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REACTION OF DICYMANTHRENYLPHENYLBISMUTH WITH CUPRIC CHLORIDE

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An oxidation–reduction reaction with the formation of CuCl, diphenyl, and chlorobenzene is found upon the action of $CuCl_2$ on $BiPh_3$ in addition to the loss of radicals from the Bi atom [1].

We have found that the substitution of two of the ligands in $BiPh_3$ by cymanthrenyl groups which differ from phenyl groups both in their electronic structure and size has virtually no effect on this reaction. Thus, the reaction of dicymanthrenylphenylbismuth (I), which we were the first to obtain from cymanthrenyllithium and $PhBiCl_2$, reacts with $CuCl_2$ to form 58% chlorocymanthrene, 21% chlorobenzene, 3% dicymanthrenyl and traces of diphenyl. This reaction carried out in acetone solution at about 20°C begins immediately upon mixing of solutions of the starting reagents, as indicated by the appearance of a colorless CuCl precipitate and disappearance of the color characteristic for $CuCl_2$ solutions. The similarity of the products obtained by the treatment of $BiPh_3$ and (I) by $CuCl_2$ indicates that these reactions proceed by the same mechanism.

EXPERIMENTAL

The reaction products were analyzed on a Tsvet 304 liquid chromatograph with a UV detector at 254 nm using 190 × 4 mm stainless steel columns packed with Silasorb 600 ($\sim$5 μm) and Silochrom C-80 ($\sim$7 μm) and hexane or 2:1 hexane–ether as the eluant. The flow rate was 1 ml/min and the inlet pressure was 4 MPa. All the measurements were carried out at 22°C. The IR spectra were carried out on a Perkin-Elmer 577 spectrometer.

Dicymanthrenylphenylbismuth (I). A solution of $PhBiCl_2$ (from 0.73 g $BiPh_3$ and 1.05 g $BiCl_3$ in 50 ml THF [3]) was added to a solution of cymanthrenyllithium (obtained from 10 ml 1N butyllithium and 2.04 g cymanthrene in 50 ml of THF [2]) at –50°C, stirred for 15 min at this temperature and then for 30 min at about 20°C. The solvent was removed in vacuum and cymanthrene was removed upon heating to 60°C. The residue was subjected to chromatography on alumina. Elution with benzene gave 2.94 g (85%) (I) as a yellow crystalline compound with mp 120°C which is soluble in most organic solvents. Found: C 38.12; H 1.94%. Calculated for $C_{22}H_{13}BiMn_2O_6$: C 38.15; H 1.88%. IR spectrum (ν, cm^{-1}): 1948, 2023 ($C\equiv O$).

Reaction of (I) with cupric chloride. A solution of $CuCl_2$ was added to a solution of 1.00 g (I) in 20 ml acetone until the appearance of a stable green color. Then, the reaction mixture was filtered and the filtrate was analyzed by liquid chromatography.

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CONCLUSIONS

A synthesis is reported for dicymanthrenylphenylbismuth which is the first representative of cymanthrenyl derivatives of trivalent bismuth. The reaction of this compound with $CuCl_2$ leads to the loss of the phenyl and cymanthrenyl ligands from the central bismuth atom.

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STRUCTURE OF PHOTOCHROMIC 1'-PHENYL-3',3'-DIMETHYL-11-NITROSPIRO(INDOLINE-2,2'-[2H-1]NAPHTHOPYRAN)

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In order to study the effect of substituents on the structure of indoline spiropyrans (SP), in particular, on the length of the C_{spiro}-O bond which is cleaved upon photoexcitation, we investigated the crystal structure of 1'-phenyl-3',3'-dimethyl-11-nitrospiro(indoline-2,2'-[2H-1]naphthopyran) (I), which contains an additional benzene ring fused at C^5-C^6 of the benzopyran fragment and a nitro group at C^{11}*. This compound gives yellow octahedral crystals with tetragonal symmetry.

The major crystallographic data for this compound are as follows: $C_{28}H_{22}N_2O_3$, a = 10.659(5), c = 19.914(7) Å, V = 2262(3) Å^3, M = 434.49, d_{calc} = 1.283(2) g/cm^3, Z = 4, space group $P4_1$. The intensities of 1282 independent nonzero reflections hk0-hk19 with $I > 2\sigma(I)$ in the range $4.2° \leqslant \theta \leqslant 57.8°$ were measured on a DAR-UM automatic diffractometer using CuKα radiation with a graphite monochromator and $(\omega - \omega/2\omega)$ laminar recording of a crystal with dimensions 0.30 × 0.30 × 0.35 mm^3. Absorption was not taken into account. The structure was solved by the direct method and refined by the full-matrix method of least squares anisotropically for the nonhydrogen atoms and isotropically for the hydrogen atoms using the Roentgen-75 programs to R = 0.040. The atomic coordinates and their errors are given in Table 1. Figure 1 gives the structure of (I). The indoline and naphthopyran fragments are approximately orthogonal to each other. The indoline fragment has compressed envelope conformation with flexure at the $N^{1'}...C^{3'}$ line of 28.5°. The naphthopyran fragment is bent along the $O^1...C^3$ and $O^1...C^4$ lines by 14.1 and 2.6°, respectively, toward the gem-methyl groups. The nitro group is twisted from the plane of the naphthalene fragment about the C^{11}—N^2 bond by 4.5°. On the whole, the conformation of (I) is analogous to that of indoline SP [1]. However, the (5-6)-fusion of an additional benzene ring in (I), in which an NO_2 group is located at C^{11}, leads to shortening of the C_{spiro}—O bond, which is cleaved upon photoexcitation, to 1.460(2) Å relative to the length of this bond in an unfused SP analog (II) (1.486(4) Å) [2]. Although the C_{spiro}—O bond length in (I) is greater than the normal C_{spiro}—O bond length in six-membered heterocycles (1.41-1.43 Å), its shortening relative to the analogous bond in (II) indicates diminution of the $n_{N^{1'}}-\sigma^*$ (C_{spiro}—O) orbital interaction in this molecule, which is reponsible for extension of the C_{spiro}—O bond [1].

Since the positions of the unshared electron pairs of $N^{1'}$ and O^1 in the $C^{22'}$—O^1 and $C^{22'}$—$N^{1'}$ bonds in (I) and (II) are the same, the diminuition in the n—σ^* interaction in (I) may be related only to a change in the electronic state of O^1 in the spiro unit. Indeed,

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