Regioselectivity

A Versatile Direct Approach to *ortho*-Substituted Azobenzenes from Benzotriazoles**

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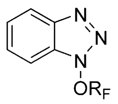
Benzotriazole (Bt) has been widely utilized by the research group of Katritzky as a synthetic auxiliary in a multitude of reactions.[1] Benzotriazole is an inexpensive, stable, and biologically innocuous compound[1a] which can be easily introduced into organic molecules. After conferring its multiple activating influences for carrying out precise transformation reactions, it can be easily removed and can generally be recycled. The early results in the chemistry of benzotriazole have been described by Katritzky and co-workers.[1e]

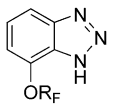
The benzotriazole ring is extremely stable and only rarely was ring cleavage encountered to give mostly products of nitrogen extrusion. For example, Grignard reagents open and modify the triazole ring and afford a variety of products.[2] Other methods for opening the benzotriazole ring are by photolysis and pyrolysis,[3] however, no actual ring opening of benzotriazole that has led to isolable azobenzenes has been reported.[1d]

We report here the pleasantly surprising chemistry of the hitherto unknown 1-[(nonafluorobutane)sulfonyl]-1*H*-benzotriazole (**3b**, BtNf) for the synthesis of *ortho*-azobenzenes in a direct and unprecedented approach.

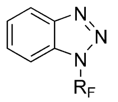
At the outset, our aim was to find out whether the perfluoroalkanesulfonates **1** and **3** derived from 1-hydroxybenzotriazole and benzotriazole, respectively, are suitable as perfluoroalknesulfonyl transfering agents for alcohols and phenols. Application of the known literature method[4] for the preparation of aryl nonafluorobutanesulfonates (nonaflates) to synthesize the nonaflate **1b** surprisingly resulted in the isolation of the rearranged product **2b**.[5] Further investigations were then concentrated on the synthesis of sulfonyl compounds **3**.



1a: $R_F = SO_2CF_3$
1b: $R_F = SO_2C_4F_9$



2a: $R_F = SO_2CF_3$
2b: $R_F = SO_2C_4F_9$



3a: $R_F = SO_2CF_3$
3b: $R_F = SO_2C_4F_9$

The lower homologue of BtNf (**3b**), the 1-[(trifluoromethyl)sulfonyl]-1*H*-1,2,3-benzotriazole (**3a**), was prepared by Katritzky et al. and some of its reactions were studied.[6] However, the skeletal structure of benzotriazole remained intact in all of these reactions. We have now prepared 1-[(nonafluorobutyl)sulfonyl]-1*H*-1,2,3-benzotriazole (BtNf, **3b**) for the first time in 89% yield by treating 1-lithiobenzotriazole with nonafluorobutanesulfonyl fluoride in 1,2-dimethoxyethane at reflux temperature. BtNf (**3b**) decomposes in the presence of light and should be kept in the dark, preferably in a refrigerator. BtNf (**3b**) was fully characterized by its spectral properties and elemental analyses (see Experimental Section).

First we examined the reaction of phenol, which was chosen as the model compound, with the trifluoromethanesulfone (triflone) **3a**. The preliminary studies with **3a** were plagued by the formation of a mixture of two products, and hence all further explorations were conducted with the homologous nonafluorobutanesulfone (nonaflone) **3b**. The fact that the nonaflate group has been shown[7] to be a better leaving group than the triflate also prompted us to carry out the study with the nonaflone-substituted benzotriazole **3b**.

We attempted first the reaction of **3b** with phenol in the presence of several bases. After some experiments, sodium hydride was found to be the base of choice, and the reaction was conducted in toluene. The major product isolated after aqueous work-up was an orange product which was shown by spectral and analytical analyses to be the azo compound **4**. Although both *ortho*- and *para*-substituted azo compounds can be expected, the structure of the major product was unambiguously assigned as the *ortho*-substituted azo compound **4**, as supported by its X-ray crystallographic analysis.[8] Only a very small amount (ca. 5%) of the *para*-substituted derivative **5** was isolated by column chromatography. Evidently, the triazole ring underwent a ring-opening reaction by nucleophilic attack of the phenoxide anion. Although the presence of a strong electron-withdrawing substituent at N1 on benzotriazole has been shown to weaken the N1–N2 bond, thus leading to ring opening of the benzotriazole, they give products of nitrogen extrusion[1d] or undergo a Dimroth rearrangement when a 4-amino substituent is present.[9] The formation of the azo compound **4** from **3b** constitutes an entirely new reaction and is an efficient method for the formation of a wide variety of differently substituted aromatic azobenzenes.

This preliminary experiment of **3b** with the phenoxide ion enabled us to identify the products from the reaction of triflone **3a** as a mixture of the *ortho*-coupled azobenzene **4** ($R_F = SO_2CF_3$) with a free phenolic group and its corresponding trifluoromethanesulfonate ester (OTf instead OH).

The mechanism for the formation of the azo compound is outlined in Scheme 1. The mesomeric anion formed by the reaction of sodium hydride with phenol attacks at the N2 position of the benzotriazole moiety. The highly electron-withdrawing nonafluorobutanesulfone group then results in the opening up of the ring which leads to **4** after proton shifts and acidic work-up. The formation of the *para*

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[**] We thank Bayer AG for the generous gift of nonafluorobutanesulfonyl fluoride. The method for the formation of azobenzenes presented here has been submitted for a patent application.

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

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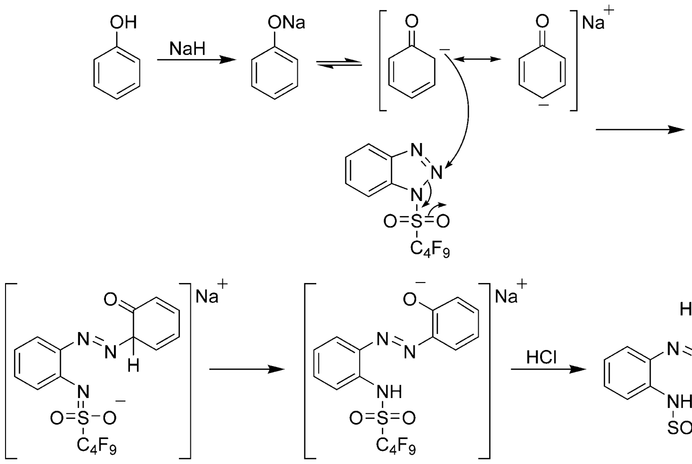
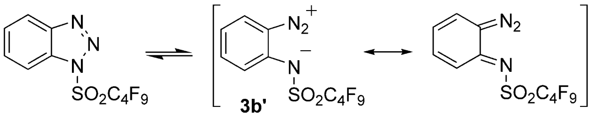


Scheme 1. Mechanism for the formation of the azo compound.

isomer can be considered to occur in a similar manner (not depicted).

Another possibility for the formation of **4** is a nucleophilic attack of the phenolate anion at the sulfur atom,[10] thus resulting in ring opening of the triazole moiety by a rearrangement reaction. However, this will lead only to the *ortho*-substituted product **4**.[11]

A mechanism involving a free diazonium intermediate existing in equilibrium with the benzotriazole **3b′** (Scheme 2) structure was also scrutinized.[12] The existence of a free diazonium species in equilibrium with the 1,2,3-triazole ring is known in the parent 1,2,3-triazole substituted with a sulfonyl group at N1. This equilibrium was confirmed by ^{1}H NMR spectroscopic studies.[13] In the benzotriazole series two compounds can be conceived to be in equilibrium with the diazo structure.



Scheme 2. Possible equilibrium involving **3b′**.

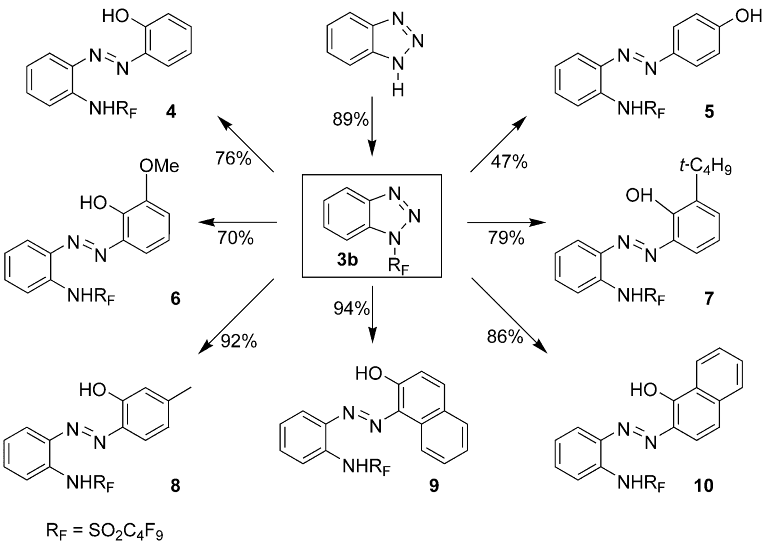
1-Nitrobenzotriazole,[14] was shown to react with amines; for example, piperidine gave an isolable piperidinium salt from the ring-opened benzotriazole. There was also a report[15] on the reversible thermochromic behavior of 1-cyanobenzotriazole, which is yellow in the melt and colorless in the crystalline state. No chemical evidence was obtained to indicate that the color might arise from ring opening to give the diazo-*N*-cyanoimine form, and no reactions of the cyano compound were reported. Experiments carried out on 1-nitrobenzotriazole by treating it with indolizine derivatives at room temperature were interpreted as an electron-transfer process, and the same process is attributed to the reaction of amines with 1-nitrobenzotriazole.[16]

Temperature-dependent NMR investigations were carried out to find out whether an equilibrium with a diazo structure does exist in the 1-nonafluorobutylsulfonylbenzotriazole **3b**. The signals in the aromatic region of the spectrum for molecule **3b** did not change when the sample was heated in [D$_6$]DMF up to a temperature of 100 °C. Spectra were recorded every 10 °C starting from ambient temperature. Above 100 °C, the compound starts to decompose to give a dark solution. No analysis of this sample could be carried out as the sample had completely decomposed.

Our coupling reactions were carried out at room temperature and on the basis of time-dependent NMR data it can be concluded that no free diazonium intermediate participates in the reaction. Also, no vibration corresponding to the N≡N group could be found in the IR spectrum of **3b**. We consider that, as far as the mechanism is concerned, the one shown in Scheme 1 is more probable, however, the other mechanism via the diazo structure cannot be completely ruled out at present.

The *para*-substituted aza compound **5**, the structure of which was proven by X-ray analysis,[17] could be obtained exclusively by conducting the reaction in *N*,*N*-dimethylformamide. This dipolar aprotic solvent probably blocks the *ortho* positions by coordination to the oxygen atom of the phenolate anion, thus directing the reaction to proceed exclusively to the *para* product **5** by the mechanism shown in Scheme 1. The lower yield of the *para* product relative to *ortho* products probably lies in the work-up from the reaction mixture containing DMF, as the yields have not yet been optimized.

A set of azobenzenes (Scheme 3) prepared by this method is listed in Table 1. The authentication of the *ortho* coupling in the reaction of benzotriazole **3b** with phenols in toluene is proved by the formation of products **6**–**8** from 2-methoxy-, 2-*tert*-butyl-, and 3-methylphenol, respectively. 2-Methoxyphenol and 2-*tert*-butylphenol gave more than 70 % of the corresponding *ortho*-coupled products **6** and **7**, respectively,



Scheme 3. Azobenzenes prepared. Solvent: toluene for **4**–**10**, DMF for **5**.

Table 1: Analytical data for azobenzenes **4**–**10**.

Product	Yield [%]	M.p. [°C]	Color	UV (MeCN) λ_{max} [nm] (ε mol^{-1} dm^3 cm^{-1})
4	76	134.2–135.1	orange	250 (11708), 321 (12021), 395 (8324)
5	47	129.5–130.0	red	250 (11334), 358 (19083)
6	70	134.0–135.0	yellowish brown	222 (23540), 333 (13380), 407 (8360)
7	79	88.7–91.3	orange	245 (11336), 326 (11559), 411 (8988)
8[a]	92	132.7–133.0	yellow	255 (22823), 325 (19315), 412 (18710)
9	94	174.0–174.7	red	212 (22617), 226 (21449), 235 (14598), 250 (8175), 277 (11095), 321 (3698), 518 (19036)
10	86	161.6–161.9	dark red	205 (40368), 245 (29965), 293 (20231), 524 (26772)

[a] The ring-opening reaction of benzotriazole **3b** proceeds quantitatively. Contains 8% of the other *ortho* isomer.

while 3-methylphenol quantitatively afforded the *ortho*-coupled azobenzenes **8** (92%) and the other *ortho* regioisomer (8%). β-Naphthol behaved in a typical way for a diazotization reaction and gave the *ortho* product, whereas α-naphthol showed opposite regioselectivity compared to that obtained in classical diazomethane reactions. The diazo compounds exhibit various colors depending upon the substituents (Table 1).

The *ortho* structure of the coupled products can be easily detected by the chemical shift of the phenolic OH group, which appears quite downfield at $\delta = 11$–16 ppm as a result of a hydrogen-bonding interaction with the neighboring nitrogen atom. In contrast, the phenolic OH group of the *para* product is found within the normal range of $\delta = 5$–6 ppm.

The aromatic azo compounds behave differently[18,19] in many of their reactions compared to the aliphatic diazo compounds.[20,21] Aromatic azo compounds are the largest and most important group of dyes used in the dye industry.[18,22–26] They have also found use in diazo-type photocopying processes and diazosulfonates are also beneficial as fungicides.[26] Although aromatic azo compounds are only represented to a marginal extent in pharmaceutical preparations,[27] azo groups have recently been included as substituents in some polycyclic compounds used as probes for chemical genetic studies.[28] Some other recent applications include their use for color marking of substrates in combinatorial chemistry[29] and in photosensitive nanocomposites.[30]

Aromatic azo compounds are still manufactured by the single most important synthetic route, that is, diazotization of aromatic amines followed by coupling with suitable acceptors.[18,22–26] In classical diazotization reactions, that is, treating a diazonium salt with an aromatic phenol or aniline derivative, the azo group usually does not enter at random, and for the phenol derivatives, the attack is always at the position *para* to the activating OH group. If this position is hindered, coupling will sometimes take place in the *ortho* position, albeit at a much slower rate.[24]

The Wallach rearrangement of azoxybenzenes[31] affords predominantly *p*-hydroxyazobenzenes. The thermolysis of 1:1 complexes of azoxybenzenes with $SbCl_5$ was reported[31] to give *o*-azobenzenes, but only in two instances were good yields obtained. The drawback of this reaction is that it necessitates the use of a harsh chemical ($SbCl_5$) and the prior preparation of azo compounds by a normal azo-coupling reaction and then oxidation to azoxybenzenes.

Of the two reported patent procedures, one describes the formation of the *ortho*-substituted azo-coupled product of α-naphthol in a heterogeneous water–organic solvent mixture (for example, water–dichloromethane) in 26% yield[32] and the other leads to *ortho* products only under strong alkaline conditions.[33] In the latter case, the intermediate formation of the mesomeric *o*-benzoquinone diazide is probably responsible for the *ortho* coupling.[33b] These variations in the reaction conditions have been done only in the case of α-naphthol to obtain various types of substituted azo dyes useful in the dye industry.

Bearing in mind the above mentioned literature data, to the best of our knowledge there exists no expedient direct method for the preparation of *ortho*-azobenzenes by a straight coupling reaction. Besides diazotization of aromatic amines, there are only a few methods, for example, diazotization of aryl hydrazines, transfer of an azo group by tosyl azides, known for the preparation of azobenzenes.[18,34,35]

In conclusion, the method presented here offers access to a wide palette of aromatic azo compounds by varying both the benzotriazole component as well as the nucleophile. Moreover, a total switch in the direction of attachment of the azo substituent can be envisaged. Although our investigations on this new reaction sequence continue, we believe that the above preliminary results provide ambitious guidelines for the preparation of keynote prototypes of *ortho*-substituted azobenzenes.

Experimental Section

3b: A 1.6 M solution of BuLi in hexanes (9.4 mL, 15 mmol) was added slowly to a stirred solution of **1** (1.8 g, 15 mmol) in anhydrous 1,2-dimethoxyethane (50 mL) at 0 °C under argon. After 1 h, nonafluorobutanesulfonyl fluoride (4.75 mL, 22.4 mmol) was added dropwise. The reaction mixture was stirred under reflux for about 3 h, with the progress of the reaction monitored by TLC. After completion of the reaction, the mixture was cooled to RT, and diluted with diethyl ether (100 mL). The organic layer was washed with aqueous saturated NH_4Cl solution (2 ×) and water (1 ×). After drying (Na_2SO_4), filtration, and removal of the solvent, the crude product was purified by chromatography on silica gel under protection from light (eluent: petroleum ether (b.p. 60–90 °C)/EtOAc, 4:1) to give **3b**; yield: 5.33 g (89%); m.p. 46.1–46.8 °C. IR (KBr): $\tilde{\nu} = 1356, 1193$ (SO_2), 1271, 1138, 1028 cm^{-1} (C-F); UV/Vis (MeCN): λ (ε mol^{-1} dm^3 cm^{-1}) = 211 (10650), 253 (5477), 293 (1477), 409 nm (352); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 8.23$ (d, $J_{6,7} = 8.22$ Hz, 1H, H7), 7.98 (d, $J_{4,5} = 8.30$ Hz, 1H, H4), 7.75–7.85 (t, $J = 8.34$, 8.04 Hz, 1H, H6), 7.55–7.64 ppm (dd, $J = 8.84$, 7.53 Hz, 1H, H5); ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 145.3$ (C9), 132.1 (C8), 131.9 (C6), 127.2 (C5), 121.4 (C7), 111.8 ppm (C4); EI-MS: $m/z = 400.9$. Elemental analysis calcd for $C_{10}H_4F_9N_3O_2S$: C 29.94, H 1.00, N 10.47, S 7.99; found: C 30.06, H 0.93, N 10.36, S 8.16.

4: NaH (0.12 g, 60% suspension in oil) was added to a stirred solution of phenol (0.28 g, 3 mmol) and **3b** (1 g, 2.5 mmol) in anhydrous toluene (50 mL) at room temperature under argon. The mixture was allowed to stir for 7 h while controlling the progress of the reaction by TLC. At the end of this period, EtOAc (100 mL) and water (25 mL) were added, and the suspension was treated with conc. HCl until the color of the organic phase changed from red to orange-red. The aqueous phase must remain colorless during this time. The organic phase was separated, dried (Na_2SO_4), filtered, and the solvent was evaporated. The crude product was purified by chromatography over silica gel (eluent: petroleum ether (b.p. 60–90 °C)/EtOAc (30:1) containing 1 % AcOH) to afford **4**; yield: 0.94 g (76 %); m.p. 134.2–135.1 °C (petroleum ether (bp 60–90 °C)). IR (KBr): $\tilde{\nu} = 3441$ (NH, OH), 1349, 1184 (SO_2), 1285, 1252, 1135 cm^{-1} (CF); UV/Vis (MeCN): λ ($\varepsilon\,mol^{-1}\,dm^3\,cm^{-1}$) = 250 (11708), 321 (12021), 395 nm (8324); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 12.00$ (s, 1H, OH), 11.86 (s, 1H, NH), 7.82–7.87 (m, 2H, H3, H6), 7.75 (d, $J = 7.92$ Hz, 1H, H3′), 7.44–7.50 (dd, $J = 7.32, 8.52$ Hz, 1H, H5), 7.37–7.44 (m, 2H, H4, H4′), 7.12–7.08 (t, $J = 7.32$, 7.92 Hz, 1H, H5′), 7.06 ppm (d, $J = 8.58$ Hz, 1H, H6′); ^{13}C NMR (600 MHz, $CDCl_3$): $\delta = 153.08$ (C2′), 137.34 (C2), 135.98 (C1′), 134.80 (C3′), 132.44 (C5), 131.43 (C4′), 130.27 (C6), 129.83 (C1), 126.12 (C4), 120.83 (C5′), 120.41 (C3), 118.72 ppm (C6′); EI-MS: $m/z = 494.9$ [M^+]. Elemental analysis calcd for $C_{16}H_{10}F_9N_3O_3S$: C 38.80, H 2.03, N 8.48, S 6.47; found: C 38.62, H 1.99, N 8.33, S 6.52.

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