UDC 542.953 + 547.78

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

G. I. Braz, G. V. Myasnikova, and A. Ya. Yakubovich

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, p. 147, 1965

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

1. F. King, R. Acheson, J. Chem. Soc., 1396, 1949.

2. E. L. Zaitseva, G. I. Braz, A. Ya. Yakubovich, V. P. Bazov, R. M. Gitina, L. G. Petrova, and I. M. Filatova, ZhVKhO, 8, 353, 1963.

3. E. L. Zaitseva, R. M. Gitina, A. Ya. Yakubovich, G. I. Braz, L. G. Petrova, and V. P. Bazov, ZhOKh, 34, 2816, 1964.

7 May 1964

Karpov Institute of Physical Chemistry, Moscow

UDC 542.945.2 + 547.73

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

M. G. Voronkov and V. E. Udre

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, p. 148, 1965

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.

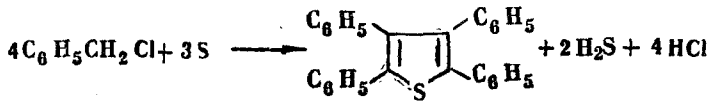
I (m.p. 185°) is formed in 68% yield by reacting sulfur with benzyl chloride, the reaction proceeding at 200-240° according to the equation

*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.

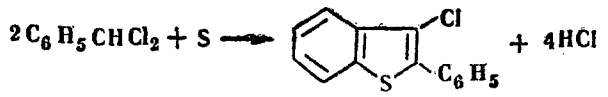
***From diethyl bisiminosuccinate dihydrochloride.

****From diethyl bisiminoadipate dihydrochloride.



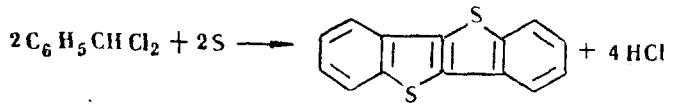
The product of reaction of sulfur with p-chlorobenzyl bromide under the same conditions is the hitherto unknown compound tetrakis-p-chlorophenylthiophene (yield 25-30%). Found: C 63.51; H 3.20; S 6.23; Cl 26.79%. Calculated for $C_{28}H_{16}Cl_4S$: C 63.87; H 3.05; S 6.09; Cl 26.99%.

Benzylidene chloride reacts with sulfur at 220-250° to give II (yield 51%)



This compound, also previously undescribed, melts at 64°. Found: C 68.5; H 3.54; S 13.28; Cl 14.23%. Calculated for $C_{14}H_9SCl$: C 68.70; H 3.70; S 13.10; Cl 14.48%.

When sulfur reacts with benzylidene chloride at higher temperatures (250°-300°) III is formed, the yield exceeding 60% (m.p. 215°).



Benzylidene bromide reacts similarly with sulfur, but the yield of III is under 10%.

Unlike the mono- and dichloro-derivatives, benzotrichloride undergoes practically no reaction with sulfur when they are heated together for a long time at 225-240°.

16 October 1964

Institute of Organic Synthesis AS Latvian SSR, Riga

UDC 54.859 + 542.959

SYNTHESIS OF PYRIMIDO[4, 5-b][1, 4]THIAZINE DERIVATIVES

T. S. Safonova and M. P. Nemeryuk

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, p. 149, 1965

The pyrimido[4, 5-b][1, 4]thiazine system is practically uninvestigated, the only method described being the synthesis of certain 5H, 7H-pyrimido[4, 5-b][1, 4]thiazoles-6 (see [1, 2]). With a view to obtaining derivatives of the pyrimido[4, 5-b][1, 4]thiazine system, a study is being made of the reaction of 5-amino-6-mercaptopyrimidines with α-halogenoketones.

Reacting 4-methoxy-5-amino-6-mercaptopyrimidine with α-bromoacetophenone and its p-bromo derivative gives, respectively: 4-methoxy-6-phenyl- and 4-methoxy-6(p-bromphenyl)pyrimido[4, 5-b][1, 4]thiazines (I and II). Reaction of 2, 5-diamino-4-methyl-6-mercaptopyrimidine with chloroacetone, α-chloroethylmethyl ketone, bromoacetophenone, and its p-bromo- and p-nitro derivatives gives the corresponding 2-amino-4-methyl-6-alkyl(aryl)pyrimido[4, 5-b][1, 4]-thiazines (III-VII).

4-Methoxy-6-phenylpyrimido[4, 5-b][1, 4]thiazine (I) m.p. 176-178° (from ethanol). Found: C 60.84; H 4.51; N 16.23; S 12.43%. $C_{13}H_{11}N_3OS$. Calculated: C 60.68; H 4.32; N 16.33; S 12.46%.

4-Methoxy-6-(p-bromphenyl)pyrimido[4, 5-b][1, 4]thiazine (II) m.p. 175-177° (from ethanol). Found: C 46.50; H 2.98; Br 23.80; N 12.55; S 9.66%. $C_{13}H_{10}BrN_3OS$. Calculated: C 46.44; H 2.99; Br 23.77; N 12.50; S 9.54%.

2-Amino-4, 6-dimethylpyrimido[4, 5-b][1, 4]thiazine (III) m.p. 223-224° (from dimethylformamide). Found: C 49.49; H 5.04; N 29.04; S 16.42%. $C_8H_{10}N_4S$. Calculated: C 49.45; H 5.20; N 28.83; S 16.50%.

2-Amino-4, 6, 7-trimethylpyrimido[4, 5-b][1, 4]thiazine (IV) m.p. 200-202.5° (from ethanol). Found: C 52.15; H 5.97; N 26.91; S 15.24%. $C_9H_{12}N_4S$: Calculated: C 51.89; H 5.80; N 26.90; S 15.39%.

2-Amino-4-methyl-6-phenylpyrimido[4, 5-b][1, 4]thiazine (V) m.p. 281-282° (from ethanol). Found: C 60.60; H 4.55; N 22.15; S 12.41%. $C_{13}H_{12}N_4S$. Calculated: C 60.91; H 4.72; N 21.86; S 12.51%.