SYNTHESIS OF UNSYMMETRICAL RADICALS — TRIPHENYLMETHYL DERIVATIVES — CONTAINING MULTIPLE AND SINGLE BONDS

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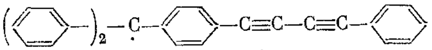
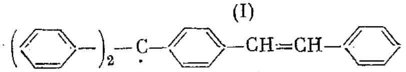
As a continuation of our research on the synthesis of substituted triphenylmethyl radicals [1-3], in the present communication we report the synthesis and EPR spectra of the unsymmetrical radicals: diphenyl-(p-phenylbutadiynyl)phenylmethyl (I), diphenyl-(p-phenylethenyl)phenylmethyl (II), and diphenyl-(p-phenylethyl)phenylmethyl (III)


(I)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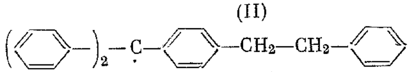
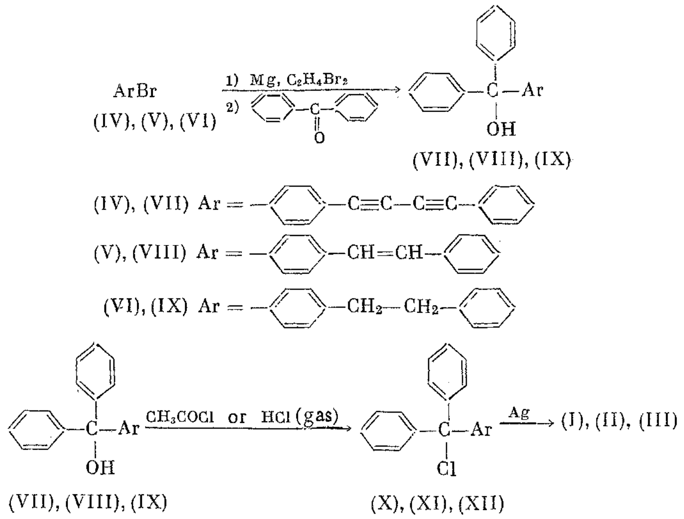

(III)

Radicals (I)-(III) were obtained by the scheme:



The Grignard reagents were obtained from the bromo derivatives (IV-(VI) by the method given in [1], which is characterized by the fact that the Mg is used in strictly stoichiometric amounts, while iodine and 1,2-dibromoethane are used to activate the Mg.

The Grignard reagents obtained from (IV)-(VI) proved to have little activity in the reaction with benzophenone. Thus, 15 h was required for the formation of (VIII) and the yield was 28%. An increase in the reaction time and temperature enhances tarring of the mixture. The reaction of (p-dibenzyl)magnesium bromide with benzophenone takes more than 4 days and gives (IX) in 18% yield.

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Tertiary alcohol (IX) was also obtained by the hydrogenation of (VIII) on skeletal Ni in a 1 : 1 dioxane–alcohol mixture, but the hydrogenation product could not be isolated in the crystalline form. The IR spectra of the (IX) samples, obtained by the two methods, coincide completely.

Replacement of the alcohol group by chlorine proceeds either by treatment with dry CH_3COCl [in the case of carbinol (VIII)], or by the passage of HCl gas into a solution of carbinol (VII) in acetic anhydride, or into a solution of carbinol (IX) in petroleum ether.

Radicals (I)-(III) are formed by shaking 0.02 M solutions of chlorides (X)-(XII) in absolute toluene with finely-dispersed silver. The solutions of radicals (I)-(III) are respectively colored yellow, dark green, and yellow, and are stable at ~20°C for several hours.

EXPERIMENTAL METHOD

The EPR spectra of the radicals were taken on a Varian E-3 spectrometer, either at room temperature [for (I) and (III)] or at a lower temperature [for (II)], in evacuated ampuls equipped with special outlets, which made it possible to mix the components immediately before photographing. The hyperfine structure of the EPR spectra differs: in the spectrum of radical (I) there are 28 lines with a minimum splitting of 1.08 G, in the case of radical (II) there are more than 100 lines with a minimum splitting of 0.15 G, while radical (III) gives ~50 lines with a minimum splitting of 0.4 G.

Diphenyl-(p-phenylbutadiynylphenyl)chloromethane (X). With cooling in an ice–water mixture, HCl gas was passed through a solution of 0.78 g of (VII) [1] in 15 ml of $(CH_3CO)_2O$ for 2 h. The obtained precipitate was filtered, washed in succession with acetic anhydride and petroleum ether (bp 30-70°), and dried in vacuo. We obtained 0.61 g (71% yield) of (X), mp 131-132°. Found: Cl 8.72. $C_{29}H_{19}Cl$. Calculated: Cl 8.80%.

Diphenyl-(p-phenylethynylphenyl)carbinol (VIII). The Grignard reagent was obtained from 8.85 g of (V), 5.65 g of Mg, and 17.5 ml of 1,2-dibromoethane in a mixture of 100 ml of absolute ether and 15 ml of absolute benzene, the same as in the synthesis of (VII) [1]. Then, with cooling in ice water, a solution of 4.5 g of benzophenone in 20 ml of absolute ether was added in 1 h. The reaction mixture was stirred for 2.5 h and then allowed to stand overnight. The next day the mixture was stirred for another 30 min at ether reflux, after which it was decomposed with dilute HCl solution. After the usual workup the ether solution was evaporated, while the residue was chromatographed on Al_2O_3 (III activity), and the mixture was eluted in succession with benzene and 2 : 1 benzene–ether mixture. We isolated 2.53 g (28%) of (VIII), mp 141-143°. Found: C 89.25; H 6.22%. $C_{27}H_{22}O$. Calculated: C 89.47; H 6.12%. Infrared spectrum (ν, cm^{-1}): 3600 m (OH), 980 s [=CH(trans)].

Diphenyl-(p-phenylethynyl)phenylchloromethane (XI). A mixture of 0.230 g of (VIII) and 5 ml of CH_3COCl was refluxed for 30 min, evaporated to minimum volume, and allowed to stand in the refrigerator. The obtained crystals were filtered, washed with petroleum ether (bp 30-45°), and dried in vacuo. We obtained 0.18 g (71%) of (XI), mp 131-133° (from a C_6H_6–hexane mixture). Found: Cl 9.37%. $C_{27}H_{21}Cl$. Calculated: Cl 9.31%.

Diphenyl-(p-phenylethylphenyl)carbinol (IX). 1) To the Grignard reagent, obtained from 10 g of (VI) [4], 5.50 g of Mg, and 16.4 ml of 1,2-dibromoethane in 120 ml of ether, was added in an N_2 stream, with cooling in ice water, a solution of 4.88 g of benzophenone in 20 ml of absolute ether in 40 min. The mixture was allowed to stand for 4 days, with periodic shaking. Then the mixture was refluxed for 5 h, cooled, and decomposed with dilute HCl solution. After the usual workup the ether solution was evaporated to minimum volume, the excess benzophenone was filtered off, and the filtrate was chromatographed on Al_2O_3 (III activity), using benzene and a 1 : 1 benzene–ether mixture for elution. After repeated chromatographing of the fraction rich in (IX) we obtained 1.72 g (18%) of a viscous liquid, which crystallized on standing, mp 71.5-72.5° (from alcohol). Found: C 89.08; H 6.73%. $C_{27}H_{24}O$. Calculated: C 88.97; H 6.64%. Infrared spectrum (ν, cm^{-1}): 2865, 2937 s, 1445 m (CH_2), 3612 m (OH).

2) A solution of 0.46 g of (VIII) in a mixture of 20 ml of alcohol and 10 ml of dioxane was hydrogenated on skeletal Ni at room temperature. The solvent was evaporated, while the residue was chromatographed on Al_2O_3 (III activity). For elution we successively used benzene and a 1 : 1 benzene–ether mixture. We obtained 0.30 g of (IX) as a viscous liquid. The IR spectrum was identical with the IR spectrum of the above-obtained sample.

Diphenyl-(p-phenylethylphenyl)chloromethane (XII). $MgSO_4$ was added to a solution of 0.29 g of (IX) in a mixture of 14 ml of petroleum ether (bp 30-45°) and 2 ml of absolute ether, after which HCl was passed in for 2 h, with cooling in an ice–water mixture. The filtrate was evaporated to dryness. We obtained 0.26 g (93%) of (XII) as a viscous liquid. Infrared spectrum (ν, cm^{-1}): 1450 m, 2860 and 2930 s (CH_2).

CONCLUSIONS

We synthesized some unsymmetrical radicals of the triphenylmethyl type, which contained multiple and single bonds in the substituents, and made a study of their EPR spectra.

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