LETTERS TO THE EDITOR

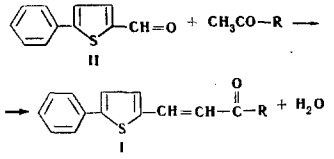
SYNTHESIS OF α, β-UNSATURATED KETONES OF THE 2-PHENYLTHIOPHENE SERIES

A. E. Lipkin and S. I. Borisov

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

UDC 547.733:542.953

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:



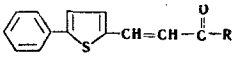
The compounds I that we synthesized (see table) are mainly yellow crystalline substances. They all possess characteristic halochromic properties.

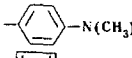
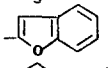
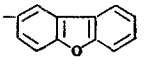
REFERENCES

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.

19 November 1966 Kuibyshev Polytechnic Institute, Kuibyshev



R	Mp, °C	Empirical formula	S, % found	S, % calculated	Yield, %
	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

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

GENERAL METHOD FOR THE SYNTHESIS OF CYCLIC SULFIDES

V. I. Dronov and V. P. Krivonogov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, pp. 952–953, 1968

UDC 547.665.07:543.422.4

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.