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

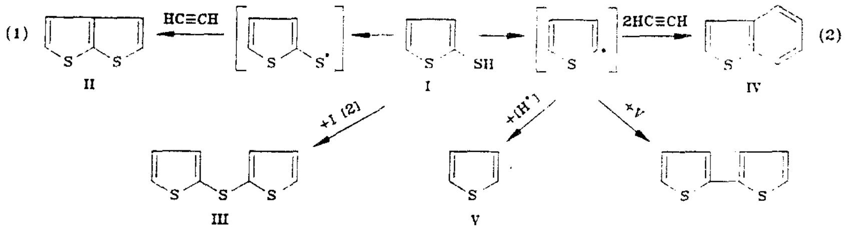
N. V. Russavskaya, N. A. Korchevin,
É. N. Sukhomazova, É. N. Deryagina,
and M. G. Voronkov

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.

0009-3122/89/2511-1313 $12.50

LITERATURE CITED

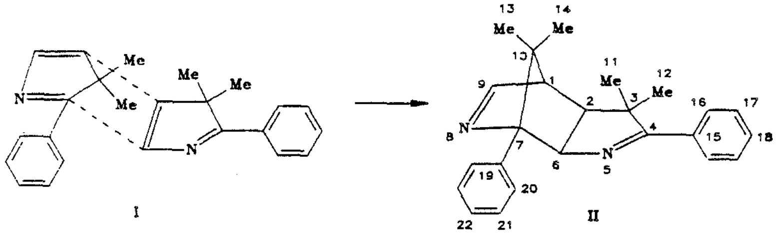
1. É. N. Sukhomazova, N. V. Russavskaya, N. A. Korchevin, É. N. Deryagina, and M. G. Voronkov, Zh. Org. Khim., 25, 1506 (1989).
2. M. G. Voronkov, É. N. Deryagina, L. K. Papernaya, É. N. Sukhomazova, N. A. Korchevin, and G. G. Efremova, Khim. Geterotsikl. Soedin., No. 12, 1614 (1986).
3. N. A. Korchevin, É. N. Sukhomazova, L. P. Turchaninova, G. G. Efremova, N. A. Kalinina, É. N. Deryagina, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 8, 1041 (1988).

DIENE AUTOCONDENSATION OF 3,3-DIMETHYL-2-PHENYL-AND 3,3-DIMETHYL-2-(2-THIENYL)-3H-PYRROLES

B. A. Trofimov, S. G. Shevchenko,
S. E. Korostova, A. I. Mikhaleva,
M. V. Sigalov, and L. B. Krivdin

UDC 547.741.04:543.422.25

As exemplified by 3,3-diethyl-2-phenyl- and 3,3-dimethyl-2-(2-thienyl)-3H-pyrroles (obtained respectively from isopropylphenyl- and isopropyl(2-thienyl)ketoximes and acetylene [1]), we have found a new modification of the Diels–Alder condensation. This is the dimerization of 3H-pyrroles in which one molecule of 3H-pyrrole acts as an azadiene, and the other as a dienophile component:



I

II

3H-Pyrrole (I), 3.42 g, 77% pure, was kept in a glass ampul at 5-7°C for 9.5 months. The resulting crystals were washed with hexane to yield 0.6 g (23%) of 3,3,10,10-tetramethyl-4,7-diphenyl-5,8-diazatricyclo[4.3.1.$0^{2,6}$]deca-4,8-diene (II), mp 169-170°C. The mass spectrum of (II) contains the peak of the molecular ion [M^+ 342]. ^{13}C NMR spectrum (acetone-D_6): 178.41 $C_{(4)}$; 171.96 $C_{(9)}$; 139.98 $C_{(19)}$; 135.75 $C_{(15)}$; 129.92 $C_{(18)}$; 129.19; 128.65; 128.47 $C_{(16)}$; $C_{(17)}$, $C_{(20)}$; 127.42 $C_{(22)}$; 85.03 $C_{(7)}$; 81.12 $C_{(6)}$; 64.14 $C_{(3)}$; 61.70 $C_{(1)}$; 56.67 $C_{(12)}$; 50.23 $C_{(10)}$; 31.95; 22.35; 20.35; 20.07 ppm $Me_{(13)}$, $Me_{(14)}$, $Me_{(11)}$, $Me_{(12)}$. PMR spectrum (benzene-D_6): 8.27 (1H, s, 9-H); 7.3-7.8 (10H, m, Ph); 5.6 (1H, d, 6-H, $^3J_{26} = 7.0$ Hz); 2.53 (1H, d.d, 2-H, $^3J_{12} = 4.0$ Hz); 2.41 (1H, d, 1-H, $^3J_{12} = 4.0$ Hz); 1.17 (3H, s, 13-Me); 1.00 (3H, s, 14-Me); 0.85 (3H, s, 11-Me); 0.56 ppm (3H, s, 12-Me). IR spectrum (KBr): 1490, 1580 (=CH, Ph), 3010, 3065 (C–H, Ph), 1600 (C=N), 1190 cm^{-1} ($>C(Me)_2$). The C, H, and N contents agree with the calculated values.

Of the four theoretically possible isomeric arrangements of the gem-dimethyl groups and phenyl radicals with respect to the position of nitrogen, and from the articulation of the structure, preference was given to structure (II) on the basis of multiplicity analysis and signal location in the PMR and ^{13}C NMR spectra. The signals at 178.41 and 171.96 ppm in the ^{13}C NMR spectrum are unequivocally assigned to the imine $C_{(4)}$ and $C_{(9)}$ atoms; this rejects participation of C=N bonds in the condensation.

3,3-Dimethyl-2-(2-thienyl)-3H-pyrrole is dimerized similarly in 20% yield.

The new reaction makes possible a simple approach to the hitherto unknown tricyclic systems with a partially hydrogenated pyrrolpyridine nucleus.

Irkutsk Institute of Organic Chemistry, Siberian Division, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1566-1567, November, 1989. Original article submitted December 6, 1988.