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SYNTHESIS OF 1,3,4,6,7,9-HEXAMETHYLPHENALENE

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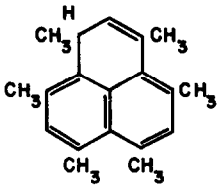
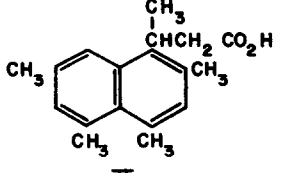
Although a few methylphenalenes have been reported (1) no polymethylphenalene susceptible of forming a symmetrical cation has yet been prepared; even the simplest, the 2,5,8-trimethylphenalenium cation, is unknown. We have now synthesized 1,3,4,6,7,9-hexamethylphenalene (I) by the method described below.



I

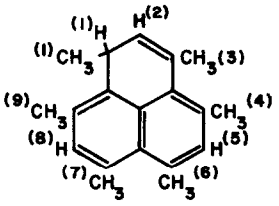
The Grignard reagent prepared from 3,5-dimethylbenzyl chloride (α-chloromesitylene) treated with pentanedione-2,4 in ether afforded a 70-75% yield of the new β-hydroxyketone, 4-hydroxy-4-methyl-5-(3,5-dimethylphenyl)-2-pentanone. Cyclodehydration of the β-hydroxyketone produced 1,3,6,8-tetramethylnaphthalene, m.p. 80-1°, in 85% yield. Bromination with 1 mole of bromine in carbon tetrachloride at 0-5° in diffused light gave a 95% yield of 1-bromo-2,4,5,7-tetramethylnaphthalene, m.p. 40°, after distillation under 0.03 mm. and recrystallization from petroleum ether. 2,4,5,7-Tetramethyl-1-naphthoic acid, m.p. 163-4°, was obtained in good yield by carbonation of the Grignard reagent prepared from the bromide. The acid was converted into the acid chloride and then 1-acetyl-2,4,5,7-tetramethylnaphthalene as described by Adams and Binder (2) for a lower homologue. Reduction with lithium aluminium hydride in ether gave the alcohol, m.p. 83°. It was converted into the bromide and the latter was treated with sodiomalonic ester as described by Bachmann and Edgerton (3). β-(2,4,5,7-Tetramethyl-1-naphthyl)-butyric acid (II), m.p 121°, was obtained as reported for a lower homologue by Reid and Sutherland (4)



II

Cyclization of II in liquid hydrogen fluoride gave a ketone which did not crystallize but formed a 2,4-dinitrophenylhydrazone, m.p. 259-260°. Treatment of the liquid ketone with methylmagnesium iodide also gave an oil. However, on adding a solution of chloranil in acetone or acetonitrile and a few drops of

perchloric acid to a solution of the oil in acetone a golden yellow precipitate came down which analyzed correctly for the perchlorate of the expected hexamethylphenalene. Reduction of the perchlorate with lithium aluminium hydride in ether gave an oil which was dissolved in pentane. The solution was filtered through neutral alumina and evaporated. The oily residue crystallized at once on adding methyl alcohol to a hard white solid, m.p. 89-90°, even after recrystallization from methyl alcohol. Its NMR spectrum was entirely consistent with structure I as was the result of microanalysis.



I

NMR SPECTRUM OF I

(Solvent: $CDCl_3$)

δ (ppm)		Relative Intensities	Kind of Proton
1.09	doublet	3	(1) CH_3
2.26	singlet	3	(3) CH_3
2.40	singlet	3	(4) or (9) CH_3
2.58	singlet	3	(4) or (9) CH_3
2.84	singlet	6	(6) and (7) CH_3
3.85	multiplet	1	(1) H
6.09	multiplet	1	(2) H
6.95 and 7.03		2	(5) and (8) H

Acknowledgements

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References

1. D.H. Reid, Quart. Rev. Vol. XIX, No. 3, 1965.
2. R. Adams and L.O. Binder, J.Amer.Chem.Soc. 63, 2773 (1941).
3. W.E. Bachmann and R.O. Edgerton, J.Amer.Chem.Soc. 62, 2221 (1940).
4. D.H. Reid and R.G. Sutherland, J.Chem.Soc. 3295 (1963).

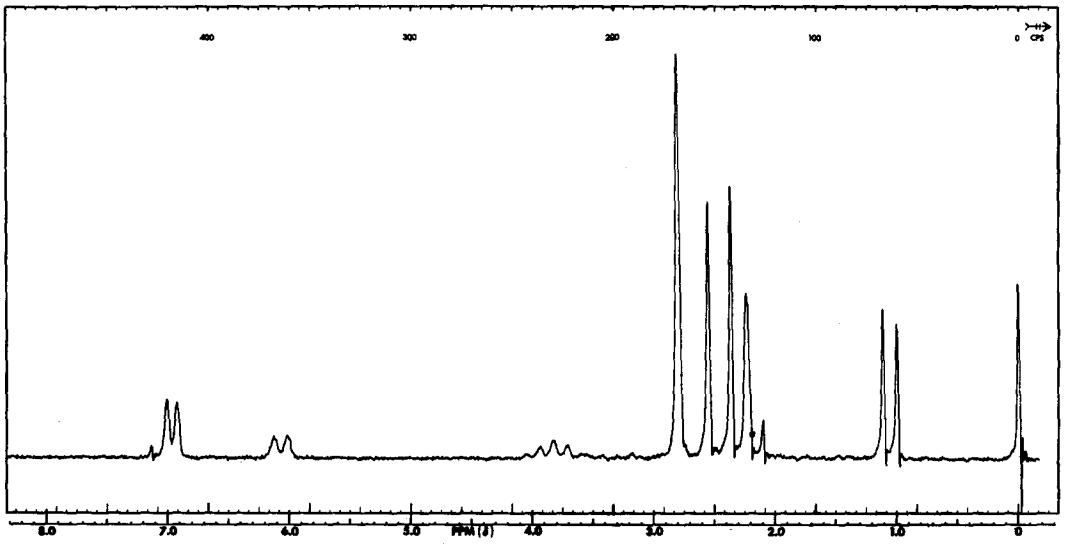

Fig. 1. NMR spectrum of 1,3,4,6,7,9-hexamethylphenalene

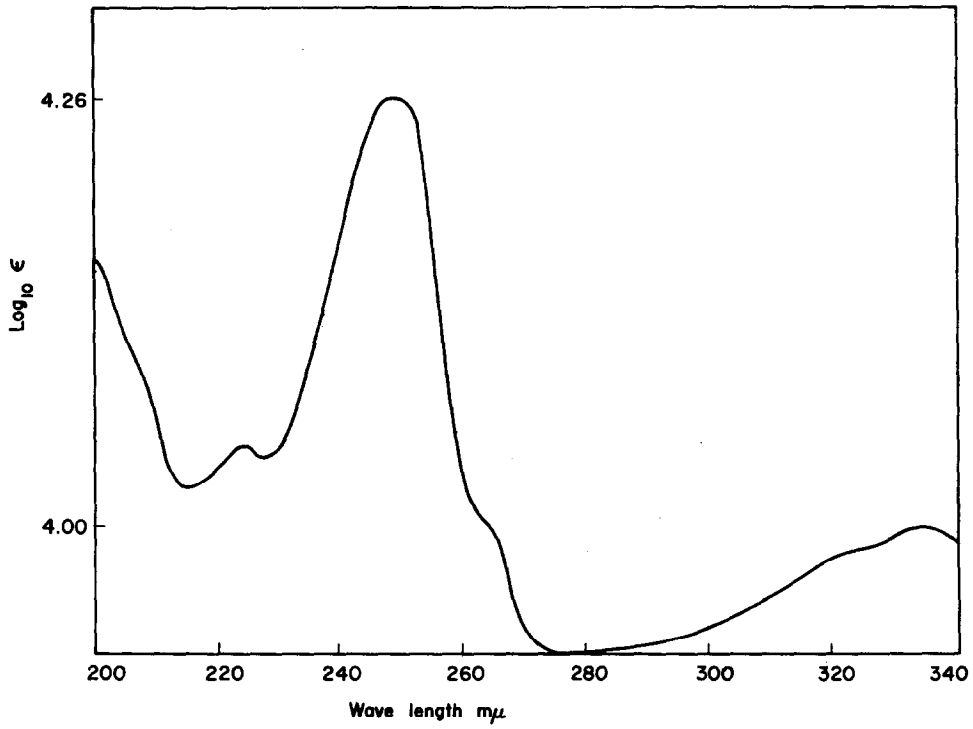

Fig. 2.- Ultraviolet absorption spectrum of 1,3,4,6,7,9-hexamethylphenalene in ethanol, principal maxima and log ε values.