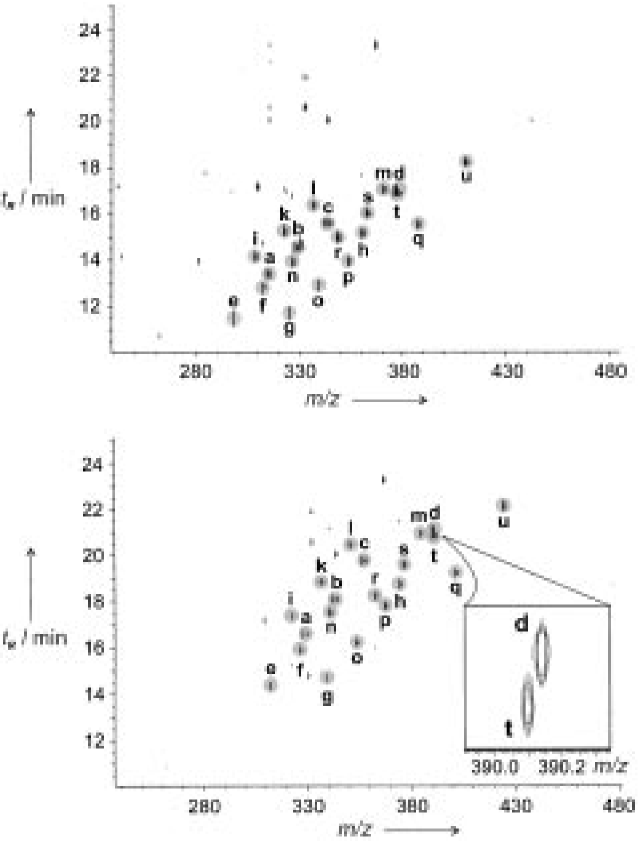


Figure 2. LC-MS contour plots (mass-to-charge ratio versus retention time) using HPLC-ESI-FT-ICR-MS. A collection of 20 pyrazole acids **15a–u** (top) were converted into their corresponding methyl esters **16a–u** (bottom) by treatment with resin **4a**. Coeluting compounds **16d** and **16t** were resolved having a mass difference of 0.042 Da.

In summary, we have demonstrated that the alkylating polymers **4a**, **b**, **d**, and **e** are very efficient and versatile esterification reagents that allow the conversion of diverse, highly functionalized substrates under extremely mild reaction conditions. The novel reagents might be of value especially in the parallel conversion of mixtures of highly functionalized compound collections such as those used in lead-optimization efforts. Alkylating polymers should be useful as well in flow-through applications allowing in situ conversions, for example, in gas chromatography. Further potential applications of the presented alkylation reagents can be expected for other nucleophiles besides carboxylates, such as for alcohols, phenols, amines, thiols, and various C-nucleophiles including the cyanide ion.

Experimental Section

Attachment of *para*-nitrophenol to Merrifield resin: Chloromethylated polystyrene resin (0.5 g, 1.0 mmol, 200–400 mesh cross-linked with 1% divinylbenzene, loading 2.0 mmol g^{-1}) was suspended in a solution of *para*-nitrophenol (5 mmol, 696 mg) in DMF (5 mL). Cs_2CO_3 (2 mmol, 652 mg) was added and the reaction mixture was agitated for 3 h at 80 °C. The resin was washed at RT with DMF, CH_2Cl_2, MeOH, CH_2Cl_2, and MeOH (each five times) and dried in vacuo to furnish resin **1**. IR: $\vartheta = 1339$, 1495, 1592 cm^{-1}.

Reduction of the nitro group and diazotation: Resin **1** was treated with a 2 M solution of $SnCl_2 \cdot 2H_2O$ in DMF (450 mg per mL solution) for 16 h at RT and subjected to the washing and drying procedure described above to furnish resin **2** (IR: $\vartheta = 2581$ cm^{-1} (NH_3^+)) with a loading of 1.63 mmol g^{-1} (elemental analysis). Resin **2** (1.0 mmol) was suspended in CH_2Cl_2 and cooled to −18 °C. *tert*-Butylnitrite was then added (10 mmol, 988 μL). After 4 h the diazonium resin **3** was washed with cold CH_2Cl_2 (five times) and cooled again to −18 °C. IR: $\vartheta = 2238$ cm^{-1} (N_2^+).

Triazene formation: The intermediate diazonium resin **3** was treated with a 2 M solution of an amine in THF at −18 °C and warmed to RT. After 4 h, washing and drying furnished resins **4a–e** with a loading of 1.54 mmol g^{-1} for resin **4a** starting from 2.0 mmol g^{-1} of chloromethyl groups. For further loadings of **4a–e** consult the Supporting Information.

Representative example of the alkylation of acids: Acid **5a** (5 mg) was dissolved in CH_2Cl_2 (5 mL) (or CH_2Cl_2/MeOH 9/1, or THF, or dioxane) and treated with resin **4b** (5 equiv) for 6 h. The resin was washed with CH_2Cl_2, MeOH, and CH_2Cl_2 (each two times with 2.5 mL) and the solvent was removed by evaporation to furnish 5.3 mg of the *n*-butyl ester (79.5% yield). HPLC analysis was conducted to determine the purity of the products (see Table 1).

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[1] *Combinatorial Chemistry—Synthesis, Analysis, Screening* (Ed.: G. Jung), Wiley-VCH, Weinheim, **1999**.

[2] *Combinatorial Peptide and Nonpeptide Libraries* (Ed.: G. Jung), VCH, Weinheim, **1996**.

[3] D. L. Flynn, R. V. Devraj, W. Naing, J. J. Parlow, J. J. Weidner, S. L. Yang, *Med. Chem. Res.* **1998**, *8*, 219–243.

[4] J. Rademann, W. Kraas, B. Dörner, *Nachr. Chem.* **2000**, *48*, 280–283, and references therein.

[5] A. Akelah, D. C. Sherrington, *Chem. Rev.* **1981**, *81*, 557–587.

[6] *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), Wiley, Chichester, **1995**.

[7] J. K. Rueter, S. O. Nortey, E. W. Baxter, G. C. Leo, A. B. Reitz, *Tetrahedron Lett.* **1998**, *39*, 975–978.

[8] E. H. White, H. Scherrer, *Tetrahedron Lett.* **1961**, *21*, 758–762.

[9] A. Baeyer, C. Jaeger, *Ber. Dtsch. Chem. Ges.* **1875**, *8*, 148–150.

[10] H. Goldschmidt, J. Holm, *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 1016–1026.

[11] O. Wallach, *Justus Liebigs Ann. Chem.* **1886**, *235*, 233–255.

[12] M. L. Gross, H. D. Blank, W. M. Welch, *J. Org. Chem.* **1993**, *58*, 2104–2109.

[13] J. K. Young, J. C. Nelson, J. S. Moore, *J. Am. Chem. Soc.* **1994**, *116*, 10841–10842.

[14] S. Bräse, J. Köbberling, D. Enders, R. Lazny, M. Wang, S. Brandtner, *Tetrahedron Lett.* **1999**, *40*, 2105–2108.

[15] T. B. Patrick, R. P. Willaredt, D. J. DeGonia, *J. Org. Chem.* **1985**, *50*, 2232–2235.

[16] L. Dunsch, B. Gollas, A. Neudeck, A. Petr, B. Speiser, H. Stahl, *Chem. Ber.* **1994**, *127*, 2423–2429.

[17] A. A. R. Laila, *Gazz. Chim. Ital.* **1989**, *119*, 453–456.

[18] E. H. White, H. M. Maskill, D. J. Woodcock, M. A. Schroeder, *Tetrahedron Lett.* **1969**, *11*, 1713–1716.

[19] **5** (2 mg mL^{-1}) was treated with resin **4a** (2 equiv) in CH_2Cl_2. In order to determine the reaction order the ratio between the starting materials and products was measured after 0, 5, 10, 20, 30, 90, and 330 min. The inverse concentration of the starting acids were plotted against the reaction time. Linear regression indicated a second-order reaction ($R = 0.9932$). The rate constant was determined to be (0.38 ± 0.02) M^{-1}s^{-1}, which corresponds to a $t_{1/2}$ of 4 min.

[20] A. Mangia, A. Scandroglio, *Tetrahedron Lett.* **1978**, *19*, 5219 – 5220.
[21] A suspension of resin **4d** and *N*-Fmoc-phenylalaninol (3 equiv; Fmoc = 9-fluorenylmethoxycarbonyl) was treated with trimethylsilyl trifluoromethylsulfonate (TMSOTf, 1 equiv) and resulted in immediate gas evolution. Only traces of the benzylated product were identified by ESI-MS.
[22] P. Grosche, A. Höltzel, T. B. Walk, A. W. Trautwein, G. Jung, *Synthesis* **1999**, 1961 – 1970.

Molecular Switching in the Near Infrared (NIR) with a Functionalized Boron – Dipyrromethene Dye[**]

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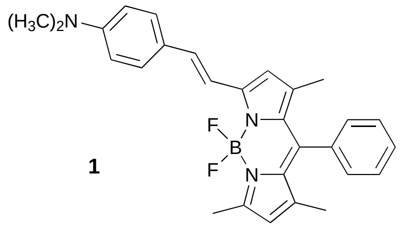
Recent developments in supramolecular chemistry and nanotechnology have stimulated interest in the design and the construction of molecular signaling systems capable of performing photo- and substrate-induced logic functions or redox-based switching actions.[1] At the molecular level, photons, that is their absorption or emission, often are the vehicle of choice for transduction of an electrochemically[2] or photochemically[3] generated signal. Examples range from photonic switches[4] to photo- or electrochromic devices[5] and to advanced micro- or nanomachines.[6] In particular, multifunctional dyes that are sensitive toward both external physical and chemical triggers provide a versatile basis for the construction of sophisticated switches that communicate, for instance, through changes in electrochromic and/or fluorescence properties. Over the past few years, the boron – dipyrromethene (BDP) chromophore has gained in importance in the design of such systems[2c, 3b, 7–9] since the BDP core is comparatively readily oxidized and reduced,[2c] a prerequisite for fluorescent switches relying on electron or charge transfer (CT),[3b, 7, 8] as well as for the generation of stable radical ions that show electrogenerated chemiluminescence upon charge recombination.[2c] In these systems, the *meso*-substituted BDP chromophore acts as in donor(D) – acceptor(A)-substituted biaryls so that the switching process hardly influences the absorption and emission wavelengths. However, for the design of more advanced molecular ensembles it would be highly desirable to generate signal changes by substrate interaction at a site conjugated to the BDP core. Since experience has shown that creation of an extensively delocalized amino radical cation would result in strong electrochromism, introduction of a proton-sensitive amino donor group seemed most suitable for the construction of such a multifunctional electro- and photochemical molecular switch. Here, we report the synthesis and spectroscopic and electrochemical properties of the 3-dimethylaminostyryl-substituted dye **1**, which, to the best of our knowledge, is the first example of an unsymmetrically substituted BDP dye carrying an analyte-sensitive (donor) group conjugated to the core.



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Compound **1** was synthesized by condensation of the tetramethyl derivative[7b] with *p*-dimethylaminobenzaldehyde using piperidinium acetate as catalyst.

Owing to the introduction of a donor-styryl-spacer group at the 3-position the spectrosocpic behavior of **1** is more reminiscent of D – A stilbenes[10a,b] or styryl bases,[10c] in contrast to *meso*-donor-substituted BDP dyes, where no direct electronic conjugation exists between both aryl subunits.[3b, 7b] As follows from Table 1 and Figure 1, the absorp-

Table 1. Spectroscopic data of **1** and **1**-H$^+$ in different solvents at 298 K.[a]

	Solvent	λ_{abs} [nm]	ε_{max} [$M^{-1}cm^{-1}$]	λ_f [nm]	Φ_f	τ_f [ns]	k_f[b] [$10^8 s^{-1}$]	k_{nr}[b] [$10^8 s^{-1}$]
1	MeCN	597	75000	731	0.13	0.94	1.4	9.2
1	THF	603	89000	672	0.58	3.21	1.8	1.3
1	Et_2O	594	98000	638	0.83	3.88	2.1	0.4
1	Bu_2O	598	101000	630	0.87	3.73	2.3	0.3
1	hexane	596	n.d.[c]	611	0.97	3.84	2.5	0.1
1-H$^+$	MeCN	553	100000	563	0.97	4.38	2.2	0.1
1-H$^+$	THF	558	100000	566	0.85	4.02	2.1	0.3
1-H$^+$	Et_2O	556	101000	563	0.90	4.24	2.1	0.2

[a] Experimental conditions: $c(\mathbf{1}) = 1 \times 10^{-6}$ M, $\lambda_{exc} = 545$ and 595 nm for steady-state, 500 and 578 nm for time-resolved fluorescence measurements, proton source $HClO_4$. [b] $k_f = \Phi_f/\tau_f$, $k_{nr} = (1 - \Phi_f)/\tau_f$. [c] Not determined due to low solubility.

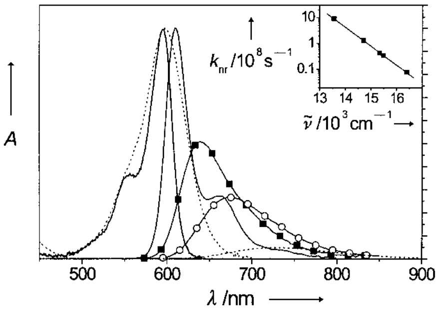

Figure 1. Absorption (normalized; absorption *A*) and emission spectra (fluorescence intensity *F*) of **1** at 298 K (——: in hexane, ■: in Bu_2O, ○: in THF, - - - -: in MeCN; absorption spectra in THF and Bu_2O omitted for better clarity, experimental conditions, see Table 1). In the inset, a plot of $\ln k_{nr}$ versus the emission maximum is shown (—— fit; $r = 0.999$).

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