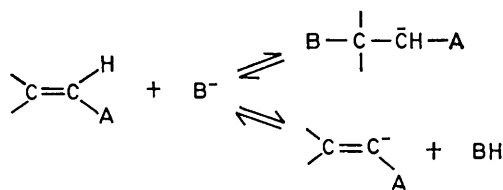


Vinyl Carbanions. Part 4.† Use of Vinyl Carbanions derived from $\beta\beta$ -Diphenylacrylonitrile as Nucleophiles

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Vinyl carbanions of the type $\text{Ph}_2\text{C}=\bar{\text{C}}\cdot\text{CN}$ (1a) were formed by treating $\beta\beta$ -diphenylacrylonitrile (1) with BuLi in tetrahydrofuran, at -78°C . These vinyl carbanions were applied as nucleophiles in addition and S_{N} -type reactions with the following electrophiles: $\beta\beta$ -diphenylacrylonitrile, benzophenone, *trans*- α -cyanostilbene, carbon dioxide, and alkyl iodides. The addition of (1a) to (1) took place at $\text{C}(\alpha)$ and afforded the addition product 1,1,4,4-tetraphenyl-2,3-dicyanobut-1-ene, and the addition-elimination products 1,1,4,4-tetraphenyl-2-cyanobutadiene and 1,1,4,4-tetraphenyl-2-butyl-3-cyanobut-1-ene. With *trans*- α -cyanostilbene, the Michael addition product was formed. A common by-product in all reactions was 1,1-diphenylhex-1-ene.

ANIONS react with activated olefins having an α -vinyl hydrogen atom, both as nucleophiles (Michael addition) and as bases, simultaneously:



A = electronegative group.

A few kinetic studies of reactions of bases with $\beta\beta$ -disubstituted olefins in which vinyl carbanions were involved as intermediates were recently reported. The mechanism of alkoxide-catalysed hydrogen-deuterium exchange reactions of 2,2,4,6,6-pentamethylcyclohexylideneacetonitrile¹ of the corresponding ketone,² of fluorene-9-ylideneacetonitrile,³ and of the alkoxide-catalysed isomerization of *cis*- and *trans*-3-(2-bromophenyl)-3-phenylacrylonitrile,⁴ were studied kinetically with regard to the existence of the derived vinyl carbanions as intermediates and their configurational stability. The $\beta\beta$ -disubstitution of these acrylonitrile derivatives depressed the nucleophilic attack at the β -carbon atom. No Michael addition products were

† Part 3, ref. 12.

¹ H. M. Walborsky and L. M. Turner, *J. Amer. Chem. Soc.*, 1972, **94**, 2273.

² J. F. Arnett and H. M. Walborsky, *J. Org. Chem.*, 1972, **37**, 3678.

³ B. A. Feit, L. Bohor, and S. Rubinaut, *J.C.S. Perkin II*, 1976, 253.

⁴ G. Djamal and B. A. Feit, unpublished results.

detected and no other evidence was observed in the above mentioned studies for a nucleophilic attack at this site. Methoxide ions add to $\beta\beta$ -diphenylnitroethylene to give the corresponding β -methyl ether,⁵ indicating that a stronger activating substituent may compensate for the steric hindrance effect. Anions add to activated double bonds at $\text{C}(\alpha)$ if $\text{C}(\beta)$ is sterically hindered. Addition products and/or addition-elimination products are obtained. Ethoxide ions add, for example, to $\beta\beta$ -diphenylfluoroethylene to give $\text{Ph}_2\text{CH}\cdot\text{CH}(\text{F})\text{OEt}$ and $\text{Ph}_2\text{C}=\text{CH}\cdot\text{OEt}$ ⁶ and 1,1-diphenylethylene reacts with butyl-lithium followed by an H^- elimination (in the presence of an H^- acceptor) to give 1,1-diphenylhex-1-ene.⁷ Köbrich and his co-workers^{8,9} studied extensively the reaction of various electrophiles with vinyl carbanions derived from $\beta\beta$ -disubstituted- α -halogeno- and $\alpha\alpha$ -dihalogeno-ethylenes. The corresponding vinyl carbanions were prepared by acid-base type reactions and by metal-halogen exchange reactions. Only a few other cases were reported where activated olefins carrying one typical electronegative substituent (not halogen) were involved in base-catalysed nucleophilic reactions. Terminally unsaturated dimers of crotonic¹⁰ and acrylic¹¹ esters,

⁵ R. Anschütz and A. Hilbert, *Ber.*, 1924, **57**, 1698.

⁶ E. F. Silversmith and D. Smith, *J. Org. Chem.*, 1958, **23**, 427.

⁷ M. T. Reetze and D. Schinzer, *Angew. Chem. Internat. Edn.*, 1977, **16**, 44.

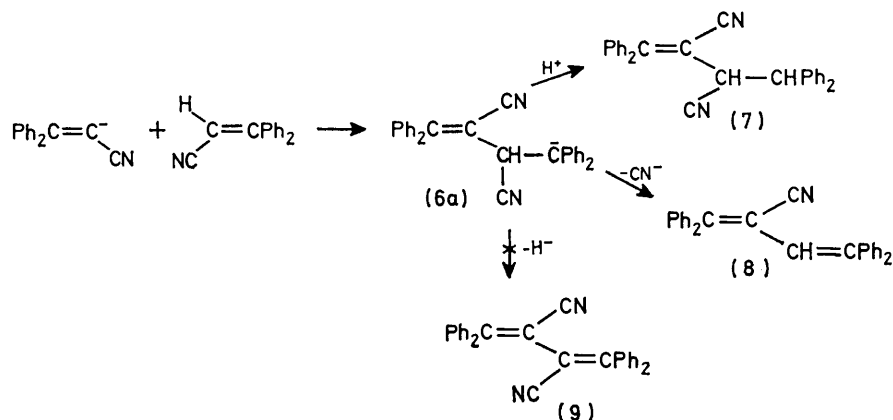
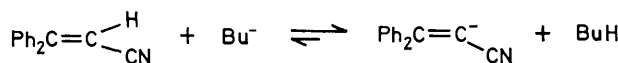
⁸ G. Köbrich, *Angew. Chem. Internat. Edn.*, 1967, **6**, 41.

⁹ G. Köbrich, *Angew. Chem. Internat. Edn.*, 1972, **11**, 473.

¹⁰ J. Shabtai and H. Pines, *J. Org. Chem.*, 1965, **30**, 3854.

¹¹ B. A. Feit, *European Polymer J.*, 1967, **3**, 523.

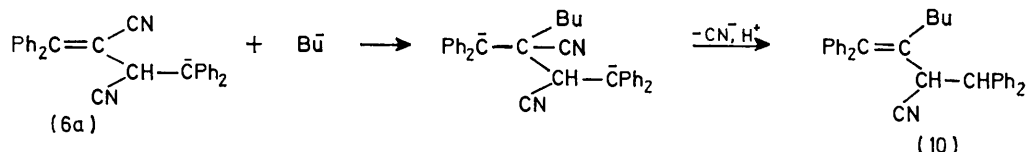
$\text{CH}_3\text{CH}=\text{C}(\text{CO}_2\text{R})\cdot\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{R}$ and $\text{CH}_2=\text{C}(\text{CO}_2\text{R})\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{R}$, respectively, were formed by a nucleophilic addition of the derived vinyl carbanions to the activated olefin. Reactions involving such carbanions



as nucleophiles might be of great significance to organic synthesis, by making possible the attachment to a carbon atom of both a double bond and a functional group in one step.

RESULTS AND DISCUSSION

Vinyl carbanions of the type $\text{Ph}_2\text{C}=\text{C}^-\text{CN}$ (1a) derived from $\beta\beta$ -diphenylacrylonitrile (1) by treating it with



BuLi , were used as nucleophiles in addition and substitution reactions. These vinyl carbanions were treated in THF at low temperature with various electrophiles yielding the expected products, along with some by-products.

We have recently found¹² that when no electrophile was added to the (1)- BuLi -tetrahydrofuran (THF) reaction mixture, addition of Bu^- at $\text{C}(\alpha)$ of (1) took place, followed by elimination of either CN^- or H^- to yield the olefins (2) and (3) in Scheme 1.

A third compound obtained was 3,3-diphenylpropionitrile (4) which resulted from a nucleophilic addition of an hydride ion to (1). Out of these compounds only 1,1-diphenylhex-1-ene (2) was formed as a by-product in the presently investigated system while the two other expected products (3) and (4) were not detected.

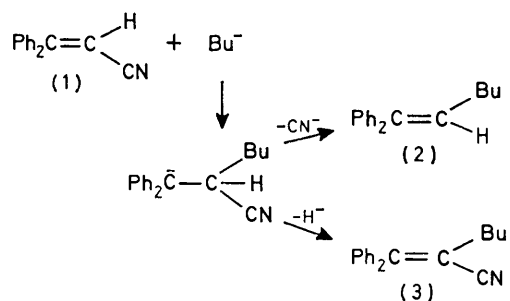
A solution of (1) was added to an equimolar mixture of (1) and BuLi (the final ratio of $[(1)] : [\text{BuLi}] = 2$) at -78°C . The dimeric addition compound (7) was the main product, while the addition-elimination product (8) was obtained in low yields. The overall high yield

¹² U. Melamed and B. A. Feit, preceding paper.

of these dimers indicates that a fast acid-base type equilibrium is first established, followed by a relatively slow addition of the conjugate base (1a) to the double bond of (1).

When equimolar concentrations of BuLi and (1) were allowed to react instead of an excess of (1) being used, addition of (1a) to (1) was still the preferred pathway. We suggest, however, that the chemically modified dimer 2-butyl-3-cyano-1,1,4,4-tetraphenylbut-1-ene (10) obtained in this case is derived from the primarily formed addition product (6a) by an addition-elimination mechanism as follows:

The dimer (8) and the olefin (2) were also formed in low yields. The dimer (8) could be recovered only as a mixture with (7). Subtraction of the absorption bands of (7) from the n.m.r. spectrum of this mixture gave the

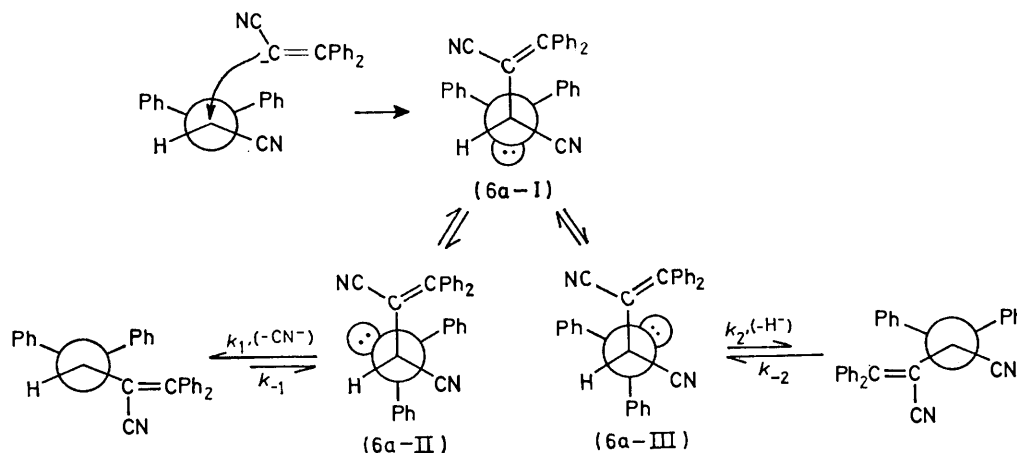


SCHEME 1

absorption bands of the assigned structure of (8): $\tau(\text{CDCl}_3)$ 3.50 (s, 1 H) and 3.20–2.50 (m, 20 H). The vinylic hydrogen atom, being also in an allylic position, gives rise to an absorption band in a relatively low field. Some minor fractions obtained by chromatography had aromatic hydrogens only, as evident from their n.m.r.

spectra. It is interesting to note in this regard that heating a mixture of (7) and (8) in $\text{Bu}^t\text{OH}-\text{Bu}^t\text{O}^-\text{K}^+$ under reflux gave an unidentified product containing only aromatic hydrogens (n.m.r. evidence). Such a compound might be 1,1,4,4-tetraphenylbutatriene, $\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{CPh}_2$, formed by base-catalysed elimination

crease in the reaction temperature to 0°C still gave, in the main, structurally modified addition products (see later). With the much less bulky nucleophile Bu^- , the less-stable conformer of the initially formed intermediate carbanion could rotate to the more stable conformers (suitable for elimination of CN^- or H^-) even

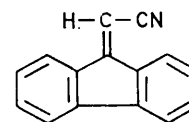


SCHEME 2

of HCN. This compound has been formed under similar conditions from $\beta\beta$ -diphenylnitroethylene.¹³

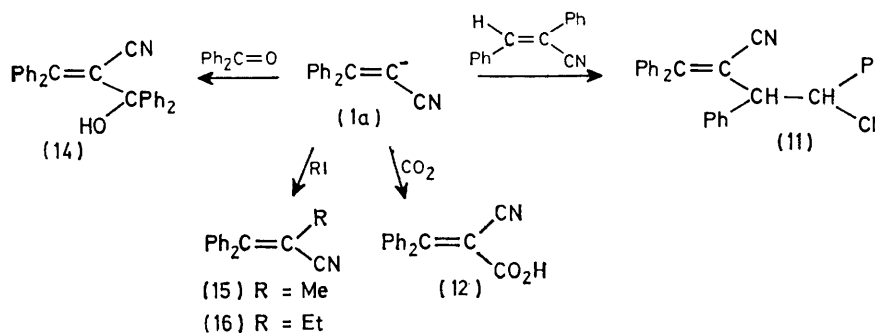
Two profound differences with respect to the products formed are revealed on comparing the nucleophilic additions of the vinyl carbanion (1a) and that of Bu^- to the double bond of (1). The reaction of (1) with BuLi afforded the two possible addition-elimination products [Scheme 1],¹² whereas its reaction with (1a) gave mainly the addition product (7) and one addition-elimination product (8) only in a low yield. The conformational equilibrium (see Scheme 2) for the carbanionic intermediate (6a) suggests that it should be

at a temperature of -78°C .¹² Olefins (8) and (9) can be formed from conformers (6a-II) and (6a-III) respectively by elimination of CN^- or H^- . The olefin (8)



(13)

was obtained in low yield but the olefin (9) not at all, in spite of the fact that the stability of the two conformers



SCHEME 3

highly populated with the relatively more stable conformers (6a-II) and (6a-III). However the relatively high yield of the addition product (7), derived from the primarily formed conformer (6a-I), indicates that the high barrier for rotation around the C(3)-C(4) bond of this conformer, combined with the very low reaction temperature, restricted the conversion of conformer (6a-I) into conformers (6a-II) and (6a-III). An in-

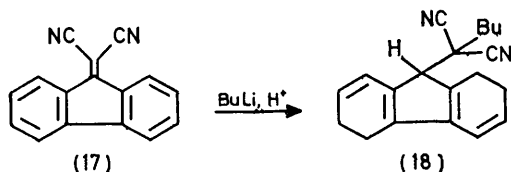
should be about the same. This result might be due to the large differences in the relative nucleophilicities and leaving group abilities of the CN^- and H^- anions, which lead to the following relation for the rate constants (Scheme 2): $k_1 \gg k_2$, $k_{-2} \gg k_{-1}$, $k_1 \gg k_{-1}$, and $k_{-2} \gg k_2$.

The possible general synthetic application of vinyl carbanions of the type (1a) was demonstrated in some nucleophilic addition and substitution reactions in which *trans*- α -cyanostilbene, carbon dioxide, benzophenone, and alkyl iodides were used as electrophilic

¹³ W. M. Jones and C. D. Broaddus, *J. Org. Chem.*, 1961, **26**, 2316.

substrates (Scheme 3). The expected addition and substitution products were obtained in good yields along with some by-products (see Experimental section).

The reaction of $\beta\beta$ -diphenylacrylonitrile (1) with BuLi did not result in formation of the addition product $\text{Ph}_2\text{CH}\cdot\text{CH}(\text{CN})\cdot(\text{CH}_2)_3\text{CH}_3$.¹² Fluorene-9-ylideneacetonitrile (13) on the other hand is more susceptible to this kind of addition due to the possible stabilization of the intermediate carbanion by the fluorene ring system. Fluorene-9-ylidenemalonitrile (17), for example, afforded by reaction with BuLi the addition product (18) as the result of such a stabilizing effect:



The vinyl carbanion derived from (13) was therefore prepared by treating the olefin with a poor nucleophile, lithium di-isopropylamide. The vinyl carbanion thus prepared was treated with carbon dioxide to give the corresponding carboxylic acid which was further converted into the methyl ester derivative.

EXPERIMENTAL

General.—M.p.s are uncorrected. N.m.r. spectra were taken on JEOL MH60 spectrometer, SiMe_4 being used as an internal standard. I.r. spectra were recorded on a Perkin-Elmer model 157 spectrometer.

Materials.—Tetrahydrofuran, analytical grade (Merck) was dried by sodionaphthalene, and fractionally distilled under nitrogen into flasks fitted with self-sealing rubber caps. Aliquot portions were removed from the flask with syringes by applying a nitrogen pressure. $\beta\beta$ -Diphenylacrylonitrile (1) was prepared by condensation of benzophenone with acetonitrile in the presence of sodamide¹⁴ and dehydration of the resulting alcohol with formic acid. *trans*- α -Cyanostilbene (5)¹⁵ and fluorene-9-ylidenemalonitrile (17)¹⁶ were prepared according to known methods and 1,1-diphenylhex-1-ene (2) was prepared¹⁷ by treating phenylmagnesium bromide with ethyl caproate, followed by dehydration of the alcohol obtained. Fluorene-9-ylideneacetonitrile was prepared by hydrolysis of ethyl α -cyano- α -fluorene-9-ylideneacetate. The cyano-ester (10 g, 0.04 mol) was refluxed with a solution of sodium ethoxide [Na (1.02 g, 0.044 mol) in EtOH (150 ml)] for 30 h. Recrystallization of the crude product recovered afforded the pure product (7 g, 75%), m.p. 109 °C (from MeOH).

Dimerization of $\beta\beta$ -Diphenylacrylonitrile (1) in the Presence of Butyl-lithium.—This reaction was carried out under nitrogen in a three-necked flask equipped with a magnetic stirrer and a dropping funnel. The flask and the 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. THF (30 ml) was introduced into the flask and cooled to -78 °C

(acetone–solid CO_2). A solution of butyl-lithium (3.3 mmol) in hexane (1.5 ml) was added to the THF. A solution of (1) (0.75 g, 3.3 mmol) in THF (10 ml) was then added dropwise through the funnel. The mixture was stirred for 5 min and a further portion of (1) (0.75 g, 3.3 mmol) dissolved in THF (10 ml) was added. The reaction mixture was then stirred for 10 min at -78 °C, and then poured into dilute hydrochloric acid. The aqueous mixture was extracted with ether. The crude residue recovered from the ethereal extracts was chromatographed on a neutral alumina column to yield the following products: (a) 2,3-dicyano-1,1,4,4-tetraphenylbut-1-ene (7) (0.75 g, 50%), m.p. 160 °C (from ethanol), $\tau(\text{CDCl}_3)$ 5.75 (1 H, d, $J = 8$ Hz, $-\text{CH}(\text{CN})$), 5.35 (1 H, d, $J = 8$ Hz, Ph_2CH), 3.40–2.90 (4 H, m, ArH), and 2.90–2.40 (16 H, m, ArH); (b) 1,1-diphenylhex-1-ene (2) (0.150 g, 10%), $\tau(\text{CDCl}_3)$ 9.20 (3 H, t, $J = 4$ Hz), 8.90–8.30 (4 H, m), 8.15–7.70 (2 H, m, $-\text{C}=\text{C}-\text{CH}_2-$), 4.00 (1 H, t, $J = 4$ Hz), and 3.00–2.50 (10 H, m, ArH); (c) 2-cyano-1,1,4,4-tetraphenylbutadiene (8) (0.15 g, 10%), $\tau(\text{CDCl}_3)$ 3.50 (1 H, s, $\text{C}=\text{CH}$) and 3.20–2.50 (20 H, m, ArH).

The reaction was also carried out at 0 °C. The order of addition of reactants was changed. A solution of butyl-lithium (5.0 mmol) in hexane (2.3 ml) was added dropwise to a solution of (1) (1.02 g, 5.0 mmol) dissolved in THF (50 ml) at 0 °C. The reaction mixture was stirred for 5 min at 0 °C and then poured into dilute hydrochloric acid; there was a 60% conversion of (1). The crude mixture of reaction products was chromatographed on a neutral alumina column to yield the following compounds: (a) 1,1-diphenylhex-1-ene (2) (0.12 g, 10%); (b) 2-cyano-1,1,4,4-tetraphenylbutadiene (8) (0.19 g, 10%); (c) 2-butyl-3-cyano-1,1,4,4-tetraphenylbut-1-ene (10) (1 g, 40%), m.p. 120 °C (from EtOH) (Found: C, 89.9; H, 6.9; N, 3.15. $\text{C}_{33}\text{H}_{31}\text{N}$ requires C, 89.79; H, 7.05; N, 3.16), $\tau(\text{CDCl}_3)$ 9.70–8.50 (7 H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.95 (2 H, m, $\text{C}=\text{C}-\text{CH}_2$), 5.70 (1 H, d, $J = 7$ Hz, CHPh), 4.45 (1 H, d, $J = 7$ Hz, $\text{C}=\text{C}-\text{CH}-\text{CN}$), and 3.10–2.30 (20 H, m, ArH).

Reaction of $\beta\beta$ -Diphenylacrylonitrile with *trans*- α -Cyanostilbene (5) in the Presence of Butyl-lithium.—The experimental conditions were the same as those described for the dimerization of (1) at -78 °C. A solution of (5) (0.75 g, 3.3 mmol) dissolved in THF (10 ml) was added to a cooled solution (-78 °C) of butyl-lithium in THF; there was a 76% conversion of (1). The mixture of products was chromatographed to give the addition product 2,4-dicyano-1,1,3,4-tetraphenylbut-1-ene (11) (0.95 g, 63%), m.p. 130 °C (from EtOH) (Found: C, 87.1; H, 5.7; N, 6.9. $\text{C}_{28}\text{H}_{23}\text{N}_2$ requires C, 87.37; H, 5.78; N, 7.05%), $\tau(\text{CDCl}_3)$ 5.90 [1 H, d, $J = 9$ Hz, $\text{C}=\text{C}(\text{CN})\text{CH}(\text{Ph})$], 5.35 [1 H, d, $J = 9$ Hz, $\text{CH}(\text{Ph})\text{CN}$], 3.60–3.20 (2 H, m, ArH), and 3.20–2.10 (18 H, m, ArH); 1,1-diphenylhex-1-ene (2) was obtained as a by-product (0.11 g, 13%).

2-Cyano-3,3-diphenylacrylic Acid (12).—The experimental conditions were the same as those described for the dimerization of (1) at -78 °C. A solution of butyl-lithium (1.1 mol) in hexane (5 ml) was added to THF (40 ml) cooled to -78 °C. A solution of $\beta\beta$ -diphenylacrylonitrile (1) (2.05 g, 1.1 mmol) in THF (10 ml) was then added dropwise to the THF–BuLi solution. The dark solution formed was stirred for 2 min at -78 °C and then crushed, solid CO_2 in ether was added. The pink mixture was stirred for 10 min and then poured into water. The

¹⁴ C. Runti and L. Sindellari, *Boll. Chem. Farm.*, 1960, **99**, 499.

¹⁵ E. C. Horning, *Org. Synth.*, 1962, Coll. Vol. III, p. 715.

¹⁶ M. Rabinovitz, I. Agranat, and E. D. Bergmann, *J. Chem. Soc. (B)*, 1967, 1281.

¹⁷ T. K. Serijan and P. H. Wise, *J. Amer. Chem. Soc.*, 1951, **73**, 5191.

aqueous layer was separated and acidified to pH 3 with hydrochloric acid. The white precipitate formed was separated to give, after crystallization, 2-cyano-3,3-diphenylacrylic acid (12) (1.8 g, 75%), m.p. 212 °C¹⁸ (from acetone-benzene); ν_{\max} . 2 200 (CN) and 1 710 cm⁻¹ (C=O). The cyano-acid (12) was converted into the corresponding methyl ester (13) by treatment with diazomethane: τ (CDCl₃) 6.35 (3 H, s, OCH₃) and 3.00–2.40 (10 H, m, ArH); 1,1-diphenylhex-1-ene (2) was obtained as a by-product (0.24 g, 10%).

2-Cyano-1,1,3,3-tetraphenylprop-2-en-1-ol (14).—The experimental conditions were as described above. A solution of butyl-lithium (3.3 mmol) in hexane (1.5 ml) was added to THF (30 ml) cooled to –78 °C. A solution of $\beta\beta$ -diphenylacrylonitrile (1) (1.5 g, 6.6 mmol) in THF (10 ml) was then added dropwise. The resulting mixture was stirred for 2 min and then a solution of benzophenone (0.6 g, 3.3 mmol) in THF (10 ml) was added to it dropwise. After a further period of stirring (30 min) at –78 °C, the reaction mixture was poured into dilute hydrochloric acid (pH 5). Extractions with ether afforded a crude mixture which was separated on a neutral alumina column to give the required product 2-cyano-1,1,3,3-tetraphenylprop-2-en-1-ol (14) (0.68 g, 25%) as white needles of m.p. 149 °C (from EtOH), τ (CDCl₃) 7.35 (1 H, s, OH), 3.20–2.00 (20 H, m, ArH), ν_{\max} . (CHCl₃) 3 550 (OH) and 2 210 cm⁻¹ (CN); $m/e = 387$ (M^+); 1,1-diphenylhex-1-ene (2) (0.09 g, 10%) and the dimer 2,3-dicyano-1,1,4,4-tetraphenylbut-1-ene (7) (0.22 g, 15%) were also recovered.

2-Methyl- and 2-Ethyl-3,3-diphenylacrylonitrile (15) and (16).—A solution of butyl-lithium (8.8 mmol) in hexane (4 ml) was added to THF (30 ml) at –78 °C. A solution of $\beta\beta$ -diphenylacrylonitrile (1) (1.5 g, 7.3 mmol) in THF (10 ml) was then added dropwise. The resulting mixture was stirred for 10 min and then methyl iodide (0.142 g, 0.01 mol) was added to it in one portion. Stirring was continued for 15 min at –78 °C. The reaction mixture was poured into water and extracted with ether. The crude mixture recovered from the ethereal extracts was chromatographed to give 2-methyl-3,3-diphenylacrylonitrile (15) (1.25 g, 80%), m.p. 60 °C¹⁹ (from EtOH), τ (CDCl₃) 8.00 (3 H, s, CH₃) and 3.00–2.40 (10 H, m, ArH); 1,1-diphenyl-

hex-1-ene (2) was also obtained in a 20% (0.35 g) yield. Using ethyl iodide under the same experimental conditions afforded 2-ethyl-3,3-diphenylacrylonitrile (16) (1.3 g, 75%), m.p. 75 °C (EtOH) (lit.,¹⁹ 76 °C), τ (CDCl₃) 8.80 (3 H, t, $J = 5$ Hz, CH₂CH₃), 7.70 (2 H, q, $J = 5$ Hz, CH₂CH₃), and 3.10–2.50 (10 H, m, ArH); 1,1-diphenylhex-1-ene (2) was also obtained (0.43 g, 25%).

1,1-Dicyano-1-fluoren-9-ylpentane (18).—The experimental procedure used was as described above for the dimerization of (1). A solution of butyl-lithium (5.0 mmol) in hexane (2.3 ml), and a solution of fluoren-9-ylidenemalonitrile (1.15 g, 5.0 mmol) in THF (10 ml) were used. The crude products were chromatographed on a neutral alumina column. An addition product, 1,1-dicyano-1-fluoren-9-ylpentane (18) was obtained (0.49 g, 30%), m.p. 95 °C (from EtOH) (Found: C, 83.0; H, 6.3; N, 9.3. C₂₀H₁₈N₂ requires C, 82.90; H, 6.30; N, 9.80%), τ (CDCl₃) 9.70–8.00 (7 H, m), 7.90–7.40 [2 H, m, C(CN)₂CH₂], 6.00 (1 H, s, fluorenyl 9-H), and 2.80–2.00 (8 H, m, ArH). Several other products which were recovered by the chromatography were impure (t.l.c.) and not identified.

Cyano(fluoren-9-yl)acetic Acid.—The experimental procedure used was as described above. Lithium di-isopropylamide was first prepared by adding a solution of butyl-lithium (4.4 mmol) in hexane (2 ml) to isopropylamine (0.73 g, 5.2 mmol) at –78 °C. (The isopropylamine was distilled over barium oxide prior to its application.) The resulting solution of lithium di-isopropylamide was diluted by THF (37 ml). A solution of fluoren-9-ylideneacetonitrile (0.9 g, 4.4 mmol) in THF (10 ml) was added dropwise during 5 min at –78 °C. After it had been stirred for 5 min crushed dry ice was added to the reaction mixture which after a further period of stirring (10 min) was poured into dilute hydrochloric acid. The red precipitate formed was recovered to give cyano(fluoren-9-yl)acetic acid (0.28 g, 25%), m.p. 212 °C (lit.,²⁰ m.p. 212 °C) (from EtOH). Reaction of the acid with diazomethane gave the corresponding methyl ester, m.p. 85–87 °C (from EtOH), τ (CDCl₃) 6.00 (3 H, s, –OCH₃), 2.80–2.30 (6 H, m, ArH), 2.20–1.90 (1 H, m, fluorenyl 1-H, *cis* to CN), and 1.60–1.40 (1 H, m, fluorenyl 8-H, *cis* to COOCH₃).

[7/1276 Received, 18th July, 1977]

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¹⁹ W. Chodkiewicz, P. Cadiot, A. Willemart, and S. Prevost, *Bull. Soc. chim. France*, 1958, 1586.

²⁰ E. J. Gragoe, C. M. Robb, and J. M. Sprague, *J. Org. Chem.*, 1950, 15, 381.