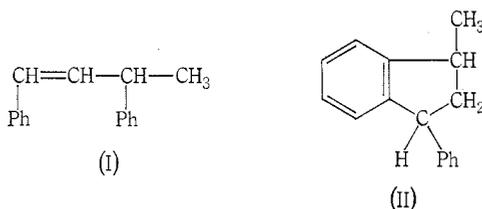


THE PREPARATION OF 1,3-DIPHENYLBUT-1-ENE

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In connection with the study of the polymerization of styrene, initiated by trityl perchlorate, we have been searching for a simple and convenient method for the preparation of 1,3-diphenylbut-1-ene (I). In 1936 Risi and Gauvin¹ showed that styrene dimer, obtained from the reaction of monomeric styrene with aqueous sulphuric acid solution, was a mixture of (I) and 1-methyl-3-phenylindan (II). This was confirmed by Spoerri and Rosen² in 1950 and later by Corson *et al.*³ To our knowledge there is no published work on the preparation of (I) as the only dimer from the dimerization of styrene, although Rosen⁴ pointed out that the overall yield of the unsaturated dimer (I) would be favoured by lower reaction temperature and lower concentration of sulphuric acid solution. We report here the modification of the method of Risi and Gauvin to give (I) with no saturated dimer (II) produced.



The concentration of aqueous sulphuric acid solution was the most critical factor, whereas the reaction temperature and reaction time were comparatively less important. Heating one part (by volume) of styrene with five parts of 50% aqueous sulphuric acid solution at 110–115° for 100 min were the optimum conditions to give the unsaturated dimer in high yield. The absence of saturated dimer was confirmed by bromination and hydrogenation. The n.m.r. spectrum of the dimer showed a doublet at δ 1.41 (3H, J 7 Hz) and multiplets at δ 3.5 (1H), δ 6.26 (2H), and δ 7.14 (10H). The i.r. spectrum of the dimer is identical to that reported for (I);⁵ however, the n.m.r. spectrum was considerably different to those reported by Seyferth and Fogel⁶

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¹ Risi, P. J., and Gauvin, D., *Can. J. Res. (B)*, 1936, **14**, 255.

² Spoerri, P. E., and Rosen, M. J., *J. Am. chem. Soc.*, 1950, **72**, 4918.

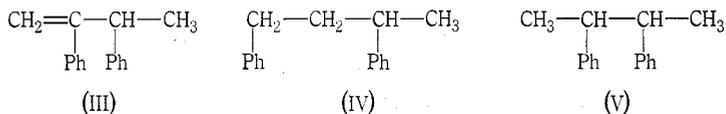
³ Corson, B. B., Dorsky, J., Nickels, J. E., Kutz, W. M., and Thayer, H. I., *J. org. Chem.*, 1954, **19**, 17.

⁴ Rosen, M. J., *J. org. Chem.*, 1953, **18**, 1701.

⁵ Mayo, F. R., *J. Am. chem. Soc.*, 1968, **90**, 1289.

⁶ Seyferth, D., and Fogel, J., *J. organomet. Chem.*, 1966, **6**, 205.

for the *cis* and *trans* isomers of (I). These authors found the 2-vinyl and 1-vinyl protons at δ 5.71 (J 10 Hz) and δ 6.41 (J 11.5 Hz) respectively for the *trans* isomer and at δ 5.7 and δ 6.28 (J 2 Hz) respectively for the *cis* isomer. Of the alternative dimeric products, (III) would be compatible with our observed data. As the vinylic protons appear at almost the same chemical shift, the n.m.r. spectrum cannot distinguish between (I) and (III), and the dimer was hydrogenated to give the dihydro-dimer which may have either structure (IV) or (V) derived from the corresponding structure (I) or (III) respectively.



The n.m.r. spectrum of the hydrogenated product showed a doublet at δ 1.25 (3H, J 7 Hz) and multiplets at δ 1.9 (2H), δ 2.5 (2H), δ 2.7 (1H), and δ 7.08 (10H). This clearly indicates structure (IV) where the signals due to the aliphatic protons may be assigned thus: δ 2.5, δ 1.9, δ 2.7, and δ 1.25 to the 1, 2, 3, and 4 protons respectively where the asymmetric centre at position 3 causes the methylene protons to be non-equivalent. Furthermore, the i.r. spectrum of the hydrogenation product agrees well with the published curve of (IV).⁵ Thus the structure of our dimeric product must be (I) in which the vinylic protons have almost the same chemical shift occurring at δ 6.26, but the discrepancy between this work and the work of Seyferth and Fogel⁶ remains unexplained.

Experimental

The boiling point was uncorrected. The molecular weight was determined with a Mechrolab vapour pressure osmometer 301A. The ultraviolet spectrum (1,2-dichloroethane) was recorded on a Unicam SP800 spectrometer. Infrared spectra (liquid film on NaCl) were taken on a Perkin-Elmer 421 spectrometer; only those bands in the range of 600–1100 cm^{-1} are reported here. Nuclear magnetic resonance spectra were obtained on a Varian HA100 spectrometer, in CCl_4 , with TMS (δ 0.0) as an internal reference. The mass spectrum (10 eV) was obtained on a AEI spectrometer MS9; only those peaks greater than 10% of base peak are reported here. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

1,3-Diphenylbut-1-ene (I)

A typical preparation run is described as follows. Styrene monomer (Monsanto) was washed free from inhibitor with 10% NaOH solution and distilled water, dried (CaCl_2 then BaO), and vacuum-distilled. The middle fraction of the distillate was used for the dimerization reaction. The purified styrene monomer (50 ml) was added to sulphuric acid (250 ml, 50%, May & Baker, A. R.) (a higher yield of (I) was obtained if the H_2SO_4 solution was made with a conductance grade of distilled water) in a flask equipped with a sealed stirrer, a reflux condenser, and a thermometer dipping into the reaction mixture under a nitrogen atmosphere. The reaction mixture was maintained at 110–115° and stirred vigorously for 100 min. The reaction mixture was diluted with distilled water (500 ml) and the oily layer was separated and washed with a saturated solution of NaHCO_3 (2×100 ml) and with distilled water until neutral to litmus. (The acid layer was discarded without attempting to extract the small amount of dimeric product dissolved in it, to avoid possible contamination.) The oily layer was dried (CaCl_2 , 12 hr) and distilled through a 12-in. Vigreux column to give 35 g (70%) of dimer (*cis* and *trans* isomers not resolved), b.p. 138°/1.5 mm; n_D^{20} 1.5900; mol. wt., 210 (Found: C, 92.3; H, 7.9. Calc. for $\text{C}_{16}\text{H}_{16}$: C, 92.3; H, 7.7%).

A quantity (8 g) of higher polymer was recovered (mainly trimer of mol. wt. 330). The dimer was shown to contain 1.1 double bond per molecule as determined by the standard bromination method.⁷ U.v.: λ_{\max} (ϵ) 253 (19700), 285 (1950), 294 nm (1140); i.r.: λ_{\max} 690, 735, 750, 830, 905, 960, 980sh, 995sh, 1005, and 1025 cm^{-1} ; mass spectrum: m/e (relative intensity) 209 (17), 208 (100), 207 (14), 194 (14), 193 (83), 179 (19), 178 (26), 165 (10), 130 (30), 129 (18), 116 (13), 115 (97), 105 (14), 91 (45), 88 (11), 77 (19); n.m.r.: δ 1.41 (d, 3, J 7 Hz, CH_3), δ 3.5 (m, 1, CH), δ 6.26 (m, 2, $\text{CH}=\text{CH}$), δ 7.14 (m, 10, Ph).

1,3-Diphenylbutane (IV)

Compound (I) was hydrogenated in ethanol at room temperature and pressure over Adams catalyst. The solution was filtered and the ethanol removed under reduced pressure. The oil was chromatographed on a column of silica gel, and eluted with benzene to give 1,3-diphenylbutane (IV) as a colourless oil (95% yield) (Found: C, 91.4; H, 8.4. Calc. for $\text{C}_{16}\text{H}_{18}$: C, 91.4; H, 8.6%). I.r.: 695, 750, 836, 905, 960, 995sh, and 1025 cm^{-1} ; n.m.r.: δ 1.25 (d, 3, J 7.0 Hz, CH_3), δ 2.9 (m, 2, C2), δ 2.5 (m, 2, C1 partly overlap with the peaks of methinyl proton), δ 2.7 (m, 1, C3), δ 7.08 (m, 10, Ph).

⁷ Polgar, A., and Jungnickel, J. L., in "Organic Analysis". (Eds. J. Mitchell, I. M. Kolthoff, E. S. Proskauer, and A. Weissberger.) Vol. 3, p. 234. (Interscience: New York 1956.)