

## SYNTHESIS OF 2-ALKYL(ARYL)-SUBSTITUTED BENZOXAZOLES FROM IMINOESTERS

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It is found that the preparation of 2-substituted benzoxazoles by condensing o-aminophenol with imino esters (only one or two examples of which have, in all, been given [1]) is of general application. For example, by stirring o-aminophenol with iminoester hydrochlorides for 3-6 hr in chloroform, various 2-alkyl-(aryl)-substituted benzoxazoles can be synthesized in good yield at room temperature. The following benzoxazoles were prepared by this method: 2-Methyl-, yield 76%, b. 88-88.5° (12 mm),  $d_4^{20}$  1.1294,  $n_D^{20}$  1.5490. Found: C 72.47; H 5.35; N 10.60%. Calculated for  $C_8H_7NO$ : C 72.18; H 5.26; N 10.52%. 2-Perfluoromethyl-\*, 52.5%, b.p. 62.5-63° (19 mm),  $d_4^{20}$  1.3571,  $n_D^{20}$  1.4579. Found: C 51.37; H 2.35; N 7.59%. Calculated for  $C_8H_4F_3NO$ : C 51.35; H 2.16; N 7.48%. 2-n-Propyl-, 70%, b.p. 97° (8 mm),  $d_4^{20}$  1.0592,  $n_D^{20}$  1.5335. Found: C 74.61; H 6.82; N 8.78%. Calculated for  $C_{10}H_{11}NO$ : C 74.55; H 6.77; N 8.69%. 2-Perfluoro-n-propyl-\*\*, 55%, b.p. 85° (22 mm),  $d_4^{20}$  1.5028,  $n_D^{20}$  1.4198. Found: C 41.60; H 1.50; N 4.68%. Calculated for  $C_{10}H_4F_7NO$ : C 41.80; H 1.39; N 4.86%; 2-Benzyl-, 70%, b.p. 175° (9 mm); m.p. 28-30°,  $n_D^{20}$  1.5990 (supercooled melt). Found: C 6.64%. Calculated for  $C_{14}H_{11}NO$ : N 6.70%. 2-Phenyl, 82.5%, m.p. 101-102° (from alcohol). Found: N 6.95%. Calculated for  $C_{13}H_9NO$ : N 7.18%. 1,2-Di(benzoxazolyl-2)-ethane\*\*\*, 55%, m.p. 191-192° (from alcohol). Found: C 72.42; H 4.58; N 9.96%. Calculated for  $C_{16}H_{12}N_2O_2$ : C 72.72; H 4.54; N 10.61%. 1,4-Di(benzoxazolyl-2)butane\*\*\*\*, 70%, m.p. 129.5-130.2° (from alcohol). Found: C 74.06; H 5.48; N 9.69. Calculated for  $C_{18}H_{16}N_2O_2$ : C 73.96; H 5.48; N 9.59%.

2-Alkyl(aryl)-substituted benzoxazoles can also be successfully obtained by condensing o-aminophenol with iminoesters in the form of free bases. The reaction is carried out in dry dioxane by stirring the reactants together for some hours at 98-100°. However, this method gives somewhat lower yields of benzoxazoles.

## REFERENCES

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## NEW METHODS OF SYNTHESIS FOR TETRAPHENYLTHIOPHENE, 2-PHENYL-3-CHLOROTHIONAPHTHENE AND THIONAPHTHENO[3,2-b]THIONAPHTHENE

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In investigating the action of sulfur on arylhalogenoalkanes, new methods of synthesizing tetraphenylthiophene (I), 2-phenyl-3-chloronaphthene (II), and thionaphtheno[3,2-b]thionaphthene (III) were discovered.

I (m.p. 185°) is formed in 68% yield by reacting sulfur with benzyl chloride, the reaction proceeding at 200-240° according to the equation

\*From methyl iminotrifluoroacetate [2] in the presence of 1 equiv.  $CF_3COOH$ .\*\*From methyl iminoperfluorobutyric acid [3] in the presence of 1 equiv.  $C_3F_7COOH$ .

\*\*\*From diethyl bisiminosuccinate dihydrochloride.

\*\*\*\*From diethyl bisiminoadipate dihydrochloride.