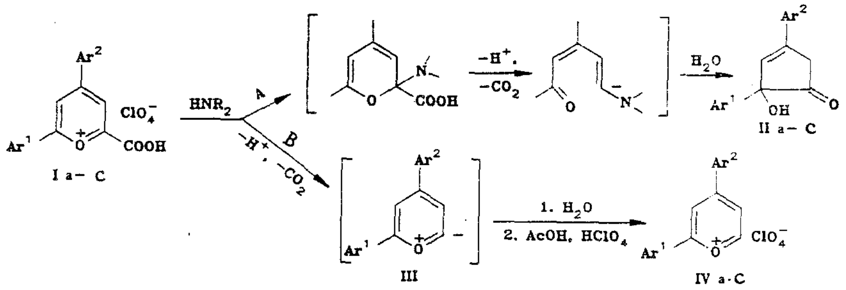
DUAL REACTING OF MONOCYCLIC α-CARBOXYPYRYLIUM SALTS IN REACTION WITH SECONDARY AMINES

N. V. Kholodova, V. G. Brovchenko,
A. I. Pyshchev, and E. V. Kuznetsov

UDC 547.814.1'514.7

In reaction with secondary amines in benzene, 1-aryl-3-carboxy-2-benzo-pyrylium salts become decarboxylated with simultaneous contraction of the heteroring, concluded with formation of benzo-annealed acyloins [1, 2].

We found that α-carboxypyrylium salts I, obviously, because of a lesser tendency to add nucleophile, compared with the benzo-[c]-annealed analogs, react under these conditions through two paths:



I—IV a $Ar^1 = Ar^2 = C_6H_5$; b $Ar^1 = C_6H_5$, $Ar^2 = p\text{-}CH_3OC_6H_4$; c $Ar^1 = p\text{-}NO_2C_6H_4$, $Ar^2 = C_6H_5$

After evaporation, treatment with water and chromatography of the reaction mixture on a column with Al_2O_3 (colorless fractions with R_f 0.4), acyloins IIa-c were obtained in yields of 15-40%, which are clearly formed by intramolecular condensation (path A).

After the evaporation of the colored fractions with R_f 0.9, oily products are obtained, dissolution of which in acetic acid and addition of 70% $HClO_4$ gave the previously difficulty obtainable α-unsubstituted pyrylium salts IVa-c [3] in yields similar to those indicated above. The formation of these salts presumes an intermediate formation of type III ylides (path B) as in reactions of α-carboxypyrylium salts with carbonyl compounds [4].

<u>2-Hydroxy-2,4-diphenylcyclopent-3-enone (IIa)</u>. mp 122-124°C. IR spectrum (KBr): 1582, 1594 (C=C, arom.), 1688 (C=O), 3435 cm^{-1} (O-H). PMR spectrum ($CDCl_3$): 3.28 (2H, s, CH_2), 4.10 (1H, s, OH), 6.50 (1H, s, CH), 7.00-7.65 ppm (10H, m, arom.).

<u>4-(4-Methoxyphenyl)-2-hydroxy-2-phenylcyclopent-3-enone (IIb)</u>. mp 134-135°C. IR spectrum (KBr): 1581, 1600 (C=C, arom.), 1674 (C=O), 3395 cm^{-1} (OH). PMR spectrum ($CDCl_3$): 3.30 (2H, s, CH_2), 3.72 (3H, s, CH_3O), 4.35 (1H, s, OH), 6.40 (1H, s, CH), 6.75-7.40 ppm (9H, m, arom.).

<u>2-(4-Nitrophenyl)-2-hydroxy-2-phenylcyclopent-3-enone (IIc)</u>. mp 128-129°C. IR spectrum (KBr): 1568, 1594 (C=C, arom.), 1688 (C=O), 3434 cm^{-1} (OH).

<u>2,4-Diphenylpyrylium Perchlorate (IVa)</u>. mp 198-200°C, according to the data in [3], mp 218-219°C. IR spectrum (KBr): 1088 (ClO_4^-), 1594, 1621 cm^{-1} (C=C, arom.).

<u>4-(4-Methoxyphenyl)-2-phenylpyrylium Perchlorate (IVb)</u>. mp 254-255°C. IR spectrum (KBr): 1090 (ClO_4^-), 1594, 1621 cm^{-1} (C=C, arom.). PMR spectrum ($CDCl_3$): 3.60 (3H, s, CH_3O), 6.72-8.05 ppm (12H, arom.).

Scientific Research Institute of Physical and Organic Chemistry of the Rostov State University, Rostov-on-Don 334104. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1564-1565, November, 1989. Original article submitted Janaury 25, 1989.

2-(4-Nitrophenyl)-4-phenylpyrylium Perchlorate (IVc). mp 178-180°C. IR spectrum (KBr): 1090 (ClO_4^-), 1580, 1620 cm^{-1} (C=C, arom.).

LITERATURE CITED

1. V. G. Brovchenko and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 1, 125 (1986).
2. Yu. A. Zhdanov, V. G. Brovchenko, N. A. Klyuev, and E. V. Kuznetsov, Khim., Geoterotsikl. Soedin., No. 4, 454 (1989).
3. S. M. Luk'yanov, A. V. Koblik, G. N. Dorofeenko, Zh. Org. Khim., 12, 2267 (1976).
4. Yu. P. Andreichikov, N. V. Kholodova, and G. N. Dorofeenko, Dokl. Akad. Nauk SSSR, 236, 1364 (1977).

HIGH-TEMPERATURE REACTION OF 2-THIOPHENETHIOL WITH ACETYLENE

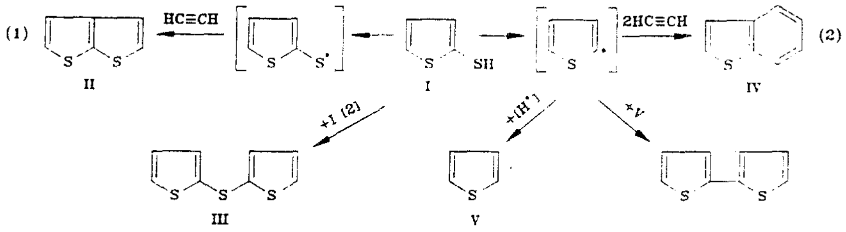
N. V. Russavskaya, N. A. Korchevin,
É. N. Sukhomazova, É. N. Deryagina,
and M. G. Voronkov

UDC 547.737.07'314.2:541.11

Thiophenol reacts with acetylene at 550-650°C with the formation of benzo[b]thiophene in 70-93% yield [1]. We have determined that the reaction of 2-thiophenethiol (I) under similar conditions (500-600°C) affords not only the expected thieno[2,3-b]thiophene (II), but also bis(2-thienyl) sulfide (III) as well as thiophene and benzo[b]thiophene (IV). At temperatures above 530°C, dithienyls are additionally formed.

At 500°C, with a 1:1 reagent ratio, the main reaction product was sulfide III (76% yield), and the yields of thienothiophene II and benzothiophene IV were only 12 and 6%, respectively. An increase of the mole fraction of acetylene [1:(2-3)] resulted in an increase of the yield of reaction products II (up to 40-50%) and IV (up to 15-20%) and a decrease of the yield of sulfide III to 40-30%. The maximum yield of thieno[2,3-b]thiophene (52%) was attained at 550°C (1:2 reagent ratio). A further temperature increase (to 600°C) resulted in the formation, preferentially, of thiophene (20%), benzothiophene IV (25%), and dithienyls (8%).

The complex nature of the conversions of 2-thiophenethiol in the high-temperature reaction with acetylene (unlike in the case of thiophenol [1]) may be due to the dual primary thermal decomposition of thiol I occurring at the S—H and C—S bonds:



Thus, in this case, acetylene acts as a trap both of thiyl radicals [reaction (I)] and C radicals [reaction (2)]. The latter are trapped less efficiently.

The reaction was carried out in a tubular quartz reactor (250 × 15 mm) in an annular gap (3 mm) formed by the walls of the reaction tube and a thermocouple housing. 2-Thiophenethiol was fed into the reaction zone with an automatic dispenser at a rate of 3.2 ml/h. The acetylene feed rate depended on the reagent ratio (0.8-2.5 liters/h). The reaction products were identified by GLC (comparison with known samples) and chromatography—mass spectrometry. Thienothiophene II was recovered by distillation in vacuo (110-120°C at 13 mm) and purified by preparative GLC. According to PMR data (acetone-D_6), the reaction products contained no thieno[3,4-b]thiophene (cf. [3]).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1565-1566, November, 1989. Original article submitted February 2, 1989.