

liarities of the effect observed for birefringence (the non-quadratic dependence of the effect, exceeding the molecular effect by 4 orders of magnitude), note that it is proportional to the magnetic anisotropy of supramolecular structures $\Delta\chi$, at least a weak magnetic field. The molar constants of the effect of magnetic birefringence³ ${}^mP_0 \sim \Delta\alpha\Delta\chi$ approximated to a zero magnetic field are equal to $6.3 \cdot 10^{-11}$, $7.3 \cdot 10^{-11}$, $1.5 \cdot 10^{-7} \text{ cm}^3 \text{ mol}^{-1}$ for La, Gd and Dy derivatives, respectively.

The similar chemical properties of rare-earth ions, along with the IR and NMR data for solutions and for the condensed phase suggest that the solutions of the complexes studied have the same structure, and, hence, the same anisotropy of electronic polarizability ($\Delta\alpha$) of their objects. Thus the ratio of the anisotropy for the magnetic susceptibilities of the associates, and, in the approximation of axial symmetry, of the remaining complexes ($\Delta\chi_m$) is approximately equal to the ratio of the mP_0 constants: $\Delta\chi_m(\text{La})/\Delta\chi_m(\text{Gd})/\Delta\chi_m(\text{Dy}) \cong 1/1.2/2.4 \cdot 10^3$. Analogous results were obtained for solutions of the complexes in chloroform and benzene.

The liquid crystal complexes of diamagnetic lanthanum and paramagnetic ($S = 7/2$, $\mu_{\text{eff}} = 7.9 \text{ M.B.}$) gadolinium (in S state), which have similar compositions and structures, possess magnetic anisotropy typical of mesogenes. The paramagnetic complex of Dy is characterized by magnetic anisotropy, significantly exceeding the anisotropy of known organic and metal-containing mesogenes.

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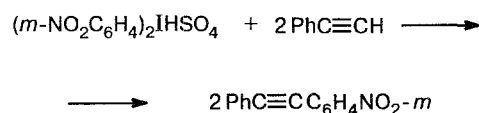
Palladium-catalyzed condensation of symmetrical diaryliodonium salts with phenylacetylene in aqueous media

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It is known that the condensation of terminal acetylenes with aryl halides proceeds the most efficiently if palladium complexes and copper (I) halides in the presence of base are used simultaneously.^{1,2}

We found that in the presence of 1 mol. % of $\text{PdCl}_2(\text{PPh}_3)_2$, 2 mol. % of CuI , and 2 eq. of Bu_3N phenylacetylene reacts easily with diaryliodonium salts in DMF at ambient temperature to afford substituted tolans in quantitative yields, e.g., *m*-nitrotolan was obtained in 94 % yield.

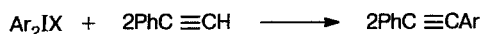


It should be noted that both of the aryl groups of the iodonium salt are involved in the cross-coupling. The diaryliodonium salt evidently interacts with phenylacetylene at the first stage, and the resulting aryl iodide reacts with phenylacetylene (see Ref. 3).

K_2CO_3 can be successfully used instead of Bu_3N if the reaction is carried out in aqueous DMF ($\text{DMF}:\text{H}_2\text{O} = 9:1$)³. In this case, the yield of *m*-nitrotolan reaches 96 %.

One can avoid using organic solvents and carry out the reaction in water in the presence of K_2CO_3 and a catalytic amount of Bu_3N .

$(m\text{-NO}_2\text{C}_6\text{H}_4)_2\text{IHSO}_4$ (0.5 mmol), phenylacetylene (1.3 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.01 mmol), CuI (0.02 mmol), Bu_3N (0.1 mmol), K_2CO_3 (2 mmol), and H_2O (2 mL) were placed into a flask equipped with a magnetic stirrer and a reflux condenser under Ar. The reaction mixture was stirred at



Ar = Ph (85 %), *p*-MeC₆H₄ (77 %), *m*-NO₂C₆H₄ (85 %)

X = HSO₄, CF₃COO, BF₄

ambient temperature for 1.5 h, and then it was extracted with ether. The ethereal extracts were washed with water and dried over Na₂SO₄. After removal of the solvent and recrystallization from MeOH, *m*-nitrotolan (0.189 g, 85 %) was obtained.

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The first example of metallation of an organogermanium hydride with an alkali metal under mild conditions: synthesis of 2,3,4,5-tetraphenyl-1,1-bis(trimethylsilyl)-1-germa-2,4-cyclopentadiene

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Germanium-centered anions of the R₃Ge[−] type are important intermediates in the synthesis of compounds containing germanium-element bonds. However, the set of convenient methods for generating them is quite limited.¹ In particular, metallation of the RGeH₃ hydrides under the action of alkali metals to form RGeH₂M (M = Li, Na)² requires the use of liquid ammonia and ethylamine as solvents. It cannot be excluded that the amides of alkali metals and not the metals themselves are the metallating agents under these conditions.

We found that 2,3,4,5-tetraphenyl-1-germa-2,4-cyclopentadiene (**1**) is metallated under the action of lithium or sodium (THF, 20 °C).

The evolution of hydrogen was observed in the course of the reaction. The signal of H—Ge disappeared completely in the ¹H NMR spectrum (δ 5.44) (in THF-d₈). The cherry-red solution obtained was diamagnetic and, evidently, it contained dianion **2**. However, attempts of its alkylation with MeCl or MeI or silylation with Me₃SiCl were unsuccessful. In all of these cases, only formation of germanium-containing polymers was observed. According to the GLC-MS data, Me₃SiSiMe₃, i.e.,

