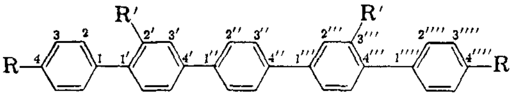
Communications TO THE EDITOR

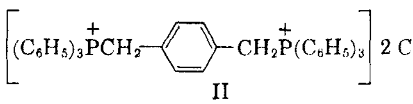
Synthesis of *p*-Quinquephenyl, 4,4''''-, and 2',3'''-Dimethyl-*p*-quinquephenyl

Sir:

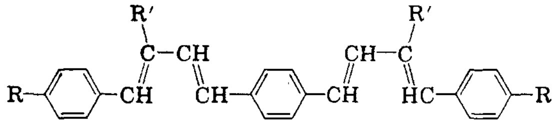
Previous syntheses of *p*-quinquephenyl (I; R = R' = H) have involved the reaction of biphenyllithium with cyclohexandione-1,4 followed by dehydration and air oxidation[1]; the Gatterman coupling reaction of benzenediazonium formate with copper[2]; the Ullmann coupling of 4-iodoterphenyl and 4-iodobiphenyl with silver[2]; the catalytic reduction of *p*-dibromobenzene[3]; and the Friedel-Crafts reaction of cyclohexene with terphenyl, followed by dehydrogenation.[4] These have yielded trace or, at best, poor yields of the hydrocarbon. We now wish to report the preparation of *p*-quinquephenyl and two derivatives utilizing the Wittig reaction for the synthesis of intermediates.



I



II



III

p-Xylylene dichloride when allowed to react with triphenylphosphine in refluxing dimethylformamide was converted in 95% yield to *p*-xylylene-bis(triphenylphosphonium chloride) [II, m.p. > 400°; *Anal.* Calcd. for $C_{44}H_{38}P_2Cl_2$: Cl, 10.16. Found: Cl (total), 10.04, 10.00; Cl (ionic), 10.15, 10.00, and for the dihydrate, calcd. for $C_{44}H_{38}P_2Cl_2 \cdot 2H_2O$: C, 71.8; H, 5.7; Cl, 9.7. Found: C, 71.6, 71.8; H, 5.9, 5.9; Cl (ionic) 9.7, 9.8; Cl (total), 9.6, 9.8]. Reaction of II with cinnamaldehyde in ethanol with lithium ethoxide as base gave a 75% yield of a mixture of *cis* and *trans* isomers of 1,4-bis(4-phenylbutadienyl)benzene[5] (III; R = R' = H; m.p. 290–293°; *Anal.* Calcd. for $C_{26}H_{22}$: C, 93.4; H, 6.6; Found: C, 93.3, 93.3; H, 6.5, 6.6), which was isomerized to all *trans* configuration with iodine.

The method reported by Lohaus[6] for the conversion of 1,4-diphenylbutadiene to terphenyl was adapted to the synthesis of quinquephenyl (I, R = R' = H). III (R = R' = H) was readily condensed with diethyl acetylenedicarboxylate in *o*-dichlorobenzene. Saponification gave a brilliant yellow solution containing potassium tetrahydroquinquephenyl tetracarboxylate. This substance was oxidized and decarboxylated by reaction with potassium fericyanide to give a 52% yield, after sublimation, of *p*-quinquephenyl, m.p. 385–390°.

Reaction of the bis-"ylide" derived from II with substituted cinnamaldehydes should ultimately lead to derivatives of *p*-quinquephenyl. When *p*-methylcinnamaldehyde was employed, 1,4-bis[4(*p*-tolyl)butadienyl]benzene (III; R = CH_3, R' = H; m.p. 315–320°; *Anal.* Calcd. for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.6, 92.7; H, 7.14, 7.52) resulted. This was converted to 4,4''''-dimethyl-*p*-quinquephenyl (I; R = CH_3, R' = H; m.p. 400°; *Anal.*, Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.59, 93.65; H, 6.48, 6.57). 1,4-Bis(3-methyl-4-phenylbutadienyl)benzene (III; R' = CH_3, R = H; m.p. 235–237°; *Anal.* Found: 92.81, 92.77, H, 7.51, 7.31) was prepared by reaction of II with α-methylcinnamaldehyde. This was converted to 2',3'''-dimethyl-*p*-quinquephenyl (I; R' = CH_3, R = H; m.p. 217–218°; *Anal.* Found: C, 93.57, 93.61; H, 6.43, 6.46).

This is by far the best preparative method for *p*-quinquephenyl reported to date. The methylated compounds represent the first derivatives of this hydrocarbon synthesized, and by an unambiguous route.

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[2] O. Gerngross and M. Dunkel, *Chem. Ber.*, **57B**, 739 (1924).

[3] M. Busch, W. Weber, C. Darboven, W. Renner, H. J. Hahn, G. Mathauser, F. Stratz, K. Zitzmann, and H. Engelhardt, *J prakt. Chem.*, **146**, 1 (1936).

[4] Buu-Hoï and P. Cagniant, *Compt. rend.*, **216**, 381 (1943).

[5] G. Drefahl and G. Plotner, *Chem. Ber.*, **91**, 1274 (1958) have reported the synthesis of this compound by the conventional Perkin or Kuhn condensation in 25% yield.

[6] H. Lohaus, *Ann.*, **516**, 295 (1935).