77.4 (d, ≡CCF, J = 32 Hz); 87.8 (d, ≡CCH$_2$, J = 9 Hz); 126.8, 128.2, 128.5 (Ph); 134.7 (C-1, Ph).

MS (m/z): 216 [M]$^+$. Found (%): C, 83.38; H, 8.01. $C_{15}H_{17}F$. Calculated (%): C, 83.29; H, 7.92.

7-Fluoro-7-(phenylethynyl)bicyclo[4.2.0]heptane (7d) was obtained in 69% yield from tetrahalide **1b** and cyclohexene by method *ii* (isomer ratio *endo*-F : *exo*-F = 4.5 : 1).

^{1}H NMR, δ: 1.20—2.10 (m, 12 H, 4 CH$_2$ and 2 CH); 7.30—7.60 (m, 5 H, Ph). *endo*-(F)-Isomer. ^{13}C NMR, δ: 19.0 (2 CH$_2$); 20.8 (d, 2 CH$_2$, J = 3 Hz); 22.4 (d, 2 CH, J = 14 Hz); 76.9 (d, CF, J = 208 Hz); 82.6 (d, ≡CCF, J = 30 Hz); 93.4 (d, ≡CCH$_2$, J = 10 Hz); 122.3 (d, C-1, Ph, J = 3 Hz); 128.4, 128.7, 131.6 (Ph). ^{19}F NMR, δ ($CFCl_3$): −163.6. *exo*-(F)-Isomer. Partial ^{13}C NMR spectrum, δ: 17.7 (d, 2 CH$_2$, J = 3 Hz); 21.3 (d, 2 CH, J = 14 Hz); 21.4 (d, 2 CH$_2$, J = 2 Hz); 128.3, 128.5, 131.7 (Ph). ^{19}F NMR, δ ($CFCl_3$): −199.7. Found (%): C, 83.92; H, 7.15. $C_{15}H_{15}F$. Calculated (%): C, 84.08; H, 7.06.

gem-(Alk-1-ynyl)fluorocyclopropanes obtained by the addition of (alk-1-ynyl)fluorocarbenes to olefins are of great interest as probable physiologically active compounds and synthons in organic syntheses.

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Allylzinc bromide: reductive *trans*-1,3-diallylation of isoquinoline and intramolecular cyclization of 2,4-dizinc derivative

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Pyrrole, isoquinoline, and pyridines treated successively with triallylborane and alcohol undergo reductive *trans*-α,α′-diallylation.[1,2] These stereospecific reactions accompanied by the destruction of aromatic system of the corresponding heterocyclic systems occur under mild conditions (20—100 °C) and are not complicated by side processes. The only disadvantage of these reactions is the necessity to obtain triallyborane. The latter is an accessible reagent but easily oxidized and hydrolyzed in air, and work with it requires certain skills. Therefore, we started to search for more convenient routes for reductive α,α′-diallylation of nitrogen heterocycles.

In this report, we present the first results of studying the transformations of isoquinoline under the action of

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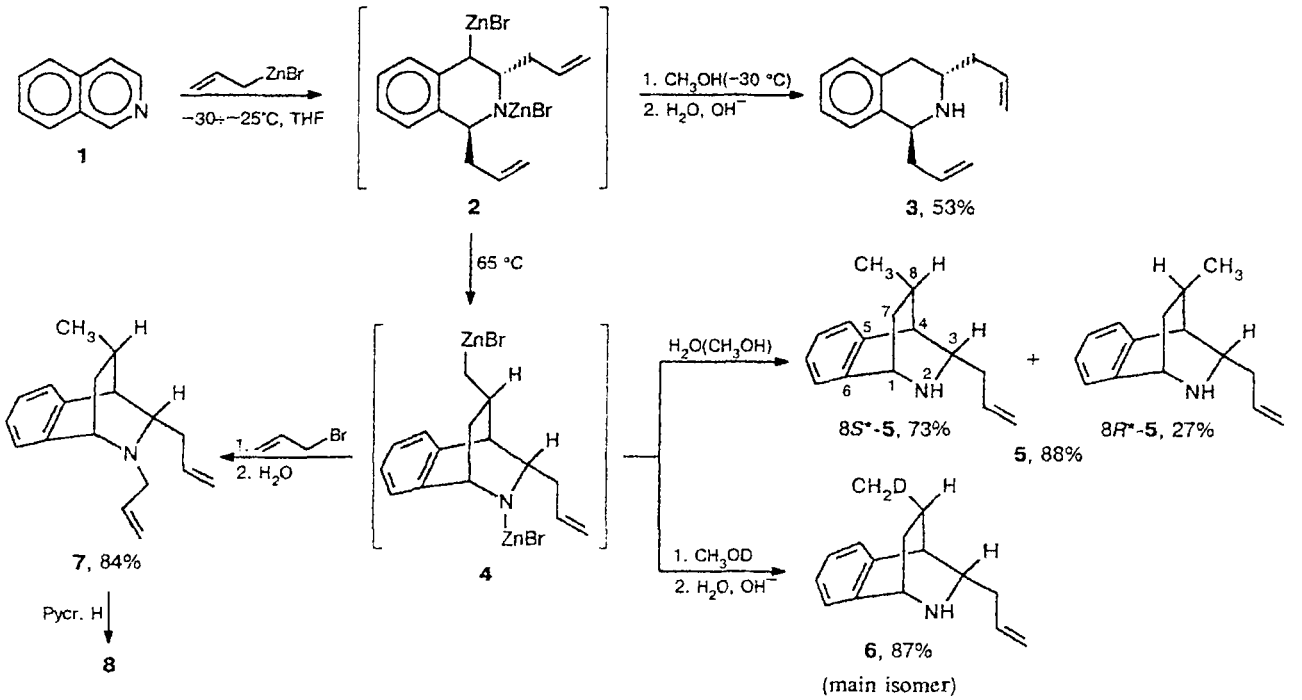
Scheme 1



Note. Pycr. H is picric acid.

allylzinc bromide. The latter was prepared from zinc and allyl bromide in THF[3—5] (the concentration was ~2 mol L^{-1}).

We have established that the heterocyclic fragment of isoquinoline adds readily two equivalents of allylzinc bromide (first at the C(1)=N bond and then at C(3)=C(4)) to form dizinc derivative **2**, which further transformations are determined by the reaction conditions (Scheme 1).

The reaction of **1** with AllZnBr at −30 °C (36 h) followed by treatment of the mixture with methanol (2 equiv., −30 °C) and a solution of NaOH (20 °C) resulted in the formation of *trans*-1,3-diallyl-1,2,3,4-tetrahydroisoquinoline (**3**) in 53% yield (b.p. 104—105 °C (2 Torr), *cf.* Ref. 6). No other products were detected. When the reaction of **1** with AllZnBr is carried out at ~20 °C (30 min), a mixture of 8*S**-methyl-3β-allyl-2-aza-5,6-benzobicyclo[2.2.2]octane (8*S**-**5**) and its 8*R**-methyl isomer (8*R**-**5**) in 7 : 3 ratio is formed with an overall yield of 64% along with **3** (20%). Heating of a mixture of **1** and allylzinc bromide in THF at 65 °C for 30 min followed by the hydrolysis of the dizinc derivative **4** that formed resulted in the formation of only tricyclic compound **5** in 88% yield (8*S**-**5** : 8*R**-**5** = 7 : 3, b.p. 122—123 °C (2 Torr), $n_D^{23.5}$ 1.5455). Found (%): C, 84.35; H, 9.05; N, 6.61. $C_{15}H_{19}N$. Calculated (%): C, 84.46; H, 8.98; N, 6.57.

Dizinc derivative **2** is transformed into tricyclic compound **4** by the addition of the benzylzinc fragment to the double bond of the 1-allyl group. The predominant formation of 8*S**-isomer **4** is most likely caused by the electronic effect of the benzene ring on the orientation of the carbon atoms of the double bond and the 4-ZnBr group in the transition state.

The successive treatment of **4** with deuteromethanol and alkali resulted in the formation of deuterated tricycle **6** in 87% yield (isomer ratio ~7 : 3, δ ^{2}H 0.62 and 1.21; δ ^{13}C (8-CH_2D) 21.15 and 18.55, respectively, triplets, $^1J_{C,D}$ = 19 Hz).

N-Allyl derivative **7** (84%) with the same ratio of isomers (b.p. 131—133 °C, $n_D^{23.5}$ 1.5275) was obtained by the successive treatment of a mixture of isomers **4** with excess allyl bromide (5 equiv., 14 h, 20 °C) and 2-propanol (3 equiv., 20 °C, THF). The reaction of **7** with CH_3I in the presence of K_2CO_3 in ethanol resulted in the formation of iodomethylate of amine **7**, fractional crystallization of which (ethanol and ethyl acetate) gave the almost pure 8*S**-isomer, m.p. 156.5—157 °C. Found (%): C, 57.78; H, 6.60; I, 32.29. $C_{19}H_{24}IN$. Calculated (%): C, 57.73; H, 6.63; I, 32.10.

The picrate of 8*S**-isomer **7** (**8**) with m.p. 126—127 °C was isolated in the pure state from a mixture of picrates obtained from a mixture of *N*-allyl amines **7** (7 : 3) and picric acid by two crystallizations from ethanol. The structure of the picrate was confirmed by X-ray diffraction analysis. Found (%): N, 11.89. $C_{24}H_{24}N_4O_7$. Calculated (%): N, 11.71.

The structures of all compounds obtained were confirmed by physicochemical methods (^{1}H, ^{2}H, and ^{13}C

NMR, COSY, APT, 2D-NOE, and mass spectrometry).

It should be noted that amine **3** has been previously obtained by the reaction of isoquinoline with triallylborane followed by treatment with alcohol,[6] which participates in the process as the reagent rather than the solvent. In this report, we describe the first example of reductive *trans*-α,α′-diallylation of the aromatic heterocycle by AllZnBr, which occurs without alcohol under very mild conditions (−30—0 °C). The surprisingly easy cyclization of dizinc derivative **2** into bicyclic compound **4** is another basic difference between the *trans*-1,3-diallylmetallation of isoquinoline by allylzinc bromide and the similar diallylboration. The stereochemistry of the benzylzinc fragment and the mechanism of its addition to the double bond remain to be elucidated.

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