LETTERS TO THE EDITOR

SYNTHESIS OF α, β-UNSATURATED KETONES OF THE 2-PHENYLTHIOPHENE SERIES

A. E. Lipkin and S. I. Borisov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, p. 952, 1968

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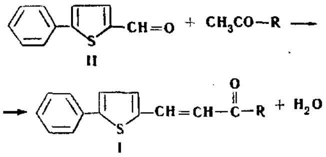
We have previously reported [1] the synthesis of α, β-unsaturated ketones based on the crotonic condensation of 2-acetyl-5-phenylthiophene with aromatic and heterocyclic aldehydes. The present communication gives information on the preparation of some α, β-unsaturated ketones of type I by the crotonic condensation of 2-formyl-5-phenylthiophene (II) [2] with aromatic and heterocyclic methyl ketones in an alkaline medium according to the equation:



The compounds I that we synthesized (see table) are mainly yellow crystalline substances. They all possess characteristic halochromic properties.

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1. A. E. Lipkin, N. I. Putokhin, and S. I. Borisov, KhGS [Chemistry of Heterocyclic Compounds], 2, 476, 1966.
2. A. E. Lipkin, N. I. Putokhin, and S. I. Borisov, KhGS [Chemistry of Heterocyclic Compounds], 3, 1020, 1967.

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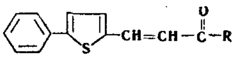
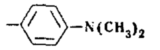
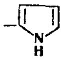
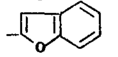
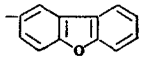


R	Mp, °C	Empirical formula	S, %		Yield, %
			found	calculated	
	184—187	$C_{21}H_{19}NOS$	9.85	9.61	74.2
	240—242	$C_{17}H_{13}NOS$	11.53	11.48	32.0
	154—157	$C_{17}H_{11}BrOS_2$	16.99	17.08	62.8
	209—212**	$C_{21}H_{14}O_2S$	9.88	9.70	54.5
	174—176**	$C_{25}H_{16}O_2S$	8.29	8.43	62.2

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* I recrystallized from 95% ethanol.
** I recrystallized from ethanol—acetone (1 : 1).

GENERAL METHOD FOR THE SYNTHESIS OF CYCLIC SULFIDES

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A general method is proposed for the synthesis of mono-, bi-, and tricyclic sulfides by the reaction of oxides of unsaturated hydrocarbons of the paraffin or naphthene series with vinylmagnesium or arylmagnesium bromides with the subsequent addition of hydrogen bromide in accordance with and contrary to Markovnikov's rule, replacement of the hydroxy group by bromine, and cyclization of the resulting dibromides with sodium sulfide to cyclic sulfides.

The method that we proposed has been confirmed experimentally on the basis of the synthesis of 2-methyl-1-thiahydrindan (I).

The reaction of cyclohexene oxide with allylmagnesium bromide by Letsinger's method [1], modified by us, provided 2-allyl-1-cyclohexanol (II) with a yield of 87%. Bp 94-96° C (15 mm), n_D^{20} 1.4778, d_4^{20} 0.9345. Found: MR_D 42.35. Calculated for $C_9H_{16}O$: MR_D 42.62. According to the literature [1], bp 94°-96° C (15 mm), n_D^{20} 1.4757.

By saturating **II** with hydrogen bromide in an atmosphere of nitrogen first in the cold and then at 100° C we obtained 1-bromo-2-(β-bromopropyl)cyclohexane (**III**), the structure of which was confirmed by its IR spectrum. Bp 99–100° C (2 mm), n_D^{20} 1.5280, d_D^{20} 1.5251. Found, %: C 38.19; H 5.70; Br 56.34; MR_D 57.09. Calculated for $C_9H_{16}Br_2$, %: C 38.03; H 5.63; Br 56.23; MR_D 57.03. Yield 86.3%.

The reaction of **III** with a threefold excess of anhydrous Na_2S in dimethylformamide at 125° C gave a 54.5% yield of **I** in the form of a mixture of cis- and trans-isomers. Bp 89°–90° C (20 mm), n_D^{20} 1.5090, d_4^{20} 0.9783. Found, %: C 57.24; H 10.35; MR_D 47.61. Calculated for $C_9H_{16}S$, %: C 57.22; H 10.25; MR_D 47.43. The structure of I was confirmed by its IR spectrum.

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1. R. L. Letsinger, J. G. Traynham, and E. Babko, J. Am. Chem. Soc., **74**, 339, 1952.

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NITRATION OF 3-METHYL-3H-IMIDAZO[4, 5-b]PYRIDINE

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, p. 953, 1968

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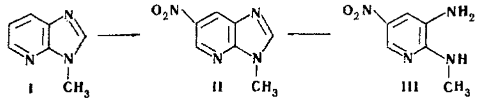
We have effected the direct introduction of a nitro group into the molecule of an imidazo[4, 5-b]pyridine for the first time. In contrast to benzimidazole, the nitration of which takes place readily even in the cold [1], 3-methyl-3H-imidazo[4, 5-b]pyridine (I) undergoes nitration with a mixture of nitric and sulfuric acids only at 140–160° C. The reaction product [yield 50%, mp 220–221° C (ethanol). Found, %: C 46.92; H 3.34; N 31.34. Calculated for $C_7H_6N_4O_2$, %: C 47.19; H 3.39; N 31.45] proved to be identical with the compound obtained from 3-amino-2-methylamino-5-nitropyridine (III) and formic acid, which shows its structure to be 3-methyl-6-nitroimidazo[4, 5-b]-pyridine (II).



No other nitro derivatives apart from **II** were detected. Compound III was obtained by the reduction with ammonium sulfide of the product of the interaction of 2-chloro-3, 5-dinitropyridine with methylamine [2]. Mp 199–200° C (water). Found, %: C 42.94; H 4.83. Calculated for $C_6H_8N_4O_2$, %: C 42.86; H 4.79.

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2. A. Hunger, I. Kebrle, A. Rossi, and K. N. Hoffman, US Patent 3004978, 1960. C. A. **56**, 4771, 1962.

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QUATERNIZATION OF 3-METHYL-3H-IMIDAZO[4, 5-b]PYRIDINE

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, p. 954, 1968

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3-Methyl-3H-imidazo[4, 5-b]pyridine (I), which has two basic centers [1], reacts with alkylating agents at the N^1 atom with the formation of monoquaternary salts. The structure of such compounds as N^1-alkyl(aryl, aralkyl)-N^3-methylimidazolium salts (II) has been shown by the oxidation of some of them ($R = CH_3, X = I$; $R = CH_2C_6H_5$, $X = Cl$) with potassium ferrocyanide in alkali at a temperature not exceeding 10° C to N^1, N^3-disubstituted imidazo[4, 5-b]pyridin-2-ones (III) ($R = CH_3, CH_2C_6H_5$). The same substances have been obtained by the methylation with dimethyl sulfate and the benzylation with dimethylphenylbenzylammonium hydroxide of 3-methylimidazo[4, 5-6]pyridin-2-ones (IV) in an alkaline medium. Compound IV was synthesized by fusing 3-amino-2-methylaminopyridine with urea at 170° C.