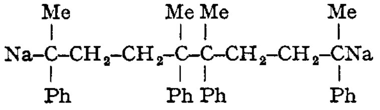
The Structure of α-Methylstyrene Tetramer

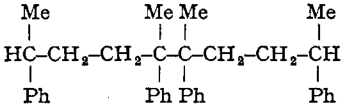
By M. N. BERGER, J. J. K. BOULTON, B. W. BROOKS, and M. J. EVANS
(*"Shell" Research Limited, Carrington, Manchester*)

THE formation of tetrameric dianions by reaction of α-methylstyrene with sodium at 20° has been reported by Szwarc *et al.*[1]

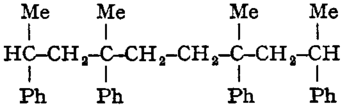
The structure of the tetramer (I) was deduced from thermodynamic considerations.[2] We have prepared a sample of the disodio-tetramer, hydrolysed it with water and examined the hydrolysate by nuclear magnetic resonance spectroscopy.



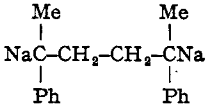
$\mathrm{Na{-}C(Me)(Ph){-}CH_2{-}CH_2{-}C(Me)(Ph){-}C(Me)(Ph){-}CH_2{-}CH_2{-}C(Me)(Ph)Na}$ (I)



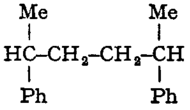
$\mathrm{HC(Me)(Ph){-}CH_2{-}CH_2{-}C(Me)(Ph){-}C(Me)(Ph){-}CH_2{-}CH_2{-}CH(Me)(Ph)}$ (II)



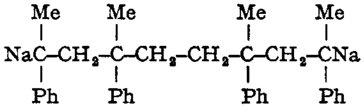
$\mathrm{HC(Me)(Ph){-}CH_2{-}C(Me)(Ph){-}CH_2{-}CH_2{-}C(Me)(Ph){-}CH_2{-}CH(Me)(Ph)}$ (III)



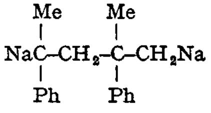
$\mathrm{NaC(Me)(Ph){-}CH_2{-}CH_2{-}C(Me)(Ph)Na}$ (IV)



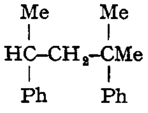
$\mathrm{HC(Me)(Ph){-}CH_2{-}CH_2{-}CH(Me)(Ph)}$ (V)



$\mathrm{NaC(Me)(Ph){-}CH_2{-}C(Me)(Ph){-}CH_2{-}CH_2{-}C(Me)(Ph){-}CH_2{-}C(Me)(Ph)Na}$ (VI)



$\mathrm{NaC(Me)(Ph){-}CH_2{-}C(Me)(Ph){-}CH_2Na}$ (VII)



$\mathrm{HC(Me)(Ph){-}CH_2{-}C(Me)(Ph)Me}$ (VIII)

The tetramer was prepared by the reaction of sodium sand with α-methylstyrene in tetrahydrofuran at 0° for 1 hr. The hydrolysed tetramer was a waxy material of molecular weight 472 (theoretical 474) as determined on a 'Mechrolab' 301 vapour pressure osmometer. High resolution n.m.r. spectra of dilute solutions of the hydrolysed tetramer in carbon tetrachloride were recorded using a Varian 100 Mc/sec. instrument. Table 1 gives the observed proton resonances, together with our assignments.

TABLE 1

Proton type	Proton resonance τ values
Aromatic	3·1
Aliphatic	7·7—9·2
Methine	7·7
Methylene	7·9—*ca.* 9
Methyl	8·5—9·2

Table 2 gives the relevant peak area ratios associated with these resonances.

TABLE 2

Proton ratios	Calculated for hydrolysed (I)	Observed in tetramer
Aromatic : aliphatic	1 : 1·10	1 : 1·10
Methine : (methyl + methylene)	1 : 10	1 : 9·2

The experimentally determined methine : (methyl + methylene) proton ratios accord with the structure (II or III). Szwarc *et al.*[1] report that cleavage of disodio-tetramer with sodium produces a disodio-dimer. Cleavage of compound (I) by sodium will produce a material with the structure (IV) which on hydrolysis will yield a dimer (V). Sodium cleavage of compound (VI) would yield a material of structure (VII) which on hydrolysis would yield a dimer (VIII).

We have therefore prepared a disodio-dimer by prolonged reaction (24 hr.) of sodium with α-methylstyrene and hydrolysed this product with water. N.m.r. spectra of the dimer showed that the proton ratio methine : (methyl + methylene) is 1 : 5·2 (τ values as for tetramer). This accords with the ratio expected from structure (V) (*i.e.*, 1 : 5·0) but not with the ratio expected from structure (VIII) (*i.e.*, 1 : 11).

We therefore conclude, in agreement with Szwarc *et al.*,[1] that only structure (I) is possible for the tetramer.

(*Received, November 7th,* 1966; *Com.* 865.)

---

[1] C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, 1962, **66**, 904.
[2] A. Vrancken, J. Smid, and M. Szwarc, *Trans. Faraday Soc.*, 1962, **58**, 2036.