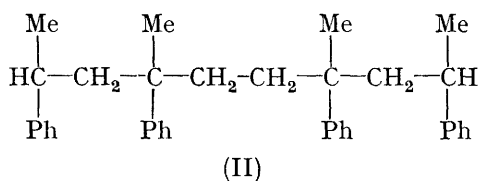
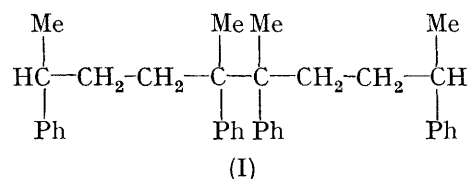


Synthesis of 1,4-Substituted 1,4-diphenylbutanes

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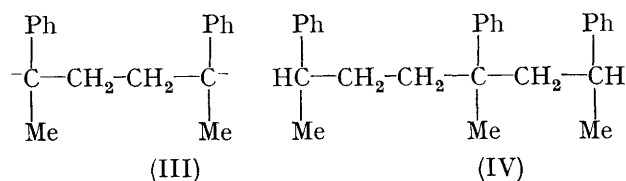
A number of derivatives of 1,4-diphenylbutane have been prepared using a simple one-step process from styrene and α -methylstyrene. The n.m.r. spectra of the products are included.

In the course of an investigation¹ to distinguish by direct synthesis between two postulated structures of α -methylstyrene tetramer,^{2,3} (I) and (II), prepared

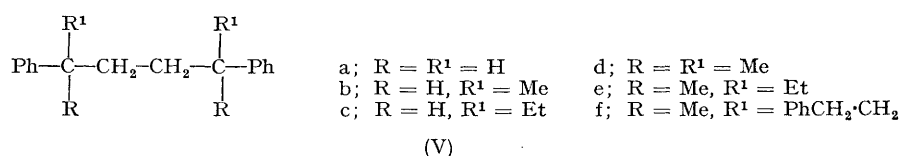


anionically, a modification to a procedure by Weyenberg⁴ was developed. We describe its use as an

Weyenberg prepared 2,5-diphenylhexane by the reaction of α -methylstyrene with lithium, the dimeric dianion (III) so formed being protonated as it is formed. We have carried out a series of similar reactions with styrene and α -methylstyrene but replacing ethanol with various alkyl and aralkyl halides as the terminating agents. Although the dimeric dianion is mainly pro-



tonated in the presence of ethanol smaller amounts of oligomers are formed by anionic addition to monomer before protonation. Thus in the preparation of 2,5-diphenylhexane we found the residue from the distillation



Olefin	Trapping agent for the dianion	Product	B.p. (or m.p.) (°C)	Yield (%)	N.m.r. spectra
Styrene	EtOH	(Va)	134/1.5 mm. (52—53°) ^a	74	τ 2.94 (10H, m, aromatic), τ 7.49 (4H, t, PhCH ₂), τ 8.44 (4H, m, PhCH ₂ CH ₂)
Styrene	MeI	(Vb)	140—142/1.5 mm. ^b	71	τ 2.93 (10H, m, aromatic), <i>ca</i> τ 7.5 (2H, m, PhCH), τ 8.54 (4H, t, PhCHCH ₂), τ 8.90 (6H, d, PhCHCH ₃)
Styrene	EtI	(Vc)	148—150/0.5 mm.	64	τ 2.92 (10H, m, aromatic), <i>ca</i> τ 7.7 (2H, m, PhCH), τ 8.52 (8H, m, PhCHCH ₂), τ 9.35 (6H, t, CH ₂ CH ₃)
α -Methylstyrene	EtOH	(Vb)	140/1.5 mm. ^b	68	
α -Methylstyrene	MeI	(Vd)	146—150/0.5 mm. (60°) ^a	63	τ 2.94 (10H, m, aromatic), τ 8.67 (4H, s, PhCCH ₂), τ 8.87 (12H, s, PhCCH ₃)
α -Methylstyrene	EtI	(Ve)	126/0.1 mm.	63	τ 2.95 (10H, m, aromatic), τ 8.1—8.8 (8H, m, PhCCH ₂), τ 8.85 (6H, s, PhCCH ₃), τ 9.44 (6H, t, CH ₂ CH ₃)
α -Methylstyrene	PhCH ₂ CH ₂ Br	(Vf)		70	τ 2.85, 2.95 (20H, m, aromatic)
α -Methylstyrene	PhMeCHBr	Polymer			τ 7.6—8.7 and 8.78 (18H, m, PhCH ₂ , PhCCH ₂ and PhCCH ₃)

Analyses: (Vc) (Found: C, 90.0; H, 9.9. C₂₀H₂₆ requires C, 90.2; H, 9.8%). (Ve) (Found: C, 89.6; H, 10.2. C₂₂H₃₀ requires C, 89.8; H, 10.2%). (Vf) (Found: C, 91.0; H, 8.6. C₃₄H₃₈ requires C, 91.4; H, 8.6%).

^a C. E. Frank, L. F. Moormeier, J. A. Scheber, and O. Homberg (*J. Org. Chem.*, 1961, **26**, 307) give m.p. 52—53°. ^b Ref. 4 gives b.p. 140°/1.5 mm. ^c This apparent triplet is actually a multiplet arising from a complex spin-spin splitting owing to the compound being a mixture of the *meso* and racemic forms. ^d H. Bredervelt and E. C. Kooyman (*Rec. Trav. chim.*, 1957, **76**, 297) give m.p. 60—61°.

efficient route to the synthesis of 1,4-substituted 1,4-diphenylbutanes.

of the product to consist almost entirely of the trimer (IV) and tetramer, (I) or (II), of α -methylstyrene.

¹ D. H. Richards and N. F. Scilly, *Chem. Comm.*, 1968, No 24.

² A. Vrancken, J. Smid, and M. Szwarc, *Trans. Faraday Soc.*, 1962, **58**, 2036.

³ R. L. Williams and D. H. Richards, *Chem. Comm.*, 1967, 414.

⁴ D. R. Weyenberg, *J. Org. Chem.*, 1965, **30**, 3236.

With one exception, the procedure described has given the expected material, namely the appropriate substituted dimer as the major product. The exception was encountered in the reaction of α -methylstyrene and 1-phenethylbromide with lithium which resulted in the formation of a polymer. The mechanism of this reaction is not clear but it may be significant that it occurred with the only material capable of forming a resonance-stabilized radical.

The compounds prepared are listed in the Table.

Compounds (Va), (Vb), and (Vd) have been identified with previously reported materials and it is reasonable to assume that the previously unreported compounds (Vc), (Ve), and (Vf) possess analogous structures, and this is supported by the ^1H n.m.r. spectra.

EXPERIMENTAL

Tetrahydrofuran was dried, and purified by reflux and distillation from sodium. The alkyl halides were dried (molecular sieve) and purified by distillation, and all experiments were carried out under nitrogen. The 60 MHz ^1H n.m.r. spectra were measured in carbon disulphide solution with tetramethylsilane as internal standard using a Perkin-Elmer R 10 spectrometer.

The two following examples described are typical experiments. Light petroleum, had b.p. 60–80°.

2,5-Diphenylhexane.—A mixture of ethanol (9.1 g.) and

α -methylstyrene (23.6 g.) was added to a stirred suspension of lithium (2.8 g.) in tetrahydrofuran (100 ml.) during 15 min., at 25–35°. After 4 hr. at this temperature the mixture was filtered and the solvent evaporated. The residue was shaken with water, extracted with light petroleum and dried (sodium sulphate). Evaporation of the solvent and distillation gave 2,5-diphenylhexane (16.2 g.), b.p. 140°/1.5 mm. and a residue (4.2 g.).

The residue was separated by preparative t.l.c. on Kieselgel G using light petroleum as the developing agent. The two major components obtained were shown, by comparison of their n.m.r. spectra with those from authentic material, to be the trimer and tetramer of α -methylstyrene.³

3,6-Dimethyl 1,3,6,8-tetraphenyloctane.—A mixture of α -methylstyrene (23.6 g.) and 2-phenethylbromide (37 g.) was added to lithium (2.8 g.) in tetrahydrofuran (100 ml.). After 4 hr. at 24–35° the solution was filtered, the filtrate evaporated to remove solvent, and the residue shaken with water, extracted with ether, and dried (sodium sulphate). The solvent was evaporated leaving a pale straw-coloured viscous oil (37.0 g.). This oil (1.0 g.) was separated into one major (0.82 g., 3,6-dimethyl 1,3,6,8-tetraphenyloctane), and two minor components by t.l.c. on Kieselgel G with light petroleum.

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