

Chemical Transformation of the Dimeric Dianion of 1,1-Diphenylethylene

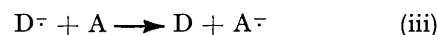
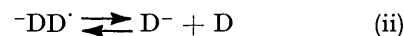
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The chemical behaviour of the dimeric dianion $^{-}\text{CPh}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Ph}_2\text{C}^{-}$ (1) derived from 1,1-diphenylethylene was examined with the intention of using the regeneration of the initial alkene as a means of detecting one-electron transfer reactions. With alkyl halides, dihalogenoalkanes, benzaldehyde, ethyl chloroformate, ethyl chloroacetate, and methyl benzoate, the dianion (1) showed conventional nucleophilic substitution and addition reactions complicated by the formation of cyclic intermediates and products, by protonation reactions, and by hydride transfer reactions. Only with methylene iodide, 1,2-dibromoethane, and iodine was the evidence indicative of electron transfer reactions.

IN recent years mechanistic pathways which involve single electron transfers have been considered as alternatives to conventional nucleophilic substitutions or additions.¹ We report an experimental attempt to distinguish between these alternatives.

It seemed possible that the behaviour of the dimeric dianion (I) generated from 1,1-diphenylethylene by reduction with alkali metals might depend on whether or not reactions involving single electron transfer were occurring. The equilibrating system involving 1,1-diphenylethylene (D), its radical anion ($\text{D}^{\cdot-}$), the dimeric dianion ($^{-}\text{DD}^{-}$), and the dimeric radical anion ($^{-}\text{DD}^{\cdot-}$) has been studied in detail by Szwarc and his co-workers.² Of particular interest was the report³ of the behaviour of $^{-}\text{DD}^{-}$ towards polycyclic aromatic hydrocarbons (A). Here electron transfer occurred from the dimeric dianion

to the aromatic substrate [equation (i)]; the dimeric radical anion so formed then dissociated to monomer and its radical anion [equation (ii)], and the latter underwent a second electron transfer [equation (iii)] or dimerized to the initial dimeric dianion $^{-}\text{DD}^{-}$.



We hoped to extend this reaction to substrates other than polycyclic aromatic hydrocarbons. Single electron transfer would generate the dimeric radical anion, which in turn should give 1,1-diphenylethylene. Should the dimeric radical anion itself prove reactive towards the substrate, products from this interaction might differ structurally from those predicted for nucleophilic substitution or addition of the dimeric dianion to the substrate.

¹ K. A. Bilevich and O. Yu. Okhlobystin, *Russ. Chem. Rev.*, 1968, **37**, 954.

² (a) G. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, 1962, **58**, 1809; (b) M. Matsuda, J. Jagur, Grodzinski, and M. Szwarc, *Proc. Roy. Soc., Ser. A*, 1965, **288**, 212; (c) J. Jagur-Grodzinski and M. Szwarc, *ibid.*, p. 224.

³ (a) J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, 1962, **58**, 2168; (b) D. Gill, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, 1964, **60**, 1424.

The products obtained by treating the dimeric dianion (1) with a variety of reagents were examined. N.m.r. spectroscopy was particularly useful for detecting the initial alkene since this possessed a vinyl proton resonance in a clear region of the spectrum.

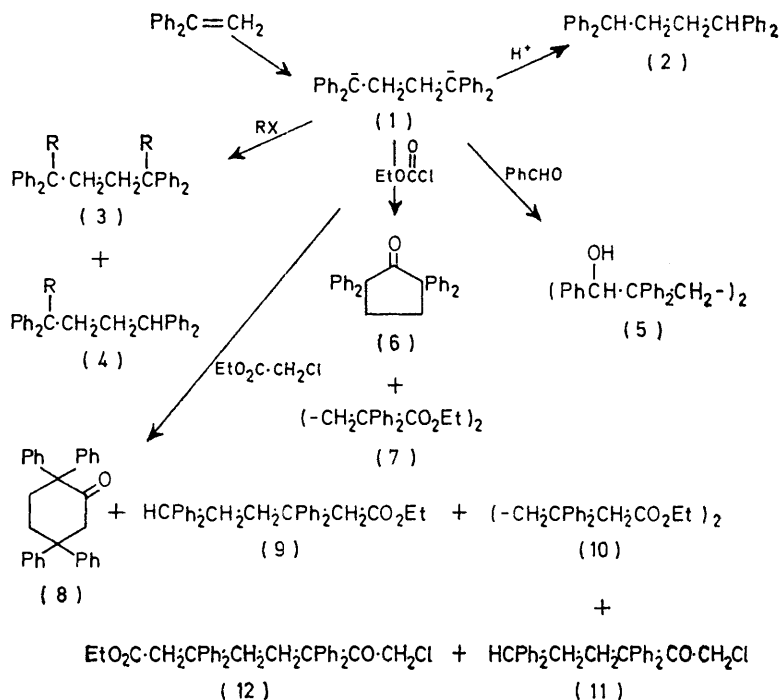
RESULTS

Protonation of the dimeric dianion (1) provided only 1,1,4,4-tetraphenylbutane (2) (see Scheme 1) in agreement with earlier observations^{2a} that the conversion of the alkene into (1) was essentially quantitative.

ethylene. The products contained the polymethylene groups of the alkylating agents but no pure compounds were isolated and the products were undoubtedly oligomeric mixtures such as those reported elsewhere.⁵

In only three instances were appreciable amounts of 1,1-diphenylethylene formed: when the dianion (1) was treated with 1,2-dibromoethane, iodine, or methylene iodide. In the first two cases, these results agreed with those of an earlier study⁵ in which the cation was lithium.

Reactions involving nucleophilic attack at a carbonyl



SCHEME 1 Reactions of the dimeric dianion of 1,1-diphenylethylene

Alkylation of (1) with alkyl halides produced minor amounts of 1,1-diphenylethylene, particularly when a specially designed flask (see Experimental section) was used to minimize inadvertent exposure of (1) to traces of oxygen. Smooth alkylation proceeded at the benzylic carbon atom giving the alkanes (3; R = Me, CH₂Ph, or Prⁱ). An exception occurred in attempted alkylation with *t*-butyl chloride: only dehydrohalogenation occurred, producing tetraphenylbutane (2).

Extensive ring-alkylation has been reported⁴ in the reaction of isopropyl halides with the vicinal dianion of benzophenone anil. Since the diphenylmethane unit was common to this last dianion and the dianion (1), attempts were made to detect ring-alkylation products in the present study. However, only tetraphenylbutane (2) and the monoalkylated product (4; R = Prⁱ) were isolated.

Alkylation with 1,3-dihalogenopropanes and 1,4-dihalogenobutanes again produced little 1,1-diphenyl-

group were examined by using benzaldehyde, ethyl chloroformate, ethyl chloroacetate, and methyl benzoate. Relatively minor amounts (5–15%) of 1,1-diphenylethylene were detected. Generally, the products expected in such reactions were observed but, in some instances, further reactions of the initially formed products occurred.

Benzaldehyde produced a diastereoisomeric mixture of 1,2,2,5,5,6-hexaphenylhexane-1,6-diols (5), both of which were isolated. One of these had been reported earlier.⁶

With ethyl chloroformate, two products were isolated, 2,2,5,5-tetraphenylcyclopentanone (6) and diethyl 2,2,5,5-tetraphenylhexanedioate (7). Some control over the ratio of these products was possible at a reaction temperature of -78°C ; here the molar ratio of reagents effectively directed the formation of either (6) or (7). However at 20°C the major product was always the cyclic ketone (6).*

Ethyl chloroacetate behaved both as an acylating and

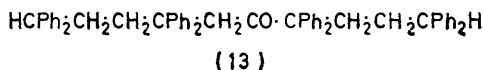
* Phosgene has been reported⁶ to produce product (6).

⁴ J. G. Smith and R. A. Turler, *J. Org. Chem.*, 1972, **37**, 126.

⁵ D. H. Richards and N. F. Scilly, *J. Chem. Soc. (C)*, 1969, 2661; *J. Polymer Sci., Part B, Polymer Letters*, 1969, **7**, 99.

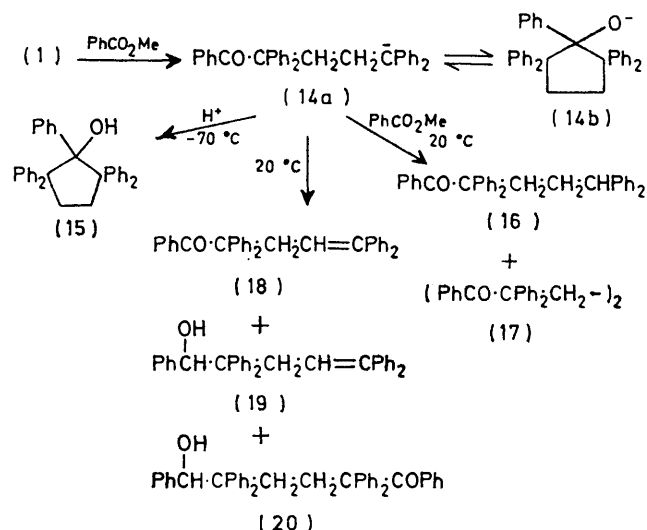
⁶ W. Schlenk and E. Bergmann, *Annalen*, 1928, **463**, 1.

as an alkylating agent. Thus the mono- and di-alkylation products ethyl 3,3,6,6-tetraphenylhexanoate (9) and diethyl 3,3,6,6-tetraphenyl-octanedioate (10) were isolated, but only small yields of the anticipated product 2,2,5,5-tetraphenylcyclohexanone (8) were detected. Attempts to increase the yield of this last product by using 1 mol. equiv. of ethyl chloroacetate were unsuccessful and led to a complicated mixture containing oligomers. One of these (13) was isolated.



Two acylation products having structures [(11) and (12)] were isolated as well. Their ^1H n.m.r. spectra were characterized by a methylene resonance at δ 4.0, much further downfield than those of compounds (8)—(10) and (13) (all at δ ca. 3.1). Mass spectra of (11) and (12) showed no molecular ion; the highest mass peak observed was the $M^+ - \text{HCl}$ fragment. Chemical analyses confirmed the presence of chlorine.

The reaction with methyl benzoate proved unexpectedly complex and sensitive to reaction conditions (see Scheme 2). At low temperatures, 1 equiv. of the ester



SCHEME 2 Reaction with methyl benzoate

produced chiefly the cyclic alcohol (15). With 2 equiv. of methyl benzoate, the open-chain mono- and di-benzoylated compounds (16) and (17) were formed.

In contrast to this, 1 equiv. of methyl benzoate at 20 °C produced the products (18)—(20). The last of these (20) could not be crystallized although it appeared to be a single component having the structure shown according to its spectroscopic properties. Oxidation converted it into the dibenzoyl derivative (17).

Benzoyl chloride and the dianion (1) have been reported⁶ to produce the cyclic alcohol (15) with m.p. different from that observed here. However, a second compound described as the benzoate of (15) was reported to have the m.p. observed here for (15). It is believed that the original identification is incorrect.

DISCUSSION

In only three cases were substantial amounts of 1,1-diphenylethylene observed, *viz.* the reactions with iodine, 1,2-dibromoethane, and methylene iodide. Richards and Scilly⁵ have also observed this behaviour [with lithium as the counterion of (1)] although with methylene bromide they reported the formation of a cyclopentane derivative. It thus appears that with easily reduced compounds electron transfer can occur giving the dimeric radical anion of (1) which dissociates to the monomeric alkene. Indeed in the case of 1,2-dibromoethane, this mechanism has been suggested,⁵ and independent evidence⁷ is available for dehalogenation of such vicinal dibromides *via* an electron transfer mechanism. The divergent results obtained with methylene iodide and bromide can be rationalized in terms of the greater ease of reduction of the iodo-compound.

With all other reagents examined, only modest amounts of 1,1-diphenylethylene were formed and the other products were not unexpected. As a chemical probe for one-electron transfers the dimeric dianion (1) proved of limited value and the limitation can be attributed to the reversible nature of the electron transfer and the relatively slow dissociation of the dimeric radical anion to 1,1-diphenylethylene.^{2c} This permits the usual nucleophilic substitution or addition reactions to occur, producing the observed products.

The failure to observe ring-alkylation products in the alkylations, in contrast to the behaviour of the benzophenone anil dianion, has two possible explanations: first, delocalization of the anionic charge in the diphenylmethyl portion of (1) could be less extensive than in the case of the benzophenone anil dianion, and secondly, the mechanisms by which the two dianions react may differ. At present, we favour the latter explanation since extensive alkylation of the benzophenone anil dianion occurs with *t*-butyl halides⁸ but only dehydrohalogenation occurs with (1).

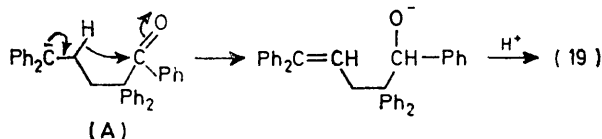
The cyclic derivatives formed on treating the dianion (1) with ethyl chloroformate or methyl benzoate [*i.e.* (6) and (15)] result from the favourable proximity of the anionic centre to the carbonyl group in the intermediate monoacylated monoanion. With ethyl chloroformate, the cyclization is rapid and it is only at -78°C that the molar ratio of reagents is effective in producing the open-chain diacylated product (7). However, with methyl benzoate it is suggested that an equilibrium exists between the cyclic alkoxide ion (14b) and the open-chain tautomer (14a). Such an equilibrium explains the preponderance of the cyclic alcohol (15) in reactions at low temperatures, but the formation of the open-chain derivatives (16) and (17) at 20 °C where protonation and acylation of (14a) can occur at significant rates.

An additional complication occurs in this last reaction when only 1 equiv. of methyl benzoate is used. Then the products (18)—(20) arise by hydride transfer from the monobenzoyl anion (14a) to a receptive carbonyl group, a

⁷ W. Adam and J. Arce, *J. Org. Chem.*, 1929, **37**, 507.

⁸ J. G. Smith, unpublished results.

reaction motivated by the conjugation of the double bond with the aromatic rings. Intermolecular hydride transfer accounts for the formation of (18) and (20). However, the especially high yield of the alkenol (19) suggests that the cyclic transition state (A) favours intramolecular hydride transfer.



With ethyl chloroacetate, the observation of both alkylation and acylation reflects the enhanced reactivity⁹ of the α -chloro-substituent to nucleophilic substitution effected by the adjacent carbonyl group. The small yield of the cyclic ketone (8), even under conditions designed to promote its formation, suggests that the strong 1,3-diaxial interactions of the phenyl substituents in (8) render the cyclization sufficiently unfavourable that competitive intermolecular reactions forming compounds such as the oligomer (13) occur.

Protonation of the intermediate anions by ethyl chloroacetate* complicated this reaction. Thus the yield of (2) was higher than normally observed and substantial amounts of the mono-alkylation (9) and mono-acylation (11) products were obtained.

In summary, the dimeric dianion (1) behaves as a bis-diphenylmethanide ion and undergoes conventional nucleophilic substitutions and additions. The occasional exception occurs when the substrate is easily reduced; here one-electron transfer can lead to regeneration of 1,1-diphenylethylene.

EXPERIMENTAL

M.p.s were determined for samples in open capillaries with a Mel-Temp apparatus. I.r. spectra were recorded on a Beckmann IR-10 spectrophotometer and n.m.r. spectra on a Varian T-60 spectrometer with tetramethylsilane as internal standard. Merck silica gel (0.05–0.2 mm) was used for column chromatography and Eastman Chromagram 6060 (silica gel) sheets were used for t.l.c. Analyses were determined by M-H-W Laboratories, Garden City, Michigan.

Petrol refers to light petroleum of boiling range 30–60° except where otherwise designated.

Reductive Metallation of 1,1-Diphenylethylene.—The usual method for preparing the dimeric dianion (1) involved shaking a mixture of the alkene (1.80 g, 0.01 mol), tetrahydrofuran (90 \pm 10 g), and sodium (1.0 g, 0.04 g atom) in a Schlenk tube for a minimum of 8 h.¹⁰ In a control run, samples of the solution were removed with a nitrogen-flushed syringe through a rubber septum and injected into methanol without exposure to air. No residual alkene was detected in the organic products after 4 h reaction time.

The deep red solution of the dianion (1) was transferred under nitrogen to a nitrogen-filled flask, cooled to -78°C , and the second reagent was injected by hypodermic syringe through a septum into the stirred cold solution.

In those cases where small amounts of 1,1-diphenylethyl-

* The lability of the methylene protons of ethyl chloroacetate is well known and is utilized in the Darzens reaction

ene might arise by inadvertent admission of oxygen, a special vessel was employed which avoided any exposure of the dianion (1) to traces of oxygen. The vessel was constructed from a 250 ml Erlenmeyer flask equipped with a standard taper joint. Attached to the flask was a side-neck constructed from 8 mm tubing capped with a septum which was used for injecting the second reagent. Also attached to the flask was a U-tube, with one branch connected to the side of the flask immediately below the central neck and the other connected to the flask wall just above the bottom. A constriction in the central area of this side arm served to retain the lump of unchanged sodium at the end of the reductive metallation.

In practice, the mixture of sodium metal, tetrahydrofuran, and the dianion (1) was sealed in the flask and stirred until the reaction was complete. The excess of sodium was removed by inverting the flask and, with a rotary motion, allowing the solution to trickle through the U-tube back into the lower portion of the flask. The sodium, which forms a metallic ball during the reaction, was retained at the constriction of the U-tube and held well above the level of the solution of the dianion (1). The solution was then cooled and subsequent reactions effected without exposure to any gas but the nitrogen contained in the flask when it was originally sealed.

Reactions with Alkyl Halides.—With the reactive halides such as benzyl chloride and methyl and isopropyl iodide, decolorization of the dianion (1) occurred at -78°C . With the less reactive halides, warming to room temperature completed the reaction. The product was isolated by diluting the solution with water and extracting with ether. Evaporation of the extract provided the crude product, whose ^1H n.m.r. spectrum enabled an estimation of the 1,1-diphenylethylene content to be made. The alkylation product (3) was isolated by treating the residue with light petroleum followed by recrystallization of the insoluble solid.

Where pure compounds were not obtained in this manner, chromatography of the products with petrol–benzene mixtures as eluants was attempted. A summary of the results is presented in Table 1.

In the case of the reaction with isopropyl halides, that portion of the products soluble in the petrol was chromatographed on silica gel with petrol containing an increasing proportion of benzene as eluant. In order of elution, the following products were obtained: 2,7-dimethyl-3,3,6,6-tetraphenyl-octane (3; R = Prⁱ) (0.102 g, 2.3%); 5-methyl-1,1,4,4-tetraphenylhexane (4; R = Prⁱ) (0.244 g, 5.5%); and the tetraphenylbutane (2) (0.111 g, 3.1%).

The monoalkylation product (4; R = Prⁱ) was an oil which slowly crystallized; m.p. $86\text{--}88^\circ$ (from hexane) (Found: C, 92.25; H, 8.2. C₃₁H₃₂ requires C, 92.0; H, 8.0%); δ (CDCl₃) 0.68 (6H, J 6 Hz, Me₂CH), 1.4–2.2 (4H, CH₂), 2.63 (1H, sept, J 6 Hz, Me₂CH), 3.65 (1H, t, J 7 Hz, CHPh₂), and 6.8–7.4 (20H, m, aromatic).

Reaction with Benzaldehyde.—The colour of the dianion (1) rapidly disappeared at -78°C after injection of benzaldehyde (1.11 g, 0.01 mol). Analysis of a sample of the product (2.85 g) showed the presence of 1,1-diphenylethylene (10–15%). Repeated recrystallization of the solid from benzene gave one diastereoisomer of 1,2,2,5,5,6-hexaphenylhexane-1,6-diol (5), m.p. $220\text{--}222^\circ$ (lit.,⁶ 212° , sinters 176°)

⁹ J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 2nd edn., 1962, p. 176.

¹⁰ J. G. Smith and C. D. Veach, *Canad. J. Chem.*, 1966, **44**, 2245.

C, 91.05; H, 6.85%); δ (CDCl₃) 1.2—2.6 (8H, m, CH₂CH₂), 3.15 (2H, s, CH₂C=O), 3.72 (2H, apparent t, *J* 7 Hz, HCPPh₂), and 6.7—7.4 (40H, m, aromatic); ν_{\max} (Nujol) 1 720 (C=O), 1 600, 1 490, 1 440, 1 370, 740, and 690 cm⁻¹; (iii) a mixture (0.85 g) from which no definite product could be obtained except the insoluble ketone (8) (0.02 g, 1%), m.p. 260—265°; (iv) the keto-ester (12) (0.10 g, 4%); (v) the diester (10) (0.30 g, 11%).

Reaction with Methyl Benzoate.—Injection of methyl benzoate (1 or 2 equiv.) into a solution of the dianion (1) at -78 °C caused a colour change from deep red to red-brown. However, decolourization of the solution occurred only on warming to room temperature. The method for isolation of the products was the same for all experiments except those in which 1 equiv. of methyl benzoate was used and the mixture warmed to room temperature. A typical procedure follows.

The crude mixture from the dianion (1) (0.005 mol) and methyl benzoate (1.36 g, 0.01 mol) (isolated by chloroform extraction) was treated with diethyl ether (20 ml) and set aside for 12 h. The insoluble 1,2,2,5,5-pentaphenylcyclopentanol (15) was filtered off (1.24 g, 53%); m.p. 238—241°, raised by recrystallization from benzene to 240—241° [lit.,⁶ 179°] (Found: C, 90.05; H, 6.2. C₃₅H₃₀O requires C, 90.1; H, 6.5%); δ (CDCl₃) 1.50 (1H, s, OH), 2.8—4.0 (4H, m, CH₂), and 6.7—7.6 (20H, m, aromatic); ν_{\max} (CHCl₃) 3 510 (OH), 1 480, 1 430, and 680 cm⁻¹.

The ether-soluble portion of the products was chromatographed on silica gel (50 g) with 1 : 1 benzene-petrol graded through benzene to benzene-5% diethyl ether as eluant. In order of elution were isolated (i) compound (2) (0.06 g, 3%) (identified by n.m.r.), 1,2,2,5,5-pentaphenylpentan-1-one (16) (0.84 g, 36%), m.p. 126—127.5° [from light petroleum (b.p. 80—100°)] (Found: C, 90.35; H, 6.55. C₃₅H₃₀O requires C, 90.1; H, 6.5%); δ (CDCl₃) 1.6—2.6 (4H, m, CH₂), 3.72 (1H, t, *J* 7 Hz, CHPh₂), and 6.8—7.6 (25H, m, aromatic); ν_{\max} (CHCl₃) 1 690 (C=O), 1 500, 1 460, 1 230, and 680 cm⁻¹; (iii) 1,2,2,5,5,6-hexaphenylhexane-1,6-dione (17) (0.20 g, 7%), m.p. 193—195° [from light petroleum (b.p. 80—100°)] [lit.,⁶ 195—196°] (Found: C, 88.2; H, 6.0. Calc. for C₄₂H₃₄O₂: C, 88.4; H, 6.0%); δ (CDCl₃) 2.19 (4H, s, CH₂) and 7.0—7.5 (30H, m, aromatic); ν_{\max} (CHCl₃) 1 690 (C=O), 1 500, 1 400, 1 220br, 1 180, and 690 cm⁻¹.

Table 3 summarizes the yields obtained under different reaction conditions.

The crude product (2.50 g) from the reaction of 1 equiv. of methyl benzoate at -78 °C for 2 h followed by warming to

22 °C for 7 h was chromatographed on silica gel (100 g) with 1 : 1 benzene-petrol graded through benzene to benzene-10% diethyl ether as eluant solvent. The following compounds, in order of elution, were isolated: (i) compound (2) (0.13 g, 7%), identified by n.m.r.; (ii) 1,2,2,5,5-pentaphenylpent-4-en-1-one (18), (0.41 g, 18%), m.p. 165.5—167.5° [from light

TABLE 3

MeOBz (mol. equiv.)	Temp. (°C)	Time (h)	Products (%)			
			(2)	(15)	(16)	(17)
1	-78	5	4	76	5	7
2	-78	3	3	53	36	7
2	22 ^a		15	2	52	24

^a 2 h At -78 °C followed by warming to 22 °C.

petroleum (b.p. 100—120°)] (Found: C, 90.6; H, 6.2. C₃₅H₂₈O requires C, 90.45; H, 6.1%); δ (CDCl₃) 3.31 (2H, d, *J* 7 Hz, CH₂), 5.92 (1H, t, *J* 7 Hz, CH), and 6.6—7.8 (25H, m, aromatic); ν_{\max} (CCl₄) 1 680 (C=O), 1 600, 1 490, 1 220, and 690 cm⁻¹; (iii) 1,2,2,5,5-pentaphenylpent-4-en-1-ol (19) (1.52 g, 65%), m.p. 133—135° [from light petroleum (b.p. 80—100°)] (Found: C, 90.25; H, 6.55. C₃₅H₃₀O requires C, 90.1; H, 6.5%); δ (CDCl₃) 2.13 (1H, s, OH), 2.75 and 2.81 (2H, m, AB portion of ABX, *J*_{AB} 15 Hz, CH₂CH=), 5.57 (1H, s, CHOH), 5.93 (1H, X portion of ABX, *J*_{AX} = *J*_{BX} = 6.5 Hz, CH₂CH=), and 6.5—7.4 (30H, m, aromatic); ν_{\max} (CCl₄) 3 500 (OH), 1 500, 1 440, and 690 cm⁻¹; (iv) 6-hydroxy-1,2,2,5,5,6-hexaphenylhexan-1-one (20) (0.29 g, 10%), an amorphous solid, δ (CDCl₃) 1.4—2.4 (5H, m, CH₂ and OH, one proton exchanged with D₂O), 5.40 (1H, s, CHOH), and 6.2—7.5 (30H, m, aromatic); ν_{\max} (CCl₄) 3 600 (OH), 1 680 (C=O), 1 500, 1 440, and 690 cm⁻¹. Treatment of the hydroxy-ketone (20) (100 mg) with chromium trioxide (100 mg) in glacial acetic acid (10 ml) resulted in an immediate colour change; t.l.c. showed oxidation was complete in 15 min. Water was added and the product isolated by ether extraction. The crude product (95 mg) was chromatographed on silica gel (10 g) giving 1,2,2,5,5,6-hexaphenylhexane-1,6-dione (75 mg), m.p. 191—194°, raised by recrystallization from light petroleum (b.p. 80—100°) to 195—196°, undepressed on admixture with authentic (17).

This research was financially supported by the National Research Council of Canada.

[4/2123 Received, 14th October, 1974]