Hetero-linked triphenylmethyl radicals and triphenylmethylcarbonium ions. Strohbusch, Frank; Zimmermann, Herbert. Univ. Freiburg, Freiburg, Fed. Rep. Ger. Tetrahedron Letters (1969), (21), 1705-8. CODEN: TELEAY ISSN: 0040-4039. Journal written in German. CAN 71:30144 AN 1969:430144 CAPLUS (Copyright (C) 2008 ACS on SciFinder (R))

Abstract

Friedel-Crafts reaction of Ph2CCl2 on Ph2O in the presence of AlCl3 yielded the carbinol 4,4'-bis(diphenylhydroxymethyl)diphenyl ether (I), m. 131-3°. Similarly, Friedel-Crafts reaction of Ph2CCl2 on Ph3N gave the carbinols 4-(diphenylhydroxymethyl)triphenylamine (II), 4,4'-bis(diphenylhydroxymethyl)triphenylamine (III) and 4,4',4"-tris(diphenylhydroxymethyl)triphenylamine (IV). With ZnCl2 as catalyst and excess Ph2CCl2 the product was mainly II, with SnCl4 mainly III, and with AlCl3 a good yield of II, III and IV was obtained. II (m. 142.3°) III (m. 181-2°), and IV (m. 240.5-41°) were converted by AcCl into the corresponding chlorides, m. 134.5-35°, 165-5.5, and 190° (decompn.), resp. Similarly I gave a chloride. Dehalogenation with mol. Ag in C6H6 or PhMe gave the corresponding radicals. Soln. of the carbinols in concd. H2SO4, or reaction of the chlorides with AgClO4 in PhMe, or with SbCl5 in CCl4 gave the corresponding cations. The amplitudes of the E.S.R. spectra of the radicals from II-IV were temp. dependent and showed 21 equidistant lines, indicating the exclusive existence of polymers. Tabulation of the spectroscopic properties of the cations showed the strong similarity of the uv spectra to those of the triphenylmethane dyestuffs. Similarly analogous is the shift of the long wave band on transition from a mono- to di-substituted system and the coincidence of both long wave bands in systems with 3-fold symmetry. The electron spectra show that the conjugation system in the cations from II-IV extends throughout the mol.
Ιν αναλογψ το τριπηενψλαμινε ιτ ισ ασσυμεδ τηατ ιν τηε χατιονσ τηε 3 βενζενε ρινγσ αρε αρρανγεδ προπ ελλερωισε αρουνδ τηε χεντραλ Ν ατομ ωιτη τηε πλανε οφ τηε ρινγσ σομε 45° rotated from the propeller plane. The cation from I is assumed to have a roof-like structure with the O atom at the apex of an isosceles triangle with a C-O-C angle of 125-40°.