

Synthesis of Dialkyl Adducts of Activated Olefins and Dienes

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A number of dialkyl adducts (phenylalkanes and olefins) of vinyl monomers and dienes have been prepared from the reactions of monomers with lithium and alkyl bromides in tetrahydrofuran. The n.m.r. spectra of the products are reported.

DIMERIC dianions, produced from activated olefins such as styrenes and dienes by reaction with alkali metals in tetrahydrofuran (THF), can be terminated *in situ* by alkylene dihalides or alkyl halides to give regular copolymers of structure (M-M-R)_n¹ or dialkyl-substituted dimers of structure R-M-M-R,^{2,3} respectively (M = monomer and R = ligand of the alkyl

higher oligomers is produced. More important, the use of excess of alkyl halide results in the formation of appreciable amounts of dialkyl-terminated monomeric products of structure R-M-R. We have explored the utility of this reaction in the synthesis of olefins and phenylalkanes.

The structural formula of the dialkyl-terminated

TABLE I
Product yields obtained at a 4 : 1 halide-monomer molar ratio

Monomer	Halide	Product	B.p. (°C)	Yield (% based on monomer)
Styrene	EtBr	EtCHPhPr ^a	217	86
	Pr ⁿ Br	Pr ⁿ CHPhBu ⁿ	126 (50 mmHg)	79
	Pr ⁿ Br *†	Pr ⁿ CHPhBu ⁿ	126 (50 mmHg)	12.3
	Pr ⁿ Cl *†	Pr ⁿ CHPhBu ⁿ	126 (50 mmHg)	50
	Pr ⁱ Br	Pr ⁱ CHPhBu ⁱ	85 (30 mmHg)	88
α-Methylstyrene	MeI	Me ₂ CPhEt	189	25
	EtBr	EtMeCPhPr ^a	220	40
	Bu ⁿ Br	Bu ⁿ MeCPhC ₅ H ₁₁	140 (50 mmHg)	24
	Bu ⁿ Cl *†	Bu ⁿ MeCPhC ₅ H ₁₁	140 (50 mmHg)	19
β-Methylstyrene	Bu ⁿ Br	Bu ⁿ CHPhCHMeBu ⁿ	103 (30 mmHg)	27
	Pr ⁿ Br	Bu ⁿ Pr ⁿ CH·CH=CH ₂	93—94 (120 mmHg)	26
Butadiene		Bu ⁿ CH=CHBu ⁿ	103 (120 mmHg)	39

* Sodium used instead of lithium. † 2 : 1 Halide-monomer ratio.

halide or alkylene dihalide). Recent work^{4,5} with α-methylstyrene has shown that these dimerically derived products are obtained in greater than 90% yield if strict adherence to the stoichiometric requirements is observed. If, however, the monomer-mono-halide molar ratio is changed appreciably from unity, large changes in the nature and the yield of products are obtained. Thus, when excess of monomer is used a significant proportion of alkyl-terminated trimers and

monomeric product requires that for its formation two molecules of alkyl halide are consumed for every molecule of monomer. However, since this reaction is in competition with several other processes, notably the formation of hydrocarbons *via* a Wurtz reaction between the alkyl halide and alkali metal and also the 'normal' reaction to produce terminated dimers, a series of

³ M. G. Pemberton, D. H. Richards, and N. F. Scilly, *European Polymer J.*, 1970, **6**, 1083.

⁴ A. Davis, D. H. Richards, and N. F. Scilly, *Makromol. Chem.*, in the press.

⁵ A. Davis, D. H. Richards, and N. F. Scilly, *Makromol. Chem.*, in the press.

¹ D. H. Richards, N. F. Scilly, and F. W. Williams, *Polymer*, 1969, **10**, 603.

² D. H. Richards and N. F. Scilly, *J. Chem. Soc. (C)*, 1969, 2661.

experiments was carried out with typical monomers in which the halide-monomer ratio was systematically increased in an attempt to determine an optimum ratio. The synthetic utility of the process was also explored by using a variety of monomers and alkyl halides. These are illustrated in Table 1; Table 2

TABLE 2
Effect of halide-monomer ratio on yield of product

Monomer	Halide	Halide-monomer molar ratio	Yield (%) based on monomer
Styrene	Pr ⁿ Br	2	57
		4	79
		6	84
α -Methylstyrene	Bu ⁿ Br	2	20
		4	24
		6	24
Butadiene	Pr ⁿ Br	2	57
		4	65
		6	65

TABLE 3

Compound	N.m.r. spectra
EtCPhPhPr ⁿ	τ 2.87 (5H, m, aromatic), 7.7—7.9 (1H, m, PhCH), 8.1—9.0 (6H, m, PhCH·CH ₂ and PhCH·CH ₂ ·CH ₂), 9.16 (3H, t, CH ₂ ·CH ₂ ·CHPh), 9.24 (3H, t, CH ₃ ·CH ₂ ·CH ₂ ·CHPh)
Pr ⁿ CHPhBu ⁿ	τ 2.90 (5H, m, aromatic), 7.3—7.8 (1H, m, PhCH), 8.2—9.0 (10H, m, PhCH·CH ₂ etc.), 9.16 (6H, t, CH ₃ ·CH ₂ ·CH ₂)
Pr ⁿ CHPhBu ^t	τ 2.92 (5H, m, aromatic), 7.5—7.9 (1H, m, PhCH), 8.1—8.9 (4H, m, PhCH·CH, PhCH·CH ₂ , and PhCH·CH ₂ ·CH), 9.16 (6H, d, PhCH·CH·CH ₃), 9.24 (6H, d, PhCH·CH ₂ ·CH·CH ₃)
Me ₂ CPhEt	τ 2.90 (5H, m, aromatic), 8.37 (2H, q, PhC·CH ₂), 8.73 (6H, s, PhC·CH ₃), 9.33 (3H, t, PhC·CH ₂ ·CH ₃)
EtMeCPhPr ⁿ	τ 2.90 (5H, m, aromatic), 8.05—8.65 (4H, m, PhC·CH ₂), 8.65—9.05 (5H, m, PhC·CH ₂ ·CH ₃ and PhC·CH ₃), 9.16 (3H, t, PhC·CH ₂ ·CH ₃), 9.35 (3H, t, PhC·CH ₂ ·CH ₂ ·CH ₃)
Bu ⁿ CHPhCHMcBu ⁿ	τ 2.90 (5H, m, aromatic), 7.4—7.9 (1H, m, PhCH), 8.1—8.55 (5H, m, PhC·CH and PhC·CH ₂), 8.55—9.0 (8H, m, PhC·CH ₂ ·CH ₂ , etc.), 9.0—9.35 (9H, m, CH ₂ ·CH ₂ ·CH ₃)
Bu ⁿ MeCPhC ₅ H ₁₁	τ 2.86 (5H, m, aromatic), 8.2—8.6 (4H, m, PhC·CH ₂), 8.6—9.0 (10H, m, PhC·CH ₂ ·CH ₂ and PhC·CH ₂ ·CH ₂ ·CH ₂ etc.), 8.75 (3H, s, PhC·CH ₃), 9.20 (6H, t, CH ₂ ·CH ₂ ·CH ₃)
Bu ⁿ Pr ⁿ CH·CH=CH ₂	τ 4.65—4.80 (1H, m, CH=CH ₂), 5.10 (2H, d, CH=CH ₂), 7.9—8.4 (1H, m, CH·CH=), 8.6—9.0 (10H, m, 5 × CH ₂), 9.13 (6H, t, 2 × CH ₃)
Bu ⁿ CH=CHBu ⁿ	τ 4.6—4.8 (2H, m, CH=), 7.8—8.25 (4H, m, CH ₂ ·CH=), 8.5—8.9 (8H, m, =CH·CH ₂ ·CH ₂ and =CH·CH ₂ ·CH ₂ ·CH ₂), 9.10 (6H, t, 2 × CH ₃)

indicates the effect of the degree of excess of halide on the percentage conversion into the required product. These products were identified by their ¹H n.m.r. spectra (Table 3).

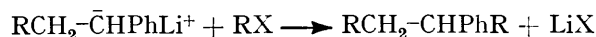
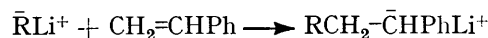
Satisfactory yields of product were obtained at a

⁶ K. Ziegler, E. Eimers, W. Heckelhammer, and H. Wilms, *Annalen*, 1950, **567**, 43.

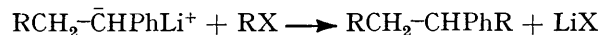
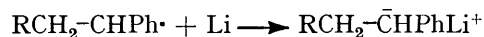
halide-monomer molar ratio of 4:1, *i.e.* a twofold excess of halide. Bromides and chlorides apparently undergo this reaction with about equal facility. Although in all but one of the examples given lithium was used, this may be replaced by sodium, generally at the expense of lower yields.

Surprisingly, the yield of products obtained with α -methylstyrene or butadiene appears to be relatively unaffected by the degree of excess of alkyl halide used, whereas with styrene a significant increase with increasing excess of alkyl halide was observed. Two products were obtained when butadiene was used because the butadiene monoalkyl intermediate can add the second alkyl ligand at either the 2- or the 4-position.

Ziegler *et al.*⁶ have described the reaction of alkyl-lithium with monomers such as styrene or butadiene and alkyl halides to give dialkyl monomer adducts of the structures reported here. This method, requiring the initial preparation of alkyl-lithium, is, however, a two-stage process, and consequently lacks the ease and simplicity of the one herein described. It does suggest that the mechanism involves an initial reaction of the alkyl halide with lithium to form the alkyl-lithium followed by addition of the alkyl-lithium to the monomer before termination with a second alkyl halide molecule, *i.e.* with styrene:



There is, however, an alternative mechanism where the initial reaction is that of monomer with the metal to form a radical anion which then reacts as shown for styrene:



The formation of monomer radical anions has been established as occurring in the initiation step of anionic 'living' polymerisations⁷ where powerful cation-solvating solvents such as THF are used. The two mechanisms may be distinguished by examining the structure of the dimer diadducts also formed in this process. The formation of 1,4-substituted 1,4-diphenylbutanes from styrene would require the formation of monomer radical anions and their subsequent tail-to-tail dimerisation, followed by reaction of these dimer dianions with alkyl halide. Alternatively, the presence of 1,4-substituted 1,3-diphenylbutanes would indicate that the mechanism proceeds *via* initial formation of alkyl-lithium and its head-to-tail addition of two monomer units before termination. This problem has been studied in some detail^{4,5} and it has been shown that

⁷ M. Szwarc, 'Carbanions, Living Polymers, and Electron Transfer Processes,' Interscience, New York, 1968, p. 367.

whilst both mechanisms are operating concurrently, the predominating reaction pathway at these high alkyl halide-monomer ratios is *via* initial alkyl-lithium formation.

Although variation of reaction parameters such as temperature concentration, alkali metal surface area, *etc.* has not yet been studied, it can be seen that the method offers a simple one-stage route for preparing novel linear alkanes and alkenes.

EXPERIMENTAL

All reactions were carried out under nitrogen. THF was purified by double distillation from sodium wire. All monomers and alkyl halides were dried and fractionally distilled immediately before use. The lithium metal used was prepared by cutting standard lithium rods into slices about 3–4 mm thick; sodium was used as a wire.

¹H N.m.r. spectra were obtained with a Perkin-Elmer R10 spectrometer for solutions in carbon disulphide with tetramethylsilane as internal standard. The yields recorded in the Tables were obtained by g.l.c. (internal standard).

The experimental details of two typical reactions are given.

4-Phenyloctane.—A mixture of styrene (20.8 g) and n-propyl bromide (98.4 g) was added to a stirred suspension of lithium (5.6 g) in THF (300 ml) at 25–30 °C, and the reaction was allowed to proceed for 3 h. The mixture was filtered to remove excess of lithium, the solvent was removed on a rotary evaporator, and the residue was shaken with water and extracted with ether. The extract was dried (MgSO₄) and evaporated and the residue was distilled to yield 4-phenyloctane, b.p. 126° at 50 mmHg.

3-Propylhept-1-ene and Dec-5-ene.—Butadiene (10.8 g) was distilled into a stirred suspension of lithium (5.6 g) in THF (300 ml) maintained at –15 °C, propyl bromide (98.4 g) was added immediately, and the reaction temperature was maintained at –15 °C for 3 h. The mixture was worked up as in the previous example, and fractionated (1 m spinning-band column) to give 3-n-propylhept-1-ene, b.p. 93–94° at 120 mmHg and dec-5-ene, b.p. 103° at 120 mmHg.

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