A NEW CATALYTIC REACTION OF ELEMENTAL SULFUR WITH ACETYLENES BY THE ACTION OF COBALT COMPLEXES

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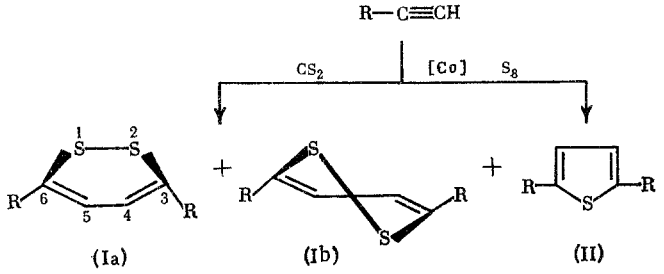
We are the first to report that the reaction of 1-hexyne with CS_2 taken in 3:1 mole ratio by the action of a catalyst prepared by the reduction of Co(2-ethylhexanoate)$_2$ by triethylaluminum in the presence of absolute DMSO (Co:Al:DMSO = 1:3:10-20) in absolute toluene solution at 150°C for 6 h gives a 1:1 mixture of stereoisomeric 1,2-dithia-3,6-dibutyl-3,5-cyclohexadienes (Ia) and (Ib) in about 40% total yield. By analogy, 1-hexyne and S_8 (S_α-cyclooctasulfane) give 40% disulfides (Ia) and (Ib), 15% 2,5-dibutylthiophene (II), and about 45% of a mixture of 1,3,4- and 1,3,5-tributylbenzenes (III) in 45% total yield identified by comparison with authentic samples [1].

The ^{13}C NMR spectrum of (I) has a double set of signals of virtually identical intensity. The upfield signals (13.7-36.4 ppm) are related to the butyl groups. The singlets at 139.7 and 140.7 ppm correspond to substituted atoms at C^3 and C^6 of the six-membered ring, while the doublets at 115.02 and 115.54 ppm are related to C^4 and C^5. The doubling of the signals in the ^{13}C NMR spectrum is apparently a result of the formation of two conformers or isomers differing in the symmetry elements (Ia) and (Ib), which are frozen at ∿20°C. A symmetry plane σ is found for (Ia) which is perpendicular to the S–S and C^2–C^3 bonds and this compound apparently has boat form, while (Ib) has a twofold axis C_2 and half-chair or twist form:



7(11) 8(12) 9(13) 10(14)
R = CH_2 CH_2 CH_2 CH_3

Derivatives (I) and (II) were separated and purified by vacuum distillation. 1,2-Dithia-3,6-dibutyl-3,5-cyclohexadiene (Ia,b), bp 95-97°C (2 mm), $n^{20}D$ 1.5475. IR spectrum (ν, cm^{-1}): 620, 760, 920, 1070, 2940, 3020. ^{13}C NMR spectrum (δ, ppm): 13.77 q (C^{10}, C^{14}), 21.93 t (C^9, C^{13}), 30.58 t, 30.65 t (C^8, C^{12}), 36.07 t, 36.42 t (C^7, C^{11}) 115.02 d, 115.54 d (C^4, C^5), 139.73 s, 140.41 s (C^3, C^6). Found, %: C 63.20; H 8.58; S 28.16. Calculated, %: C 63.16; H 8.77; S 28.07. M^+ 228.

2,5-Dibutylthiophene (II), bp 82-83 (2 mm), $n^{20}D$ 1.4940 [2].

LITERATURE CITED

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