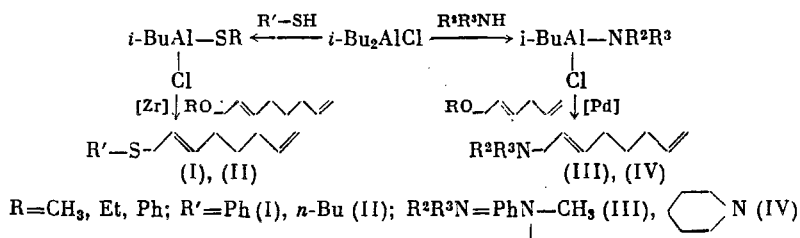


NEW METHOD FOR THE SYNTHESIS OF HIGHER UNSATURATED SULFIDES AND
AMINES INVOLVING ZIRCONIUM AND PALLADIUM COMPLEX CATALYSTS

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UDC 542.97:547.379.1:547.333

We are the first to report that aluminum mercaptides or amides obtained in situ by the action of alkylthiols, arylthiols, or secondary amines with $(i\text{-Bu})_2\text{AlCl}$ in CH_2Cl_2 reacts with 2,7-octadienyl ethers in the presence of catalytic amounts of Cp_2ZrCl_2 or $\text{Pd}(\text{acac})_2 + 2\text{Ph}_3\text{P}$ at 35-40°C over 6-8 h to give the corresponding alkyl or aryl 2,7-octadienyl sulfides or tertiary amines in 65-96% yield.



Unsaturated sulfides or amines are not formed in the absence of catalyst or $(i\text{-Bu})_2\text{AlCl}$. Products (III) and (IV) are identified by comparison with authentic samples [1]. Phenyl 2E,7-octadienyl sulfide (I): $n_D^{25} 1.5566$. IR spectrum (ν , cm^{-1}): 3050, 1640, 1580, 1480, 1440, 1000, 975, 915, 740, 690. PMR spectrum (δ , ppm): 0.90-1.58 m (2H, CH_2), 1.66-2.10 m (4H, CH_2), 3.33 d (2H, S-CH_2 , $J = 5$ Hz), 4.60-5.83 m (5H, olefinic), 7.15 s (5H, Ph). M^+ 218.

5-Thia-7E,12-tridecadiene (II): $n_D^{27} 1.4782$. IR spectrum (ν , cm^{-1}): 3040, 1640, 990, 960, 905, 740. PMR spectrum (δ , ppm, J , Hz): 0.87 t (3H, CH_3 , $J = 7$ Hz), 1.10-1.75 m (6H, CH_2), 1.80-2.15 m (4H, CH_2), 2.33 t (2H, $\text{CH}_2\text{-S}$, $J = 7$ Hz), 2.95 d (2H, S-CH_2 , $J = 5$ Hz), 4.67-5.92 m (5H, olefinic). ^{13}C NMR spectrum (δ , ppm): 13.69 q (C^1), 22.02 t (C^2), 31.64 t (C^3), 30.30 t (C^4), 33.90 t (C^6), 132.93 d (C^7), 126.52 d (C^8), 31.55 t (C^9), 28.61 t (C^{10}), 32.20 t (C^{11}), 138.48 d (C^{12}), 114.56 t (C^{13}). M^+ 198.

LITERATURE CITED

1. S. Takahashi, T. Shibano, and N. Hagihara, Bull. Chem. Soc. Jpn., 41, 454 (1968).