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A NOVEL SYNTHESIS OF 2,4-DIMETHYL-1-(4-HYDROXYPHENYL)PYRROLE-3-THIOL

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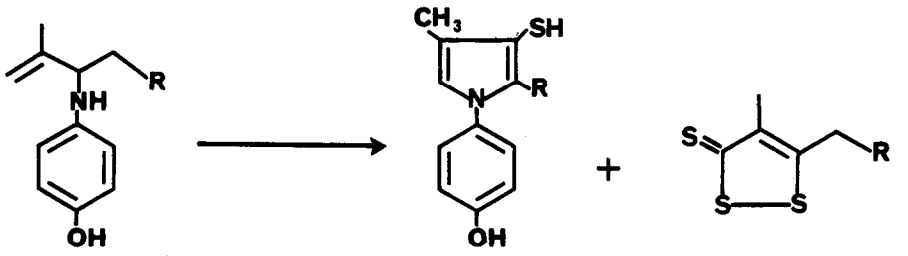
The literature on pyrrolethiols is extremely scanty and no systematic synthetic methods for such thiols have been described. During our investigations of the synergistic interaction[1] of the sulphur and urethane vulcanizing systems for olefinic rubbers we have found that N-(1-ethyl-2-methylprop-2-enyl)-p-aminophenol[2] (1; R = CH_3) reacts with sulphur in the presence of bis(dimethyldithiocarbamato)zinc at elevated temperatures, 140° for 60 h, to yield 2,4-dimethyl-1-(4-hydroxyphenyl)pyrrole-3-thiol (2; R = CH_3), m.p. 157-8°, in 45% yield. The structure of the product was established by elemental analysis ($C_{12}H_{13}NOS$ requires : C, 65.7; H, 5.94; N, 6.4; S, 14.6. Found : C, 65.6; H, 5.8; N, 6.3; S, 14.6%) and its ^{1}H-NMR spectrum (DMSO-d_6): δ , 1.81, 3H, doublet (J = 1 Hz) (4-CH_3); 2.05, 3H, singlet (2-CH_3); 6.23, 4H, AB quartet (Ar-H); 6.45, 1H, singlet (SH); 6.85, 1H, quartet (J = 1 Hz) (pyrrole-H); 8.2 ppm, 1H, broad singlet (OH). The mass spectrum was consistent with a 1-phenylpyrrole structure[3] : m/e 219 M^+, m/e 218 [M^+-H], m/e 202 [M^+-OH], m/e 186 [M^+-SH], m/e 126 [M^+-C_6H_5O], m/e 125 [M^+-C_6H_6O], m/e 93 [M^+-C_6H_8NS].

5-Ethyl-4-methyl-1,2-dithiole-3-thione (3; R = CH_3), m.p. 28-9° (lit.,[4] 28°), was also isolated (18%) from the reaction products. The other products : zinc sulphide, N,N-dimethylthioformamide, tetramethylthiourea, and trimethylthiourea, were all derived from bis(dimethyldithiocarbamato)zinc and identified by comparison with authentic specimens.



(1) (2) (3)

N-(1-Propyl-2-methylprop-2-enyl)-p-aminophenol (1; R = C_2H_5) reacted in an analogous manner to yield the dithiolethione (3; R = C_2H_5) and 2-ethyl-1--(4-hydroxyphenyl)-4-methylpyrrole-3-thiol (2; R = C_2H_5), m.p. 121.5-122.5°, in 48% yield. The ^{1}H-NMR spectrum of the latter (DMSO-d_6) was similar to that of the dimethyl derivative except that the 2-methyl signal was replaced by peaks at 2.52 ppm, 2H, quartet (J = 8 Hz) (2-$\underline{CH_2}CH_3$) and 1.02 ppm, 3H, triplet (J = 8 Hz) (2-$CH_2\underline{CH_3}$).

The reaction pathway to the pyrrolethiols (2) is clearly a multi-step one, involving sulphuration, nitrogen migration, cyclization and dehydrogenation, and appears to be related to the Willgerodt-Kindler class of reactions.[5] After treatment for shorter times, when the aminophenol (1; R = CH_3) had not completely reacted, the thiol (2; R = CH_3) was isolated but no additional products could be detected. 1,2-Dithiole-3-thiones are often isolated as low-yield end-products of sulphuration of many types of unsaturated substrate,[6] apparently because of their high thermodynamic stability.

1. C.S.L. Baker, D. Barnard, M. Porter, L.G. Manino and S.A. Westley, Proc. Int. Rubb. Conf., Brighton, 1972, G2-1.

2. G.T. Knight and B. Pepper, J. Chem. Soc. Chem. Comm., 1971, 1507.

3. H. El Khadem, L.A. Kemler, Z. M. El Shafei, M.M.A. Abdel Rahman and S. El Sadany, J. Heterocycl. Chem., 1972, 9, 1413.

4. A. Thuillier and J. Vialle, Bull. Soc. Chim. France, 1962, 2187.

5. F. Asinger, W. Schäfer, K. Halcour, A. Saus and H. Triem, Angew. Chem. Int. Ed. Eng., 1964, 3, 19.

6. P.A. Landis, Chem. Rev., 1965, 65, 237; N. Lozac'h and J. Vialle, in N. Kharasch and C.Y. Meyers, Eds., Organic Sulfur Compounds, Vol. 2 (Pergamon Press, 1966), Chap. 10; N. Lozac'h, Quart. Reports Sulfur Chem., 1968., 1968, 3, 367.