# Lithium Tetrafluoroborate-Assisted Reactions of N-(α-Aminoalkyl)benzotriazoles with Olefins and 1,3-Dienes. New Syntheses of 1,2,5,6-Tetrahydropyridinium Salts, 1,2,3,4-Tetrahydroquinolines, and Some Related Heterocyclic Systems

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*Received December 11, 1992*

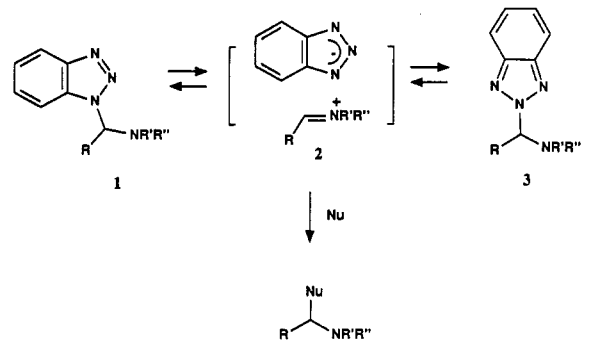
Lithium tetrafluoroborate efficiently assists the ionization of N-(α-aminoalkyl)benzotriazoles in tetrahydrofuran solution to generate reactive iminium intermediates, which can be trapped with electron-rich olefins and with 1,3-dienes. Hetero Diels–Alder cycloadditions of N-(α-dialkylaminoalkyl)benzotriazoles and lithium tetrafluoroborate with 1,3-dienes thus gave 1,2,5,6-tetrahydropyridinium salts, while reactions of N-[α-(arylamino)alkyl]benzotriazoles with olefins and 1,3-dienes afforded substituted 1,2,3,4-tetrahydroquinolines, as well as examples of the new heterocyclic systems indeno[2,1-c]quinoline and pyrido[3,2,1-kl]-1,4-phenothiazine.

## Introduction

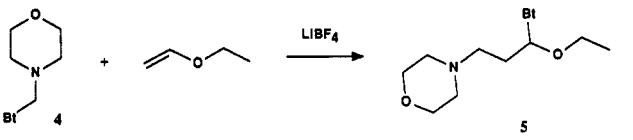
N-(α-Aminoalkyl)benzotriazoles constitute an interesting class of aminals which undergo reversible ionization in solution to generate benzotriazolate anion/iminium cation ion pairs.[1] $S_N1$-Nucleophilic substitutions of the benzotriazolyl group in compounds of type **1** and **3** by a variety of N-, O-, S-, and C-nucleophiles, proceeding *via* iminium intermediates **2**, have found numerous synthetic applications[2] (Scheme I).

Recently, acid-catalyzed additions of 1-(α-aminoalkyl)-benzotriazoles to ethyl vinyl ether or to 2,3-dihydrofuran opened a novel synthetic route to 1,3-amino ethers.[3] In this paper we describe lithium tetrafluoroborate-assisted reactions of N-(α-aminoalkyl)benzotriazoles with olefins and 1,3-dienes which provide synthetically useful routes to 1,2,5,6-tetrahydropyridinium salts and to 1,2,3,4-tetrahydroquinolines.

**Scheme I**




**Scheme II**




Bt = benzotriazolyl

## Results and Discussion

**Lithium Tetrafluoroborate-Assisted Generation of Iminium Cations from N-(α-Aminoalkyl)benzotriazoles and the Synthesis of 1,2,3,6-Tetrahydropyridinium Salts.** In spite of the easy interconversions of benzotriazol-1-yl and benzotriazol-2-yl derivatives of types **1** and **3** (Scheme I) *via* intermediate ion pairs,[1,2] N-(α-aminoalkyl)benzotriazoles do not react with aryl-substituted olefins or 1,3-dienes such as styrene or isoprene under a variety of conditions. N-(α-Aminoalkyl)benzotriazoles react with ethyl vinyl ether but only on heating (130–150 °C) and then rather slowly (cf. with ref 3). These observations are consistent with the above-mentioned isomerization proceeding *via* intimate ion pairs, which are not sufficiently reactive to attack styrene or isoprene.

We now report an efficient way of increasing the reactivity of N-(α-aminoalkyl)benzotriazoles employing lithium tetrafluoroborate.[4] Lithium perchlorate had no detectable effect in our attempted reactions of aminals **4** and **6** with ethyl vinyl ether, styrene, or isoprene in tetrahydrofuran solutions at 25–90 °C. According to $^1H$ NMR spectra, the aminals remained essentially unchanged. By contrast, lithium tetrafluoroborate increased the reactivity of N-(α-aminoalkyl)benzotriazoles dramatically. When heated in a sealed tube at 85 °C with ethyl vinyl ether in the presence of 10 mol% of lithium tetrafluoroborate, the aminal **4** gave within 20 min the addition product **5** in quantitive yield (Scheme II). These conditions are advantageous as compared to the previously reported additions of N-(α-aminoalkyl)benzotriazoles to enol ethers by heating at 130 °C for 48 h in the presence of p-toluenesulfonic acid.[3] The compound **5** was obtained

(1) Lindsay Smith, J. R.; Sadd, J. S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1181.
(2) Katritzky, A. R; Rachwal, S.; Hitchings, G. J. *Tetrahedron* **1991**, *47*, 2683.
(3) Katritzky, A. R; Rachwal, S.; Rachwal B.; Steel, P. *J. Org. Chem.* **1992**, *57*, 4932.
(4) For other synthetic methods employing lithium salts to accelerate transformations with polarized transition state, see: (a) Winstein, S.; Smith, S.; Darwish, D. *J. Am. Chem. Soc.* **1959**, *81*, 5511. (b) Pocker, Y.; Bucholz, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 2075. (c) Zefirov, N. S.; Koz'min, A. S.; Kirin, V. N.; Zhdankin, V. V.; Caple, R. *J. Org. Chem.* **1981**, *46*, 5264. (d) Grieco, P. A.; Clark, J. D.; Jagoe, C. T. *J. Am. Chem. Soc.* **1991**, *113*, 5488. (e) Pearson, W. H.; Schkeryantz, M. *J. Org. Chem.* **1992**, *57*, 2986.

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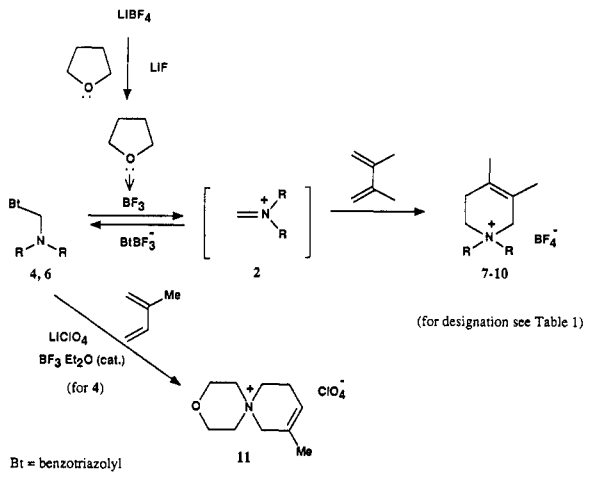
**Scheme III**



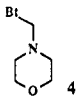
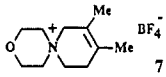
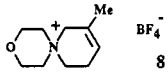
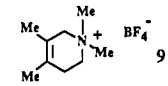
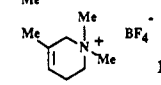
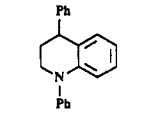
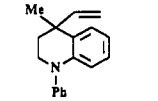
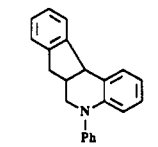
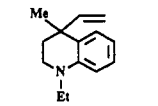
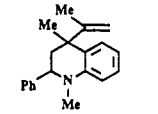
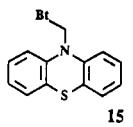
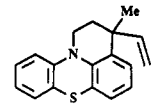
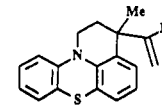

as a mixture of benzotriazol-1-yl and benzotriazol-2-yl isomers in a ratio of ca. 4:1 (by $^1$H NMR); the major isomer was isolated by column chromatography.

Iminium intermediates **2** generated from *N*-[α-(dialkylamino)alkyl]benzotriazoles **4**, **6**, and lithium tetrafluoroborate (1.25 equiv) can also be trapped with 1,3-dienes to afford 1,2,5,6-tetrahydropyridinium salts **7–10** in high yields (Scheme III, Table I). Interestingly, this reaction occurs even at 25 °C, but then requires ca. 15–20 days for completion. The optimal conditions for this transformation included heating the reagents at 85 °C for 3 h.

Hetero Diels–Alder reactions of Eschenmoser's salt,[5] of *N*,*N*,2-trimethylpropeniminium tetrafluoroborate,[6] and of iminium intermediates from α-halotrialkylamines,[7] from primary amines and aldehydes in aqueous media,[8-10] and from symmetric *N*,*N*,*N*′,*N*′-tetraalkylaminals with acetyl chloride[11] have been reported (for a review see ref 12). The regioselectivity of the reactions of aminals **4** and **6** with isoprene is analogous to that previously reported for hetero [4 + 2] cycloadditions with imines[13] or iminium intermediates from primary amines and aldehydes.[8,12] The new procedure of Scheme III is supplementary to those employing primary amines with aldehydes[12-14] and advantageous in comparison with the method of the ref 11 since we now completely utilize the aliphatic amine, and the benzotriazole produced can be easily recovered.[2] Readily available stable and crystalline *N*-(α-aminoalkyl)-benzotriazoles (for a review see ref 2) are also more convenient precursors of iminium intermediates than highly reactive and hygroscopic α-halo amines or iminium salts themselves.

The striking difference in behavior of lithium perchlorate and tetrafluoroborate in the presently described transformations suggest that the assistance of lithium tetrafluoroborate is not confined to a normal salt effects.[4a,c] Our studies find precedent in earlier work on the hydrolysis of acetals and ketals using lithium tetrafluoroborate.[14] (The application of this reagent for a cleavage of silyl ethers[15,16] and for electrooxidative cleavage of carbon–carbon bonds[17] has also been reported). On the basis of these[14] and our observations, we suggest that lithium tetrafluoroborate-assisted reactions of *N*-(α-aminoalkyl)benzotriazoles involve a partial dissociation of this salt to produce lithium fluoride and boron trifluoride. Probably, the relatively high energy of solvation of boron trifluoride in tetrahydrofuran can facilitate this reversible process (Scheme III).

**Table I. Tetrahydropyridinium Salts and Tetrahydroquinolines from *N*-(α-Aminoalkyl)benzotriazoles with 1,3-Dienes or Olefins**

| entry | aminal | substrate | product | yield (%) |
|---|---|---|---|---|
| 1 |  4 |  |  7 | 90[a] |
| 2 | 4 |  |  8 | 79 |
| 3 |  6 |  |  9 | 35 (87[a]) |
| 4 | 6 |  |  10 | 70 |
| 5 |  12 |  |  | 17 45 |
| 6 | 12 |  |  | 18 60 |
| 7 | 12 |  |  | 19 40 |
| 8 |  13 |  |  | 20 53 |
| 9 |  14 |  |  | 21[b] 58 |
| 10 |  15 |  |  | 22 85 |
| 11 | 15 |  |  | 23 80 |

[a] Yield of the tetraphenylborate. [b] Mixture of (2*R**,2*S**) and (2*S**,4*S**)-diastereoisomers in a ratio of 2.5:1.

(5) Danishefsky, S.; Kitahara, T.; McKee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 6715.
(6) Marchand-Brynaert, J.; Ghosez, L. *Tetrahedron Lett.* **1974**, 377.
(7) Böhme, H.; Hartke, K.; Müller, A. *Chem. Ber.* **1963**, *96*, 607.
(8) Larsen, S. D.; Grieco, P. A. *J. Am. Chem. Soc.* **1985**, *107*, 1768.
(9) Grieco, P. A.; Larsen, S. D.; Fobare, W. F. *Tetrahedron Lett.* **1986**, *27*, 1975.
(10) Grieco, P. A.; Larsen, S. D. *J. Org. Chem.* **1986**, *51*, 3553.
(11) Babayan, A. T.; Martyrosyan, G. T.; Grigoryan, D. V. *Zh. Org. Khim.* **1968**, *4*, 984 (Boger, D. L.; Weinreb, S. N. *Hetero Diels–Alder Methodology in Organic Synthesis*; Pergamon Press: New York, 1987; p 49.
(12) Boger, D. L.; Weinreb, S. N. *Hetero Diels-Alder Methodology in Organic Synthesis*; Pergamon Press: New York, 1987; p 49.
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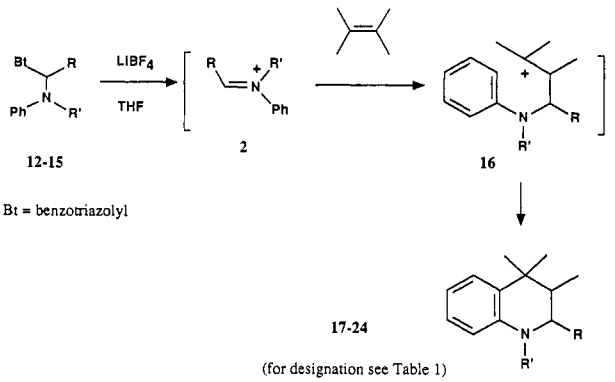
(15) Metcalf, B. W.; Burkhart, J. P.; Jund, K. *Tetrahedron Lett.* **1980**, *21*, 35.
(16) Shu, A. Y. L.; Djerassi, C. *Tetrahedron Lett.* **1981**, *22*, 4627.
(17) Torii, S.; Inokuchi, T.; Oi, R. *J. Org. Chem.* **1982**, *47*, 47.

**Scheme IV**



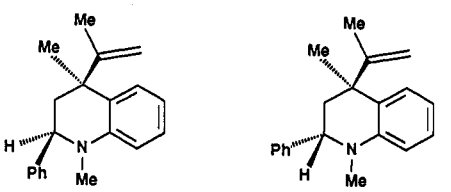

Thus, in the reactions of Schemes II and III lithium tetrafluoroborate probably acts both as a salt increasing the ionizing power of the solvent[4a] (cf. also the "doping effect"[4c]) and as a Lewis acid source. Indeed, use of 1 M lithium perchlorate in tetrahydrofuran along with catalytic amounts (ca. 7 mol %) of boron trifluoride etherate in the transformation of the aminal 4 with isoprene gave rise to the salt 11 in 55% yield (Scheme III).

**Lithium Tetrafluoroborate-Assisted Syntheses of 1,2,3,4-Tetrahydroquinolines and Related Heterocyclic Systems.** When *N*-[α-(arylamino)alkyl]benzotriazoles **12–15** were allowed to react with isoprene or 2,3-dimethylbutadiene under the conditions of Scheme III, no formation of 1,2,5,6-tetrahydropyridinium salts was observed. Instead, 1,2,3,4-tetrahydroquinolines **17–23** were isolated from reactions of aminals **12–15** with isoprene, 2,3-dimethylbutadiene, styrene, or indene as major products in 40–85% yields (Scheme IV, Table I).

This new reaction of *N*-[α-(arylamino)alkyl]benzotriazoles is closely related to a previously reported synthesis of 1,2,3,4-tetrahydroquinolines from electrochemically produced α-methoxy-*N*,*N*-dialkylanilines with electron-rich olefins in the presence of titanium tetrachloride.[18] Very recently, the construction of quinoline skeletons by the ruthenium-catalyzed oxidation of *N*-methyl-*N*-alkylanilines with *tert*-butyl hydroperoxide followed by treatment with olefins in the presence of titanium tetrachloride has been reported.[19] The presently reported reaction is also initiated by electrophilic addition of the iminium ions **2** generated under the reaction conditions to the double bond to yield new cationic species **16** that then attack intramolecularly the aromatic nucleus to yield the products **17–23** (Scheme IV). This mechanism might suggest that similar transformations could be achieved using *N*-arylamines and formaldehyde instead of *N*-[α-(arylamino)-alkyl]benzotriazoles. However, diphenylamine and paraformaldehyde with styrene or isoprene under the conditions of Scheme IV gave the expected 1,2,3,4-tetrahydroquinolines **17** and **18** only in low yields (ca. 10–20%).

We believe that the higher selectivity observed in the transformations involving aminals **12–15** reflects the relatively soft character of the iminium intermediates **2** generated as ion pairs with trifluoro(benzotriazolyl)borate anions (Scheme IV). Indeed, attempted reactions of compounds **12** and **13** with the less reactive olefins (1-decene or cyclohexene) resulted in complex mixtures of products from which no tetrahydroquinolines could be isolated (considerable decomposition of the aminals to benzotriazole and aromatic amines was detected by TLC and $^1$H NMR spectroscopy). Thus, the scope of the presently described route to tetrahydroquinolines is apparently restricted to transformations employing electron-rich olefins or 1,3-dienes. The related procedures of refs 18 and 19 cannot be applied to the synthesis of 2-substituted 1,2,3,4-tetrahydroquinolines. By contrast, the easy accessibility of α-substituted *N*-(α-aminoalkyl)-benzotriazoles[2] should provide for considerable generalization of the presently described methodology, as demonstrated by the preparation of 2-phenyltetrahydroquinoline **21** from aminal **14** (Table I).

The compound **21** has been obtained as a mixture of two diastereomers in a ratio of ca. 2.5:1 (by $^1$H NMR). Pronounced nuclear Overhauser effects observed in the $^1$H NMR spectra of the major and minor isomers of **21** enabled structural assignments of these compounds to (2*R**,4*S**) and (2*S**,4*S**) diastereomers, respectively. Thus, selective decoupling of the methyl group in position 4 of the major isomer (δ 1.48 ppm) resulted in a 15% enhancement of the H-2 resonance (*Z*-configuration), whereas analogous irradiation of the minor isomer (the methyl signal at δ 1.43 ppm) gave rise to a 12% enhancement in the intensity of the H-2′ and H-5′ signals of the phenyl group (δ 7.15 ppm), and the ring H-2 resonance was not affected in the latter case (*E*-configuration).




**21**

Reaction of the aminal **12** with indene was stereoselective and afforded *cis*-fused tetrahydroindeno[2,1-*c*]quinoline **19**, as evidenced by the value of a coupling constant between H-3 and H-9 of ca. 6.6 Hz. NMR data for compounds **17-23** (recorded at 22 °C) are in a good agreement with earlier studies and indicated an easy inversion of potentially chiral nitrogen in substituted 1,2,3,4-tetrahydroquinolines,[20,21] as no additional isomers could be detected.

Tetrahydroquinolines have found many industrial applications.[22] Recent reports include their use as components of imaging compositions,[23] recording materials,[24] photoreceptors,[25] adhesives,[26] herbicides and fungicides,[27] antiaging agents,[28] polymerization catalysts,[29] inhibitors

(18) Shono, T.; Matsumura, Y.; Inoue, K.; Ohmizu, H., Kashimura, Sh. *J. Am. Chem. Soc.* **1982**, *104*, 5753.
(19) Murahashi, Sh.-I.; Naota, T.; Nakato, T. *Synlett* **1992**, 835.
(20) Booth, H. *J. Chem. Soc.* **1964**, 1841.
(21) Nagarajan, K.; Shah, R. K.; Fuhrer, H.; Puckett, R. T.; Narasimhamurthy, M. R.; Venkatesan, K. *Helv. Chim. Acta* **1978**, *61*, 1246.
(22) Yates, F. S. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon Press: New York, 1984; Vol. 2, p 511.
(23) Jpn. Kokai 81,101,146 (*Chem. Abstr.* **1982**, *96*, 77598r).
(24) Shioi, S.; Matoba, G.; Miyake, M. Ger. Offen. DE 3,330,679 1982. (*Chem. Abstr.* **1984**, *101*, 201650q).
(25) Hirose, H.; Sawada, K.; Kinoshita, A.; Kawakami, S. Jpn. Kokai 61,77,055, 1986 (*Chem. Abstr.* **1986**, *105*, 235746y).
(26) Boeder, C. W. U.S. Pat. 4,373,077, 1983 (*Chem. Abstr.* **1983**, *98*, 144741p).
(27) Osumi, T.; Okuda, H.; Sato, M.; Takano, J. Jpn. Kokai 61,68,487, 1986 (*Chem. Abstr.* **1986**, *105*, 172511v).
(28) Knittel, H. *Dtsch. Faerber-Kal.* **1984**, *88*, 158 (*Chem. Abstr.* **1984**, *101*, 231808q).

of blood aggregation,[30] and antiarrhythmics.[31] Products **17-23** are all new, and the compound **19** is the first representative of the novel heterocyclic system of indeno-[2,1-*c*]quinoline. Analogously, from 1-[(1,4-phenothiazin-1-yl)methyl]benzotriazole (**15**) the first derivatives (**22** and **23**) of pyrido[3,2,1-*kl*]-1,4-phenothiazine have been synthesized in high yields.

## Conclusion

A new and efficient lithium tetrafluoroborate-assisted method for the generation of reactive iminium intermediates from *N*-(α-aminoalkyl)benzotriazoles under mild conditions has enabled simple preparations of 1,2,5,6-tetrahydropyridinium salts and of 1,2,3,4-tetrahydroquinolines, as well as derivatives of the two novel heterocyclic systems indeno[2,1-*c*]quinoline and pyrido[3,2,1-*kl*]-1,4-phenothiazine, from readily available benzotriazole-derived aminals and electron-rich olefins or 1,3-dienes.

## Experimental Section

**General.** Melting points were determined on a capillary melting point apparatus and are uncorrected. NMR spectra were taken for solutions in $CDCl_3$ except for salts **7-11**, which were taken in $(CD_3)_2SO$, with tetramethylsilane or solvent as internal standard for $^1H$ (300 MHz) and $^{13}C$ NMR (75 MHz), respectively. Assignments for the signals in necessary cases were confirmed by selective decouplings (for $^1H$ NMR spectra) or APT and DEPT techniques (for $^{13}C$ NMR spectra). Signals without assignment correspond to aromatic resonances. Tetrahydrofuran was distilled from sodium–benzophenone immediately before use. Reactions with water-sensitive compounds were carried out in dry nitrogen atmospheres. Column chromatography was conducted with silica gel grade 60–200 mesh. Aminals **4**, **6**, and **12-14** were prepared by literature procedures.[32]

**1-[(1,4-Phenothiazin-10-yl)methyl]benzotriazole (15).** A mixture of 1,4-phenothiazine (1.99 g, 10 mmol) and 1-(hydroxymethyl)benzotriazole (1.49 g, 10 mmol) in toluene (40 mL) was stirred under reflux with Dean–Stark adapter for 30 h. The solvent was evaporated in vacuo and the residue was crystallized from ethanol to give 2.15 g (65%) of the product: mp 168–169 °C; $^1H$ NMR δ 6.64 (s, 2 H, $CH_2$), 6.91–7.39 (m, 10 H), 7.51 (d, $J$ = 8.1 Hz, 1 H, H-7 Bt), 7.80 (d, $J$ = 8.2 Hz, 1 H, H-4 Bt); $^{13}C$ NMR δ 62.5 ($CH_2$), 110.5 (C-7 Bt), 116.8, 117.0, 119.8 (C-4 Bt), 124.0, 124.2 (C-5 Bt), 126.5, 127.6, 127.7 (C-6 Bt), 132.3 (C-7a Bt), 142.6, 146.3 (C-3a Bt). Anal. Calcd for $C_{19}H_{14}N_4S$: C, 69.07; H, 4.27; N, 16.96. Found: C, 68.80; H, 4.30; N, 16.98.

**1-(Benzotriazol-1-yl)-1-ethoxy-3-morpholinopropane and 1-(Benzotriazol-2-yl)-1-ethoxy-3-morpholinopropane (5).** A solution of **4** (0.88 mg, 4 mmol), vinyl ethyl ether (0.36 g, 4.8 mmol), and $LiBF_4$ (0.04 g, 0.4 mmol) in tetrahydrofuran (4 mL) was heated in a sealed tube at 85 °C for 20 min. The solvent was evaporated in vacuo and the residue subjected to flash column chromatography (chloroform–hexanes 1:3) to give 1.16 g (100%) of the oily product as a mixture of Bt-1 and Bt-2 isomers in a molar ratio of 3:1 (by NMR). Repeated column chromatography (diethyl ether–hexanes 1:10) afforded pure Bt-1 isomer (0.7 g, 60%) as an oil: $^1H$ NMR δ 1.15 (t, $J$ = 6.9 Hz, 3 H, Me), 2.25–2.50 [m, 8 H, $CH_2N(CH_2)CH_2CH_2$], 3.32 [dq, $J$ = 9.3, 6.9 Hz, 1 H, $OCH_A(H_B)Me$], 3.50–3.70 [m, 5 H, $OCH_A(H_B)Me$ and $CH_2OCH_2$], 6.23 (dd, $J$ = 6.1, 6.4 Hz, 1 H, H-1), 7.39 (dd, $J$ = 8.3, 7.6 Hz, 1 H, H-5′ Bt), 7.48 (dd, $J$ = 8.3, 7.6 Hz, 1 H, H-6′ Bt), 7.78 (d, $J$ = 8.3 Hz, 1 H, H-7′ Bt), 8.10 (d, $J$ = 8.3 Hz, 1 H, H-4′ Bt); $^{13}C$ NMR δ 14.6 (Me), 31.7 (C-2), 53.5 (C-3′ and C-5′ morph), 53.8 (C-3), 64.5 ($CH_2Me$), 66.8 (C-2′ and C-6′ morph), 88.8 (C-1), 111.0 (C-7′ Bt), 120.0 (C-4′ Bt), 124.1 (C-5′ Bt), 127.3 (C-6′ Bt), 131.5 (C-7a′ Bt), 146.7 (C-3a′ Bt). Anal. Calcd for $C_{15}H_{22}N_4O_2$: C, 62.05; H, 7.64; N, 19.30. Found: C, 62.15; H, 7.66; N, 19.20.

**General Procedure for the Preparation of Tetrahydropyridinium Salts 7-10.** A solution of the appropriate aminal **4** or **6** (4 mmol), 1,3-diene (4.4 mmol), and $LiBF_4$ (0.56 g, 6 mmol) in tetrahydrofuran (4 mL) was heated at 85 °C for 3 h. The mixture was cooled to 20 °C or left at 0 °C over 10 h (for the isolation of the tetrafluoroborate **9**), and the precipitated products **7–10** were filtered off and washed with tetrahydrofuran (2 × 2 mL) and diethyl ether (4 × 5 mL). Salts **7** and **9** were isolated as tetraphenylborates after evaporation of reaction mixtures *in vacuo*, treatment of the residue with a mixture of diethyl ether (20 mL) and water (40 mL), and addition of sodium tetraphenylborate (1.37 g, 4 mmol) in water (10 mL) to the separated aqueous phase. The resulting precipitates of tetraphenylborates **7** and **9** were washed with water (5 × 20 mL), diethyl ether (2 × 5 mL), and dried in a vacuum desiccator.

**6,7-Dimethyl-1-oxa-4-azoniaspiro[5.5]undec-6-ene tetraphenylborate (7):** yield 90%; mp 218–220 °C (methanol–acetone); $^1H$ NMR δ 1.59 (s, 3 H, Me-6), 1.63 (s, 3 H, Me-7), 2.22 (m, 2 H, 2 H-8), 3.29 (dd, $J$ = 4.8, 4.7 Hz, 4 H, 2 H-3 and 2 H-10), 3.49 (dd, $J$ = 6.4, 6.4 Hz, 2 H, 2 H-9), 3.83 (m, 6 H, 2 H-2, 2 H-5 and 2 H-11), 6.80 (dd, $J$ = 7.3, 7.1 Hz, 4 H, Ph), 6.94 (dd, $J$ = 7.3, 7.1 Hz, 8 H, Ph), 7.19 (m, 12 H, Ph); $^{13}C$ NMR δ 15.9 (Me-7), 17.5 (Me-6), 25.2 (C-8), 51.4 (C-9), 57.2 (2 C, C-3 and C-10), 59.6 (2 C, C-2 and C-11), 63.3 (C-5), 117.5 (C-7), 121.5 (C-4′ BPh), 124.1 (C-7), 125.3 (q, $J$ = 2.6 Hz, 2 C, C-2′ and C-6′ BPh), 135.5 (2 C, C-3′ and C-5′ BPh), 163.4 (q, $J$ = 49.1 Hz, 4 C, C-1′ BPh). Anal. Calcd for $C_{35}H_{40}BNO$: C, 83.82; H, 8.04; N, 2.79. Found: C, 83.76; H, 8.15; N, 2.83.

**6-Methyl-1-oxa-4-azoniaspiro[5.5]undec-6-ene tetrafluoroborate (8):** yield 79%: mp 185–186 °C (from methanol–diethyl ether); $^1H$ NMR δ 1.74 (s, 3 H, Me), 2.34 (m, 2 H, 2 H-8), 3.41 (dd, $J$ = 4.7, 4.6 Hz, 4 H, 2 H-3 and 2 H-10), 3.65 (dd, $J$ = 6.3, 6.1 Hz, 2 H, 2 H-9), 3.91 (m, 4 H, 2 H-2 and 2 H-11), 4.01 (br s, 2 H, 2 H-5), 5.36 (br s, 1 H, H-7); $^{13}C$ NMR δ 21.8 (Me), 24.4 (C-8), 54.8 (2 C, C-5 and C-9), 57.1 (2 C, C-3 and C-10), 59.6 (2 C, C-2 and C-11), 112.3 (C-7), 132.9 (C-6). Anal. Calcd for $C_{10}H_{18}BF_4NO$: C, 47.09; H, 7.11; N, 5.49. Found: C, 46.83; H, 7.23; N, 5.36. **Perchlorate 11.** A solution of **4** (0.44 g, 2 mmol), isoprene (0.16 g, 2.2 mmol), $LiClO_4$ (0.22 g, 2 mmol), and boron trifluoride etherate (0.02 g, 0.14 mmol) in tetrahydrofuran (2 mL) was heated at 85 °C for 3 h. The mixture was cooled to 20 °C, and precipitated crystals were filtered off, washed with tetrahydrofuran (2 × 2 mL) and diethyl ether (7 mL), and dried in a vacuum dessicator to give 0.27 g (50%) of the salt **11**: mp 195–196 °C (with dec.). Anal. Calcd for $C_{10}H_{18}ClNO_5$: C, 44.87; H, 6.78; N, 5.23. Found: C, 44.88; H, 6.68; N, 5.04.

**1,1,3,4-Tetramethyl-1,2,5,6-tetrahydropyridinium tetrafluoroborate (9):** yield 35%; mp 142–144 °C (from methanol–diethyl ether); $^1H$ NMR δ 1.59 (s, 3 H, Me-4), 1.70 (s, 3 H, Me-3), 2.32 (m, 2 H, 2 H-5), 3.03 (s, 3 H, $NMe_2$), 3.38 (dd, $J$ = 9.0 and 6.3 Hz, 2 H, 2 H-6), 3.72 (br s, 2 H, 2 H-2); $^{13}C$ NMR δ 15.7 (Me-4), 17.6 (Me-3), 26.3 (C-5), 50.6 ($NMe_2$), 57.7 ($NCH_2$), 63.2 ($NCH_2$), 118.2 (C-4), 123.6 (C-3). **Tetraphenylborate:** yield 87%; mp 231–233 °C (from methanol–acetone). Anal. Calcd for $C_{33}H_{38}BN$: C, 86,26; H, 8.34; N, 3.05. Found: C, 85.86; H, 8.33; N, 3.06.

**1,1,3-Trimethyl-1,2,5,6-tetrahydropyridinium tetrafluoroborate (10):** yield 70%; mp 265–267 °C (from methanol–diethyl ether); $^1H$ δ 1.75 (s, 3 H, Me), 2.33 (m, 2 H, 2 H-5), 3.04 (s, 6 H, $NMe_2$), 3.41 (dd, $J$ = 6.3 and 6.2 Hz, 2 H-6), 3.81 (br s, 2 H, 2 H-2), 5.39 (br s, 1 H, H-3); $^{13}C$ NMR δ 21.9 (Me), 25.3 (C-5), 50.5 ($NMe_2$), 57.7 ($NCH_2$), 59.9 ($NCH_2$), 113.2 (C-4), 132.11 (C-3). Anal. Calcd for $C_8H_{16}BF_4N$: C, 45.11; H, 7.57; N, 6.58. Found: C, 45.21; H, 7.37; N, 6.46.

**General Procedure for the Preparation of Tetrahydroquinolines 17, 18, 20, 21, Tetrahydroindeno[2,1-*c*]quinoline 19 and Tetrahydropyrido[3,2,1-*kl*]-1,4-phenothiazines 22 and 23.** A solution of the appropriate aminal **12–15** (4 mmol), olefin or 1,3-diene (4.8 mmol), and $LiBF_4$ (0.38 g, 4 mmol) in tetrahydrofuran (4 mL) was heated at 85 °C for 1 h. Solvent was evaporated *in vacuo* and the residue subjected to a flash column chromatography (hexanes–diethyl ether 30:1) to afford the corresponding products **17–23** as a first major fraction.

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**1,4-Diphenyl-1,2,3,4-tetrahydroquinoline (17)**: yield 45%; mp 59–60 °C; $^1$H NMR δ 2.10–2.40 (m, 2 H, H-3), 3.57 (m, 2 H, 2 H-2), 4.22 (dd, $J$ = 6.2, 6.1 Hz, 1 H, H-4), 6.65 (ddd, $J$ = 7.4, 7.3, 1.1 Hz, 1 H), 6.80 (dd, $J$ = 8.3, 1.1 Hz, 1 H), 6.84 (d, $J$ = 7.5 Hz, 1 H), 6.97 (m, 1 H), 7.12 (m, 1 H), 7.15–7.40 (m, 9 H); $^{13}$C NMR δ 31.2 (C-3), 43.3 (C-4), 48.1 (C-2), 115.8, 118.3, 123.9, 124.9, 126.2, 126.3 (C-4a), 126.9, 128.4, 128.6, 129.5, 130.3, 144.6, 146.1, 148.3 (C-8a). Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.04; H, 6.48; N, 4.59.

**4-Methyl-1-phenyl-4-vinyl-1,2,3,4-tetrahydroquinoline (18)**: yield 60% oil; $^1$H NMR δ 1.37 (s, 3 H, Me), 1.81 (m, 2 H, 2 H-3), 3.51 (m, 2 H, 2 H-2), 4.82 [dd, $J$ = 17.3, 1.4 Hz, 1 H, C$H_A$(H$_B$)=], 5.03 [dd, $J$ = 10.5, 1.4 Hz, 1 H, CH$_A$($H_B$)=], 5.88 (dd, $J$ = 10.5, 17.3 Hz, 1 H, CH=), 6.63 (m, 2 H), 6.81–6.88 (m, 1 H), 7.00 (m, 1 H), 7.04–7.09 (m, 1 H), 7.10–7.17 (m, 2 H), 7.20–7.30 (m, 2 H); $^{13}$C NMR δ 27.2 (Me), 35.9 (C-3), 39.4 (C-4), 47.2 (C-2), 113.3 (CH$_2$=), 116.0 (C-4 Ph), 118.1, 123.8, 124.8 (C-4a), 124.8, 126.6, 128.1, 129.4, 143.7 (C-1 Ph), 147.5 (CH=), 148.46 (C-8a). Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.38; H, 7.84; N, 5.41.

**1-Phenyl-1,2,3,9-tetrahydroindeno[2,1-*c*]quinoline (19)**: yield 40% oil; $^1$H NMR δ 2.73 (dd, $J$ = 15.9, 2.4 Hz, 1 H, H$_A$-4), 3.00 (m, 1 H, H-3), 3.18–3.32 (m, 2 H, H$_B$-4 and H$_A$-2), 3.52 (dd, $J$ = 16.0, 4.6 Hz, 1 H, H$_B$-2), 4.42 (d, $J$ = 6.6 Hz, H-9), 6.78 (dd, $J$ = 8.3, 1.0 Hz), 6.85 (ddd, $J$ = 7.4, 7.3, 1.0 Hz, 1 H), 7.00 (m, 1 H), 7.08 (m, 1 H), 7.14–7.48 (m, 8 H); $^{13}$C NMR δ 35.9 (C-4), 37.1 (C-3), 46.0 (C-9), 51.5 (C-2), 115.6, 118.5, 123.6, 124.6, 124.7 (C-9a), 125.1, 126.4, 126.6, 129.2, 129.3, 130.6, 141.3, 144.3, 146.2, 147.9 (C-13a). Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.77; H, 6.57; N, 4.58.

**1-Ethyl-4-methyl-4-vinyl-1,2,3,4-tetrahydroquinoline (20)**: yield 53% oil; $^1$H NMR δ 1.12 (t, $J$ = 7.1 Hz, 3 H, *Me*CH$_2$), 1.37 (s, 3 H, Me), 1.78 (m, 2 H, 2 H-3), 3.22 (dd, $J$ = 6.0, 5.8 Hz, 2 H, 2 H-2), 3.35 (dq, $J$ = 7.1, 3.4 Hz, 2 H, MeCH$_2$), 4.81 [dd, $J$ = 17.3, 1.5 Hz, 1 H, C$H_A$(H$_B$)=], 5.07 [dd, $J$ = 10.5, 1.5 Hz, 1 H, CH$_A$($H_B$)=], 5.90 (dd, $J$ = 17.3, 10.5 Hz, 1 H, CH=), 6.55–6.66 (m, 2 H, H-6 and H-7), 7.05 (m, 2 H, H-5 and H-8); $^{13}$C NMR δ 10.6 (MeCH$_2$), 27.2 (Me), 35.4 (C-3), 39.1 (C-4), 44.4 (CH$_2$), 45.4 (CH$_2$), 110.7, 113.1 (CH$_2$=), 115.2, 127.2, 127.4 (C-4a), 128.0, 144.1 (C-8a), 147.9 (CH=); HRMS calcd for $C_{14}H_{19}N$: 201.1507 (M$^+$), found 201.1506.

**(2*R**,4*S**)-1,4-Dimethyl-4-(1-methylethenyl)-2-phenyl-1,2,3,4-tetrahydroquinoline and (2*S**,4*S**)-1,4-Dimethyl-4-(1-methylethenyl)2-phenyl-1,2,3,4-tetrahydroquinoline (21).** Mixture of the (2*R**,4*S**) and (2*S**,4*S**) diastereomers in a ratio of 2.5:1 (by NMR): yield 58% oil; $^1$H NMR (superscript indexes *RS* and *SS* correspond to a (2*R**,4*S**) and (2*S**,4*S**) isomers, respectively) δ 1.43 (s, 0.86 H, Me$^{SS}$), 1.48 (s, 2.14 H, Me$^{RS}$), 1.60 [d, $J$ = 1.2 Hz, 4-Me$^{RS}$), 1.66 (dd, $J$ = 13.5 and 3.9 Hz, C$H_A$(H$_B$)$^{RS}$], 1.82 [d, $J$ = 0.7 Hz, 0.86 H, 4-Me$^{SS}$), 1.82 [m, 0.29 H, C$H_A$(H$_B$)$^{SS}$, overlapped with Me signal], 2.15 [dd, $J$ = 12.5 and 3.9 Hz, 0.29 H, CH$_A$($H_B$)$^{SS}$], 2.23 [dd, $J$ = 13.5, 11.7 Hz, 0.71 H, CH$_A$($H_B$)$^{RS}$], 2.67 (s, 0.86 H, NMe$^{SS}$), 2.72 (s, 2.14 H, NMe$^{RS}$), 4.13 (dd, $J$ = 12.0 and 3.9 Hz, 0.29 H, H-2$^{SS}$), 4.20 [d, $J$ = 2.0 Hz, 0.29 H, C$H_A$(H$_B$)=$^{SS}$), 4.36 (dd, $J$ = 11.7, 3.9 Hz, 0.71 H, H-2$^{RS}$), 4.89 [m, 0.29 H, CH$_A$($H_B$)=$^{SS}$], 5.00 [dq, $J$ = 1.3 and 1.2 Hz, 0.71 H, C$H_A$(H$_B$)=$^{RS}$], 5.08 [m, 0.71 H, CH$_A$($H_B$)=$^{RS}$], 6.63–7.40 (m, 9 H); $^{13}$C NMR δ 18.6 (*Me*C=$^{SS}$), 19.9 (*Me*C=$^{RS}$), 26.3 (Me$^{SS}$), 28.1 (Me$^{RS}$), 37.8 (NMe$^{RS}$), 38.1 (NMe$^{SS}$), 42.1 (C-4$^{SS}$), 42.4 (C-4$^{RS}$), 44.3 (C-3$^{SS}$), 44.7 (C-3$^{RS}$), 61.1 (C-2$^{RS}$), 61.4 (C-2$^{SS}$), 112.3 (CH$_2$=$^{SS}$), 112.5 (CH$_2$=$^{RS}$), 114.4, 116.2, 116.5, 126.6, 126.9, 127.0, 127.2, 127.4, 128.5, 128.6, 128.9, 144.5, 144.6, 146.9, 150.7 (>C=$^{RS}$), 151.3 (>C=$^{SS}$). Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.43; H, 8.39; N, 5.04.

**9-Methyl-9-vinyl-9,10,11,12-tetrahydropyrido[3,2,1-*kl*]-1,4-phenothiazine (22)**: yield 85% oil; $^1$H NMR δ 1.38 (s, 3 H, Me), 1.95 (m, 2 H, 2 H-10), 3.60 (dd, $J$ = 6.1, 5.6 Hz, 2 H, 2 H-11), 4.76 [dd, $J$ = 17.3 and 1.2 Hz, 1 H, C$H_A$(H$_B$)=], 5.09 [dd, $J$ = 10.5, 1.2 Hz, 1 H, CH$_A$($H_B$)=], 5.84 (dd, $J$ = 17.3, 10.5 Hz, CH=), 6.78–6.99 (m, 5 H), 7.05–7.13 (m, 2 H); $^{13}$C NMR δ 27.0 (Me), 34.5 (C-10), 39.2 (C-9), 42.3 (C-11), 112.9, 114.7 (CH$_2$=), 119.6, 121.8, 122.3, 122.4, 125.5, 126.6, 126.8, 127.3, 129.6, 141.1, 144.4, 146.4 (CH=). Anal. Calcd for $C_{18}H_{17}NS$: C, 77.38; H, 6.13; N, 5.01. Found: C, 77.11; H, 6.11; N, 4.96.

**9-Methyl-9-(1-methylethenyl)-9,10,11,12-tetrahydropyrido[3,2,1-*kl*]-1,4-phenothiazine (23)**: yield 80% oil; 1.45 (s, 3 H, Me), 1.71 (d, 3 H, $J$ = 0.7 Hz, MeC=), 1.79–1.92 (m, 1 H, H$_A$-10), 2.21 (ddd, $J$ = 13.6, 4.8 and 4.7 Hz, H$_B$-10), 3.56 (m, 2 H, 2H-11), 4.43 [br s, 1 H, CH$_A$(H$_B$)=], 4.90 [dd, $J$ = 1.4 and 1.3 Hz, 1 H, CH$_A$(H$_B$)=], 6.78–6.98 (m, 5 H), 7.10–7.13 (m, 2 H); $^{13}$C NMR δ 18.8 (MeC=), 26.9 (Me), 32.2 (C-10), 41.9 (C-9), 42.5 (C-11), 112.9, 115.0 (CH$_2$=), 119.4, 121.7, 122.3, 125.4, 126.4, 126.5, 126.8, 131.0, 141.0, 144.4, 150.2 (MeC=). Anal. Calcd for $C_{19}H_{19}NS$: C, 77.77; H, 6.53; N, 4.77. Found: C, 77.49; H, 6.23; N, 4.89.