SYNTHESIS OF SYMMETRICAL RADICALS OF TRIPHENYLMETHYL DERIVATIVES CONTAINING MULTIPLE AND SINGLE BONDS

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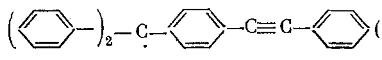
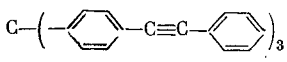
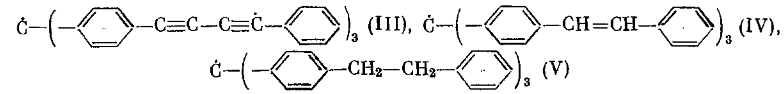
UDC 542.91:541.515:547.632.2-128

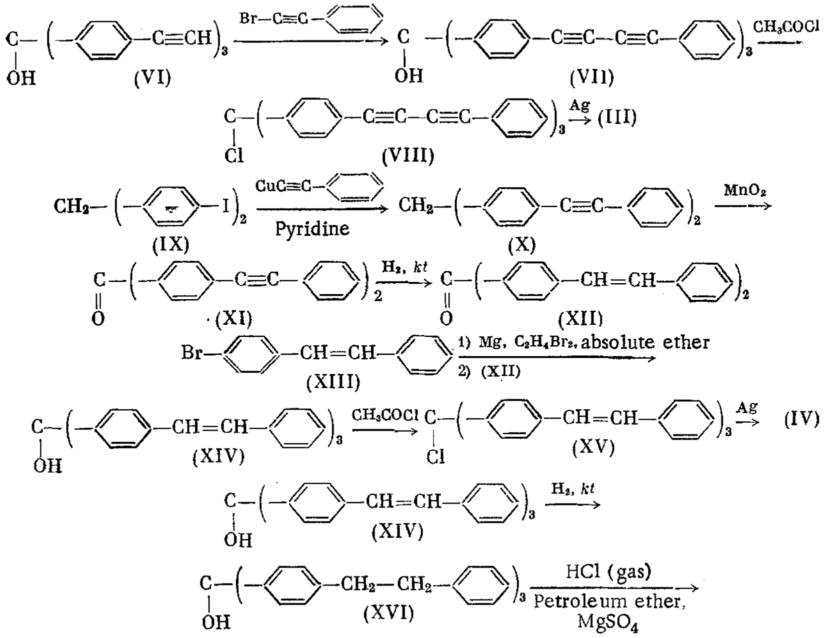
The synthesis of derivatives of the triphenylmethyl radical, containing triple bonds in the p-position (I, II), was described previously [1, 2]


(I)


(II)

In harmony with the set objective, namely to compare the ability of the triple, double and saturated bonds to transfer the spin electron density, we synthesized the free radicals (III), (IV) and (V)





The Chodkiewicz condensation of tri-(p-ethynylphenyl)carbinol (VI) [1] with ω-bromophenylacetylene proceeds in DMF with a yield of 60% in 16-17 h. Together with the main product, namely tri-(p-phenylbutadiynylphenyl)carbinol (VII), about 20% of diphenylbutadiyne is always obtained. The condensation of di-(p-iodophenyl)methane (IX) [3] with copper phenylacetylide in pyridine goes in 23 h and gives a 71% yield of

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1405-1407, June, 1973. Original article submitted November 2, 1972.

ditolanylmethane (X). The latter was oxidized with MnO_2 to ditolanyl ketone (XI) as described in [4]. The hydrogenation of (XI) to distilbenyl ketone (XII) on Lindlar catalyst (12% $Pb(OAc)_2$) can be run only in hot dioxane due to the poor solubility of (XI). The hydrogenation product is a viscous liquid and, based on the NMR and IR spectra, corresponds to the cis-isomer. cis–trans-Isomerization occurs when the compound is heated in nitrobenzene with a catalytic amount of I_2, which is corroborated by the IR spectra.

The Grignard reaction with (XIII) and cis-distilbenyl ketone (XII) was run in a N_2 atmosphere using a known amount of absolute ether and benzene. An increase in the volume of the solvent leads to the situation that the Grignard reagent deposits from solution, and further reaction is sharply retarded. The yield of tri-(p-stilbenyl)carbinol (XIV) is 57%. Tri-(p-dibenzylyl)carbinol (XVI) was obtained by the hydrogenation of (XIV) on skeletal nickel in a dioxane–alcohol mixture. The hydrogenation product is a viscous liquid. It could be isolated in the crystalline state in only 38% yield. Alcohols (VII), (XIV) and (XVI) were converted to the corresponding chloro derivatives by using either dry CH_3COCl [(VIII) and (XV)] or HCl gas and $MgSO_4$ as the water-removing agent. Radicals (III), (IV) and (V) were obtained by shaking 0.02 M solutions of (VIII), (XV) and (XVII) in absolute toluene with powdered silver [5] in evacuated sealed ampuls. The solutions of the radicals were respectively colored yellow, dark green and orange. Radicals (III) and (V) are retained in solution at room temperature for 1-2 h, while radical (IV) is retained for 1-2 days. The stability of radicals (III), (IV) and (V) was determined by the change in the intensity of the ESR signal with time. In view of their low stability the radicals were not isolated, and instead were studied as their toluene solutions. Below are enumerated the radicals and the number of unpaired electrons in 1 ml of solution: (III) $1.17 \cdot 10^{17}$; (IV) $1.03 \cdot 10^{19}$; (V) $1.2 \cdot 10^{18}$.

EXPERIMENTAL METHOD

Tri-(p-phenylbutadiynylphenyl)carbinol (VII). A solution of 1.50 g of (VI) in 30 ml of DMF was mixed with 12 ml of 30% aqueous ethylamine solution in a nitrogen atmosphere. CuCl and $NH_2OH \cdot HCl$ were added on the end of a scalpel. A solution of 5.36 g of ω-bromophenylacetylene in 10 ml of DMF was added to the mixture in drops. Immediately after loading, the temperature in the flask rose to 40°C. After 12 h the mixture was heated at 50° for 4-5 h, cooled, and poured into water. The precipitate was filtered, washed with water, and dried. By chromatography on Al_2O_3 (II activity, eluant = ether) we isolated 1.70 g (60%) of (VII), mp 240° (decompn.) (benzene–petroleum ether mixture). Found: C 93.58; H 4.82%. $C_{49}H_{28}O$. Calculated: 93.01; H 4.46%. Infrared spectrum (ν, cm^{-1}): doublet 2136 and 2212 m (–C ≡C–); 3562 s (O–H).

Tri-(p-phenylbutadiynylphenyl)chloromethane (VIII). A solution of 0.02 g of (VII) in 80 ml of CH_3COCl was refluxed until solution was complete, evaporated to 1 ml, and allowed to stand for several days at ~5°. The obtained crystals were filtered, washed with petroleum ether (bp 30-70°), and dried in vacuo. We obtained 0.10 g (49%) of (VIII), mp 150° (polymerizes). Found: Cl 5.45%. $C_{49}H_{27}Cl$. Calculated: 5.44%.

Ditolanylmethane (X). The condensation of 19 g of (IX) with 22 g of copper phenylacetylide was run as described in [6, 2] (refluxing pyridine, 23 h, N_2). After evaporation of the ether solution and recrystallization of the residue from ethanol we obtained 11.92 g (71%) of (X), mp 136-137° (from alcohol). Found: C 94.49; H 5.47%. $C_{29}H_{20}$. Calculated: C 94.54; H 5.46%. Infrared spectrum (ν, cm^{-1}): 2210 w (–C ≡ C), 2830 and 2905 w (–CH_2–).

Ditolanyl Ketone (XI). A mixture of 9.4 g of (X) and 94 g of MnO_2 was heated without a solvent for 20-24 h at 140°, after which it was extracted with 300 ml of $CHCl_3$ in a Soxhlet apparatus for 14 h. We obtained 6.24 g (62%) of (XI), mp 239-240° (from $CHCl_3$). Found: C 90.59; H 4.72%. $C_{29}H_{18}O$. Calculated: C 91.07; H 4.74%. Infrared spectrum (ν, cm^{-1}): 2210 m (–C≡C–), 1660 s (–C =O).

Distilbenyl Ketone (XII). A solution of 1 g of (XI) in 75 ml of hot dioxane was hydrogenated over Lindlar catalyst. After evaporation of the solvent we isolated 0.84 g (80%) of liquid (XII) (cis-isomer). Infrared spectrum (ν, cm^{-1}): 1660 s (–C =O), –C ≡ C– is absent. NMR spectrum: $\tau = 6.4$ ppm (doublet), J 5 Hz. When heated in nitrobenzene at 230° for 15 min the cis-isomer was converted to the trans-isomer, mp 282-283° (from $CHCl_3$). Found: C 90.20; H 5.70%. $C_{29}H_{22}O$. Calculated: C 90.12; H 5.74%. Infrared spectrum (ν, cm^{-1}): 1660 s (–C=O), 970 s (=C–H-trans).

p-Bromostilbene (XIII). We first obtained p-bromophenylbenzylcarbinol by reduction, by adding an ether solution of the exactly calculated amount of freshly prepared $LiAlH_4$ to 5 g of p-bromodesoxybenzoin [1] in 80 ml of absolute ether. The yield of (XIII) was quantitative, mp 55°. Found: Br 28.57%. $C_{14}H_{12}Br$. Calculated: Br 28.83%. Infrared spectrum (ν, cm^{-1}): 3580 m (O–H). Then 10.68 g of p-bromophenylbenzylcarbinol was dehydrated at 71-73° in 50 ml of Ac_2O to which 1 ml of conc. H_2SO_4 and 1.30 ml of water had been added. The reaction time was 1 h and 10 min. Then the mixture was cooled and poured into an ether–water mixture. The ether solution was washed until neutral, dried over $CaCl_2$, evaporated, and chromatographed on Al_2O_3 (III activity, eluant = benzene). We obtained 6.30 g (63%) of (XIII), mp 136°. From [7]: mp 139°.

Tri-(p-stilbenyl)carbinol (XIV). As described in [1], the Grignard reagent was obtained from 1.80 g of (XIII), 1.07 g of Mg and 3 ml of dibromoethane in a mixture of 17.8 ml of absolute ether and 5.8 ml of absolute benzene. Then in a N_2 stream was added 1.21 g of (XII) in 8.7 ml of absolute ether. The mixture was stirred for 4.5 h and then immediately decomposed with dilute HCl solution. After the usual workup, from the ether solution by preparative chromatography on Al_2O_3 (III activity, eluant = benzene) we isolated 1.02 g (57%) of (XIV), mp 184-186° (benzene–petroleum ether, bp 70-100°). Found: C 90.21%. H 5.99%. $C_{43}H_{34}O$. Calculated: C 90.40%; H 5.95%. Infrared spectrum (ν, cm^{-1}): 970 s (=C–H-trans), 3610 m (–O–H).

Tri-(p-stilbenyl)chloromethane (XV). To a mixture of 0.40 g of (XIV) and 4 ml of petroleum ether at reflux was added dry CH_3COCl until solution was complete (12 ml), after which the mixture was refluxed for another 10 min and then cooled. The obtained crystals were filtered and dried. We obtained 0.25 g (41.5%) of analytically pure (XV), mp 166-167°. Found: C 6.17%. $C_{43}H_{33}Cl$. Calculated: Cl 6.07%.

Tri-(p-dibenzylyl)carbinol (XVI). A solution of 1.50 g of (XIV) in a 2 : 1 dioxane–alcohol mixture was hydrogenated on skeletal nickel. Evaporation of the solvent gave 0.57 g (38%) of (XVI) with mp 78-79.5° (from petroleum ether). Found C 89.65; H 7.27%. $C_{43}H_{40}O$. Calculated: C 90.17; H 7.04%. Infrared spectrum (ν, cm^{-1}): 1450 m, 2860 and 2925 s ($-CH_2-$), 3620 m (O–H).

Tri-(p-dibenzylyl)chloromethane (XVIII). Freshly purified (XVI) (0.07 g) was dissolved in excess petroleum ether (bp 30-45°), $MgSO_4$ was added, and the mixture was saturated with HCl, with cooling in ice water. The solution was filtered from the $MgSO_4$ and evaporated to dryness. We obtained 0.06 g (73%) of a colorless noncrystallizing liquid. The IR spectrum was identical with the IR spectrum of (XVI), (ν, cm^{-1}): 1450 m, 2860 and 2925 s ($-CH_2-$), and –O–H is absent.

CONCLUSIONS

1. We synthesized some symmetrical radicals of the triphenylmethyl type, which considered triple, double and single bonds in the substituents.

2. The most stable of all of the radicals obtained in the present study is tris-(p-stilbenyl)methyl (V), which contains double bonds.

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