of CPK models suggested that the helical structure is more compact and rigid, and that the helicate provides a more favorable binding site for Na^+ ions than the nonhelicate. Finally, the observation of a modulation of the CD intensity in the MLCT region indicates that this system works as an AND device for CD output by utilizing coordination and chiral information: The Cu^I and Na^+ ions act as the input signals[4, 5] and there is only a CD response if the system receives both input signals.

All the spectral data obtained indicate unambiguously that there is an efficient and intramolecular transfer of chiral information from the binaphthyl moiety to the [Cu^I-bipyridine] complex through the coordination of an achiral Na^+ ion. This complexation makes the pseudocrown ring more rigid than in the Na^+-free [Cu^I(**1**)] complex. This rigidity results in a significant reduction in the loss of chiral information from the binaphthyl unit to the Cu^I complex through the polyether spacers and results in effective chiral communication being achieved.

Helicates such as the [Cu^I(**1**)] complex are also considered to be strong candidates for intermolecular chirality transfer since helical metal complexes have a high potential for chiral recognition and interaction with helical biomolecules such as DNA[11] and proteins with an α-helical structure. A preliminary experiment showed that [Cu^I(**1**)] bound to amino acid derivatives, thus an interaction with proteins can be expected. We are currently investigating chiral information transfer systems by using an achiral mediator for chirality.

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α-Lithiation of 1-Aryl-3,3-dialkyltriazenes and Intramolecular Conversion to Benzylamine and Tetrahydrobenzotriazine Derivatives**

Keiji Nishiwaki,* Takashi Ogawa, and Keizo Matsuo*

1-Aryl-3,3-dialkyltriazenes are utilized in many ways in organic syntheses, for example, as protective groups for aniline derivatives,[1] as precursors of benzyne,[2] as well as in diazo coupling,[3] Sandmeyer–Gattermann reactions,[4] and hydroxylation of positive ion exchange resins.[5] Recently, Nicolaou et al. showed that aryltriazenes can be used in the construction of aryl ethers, and applied this method to the synthesis of vancomycin.[6] In combinatorial chemistry, triazenes were used as linkers in solid-phase synthesis[7] and as alkylating polymers in solution-phase synthesis.[8] Haley et al. reported thermal cyclization of triazenes.[9]

Here we report on the transformation of l-aryl-3,3-dialkyltriazenes into benzylamines and dearomatized compounds, which involves a novel intramolecular carbon–carbon bond-forming reaction in which a lithiated alkyl group on the nitrogen atom in the 3-position[10] attacks the aromatic ring as a nucleophile.

The triazenes were prepared in good yields from the corresponding primary aromatic amines by standard methods ($NaNO_2$/HCl, then addition of the respective amine). The general procedure for the transformation of the triazenes into benzylamines is as follows. The triazenes were treated with *n*BuLi (1 equiv) in THF at 0 °C for 1 h, followed by the addition of electrophiles to produce the corresponding benzylamine derivatives [Eq. (1)]. The results are summarized in Table 1. The addition of Boc_2O instead of H_2O as an electrophile greatly increased the yield (entries 1 and 3). When *o*- and *p*-methylphenyltriazenes were treated as above, *m*-methylbenzylamine was formed in both cases, but the yield of the product was superior in the latter case (entries 6–8). Some *p*-substituted triazenes were transformed into *m*-substituted benzylamine derivatives (entries 9–12). In the case of the *m*-substituted triazenes, mixtures of *o*- and *p*-methylbenzylamine derivatives were obtained, but *p*-derivatives were formed predominantly (entries 7 and 13). The *m*-methoxy- and *m*-fluorophenyltriazenes produced *o*-substitut-

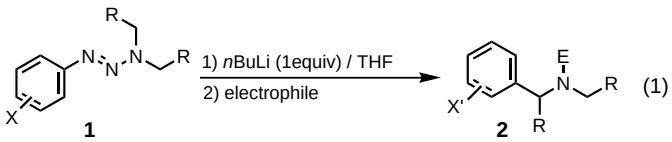

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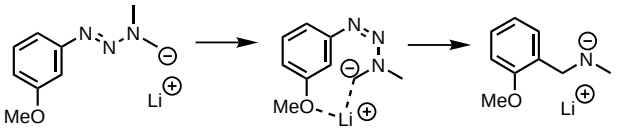
Table 1. Synthesis of benzylamine derivatives.[a]

Entry	Substrate X	Substrate R	Electrophile	Product X′	Product E	Yield [%]
1	H	H	H_2O	H	H	57
2	H	H	*n*BuBr	H	*n*Bu	78
3	H	H	Boc_2O	H	Boc	81
4	H	Me	Boc_2O	H	Boc	47
5	H	$-(CH_2)_2-$	Boc_2O	H	Boc	69
6	*o*-Me	H	H_2O	*m*-Me	H	74
7	*m*-Me	H	H_2O	*o*-, *p*-Me (1:2)	H	71
8	*p*-Me	H	H_2O	*m*-Me	H	95
9	*p*-Me	H	Boc_2O	*m*-Me	Boc	96
10	*p*-MeO	H	Boc_2O	*m*-MeO	Boc	78
11	*p*-TMS	H	Boc_2O	*m*-TMS	Boc	70
12	*p*-F	H	Boc_2O	*m*-F	Boc	89
13	*m*-Me	H	Boc_2O	*o*-, *p*-Me (1:2)	Boc	90
14	*m*-MeO	H	Boc_2O	*o*-MeO	Boc	70
15	*m*-F	H	Boc_2O	*o*-F	Boc	41
16	*m*-TMS	H	Boc_2O	*p*-TMS	Boc	81

[a] Boc = *tert*-butoxycarbonoyl; TMS = trimethylsilyl.

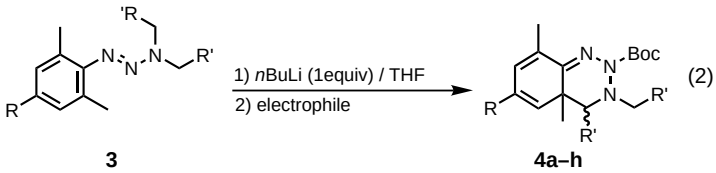
ed benzylamines in good to moderate yields (entries 14 and 15). For X = MeO, the result is explained by the chelate effect shown in Scheme 1. In the other case, the chelating and inductive effects of the F atom cause attack of the anion at that position. On the other hand, *m*-trimethylsilylphenyltriazene gave *p*-trimethylsilylbenzylamine as the sole product (entry 16), whereby steric hindrance between the trimethylsilyl group and the carbanion resulted in selectivity. Thus, the regioselectivities of the carbon–carbon bond formation are attributable to the electronic and steric features of the substituents on the aromatic ring.



Scheme 1. Chelate effect.

We obtained additional significant results by further investigation into the course of these reactions. Treating 1-aryl-3,3-dialkyltriazenes with substituents at the 2- and 6-positions of the aryl groups with *n*BuLi gave good yields of dearomatized heterocyclic compounds [Eq. (2)].[11] The results are summarized in Table 2. For R′ = Me, two diastereomers were obtained (entries 2 and 6). In contrast, triazenes derived from pyrrolidine (entries 3 and 7) and piperidine (entries 4 and 8) gave single diastereomers.

On the basis of the above results, we propose the reaction mechanism shown in Scheme 2. Deprotonation occurs at the C atom α to N3. Nucleophilic attack of the resulting anion at the *o*-position of the aryl



(2)

Table 2. Synthesis of dearomatized compounds.

Entry	Triazene 3 R	Triazene 3 R′	Product	Yield [%][a]
1	H	H	**4a**	73
2	H	Me	**4b**	64 (1:2.9)
3	H	$-(CH_2)_2-$	**4c**	75
4	H	$-(CH_2)_3-$	**4d**	58
5	Me	H	**4e**	65
6	Me	Me	**4f**	52 (1:5)
7	Me	$-(CH_2)_2-$	**4g**	85
8	Me	$-(CH_2)_3-$	**4h**	63

[a] The values in parentheses indicate diastereoselectivity. The ratio of diastereomers was determined by ^{1}H NMR spectroscopy.

group is followed by dearomatization. For R = H, two possible routes for further reaction were considered. Path a involves an intramolecular 1,2-proton shift and elimination of N_2. In path b, the proton that originated from the solvent is incorporated into the anion, after which a proton is abstracted by the anion of the solvent (HSol). For R = Me, the proton shift analogous to path a and the proton exchange as in path b can not proceed, because the dearomatized intermediate **A** has no such proton available for the rearomatization step. Consequently, the *N*-anion **A** immediately reacts with an electrophile to give a tetrahydrobenzotriazine derivative.

In conclusion, we found a new carbon–carbon bond-forming reaction by intramolecular nucleophilic attack of carbanions generated from 1-aryl-3,3-dialkyltriazenes. These reactions provide an alternative method for the preparation of benzylamine derivatives and dearomatized compounds. Further studies are in progress.

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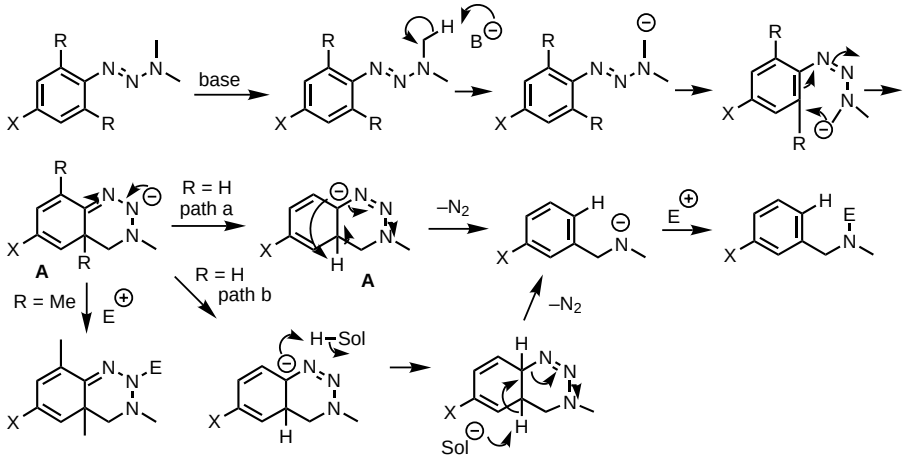

Scheme 2. Proposed mechanism.

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Fluorescent Deazaflavin – Oligonucleotide Probes for Selective Detection of DNA

Cécile Dueymes, Jean Luc Décout,* Philippe Peltié, and Marc Fontecave*

Arrays of oligonucleotide probes (DNA chips) immobilized on glass or silicon surfaces have emerged as powerful new tools for the analysis of DNA and RNA.[1] These specific DNA sensors operate through hybridization reactions which are based on the mutual recognition of two complementary nucleic acid strands that establish hydrogen bonds between their nucleic bases. Hybridization is most commonly assayed by fluorescence, and hence requires that fluorophore labels are covalently attached to the DNA target fragments to be analyzed.

This technology, however, is still fraught with a number of drawbacks and requires new developments. For example, it is still difficult to assess the quality of the oligonucleotides attached to the surface. The homogeneity and the reproducibility of the procedures for preparing the DNA-functionalized surfaces, and consequently the DNA surface density, are difficult to control. Furthermore the polymerase chain reaction (PCR) step, which serves to amplify the DNA targets, and the subsequent chemical step, for the attachment of the fluorophore to the target DNA, are responsible for significant modifications in the relative proportions of the different populations of the nucleic acids to be analyzed.

We propose that some of these problems might be simply solved if the detection label (here a fluorophore) is incorporated on the array capture DNA strand and not on the target to be detected. This strategy might have many advantages. First it greatly reduces the number of manipulations of the targets. Second, it provides a way to control the quality of the DNA array (by using standard fluorescence scanners) in the absence of the targets. Such an array requires that: 1) the fluorescence is not quenched by interaction of the fluorophore with the surface; 2) the label on the probe does not affect its affinity for its complementary oligonucleotide; and 3) the fluorescence is significantly changed as a specific consequence of hybridization of the functionalized DNA

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