LETTERS TO THE EDITOR

SAMARIUM, EUROPIUM, AND YTTERBIUM

IODOPHENYLACETYLENES AND THEIR REACTIONS

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Organometallic compounds of the Iotsich type reagents $PhC \equiv CLnI$ ($Ln^{2+} = Sm$, Eu, Yb), which are formed in the reaction of MeLnI with phenylacetylene in THF at $-20^{\circ}C$, and their reactions, have been reported for the first time.

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In the reaction of PhC=CLnI with SiMe₃Cl in THF, trimethylsilylphenylacetylene is formed in a yield of 70-80%, bp 82°C (6 mm), $n_D^{2\circ}$ 1.5260 (cf.[1]).

The reactions of PhC=CLnI with allyl bromide proceed differently, depending on the metal. The use of PhC=CSmI leads to the formation of phenylallylacetylene, in a yield of 35%, bp 60-61°C (2 mm), $n_D^{2^\circ}$ 1.5570 (cf. [2]). Yb-Iodophenylacetylene reacts with allyl bromide to form diphenyldiacetylene (87%), mp 85-86°C (cf. [3]). PhC=CEuI does not react with allyl bromide under the conditions studied (-20 to +20°C).

With phenyl propyl ketone, Eu- and Yb-iodophenylacetylenes form a mixture of products (IV), (V), and (VI) in a ratio of 1:1:4 and 1:1:1, with overall yields of 60 and 90%, respectively. With PhC \equiv CSmI, only pinacone (VI) was obtained in a yield of 40%, mp 93-94°C (cf. [4])

 $\begin{array}{c} PhC \equiv CLnI \xrightarrow{PhCOPr} PhC \equiv C - C(OH)Pr + PhC \equiv C - C = CHEt + [PrPhC(OH)]_{2} \\ \downarrow \\ Ph & Ph \\ (IV) & (V) \end{array}$

<u>1,3-Diphenyl-1-hexyn-3-ol (IV)</u>, mp 57-58°C. IR spectrum (ν, cm⁻¹): 708, 760, 1600, 3040-3090 (Ph), 2235 (-C=C-), 3460 (-OH). ¹H NMR spectrum (CC1₄, δ, ppm): 0.90 m (3H, C⁶), 1.20 m (2H, C⁵), 1.85 m (2H, C⁴), 2.47 m (1H, OH), 7.18-7.75 m (10H, 2Ph). M⁺ (massspectrometrically) 250.

<u>1,3-Diphenyl-3-hexen-1-yne (V)</u>, n_D^{22} 1.6020. IR spectrum (v, cm⁻¹): 695, 760, 1495, 1600, 3040-3085 (Ph), 840, 1660, 3020 () C=CH), 2210 (-C=C-). ¹H NMR spectrum (CC1₄, δ , ppm): 1.05 t (3H, C⁶), 2.05 q (2H, C⁵), 6.33 t (1H, C⁴), 6.98-7.70 m (10H, 2Ph). M⁺ (mass-spectrometrically) 232.

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