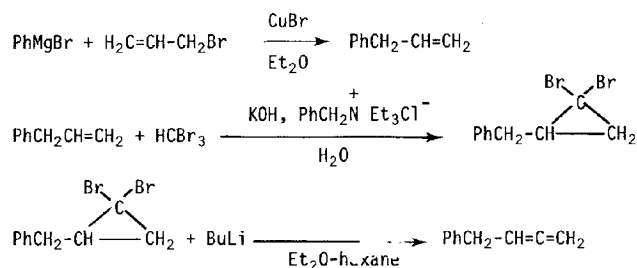


the solvents by evaporation in a water-pump vacuum was distilled through a 25-cm Vigreux column, giving the diyne ether, b.p. 50°C/1 mmHg,  $n_D^{20}$  1.5273, in 87% yield (*cis* to *trans* ratio ca. 1).

*Note 1.* Prepared in 82% yield by refluxing an ethereal solution of  $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{MgBr}^1$  for 8 h with an equivalent amount of  $\text{HC}(\text{OC}_2\text{H}_5)_3$  and subsequently hydrolysing the reaction mixture with aqueous ammonium chloride solution.  $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$  has b.p. 87°C/15 mmHg (*cis* to *trans* ratio ca. 3:2). For the preparation of  $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$  and its Grignard derivative, see Ref. 1.

*Note 2.* In view of the oxygen-sensitivity of the product, all operations during the work-up must be carried out under nitrogen.

(19) 4-Phenyl-1,2-butadiene<sup>51, 52</sup>



a. Preparation of allylbenzene

*Apparatus:* 1-l round-bottomed, three-necked flask, provided with a dropping funnel, combined with a gas inlet, a mechanical stirrer and a reflux condenser.

To a refluxing solution of phenylmagnesium bromide in 650 ml of diethyl ether, prepared from 1.15 mol of bromobenzene (see Chapter II, Exp. 5) was added 1.00 mol of allyl bromide at a rate such that refluxing was maintained (about 30 min). Thirty minutes after refluxing had stopped, a trace of copper(I) bromide was added to terminate the conversion. The reaction mixture was cautiously poured on to 500 g of finely crushed ice, then 200 ml of 4 N hydrochloric acid were added. After the remaining ice had melted the layers were separated and the aqueous layer was extracted three times with diethyl ether. The combined ethereal solutions were washed with saturated NaCl solution and dried over magnesium sulfate. The greater part of

the diethyl ether was distilled off at normal pressure through a 40-cm Vigreux column and distillation of the residue gave allylbenzene, b.p. 44°C/15 mmHg,  $n_D^{21.5}$  1.5102, in 90% yield.

b. Addition of dibromocarbene to allylbenzene<sup>50</sup>

*Apparatus:* 2-l three-necked, round-bottomed flask with a thermometer, a mechanical stirrer and a vent.

To a solution of 250 g of NaOH in 275 ml of water were added at 25°C 0.5 g of triethylbenzyl ammonium chloride, 5 ml of ethanol, 0.50 mol of allylbenzene and 1.00 mol of bromoform and the mixture was vigorously stirred. The temperature rose to about 45°C in 10-15 min and was kept at that level by occasional cooling. Stirring was continued for 10 h after the exothermic reaction had subsided. After addition of 1 l of ice-water the product was extracted with diethyl ether (for the first extraction a sufficient amount has to be used to obtain an upper layer). The combined ethereal solutions were washed with water and dried over magnesium sulfate. After the diethyl ether had been removed by evaporation in a water-pump vacuum, the residue was subjected to a high-vacuum distillation (< 0.5 mmHg), keeping the temperature of the heating bath below 100°C. The residue remaining after the unconverted bromoform had been distilled off (b.p. < 60°C/0.1-0.5 mmHg) weighed 120 g and consisted of reasonably pure adduct.

c. Preparation of 4-phenyl-1,2-butadiene (Apparatus: 1-l flask, see Fig. 1)

The 120 g of residue were dissolved in 350 ml of dry diethyl ether and a solution of 0.35 mol of butyllithium in about 280 ml of hexane was added dropwise during 30 min, while maintaining the temperature at about -60°C. After the addition the temperature was allowed to rise to -25°C and stirring at that temperature was continued for an additional 30 min. The mixture was then poured with swirling into 1 l of ice-water and the upper layer and two extracts of the aqueous layer were combined and dried over magnesium sulfate. The solvents were removed in a water-pump vacuum by means of a rotary evaporator. Distillation of the residue gave the allene, b.p. 75°C/15 mmHg,  $n_D^{21}$  1.5396, in 60% yield (based on allylbenzene).

(20) 1,2-Cyclooctadiene<sup>51, 52</sup>

