

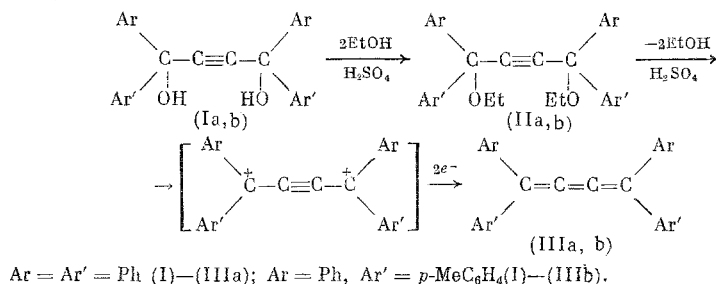
## AN UNUSUAL SYNTHESIS

## OF 1,1,4,4-TETRAARYLBUTATRIENES

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1,1,4,4-Tetraarylbutatrienes are obtained from acetylenic 1,4-diols or their ethers under reduction conditions by the action of  $\text{SnCl}_2$  in hydrochloric or sulfuric acid, hydriodic acid in acetic acid, KI in sulfuric acid and alcohol, and  $\text{PX}_3$  ( $\text{X}=\text{Cl}, \text{I}$ ) in the presence of bases [1]. We are the first to report the formation of cumulenes (IIIa) and (IIIb) by the action of 18% ethanolic  $\text{H}_2\text{SO}_4$  on 1,1,4,4-tetraaryl-2-butyne-1,4-diols (Ia) and (Ib). The electron donor required for reduction of the dicarbocation to the cumulene is presumably  $\text{SO}_2$  formed upon heating ethanol with  $\text{H}_2\text{SO}_4$  [2, 3].



**1,1,4,4-Tetraphenylbutatriene (IIIa).** A sample of 2 g glycol (Ia) was heated with 18% ethanolic  $\text{H}_2\text{SO}_4$  for 10 h at 60–70°C. White crystals of (IIa) began to precipitate after 3–5 min, mp 116–117°C [4]. PMR spectrum in  $\text{CCl}_4$  ( $\delta$ , ppm): 1.17 m (Me), 3.48 q ( $\text{OCH}_2$ ), 7.28 and 7.47 m (Ph). The crystals gradually yellowed upon heating. The crystals were filtered off, washed with aqueous ammonia and ethanol to give 1 g (80%) tetraphenylbutatriene (IIIa), mp 235°C [1]. Found: C, 94.37; H, 5.75%. Calculated for  $\text{C}_{28}\text{H}_{20}$ : C, 94.38; H, 5.61%. PMR spectrum in  $\text{CS}_2$  and  $\text{CDCl}_3$  ( $\delta$ , ppm): 7.32 and 7.51 m (Ph). UV spectrum in  $\text{CHCl}_3$ :  $\lambda_{\text{max}}$  420 nm. Mass spectrum:  $m/z$  357.

**1,4-Diphenyl-1,4-ditolylbutatriene (IIIb)** was obtained analogously in 73% yield, mp 235°C [1]. Found: C, 94.07; H, 6.34%. Calculated for  $\text{C}_{30}\text{H}_{24}$ : C, 93.72; H, 6.30%. PMR spectrum in  $\text{DMSO}-d_6$  ( $\delta$ , ppm): 2.52 s (Me), 7.46 m (Ph). IR spectrum (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1600, 1640, 3030, 3050, 3080 (Ph), 1920 w ( $\text{C}=\text{C}=\text{C}$ ).

## LITERATURE CITED

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