(47%), 3-phenylpentane (44%), and 3-phenylheptane (3%) in a total yield of 94% based on toluene. In the absence of sodium, the degree of conversion of toluene into alkylation products does not exceed 48% (*n*-propylbenzene, 30%; 3-phenylpentane, 8%, 3-phenylheptane, 5%; and *n*-pentylbenzene, 5%), and in the absence of lithium, the degree of conversion is only 18% (*n*-propylbenzene, 15%, and 3-phenylpentane, 3%).

Alkylation of naphthalene with ethene in the presence of toluene is also accelerated when both alkali metals are present in the mixture; however, in this case, the dependence of the system activity on the proportions of lithium and sodium does not pass through a clear-cut maximum. For a Li : Na ratio ranging from (1 : 5) to (4.5 : 1.5), the total yield of naphthalene alkylation products (1-ethyl-, butyl-, hexyl-, and octylnaphthalenes and their dihydro derivatives) varies in the 72—78% range. If the reaction is carried out without sodium, the yield of these products decreases to 55%, while in the absence of lithium, it diminishes to 38%. The system with Li : Na = 2 : 1 is the most active toward alkylation of naphthalene without toluene. The reaction of ethene with this system affords the above-listed alkylnaphthalenes and their dihydro derivatives in a total yield of 81%. When either lithium or sodium alone (instead of a mixture of Li and Na) is used, the degree of conversion of naphthalene into alkylation products again substantially decreases (to 60 and 32%, respectively).

Similar synergistic effects are observed in systems based on phenanthrene. For example, when the Li : Na ratio in the phenanthrene-containing system is 1 : 2, the yield of products of toluene alkylation with ethene reaches 91% of the theoretical value with respect to toluene (*n*-propylbenzene, 43%; 3-phenylpentane, 45%; and 3-phenylheptane, 3%). An increase and a decrease in this ratio both diminish the alkylation efficiency. In the absence of sodium, the degree of conversion of toluene into alkylation products is only 36% (*n*-propylbenzene, 27%; 3-phenylpentane, 3%; 3-phenylheptane, 2%; and *n*-pentylbenzene, 4%), and that without lithium is 11% (*n*-propylbenzene, 10%; and 3-phenylpentane, 1%).

Thus, the use of synergistic mixtures of lithium and sodium opens up the way to almost quantitative transformation of toluene into higher monoalkylbenzenes and to a substantial increase in the degree of conversion of naphthalene into alkylation products. The synergistic effects of alkali metals in olefin oligomerization have been described in a review.[4] In these reactions, occurring at elevated temperatures, alkali metals were used as dispersions and were not activated by addition of aromatic promoters.

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Simple synthesis of 1,4,8-triazabicyclo[5.3.0]dec-4-ene derivatives from β-amino-β-polyfluoroalkylvinyl ketones and diethylenetriamine

V. Ya. Sosnovskikh, V. A. Kutsenko, and Yu. G. Yatluk*

A. M. Gor'ky Ural State University,
51 prosp. Lenina, 620083 Ekaterinburg, Russian Federation.
Fax: +7 (343 2) 61 5978. E-mail: Vyacheslav.Sosnovskikh@usu.ru

It is known[1] that heating of β-amino-β-polyfluoroalkylvinyl ketones **1a,b** with diethylenetriamine to 90 °C over 36 h afforded a mixture of 1,5-di(polyfluoroacyl)amino-3-azapentanes and *N,N'*-(3-azapentamethylene)-bis(3-amino-3-polyfluoroalkyl-1-phenylprop-2-en-1-ones) in a ratio of 1 : 2. We found that the reactions of aminoenones **1a—d** with diethylenetriamine without a solvent at room temperature over 4—7 days afforded compounds **2a—d**, which are derivatives of the new fused triazabicyclo[5.3.0]dec-4-ene system containing a bridgehead nitrogen atom, in 64—74% and 25—33% yields in the case of the trifluoromethyl and tetrafluoroethyl substituents, respectively. In this case, diethylenetriamine acted as a trinucleophile and its reactions with aminoenones **1a—d** involved the double nucleophilic addition at the β-carbon atom with elimination of am-

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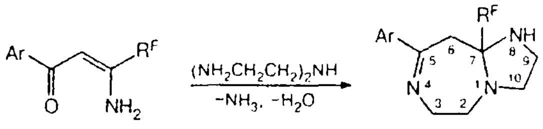
monia and the attack on the carbonyl group accompanied by liberation of a water molecule.



1a–d **2a–d**

	a	**b**	**c**	**d**
Ar	Ph	Ph	2-C_4H_3S	2-C_4H_3S
R^F	CF_3	CF_2CF_2H	CF_3	CF_2CF_2H

Evidently, the presence of a polyfluoroalkyl substituent is favorable for this reaction to proceed successfully because this substituent not only enhances the electrophilicity of the β-carbon atom but also stabilizes the imidazolidine ring, as in the cases of aminals and aminoketals.[2] The reaction under consideration is characterized by its simplicity, the availability of the initial compounds, and a rather high synthetic potential due to which this reaction is very useful in the synthesis of aza analogs of bicyclo[5.3.0]decane.

The IR spectra were recorded on an IKS-29 instrument as Nujol mulls. The ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer in $CDCl_3$ operating at 250 MHz with Me_4Si as the internal standard.

5-Phenyl-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2a). Aminoenone **1a** (215 mg, 1.0 mmol) was dissolved in diethylenetriamine (215 μL, 205 mg, 2.0 mmol). The reaction mixture was kept at –20 °C for 4–7 days. Crystals of bicycle **2a** that precipitated were washed with water and recrystallized from hexane to yield 210 mg (74%), m.p. 77–78 °C. Found (%): C, 59.43; H, 5.53; N, 14.85. $C_{14}H_{16}F_3N_3$. Calculated (%): C, 59.36; H, 5.69; N, 14.83. IR, ν/cm^{-1}: 3350 (NH), 1630 (C=N), 1580 (benzene ring). ^1H NMR, δ: 2.08 (br.s, 1 H, NH); 3.04–3.22 (m, 5 H, $C(9)H_2$, $C(10)H_2$, $C(2)\underline{H}H$); 3.31 (AB system, $\Delta\delta = 0.13$, 2 H, $C(6)H_2$, $J_{AB} = 15.4$ Hz); 3.43–3.54 (m, 1 H, $C(2)H\underline{H}$); 3.99 (dt, 1 H, $C(3)\underline{H}H$, $^2J = 16.1$ Hz, $^3J = 5.3$ Hz); 4.29 (ddd, 1 H, $C(3)H\underline{H}$, $^2J = 16.1$ Hz, $^3J = 7.7$ and 4.6 Hz); 7.37–7.40 (m, 3 H, CH arom.); 7.71–7.75 (m, 2 H, CH arom.).

5-Phenyl-7-(1,1,2,2-tetrafluoroethyl)-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2b). The yield was 33%, m.p. 100–101 °C. Found (%): C, 57.25; H, 5.52; N, 13.46. $C_{15}H_{17}F_4N_3$. Calculated (%): C, 57.14; H, 5.43; N, 13.33. IR, ν/cm^{-1}: 3400 (NH), 1630 (C=N), 1580 (benzene ring). ^1H NMR, δ: 2.04 (br.s, 1 H, NH); 2.94–3.57 (m, 6 H, $C(9)H_2$, $C(10)H_2$, $C(2)H_2$); 3.35 (AB system, $\Delta\delta = 0.19$, 2 H, $C(6)H_2$, $J_{AB} = 15.1$ Hz); 3.97 (ddd, 1 H, $C(3)\underline{H}H$, $^2J = 15.2$ Hz, $^3J = 5.7$ and 4.2 Hz); 4.25 (ddd, 1 H, $C(3)H\underline{H}$, $^2J = 15.2$ Hz, $^3J = 7.8$ and 4.5 Hz); 6.12 (tdd, 1 H, CF_2CF_2H, $^2J_{H,F} = 53.6$ Hz, $^3J_{H,F} = 7.6$ and 4.8 Hz); 7.38–7.43 (m, 3 H, CH arom.); 7.74–7.80 (m, 2 H, CH arom.).

5-(2-Thienyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2c). The yield was 64%, m.p. 140–141 °C. Found (%): C, 49.77; H, 4.68; N, 14.63. $C_{12}H_{14}F_3N_3S$. Calculated (%): C, 49.82; H, 4.88; N, 14.52. IR, ν/cm^{-1}: 3350 (NH), 3090 (=CH), 1635 (C=N), 1615 (NH), 1530 (thiophene ring). ^1H NMR, δ: 2.10 (br.s, 1 H, NH); 3.03–3.22 (m, 5 H, $C(9)H_2$, $C(10)H_2$, $C(2)\underline{H}H$); 3.28 (AB system, $\Delta\delta = 0.16$, 2 H, $C(6)H_2$, $J_{AB} = 15.3$ Hz); 3.44–3.55 (m, 1 H, $C(2)H\underline{H}$); 3.93 (dt, 1 H, $C(3)\underline{H}H$, $^2J = 16.5$ Hz, $^3J = 5.1$ Hz); 4.22 (ddd, 1 H, $C(3)H\underline{H}$, $^2J = 16.5$ Hz, $^3J = 8.1$ and 4.7 Hz); 7.04 (dd, 1 H, H(4´), $J_{H(4'),H(5')} = 5.1$ Hz, $J_{H(4'),H(3')} = 3.7$ Hz); 7.30 (dd, 1 H, H(3´), $J_{H(3'),H(5')} = 0.9$ Hz); 7.38 (dd, 1 H, H(5´)).

7-(1,1,2,2-Tetrafluoroethyl)-5-(2-thienyl)-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2d). The yield was 25%, m.p. 110–111 °C. Found (%): C, 48.74; H, 4.60; N, 13.18. $C_{13}H_{15}F_4N_3S$. Calculated (%): C, 48.59; H, 4.71; N, 13.08. IR, ν/cm^{-1}: 3395 (NH), 3075 (=CH), 1620 (C=N), 1525 (thiophene ring). ^1H NMR, δ: 2.06 (br.s, 1 H, NH); 2.91–3.55 (m, 6 H, $C(9)H_2$, $C(10)H_2$, $C(2)H_2$); 3.29 (AB system, $\Delta\delta = 0.23$, 2 H, $C(6)H_2$, $J_{AB} = 15.0$ Hz); 3.89 (ddd, 1 H, $C(3)\underline{H}H$, $^2J = 15.5$ Hz, $^3J = 5.5$ and 4.6 Hz); 4.17 (ddd, 1 H, $C(3)H\underline{H}$, $^2J = 15.5$ Hz, $^3J = 8.2$ and 4.6 Hz); 6.11 (tdd, 1 H, CF_2CF_2H, $^2J_{H,F} = 53.6$ Hz, $^3J_{H,F} = 7.6$ and 4.8 Hz); 7.04 (dd, 1 H, H(4´), $J_{H(4'),H(5')} = 5.1$ Hz, $J_{H(4'),H(3')} = 3.7$ Hz); 7.31 (dd, 1 H, H(3´), $J_{H(3'),H(5')} = 0.9$ Hz); 7.37 (dd, 1 H, H(5´)).

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