

Vinyl Carbanions. Part 3. The Reaction of $\beta\beta$ -Diphenylacrylonitrile Derivatives with Butyl-lithium

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$\beta\beta$ -Diphenylacrylonitrile (I) reacts with butyl-lithium in THF at -78° to give the derived vinyl carbanion $\text{Ph}_2\text{C}=\bar{\text{C}}-\text{CN}$ (Ia) in a rapidly established equilibrium. A competing nucleophilic addition of a butyl carbanion at the less hindered α -position, afforded the substituted olefins $\text{Ph}_2\text{C}=\text{CHBu}$ and $\text{Ph}_2\text{C}=\text{C}(\text{Bu})\text{CN}$, by elimination of either CN^- or H^- , respectively, from the intermediate carbanion. An addition product of butyl-lithium to (I) was not formed. Reactions of butyl-lithium with *trans*- α -cyanostilbene and with triphenylacrylonitrile were also carried out in THF at -78° in order to study the effect of structural variations on the site of the nucleophilic attack and on the type of products obtained.

ANIONS may react with activated olefins having an α -vinyl hydrogen both as nucleophiles (Michael addition)¹ and as bases leading to formation of the derived vinyl carbanions.²⁻⁸ These two simultaneous reactions were studied kinetically for the first time with the *trans*-cinnamionitrile-ethoxide-ethyl [²H]alcohol system.⁹ $\beta\beta$ -Disubstituted acrylonitrile derivatives, however, do not undergo nucleophilic addition at C_β due to steric hindrance. This was evident from kinetic studies of H-D exchange of 2,2,4,6,6-pentamethylcyclohexylideneacetonitrile,² of fluoren-9-ylideneacetonitrile,¹⁰ and of the

RESULTS AND DISCUSSION

(a) *Reaction of BuLi with $\beta\beta$ -Diphenylacrylonitrile (I).*—All reactions were carried out under dry conditions and under nitrogen, at -78° , THF being used as a solvent. The addition of (I) to the cooled solution of BuLi was characterized by subsequent formation of a deep red-brown colour, attributed to the presence of the derived vinyl carbanion $\text{Ph}_2\text{C}=\bar{\text{C}}-\text{CN}$ (Ia). The main products were 1,1-diphenylhex-1-ene (II), 2-cyano-1,1-diphenylhex-1-ene (III), and 3,3-diphenylpropionitrile (IV). The results are summarized in the Table. Increasing the

Reaction of $\beta\beta$ -diphenylacrylonitrile^a with BuLi in THF

[(I)] : [BuLi]	Yield (%) ^b				
	$\text{Ph}_2\text{C}=\text{C}\begin{matrix} \text{CN} \\ \text{H} \end{matrix}$ (I)	$\text{Ph}_2\text{C}=\text{C}\begin{matrix} \text{Bu} \\ \text{H} \end{matrix}$ (II)	$\text{Ph}_2\text{C}=\text{C}\begin{matrix} \text{Bu} \\ \text{CN} \end{matrix}$ (III)	$\text{Ph}_2\text{CHCH}_2\text{CN}$ (IV)	Unidentified products
2 : 1 ^c	35	15			
1 : 1	55	15	15	10	5
1 : 3	27	16	29	22	6
1 : 8	1	15	55	20	9

^a 0.1M. ^b Percent of products in the crude mixture of products. The values are averages of several experiments carried out with each ratio of [(I)] : [BuLi]. ^c Additional products isolated were the dimers 2,3-dicyano-1,1,4,4-tetraphenylbut-1-ene and 2-cyano-1,1,4,4-tetraphenylbuta-1,3-diene.¹²

cis-trans isomerization of 3-(2-bromophenyl)-3-phenylacrylonitrile.¹¹ $\beta\beta$ -Diphenylacrylonitrile (I) is therefore a good model substrate for studying the formation of vinyl carbanions by its reaction with strong bases. Vinyl carbanions derived from this olefin by treating it in THF with BuLi, were applied *in situ* as nucleophiles in various substitution and addition reactions.¹² By-products were obtained, in which the electrophilic reactant was absent.¹² The present work deals with the chemical behaviour of the BuLi-THF-(I) system in the absence of any added electrophilic reactant. The results obtained provide new information and understanding of the chemical pathways and mechanisms of base-catalysed reactions involving activated olefins, such as the Michael addition reactions, anionic polymerizations of vinyl monomers, *etc.*

concentration of BuLi in the region of [(I)] : [BuLi] = 2 : 1—1 : 8, resulted in an increase of the overall conversion of (I) and of the yield of the olefin (III). The yield of (II) remained constant (*ca.* 15%), while that of (IV) reached a limiting value (of *ca.* 20%).

BuLi may react with (I) either as a base or as a nucleophile, leading to the formation of the corresponding carbanionic intermediates. Addition products resulting from (Ic) were not obtained at all. Similar addition (at C_β) intermediates are already very unstable even if one phenyl group is attached to C_β . It was found for the addition of EtO^- to *trans*-cinnamionitrile in EtOH,⁹ that $k_{-1} \gg k_1(k_{-1}/k_1 \text{ ca. } 10^8)$, where k_1 and k_{-1} were the rate constants for the forward and reverse reactions, respectively. We suggest therefore that olefins (II) and (III) are derived from the intermediate (Ib) by elimination of either CN^- or H^- , respectively

¹ S. Patai and Z. Rappoport, 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 469.

² B. A. Feit and A. Zilkha, *J. Appl. Polymer Sci.*, 1963, **7**, 287.

³ H. M. Walborsky and L. M. Turner, *J. Amer. Chem. Soc.*, 1972, **94**, 2273.

⁴ J. F. Arnett and H. M. Walborsky, *J. Org. Chem.*, 1972, **37**, 3678.

⁵ W. M. Jones and C. D. Broaddus, *J. Org. Chem.*, 1961, **26**, 2316.

⁶ B. A. Feit, *Eur. Polymer J.*, 1967, **3**, 523.

⁷ J. Shabtai and H. Pines, *J. Org. Chem.*, 1965, **30**, 3854.

⁸ G. Maccagnani and F. Taddei, *Bolletino*, 1968, **26**, 71.

⁹ B. A. Feit, R. Pazhenchevsky, and B. Pazhenchevsky, *J. Org. Chem.*, 1976, **41**, 3246.

¹⁰ B. A. Feit, L. Bohor, and S. Rubinraut, *J.C.S. Perkin II*, 1976, 253.

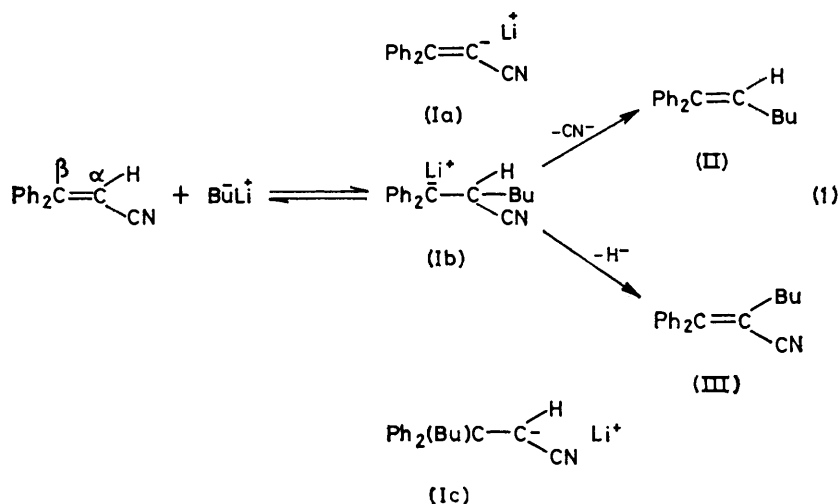
¹¹ G. Djamal and B. A. Feit, unpublished results.

¹² U. Melamed and B. A. Feit, unpublished results.

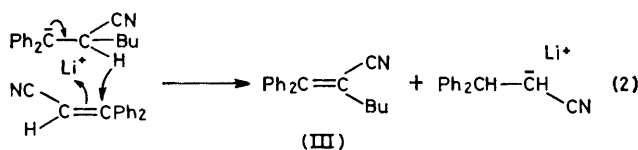
[equation (1)]. Similar vinylic nucleophilic substitutions at C_α by an addition-elimination mechanism have been observed.¹³⁻¹⁶

(II) and its saturated derivative (IV) are formed simultaneously [reaction (2)].

The fact that the yields of (III) were higher than those



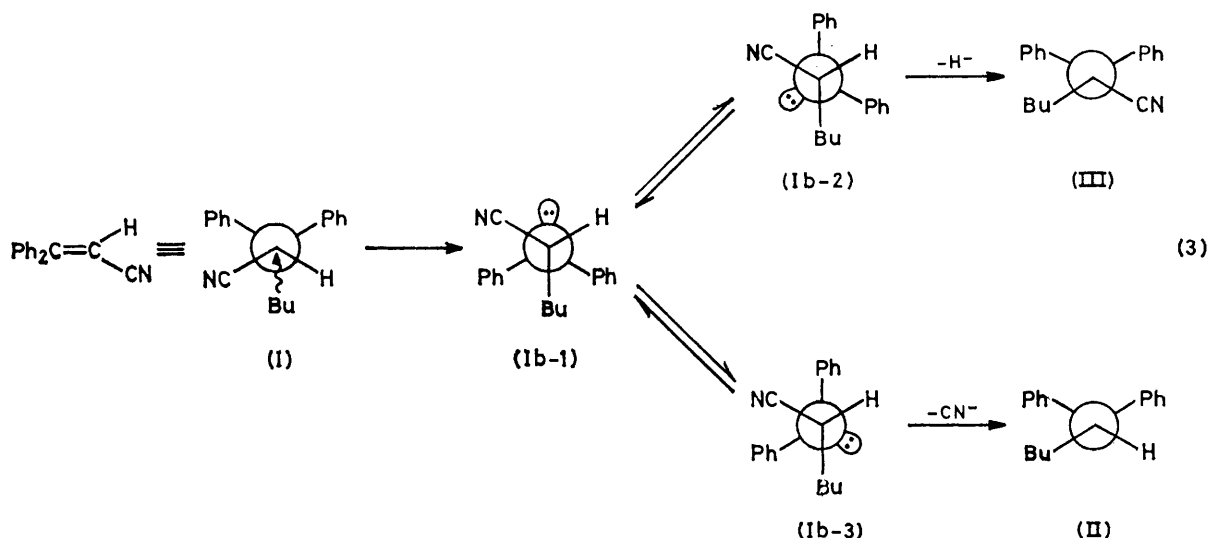
While CN^- is a common leaving group, β -elimination of H^- from sp^3 -type carbanions to form an olefinic



double bond is an unfavourable reaction. Formation of a terminal double bond in anionically polymerized 'living' polystyrene is one other case of such an elimination.¹⁷ We suggest that the H^- elimination from (Ib)

of (IV) (Table) can be explained by the possible existence of other H^- consuming reactions, such as proton abstraction from (I). The possibility that the carbanions derived from the solvent (THF) might act as H^- donors was rejected, since addition of 2,3-dihydrofuran to the mixture at -78° did not result in any increase of the yield of (III). Recent results on H^- elimination (in the presence of H^- acceptors) from carbanionic intermediates of nucleophilic addition reactions to olefins^{18,19} support the mechanism proposed [reaction (2)] for the formation of (III) and (IV).

The unexpected elimination of a hydride ion from



takes place in a multicentre-type reaction in which the electrophilic olefin (I) acts as an H^- acceptor. Olefin

the carbanion (Ib) may be rationalized by considering the stereochemical aspects of the elimination pathways for this carbanion [reaction (3)]. The conformational

¹³ G. Köbrich, *Angew. Chem. Internat. Edn.*, 1967, **6**, 41.

¹⁴ G. Köbrich, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1973.

¹⁵ E. F. Silversmith and D. Smith, *J. Org. Chem.*, 1958, **23**, 427.

¹⁶ G. Modena, *Accounts Chem. Res.*, 1971, **4**, 73.

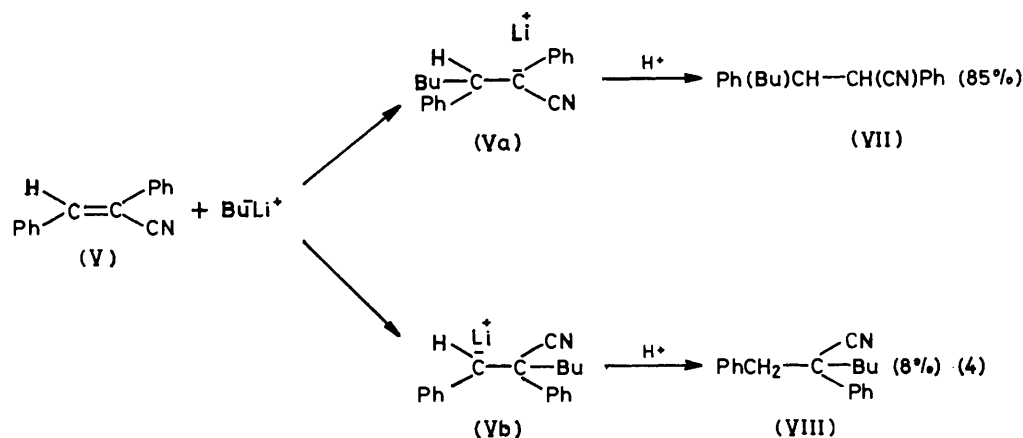
¹⁷ M. Szwarc in 'Carbanions, Living Polymers and Electron Transfer Processes,' International, New York, 1968, p. 646.

¹⁸ M. T. Reetz and D. Schinzer, *Angew. Chem. Internat. Edn.*, 1977, **16**, 44.

¹⁹ M. T. Reetz and W. Stephan, *Angew. Chem. Internat. Edn.*, 1977, **16**, 44.

equilibrium mixture is relatively highly populated with the more stable conformer (Ib-2), resulting in the elimination of H⁻ to yield (III) along with the elimination of CN⁻ to yield (II).

(b) *Reactions of BuLi with trans- α -Cyanostilbene (V) and with Triphenylacrylonitrile (VI).*—The reactions of BuLi with these two olefins, which do not have an α -vinyl hydrogen, were compared with that of $\beta\beta$ -diphenylacrylonitrile with respect to the site of the nucleophilic attack and the products formed. The reactions were carried out in THF at -78° , the ratio of reactants [olefin]:[BuLi] being 1:3. In the case of olefin (V) addition occurred both at C _{α} and C _{β} , with a preference for the less hindered C _{β} position [reaction (4)]. Eliminations of H⁻ from (Va) and of CN⁻ from (Vb) to yield the olefins BuC(Ph)=C(Ph)CN and PhCH=C(Ph)Bu, respectively, did not occur. This fact can be explained by considering the stereochemistry of the reaction in the case of a nucleophilic attack at either C _{β} [equation (5)] or C _{α} [equation (6)]. Conformer (Va-1) is relatively



stable, while conformers (Va-2) and (Va-3) are unstable due to phenyl-phenyl interactions. It might therefore be that the low population of conformer (Va-2) combined with the low leaving ability of H⁻ prevent the formation of the corresponding olefin. Similar considerations applied to the conformational equilibrium of carbanions (Vb) explain why an olefin is not formed by elimination of CN⁻.

The addition of BuLi to triphenylacrylonitrile occurred only at C _{α} , yielding the corresponding addition product and the CN⁻ elimination product [reaction (7)].

EXPERIMENTAL

Materials.— $\beta\beta$ -Diphenylacrylonitrile (I) was prepared by condensation of benzophenone and acetonitrile in the presence of sodamide,²⁰ followed by dehydration with formic acid. *trans- α -Cyanostilbene*²¹ (V) and triphenylacrylonitrile²² (VI) were prepared according to known methods. 1,1-Diphenylhex-1-ene (II) was prepared²³ by treating phenylmagnesium bromide with ethyl caproate, followed by dehydration of the alcohol obtained. The liquid olefin was purified by chromatography on a neutral alumina column.

²⁰ C. Runti and L. Sindellari, *Boll. Chem. Farm.*, 1960, **99**, 499.

²¹ *Org. Synth.*, 1962, Coll. Vol. III, 715.

A solution of butyl-lithium in hexane (Merck) was used. Its concentration was determined by titration. Tetrahydrofuran (analytical grade; Merck) was dried over sodium naphthalene and fractionally distilled under nitrogen into flasks fitted with self-sealing rubber caps. Aliquot portions were removed from these flasks with syringes by applying a nitrogen pressure.

Reaction of $\beta\beta$ -Diphenylacrylonitrile with BuLi.—The reaction was carried out under nitrogen in a three-necked flask equipped with a magnetic stirrer and a dropping funnel. The flask and the dropping funnel were fitted with self-sealing rubber caps through which liquids were introduced by syringes. The system was dried, evacuated, and flushed with dry nitrogen prior to the introduction of solvent and solutions of reactants. Tetrahydrofuran (38 ml) was introduced into the flask, and the flask cooled to -78° . A solution of BuLi (0.005 mol) in hexane (2.3 ml) was then introduced into the flask during 5 min, followed by a solution of $\beta\beta$ -diphenylacrylonitrile (1.02 g, 0.005 mol) in THF (10 ml). The dark red-brown mixture formed was stirred for 15 min and then poured into a dilute hydrochloric acid solution (0.01N). The mixture was extracted with

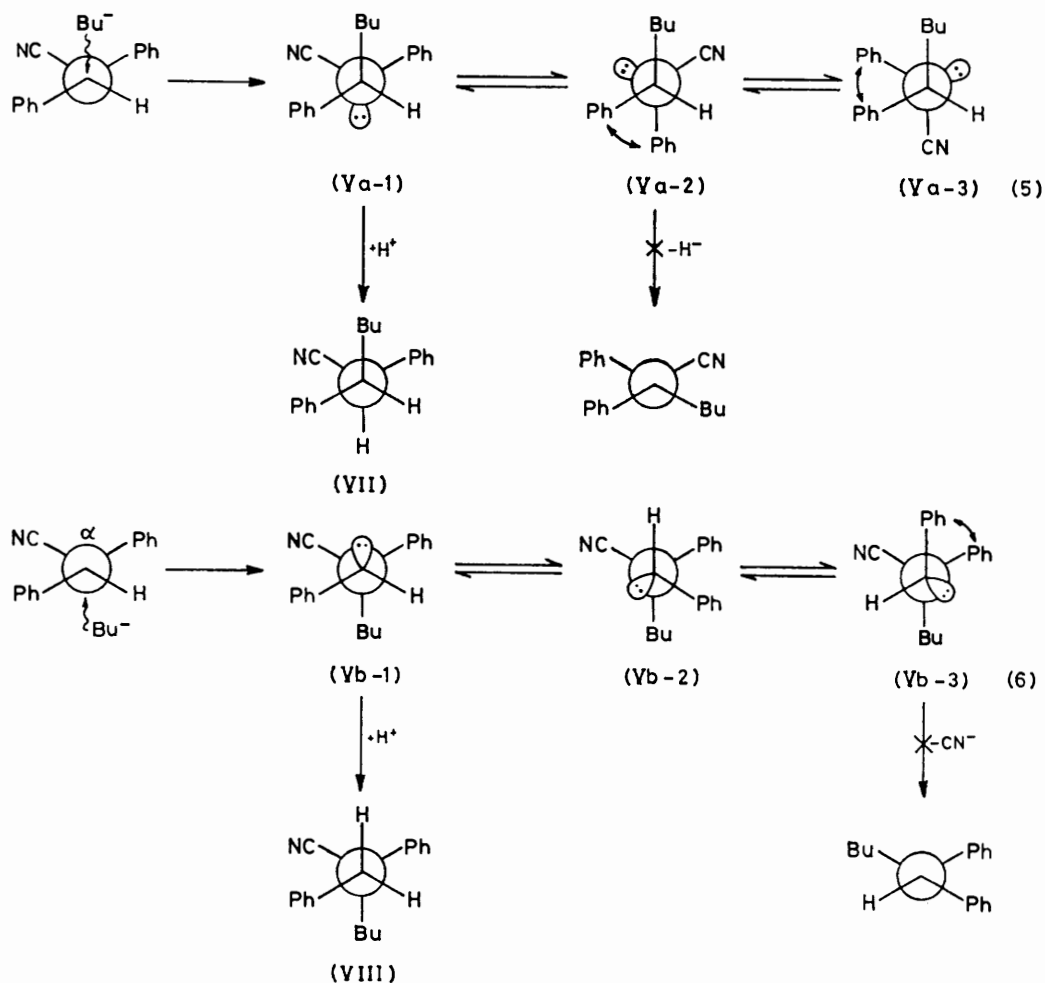
ether. The crude liquid residue recovered from the ether extracts was chromatographed on a neutral alumina column with chloroform-light petroleum as eluant to give (a) 1,1-diphenylhex-1-ene (II) (0.170 g, 15%); $\tau(\text{CDCl}_3)$ 9.20 (3 H, t, J 4 Hz), 8.90–8.30 (4 H, m), 8.15–7.70 (2 H, m), 4.00 (1 H, t, J 4 Hz), and 3.00–2.50 (10 H, m), identical with an authentic sample;²³ (b) 2-cyano-1,1-diphenylhex-1-ene (III) (0.190 g, 15%); $\tau(\text{CDCl}_3)$ 9.50–9.00 (3 H, t, J 4 Hz), 9.00–8.00 (4 H, m), 7.90–7.50 (2 H, t, J 4 Hz), and 3.10–2.50 (10 H, m); m/e 261 (M^+); and (c) 3,3-diphenylpropionitrile (IV) (0.105 g, 10%). The ¹H n.m.r. spectrum was in agreement with the assigned structure. An authentic compound was prepared as follows. A solution of $\beta\beta$ -diphenylacrylonitrile (1.02 g, 0.005 mol) in absolute ethyl alcohol (50 ml) was hydrogenated at a hydrogen pressure of 50 lb in⁻² for 24 h over a Pd-C (0.150 g) catalyst. The crude product recovered from the alcohol was chromatographed on a neutral alumina column using chloroform-light petroleum (1:4) as eluant, to yield 3,3-diphenylpropionitrile (0.400 g, 40%). (d) Unidentified products (0.050 g, 5%) were also obtained.

The same procedure was applied in the case of all other

²² *Org. Synth.*, 1963, Coll. Vol. IV, 387.

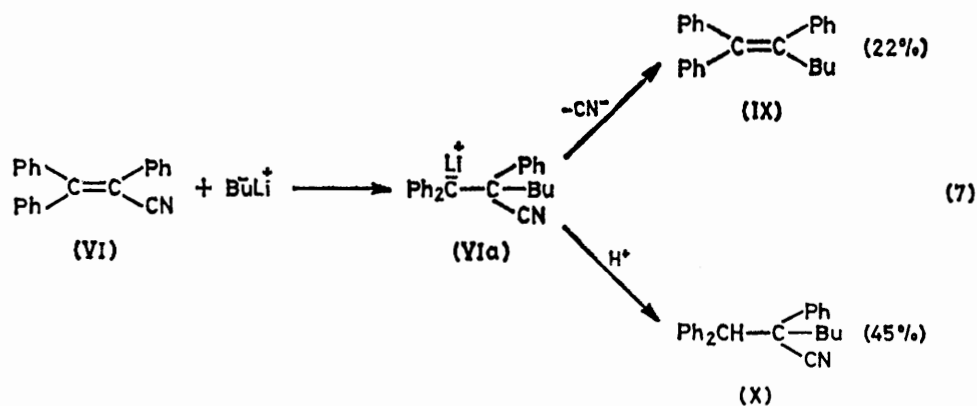
²³ T. K. Serijan and P. H. Wise, *J. Amer. Chem. Soc.*, 1951, **73**, 5191.

[BuLi] : [(I)] ratios (see Table). The total volume of the reaction mixture was kept constant (50 ml) in all experiments. stirring the mixture for an additional 15 min at -78° , it was poured into a dilute hydrochloric acid solution (0.1N). The resulting mixture was extracted with ether. The



Reaction of *trans*- α -Cyanostilbene (V) with BuLi.—The system described for the reaction of (I) with butyl-lithium was used in this case. A solution of butyl-lithium (0.011 mol) in hexane (50 ml) was added to tetrahydrofuran (30 ml),

residue recovered from the ether extracts was chromatographed on a neutral alumina column with chloroform–light petroleum as eluant, to afford two main products: (a) 1-cyano-1,2-diphenylhexane (VII) (1.05 g, 85%), m.p. 127°



cooled to -78° , and the mixture was kept for 3 min at this temperature. A solution of *trans*- α -cyanostilbene (1.02 g, 0.005 mol) in tetrahydrofuran (10 ml) was then added dropwise from the dropping funnel, during 5 min. After

(from ethyl alcohol) (Found: C, 88.4; H, 7.35; N, 4.1. $\text{C}_9\text{H}_{21}\text{N}$ requires C, 88.45; H, 7.4; N, 4.15%); $\tau(\text{CDCl}_3)$ 9.20 (3 H, t, J 4 Hz), 9.00–8.50 (4 H, m), 8.50–7.50 (2 H, m), 7.10 (1 H, q, J 5 Hz), 6.00 (1 H, d, J 4 Hz), and

3.20—2.50 (10 H, m); m/e 263 (M^+); and (b) 2-cyano-1,2-diphenylhexane (VIII) (0.100 g, 8%). Chromatography could not afford the pure compound, as it was always contaminated with (VII). The ^1H n.m.r. spectrum of (VIII) was obtained by subtracting the absorption bands of (VII) from the mixture obtained from the column. The ^1H n.m.r. spectrum of (VIII) thus obtained was in agreement with the assigned structure; $\tau(\text{CDCl}_3)$ 9.20 (3 H, t, J 4 Hz), 9.00—8.30 (4 H, m), 8.20 (2 H, t, J 5 Hz), 6.20 (2 H, s), and 3.20—2.50 (10 H, m).

Reaction of Triphenylacrylonitrile (VI) with BuLi.—The reaction system and the experimental conditions were the same as described for the reaction of (V) with butyl-lithium.

Triphenylacrylonitrile (1.41 g, 0.005 mol) and butyl-lithium (0.011 mol) were used. Chromatography on a neutral alumina column afforded two products: (a) 1,1,2-triphenylhex-2-ene (IX) (0.345 g, 22%), m.p. 91° (from ethyl alcohol); $\tau(\text{CDCl}_3)$ 9.30 (3 H, t, J 4 Hz), 9.00—8.50 (4 H, m), 7.80—7.40 (2 H, m), 3.10 (5 H, s), 2.90 (5 H, s), and 2.75 (5 H, s); and (b) 2-cyano-1,1,2-triphenylhexane (X) (0.765 g, 45%), m.p. 116° (from ethyl alcohol) (Found: C, 86.6; H, 8.1; N, 5.25. $\text{C}_{25}\text{H}_{25}\text{N}$ requires C, 86.65; H, 8.0; N, 5.35%); $\tau(\text{CDCl}_3)$ 9.50—8.50 (7 H, m), 8.45—7.90 (2 H, t, J 4 Hz), 5.40 (1 H, s), 3.50—3.30 (2 H, m), 3.10—2.40 (13 H, m); m/e 339 (M^+).

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