840. *Chalcones and Related Compounds. Part VIII.* The Preparation of Some Phenylenedi*(*arylpropenones*) (" *Dichalcones* ") *and Quinquephenyls.*

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" Dichalcones " and their heterocyclic analogues (I) and (II) have been prepared and the addition of ethyl acetoacetate and cyanoacetate to them investigated. Hydrolysis and decarboxylation of the acetoacetate adducts leads to some partially reduced quinquephenyl derivatives. The *meta*-compounds (cf. II) were usually intractable.

GERNGROSS and DUNKEL [1] first obtained *p*-quinquephenyl in low yield by a modified Gatterman reaction, but later workers preferred to use Friedel–Crafts reactions, aryllithiums,[2] or Grignard reagents [3] for synthesis of these and other polyphenyls. Few heterocyclic analogues have been prepared, although Busch *et al.*[4] reported the formation of quinquepyridyl, and the use of Ullmann reactions has yielded 2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquepyridyl and 2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethienyl.[5] The present work describes an attempt to prepare some quinquephenyl analogues by the Michael reaction by somewhat similar routes to those used in the preparation of terphenyls.[6]

Pfeiffer, Kollbach, and Haack [7] prepared " *p*-dichalcone " in 50% yield by condensing acetophenone with terephthalaldehyde in aqueous-ethanolic sodium hydroxide, but reaction in methanol, catalysed by methanolic sodium hydroxide, gave an increased yield (96%), the product crystallising from the reaction medium, and this technique was

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* Part VII, *J.*, 1958, 4193.

[1] Gerngross and Dunkel, *Ber.*, 1924, **57**, 739; cf. Gerngross, Schachnow, and Jonas, *ibid.*, p. 747.

[2] Muller and Topel, *Ber.*, 1939, **72**, 273.

[3] Woods and Tucker, *J. Amer. Chem. Soc.*, 1948, **70**, 3340; Woods and Reed, *ibid.*, 1949, **71**, 1348; Alexander, *J. Org. Chem.*, 1956, **21**, 1464; Silverman and Houk, *Analyt. Chem.*, 1955, **27**, 1957.

[4] Busch and Weber, *J. prakt. Chem.*, 1938, **146**, 1.

[5] Burstall, *J.*, 1938, 1662; Steinkopf, Leitsman, and Hofmann, *Annalen*, 1941, **546**, 180; Lease and Zechmeister, *J. Amer. Chem. Soc.*, 1947, **69**, 270.

[6] Ames and Davey, *J.*, 1957, 3480; 1958, 1794.

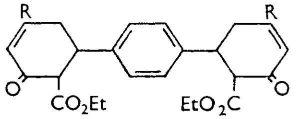
[7] Pfeiffer, Kollbach, and Haack, *Annalen*, 1928, **460**, 138.

successfully employed for the preparation of the analogous compounds (Ia—e) and (IIa—d).

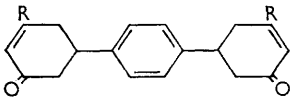
(I) $p\text{-}C_6H_4(CH{:}CH{\cdot}COR)_2$ $m\text{-}C_6H_4(CH{:}CH{\cdot}COR)_2$ (II)

R = (a) Ph, (b) 2-furyl, (c) 2-thienyl, (d) 2-pyridyl, (e) 4-pyridyl.

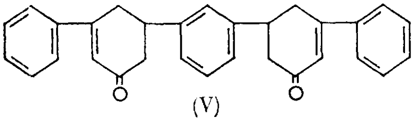
Addition of acetoacetic ester to such compounds could only be effected under the conditions described by Nadkarni, Warriar, and Wheeler[8] and even then the *meta*-compounds gave oils. Other methods of addition yielded adducts without cyclisation but this technique gave addition and cyclisation, the "*p*-dichalcone" adducts being the quinquearyl derivatives (IIIa—d). Refluxing with the calculated quantity of aqueous-ethanolic potassium hydroxide for 3 hours then afforded the diketones (IVa—e). Hydrolysis of the oils in the *meta*-series of compounds yielded a crystalline product in only one case, namely, compound (V) in the benzene series. Attempts to dehydrogenate compounds (III) and (IV) with palladised charcoal failed; with sulphur the corresponding dihydroxyquinquephenyl was obtained but the furyl and thienyl analogues decomposed.



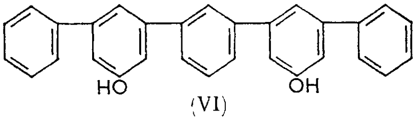
(III)



(IV)



(V)



(VI)

In an attempt to prepare *m*-quinquephenyl, the corresponding keto-ester was reduced to the diol by potassium borohydride, but dehydrogenation by sulphur yielded the dihydroxyquinquephenyl (VI).

Addition of cyanoacetic ester to "*p*-dichalcone" (Ia) by Davey and Tivey's method[9] gave only 16% yield of the required adduct but an improved yield (28%) was obtained by shaking the reactants together at room temperature for 24 hours. "*m*-Dichalcone" (IIa) under all conditions studied gave only oils. Attempts to hydrogenate the cyanoacetic adducts over Raney nickel W7 or platinic oxide failed, starting materials being recovered in quantitative yields.

EXPERIMENTAL

"p-*Dichalcones*."—(i) The method of Organic Syntheses[10] yielded 42·5% of "*p*-dichalcone" 3,3′-*p*-phenylenedi-(1-phenylprop-2-en-1-one) (Ia), m. p. 196°, raised to 201° on recrystallisation from dioxan (von Ledenfeld[11] gave m. p. 201°). (ii) To a solution of terephthalaldehyde (1·34 g., 0·01 mole) and acetophenone (2·5 g., 0·02 mole) in methanol (50 ml.), saturated methanolic sodium hydroxide solution (0·5—1·0 ml.) was added with stirring and the whole was left overnight at room temperature. Filtration and washing with cold methanol of the resulting yellow crystals gave "*p*-dichalcone," (3·24 g., 96%), m. p. 200—201°.

Addition of Acetoacetic Ester to "p-*Dichalcone*."—(i) "*p*-Dichalcone" (2·0 g., 0·0059 mole) was added to a solution of sodium (0·28 g., 0·012 g.-atom) and ethyl acetoacetate (1·6 g., 0·012 mole) in dry ethanol (50 ml.) and the mixture refluxed for 3 hr. Pouring into water and acidification of the yellow solution gave a yellow gum.

(ii) Reaction of the above materials by the method of Knoevenagel and Schmidt[12] at room temperature for 48 hr. gave a yellow gum from which crystals (200 mg.) were obtained. Recrystallisation from aqueous acetic acid gave white material of m. p. 205—206° (decomp.); from aqueous dioxan crystals, m. p. 215—216° (decomp.), were obtained.

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[8] Nadkarni, Warriar, and Wheeler, *J.*, 1937, 1798.

[9] Davey and Tivey, *J.*, 1958, 2606.

[10] *Org. Synth.*, Coll. Vol. I, 1941, p. 78.

[11] von Ledenfeld, *Monatsh.*, 1896, **27**, 971.

[12] Knoevenagel and Schmidt, *Annalen*, 1894, **281**, 58.

(iii) By Kohler's method[13] "*p*-dichalcone" (2·0 g., 0·0059 mole) in dry ethanol (100 ml.), ethyl acetoacetate (1·6 g., 0·012 mole), and diethylamine (2 ml.) at room temperature deposited in 24 hr. a solid, and addition of ether (100 ml.) to the filtrate gave a further yield (total 0·8 g., 40%). Crystallisation from 2-hydroxyethyl ether gave an *adduct*, m. p. 204° (decomp.); from butyl acetate–dioxan crystals, m. p. 221—222° (decomp.), were obtained. Finally crystallisation from ethyl methyl ketone gave material of m. p. 246° (decomp.) (Found: C, 67·1; H, 6·7. $C_{36}H_{38}O_8,2{\cdot}5H_2O$ requires C, 67·2; H, 6·8%). An attempt to cyclise this compound after vacuum-drying by refluxing it in dry ethanol with sodium for 3 hr. gave only a gum.

(iv) Refluxing "*p*-dichalcone" (2·0 g., 0·0059 mole), ethyl acetoacetate (1·6 g., 0·012 mole), and diethylamine (2 ml.) in dry ethanol (50 ml.) for 1 hr. gave a yellow solution but this afforded a gum.

(v) To a solution of sodium (0·14 g., 0·006 g.-atom) and ethyl acetoacetate (3·0 g., 0·023 mole) in dry ethanol (100 ml.), "*p*-dichalcone" (2·0 g., 0·0059 mole) was added and the mixture was refluxed for 2 hr. Cooling in ice and salt gave *diethyl* 6,6′-*phenylenedi*-(2-*oxo*-4-*phenylcyclohex*-3-*enecarboxylate*) (IIIa) which recrystallised from ethanol in pale yellow plates, m. p. 216—217° (1·7 g., 51%) (Found: C, 76·6; H, 6·2. $C_{36}H_{34}O_6$ requires C, 76·9; H, 6·1%).

Hydrolysis of the Keto-ester (IIIa).—The ester (1·7 g., 0·003 mole) was suspended in a solution of potassium hydroxide (0·6 g.) in 4 : 1 aqueous ethanol (40 ml.) and refluxed for 3 hr. Dilution with water, filtration, washing, and drying gave 5,5′-p-*phenylenedi*-(3-*phenylcyclohex*-2-*enone*) (IVa) (1·1 g., 87%), m. p. 254°, which crystallised from dioxan in white plates, m. p. 258—259° (Found: C, 86·3; H, 6·0. $C_{30}H_{26}O_2$ requires C, 86·1; H, 6·3%).

1,1′:3′,1″:4″,1‴:3‴,1⁗-*Quinquephenyl*-5′,5‴-*diol*.—The diketone (IVa) (0·5 g., 0·0012 mole) and sulphur (0·08 g., 0·0035 g.-atom) were heated at 140°. The melt resolidified after 5 min. and the temperature was then raised to 270° for 2½ hr. Extraction of the residue with methanol, then the addition of benzene and light petroleum to the extract, gave the *diol*, m. p. 200—224°, which crystallised from toluene and then from benzene in small pink crystals, m. p. 238—239° (Found: C, 86·2; H, 5·6. $C_{30}H_{22}O_2$ requires C, 86·9; H, 5·4%).

5,5′-*Phenylenedi*-(3-*phenylcyclohex*-2-*enol*).—Potassium borohydride (1·2 g.) in water was added to the ketone (IVa) (0·6 g.,) in 2-hydroxyethyl ether and left overnight. Dilution with water and acidification gave the *biscyclohexenol* (0·015 g.), m. p. 214—215° (Found: C, 85·5; H, 7·7. $C_{30}H_{30}O_2$ requires C, 85·3; H, 7·2%). Heating this product (0·96 g.) with sulphur (0·65 g.) at 240° for 3 hr. and extraction with methanol gave pink crystals, (0·5 g., 52%), m. p. 236—237° alone or mixed with the quinquephenyldiol.

"m-*Dichalcone*" [3,3′-m-*Phenylenedi*-(1-*phenylprop*-2-*en*-1-*one*)] (IIa).—Condensation of *m*-phthalaldehyde (2·68 g., 0·02 mole) and acetophenone (5 g., 0·04 mole) by the method used for the *para*-isomer gave this *product* as pale yellow needles, m. p. 200—201°, but subsequent crystallisation gave pale yellow blades, m. p. 143—144° (Found: C, 85·2; H, 5·1. $C_{30}H_{30}O_2$ requires C, 85·2; H, 5·4%).

Condensation of o-*Phthalaldehyde and Acetophenone*.—To *o*-phthalaldehyde (0·67 g., 0·005 mole) and acetophenone (1·2 g., 0·01 mole) in methanol (25 ml.), saturated methanolic sodium hydroxide (1·0 ml.) was added; the solution rapidly darkened and was set aside at room temperature for 24 hr. On dilution with water a dark oil separated. Steam-distillation removed unchanged reactants and methanol extraction of the tarry residue gave yellow needles (80 mg., 6%), m. p. 103—104° (Found: C, 81·3; H, 5·1. Calc. for $C_{16}H_{12}O_2$: C, 81·0; H, 4·9%). Infrared absorption (in $CHCl_3$ and Nujol) supported the structure as 2-benzoylindan-1-one. The crystals dissolved in sodium hydroxide solution and gave a dark green colour with ferric chloride. Thiele and Falk[14] give m. p. 98·5°; Robinson and Shah[15] give m. p. 104°.

Addition of Cyanoacetic ester to "p-*Dichalcone*."—(i) "*p*-Dichalcone" (1·0 g., 0·0029 mole) and ethyl cyanoacetate (0·67 g., 0·005 mole) in dry ethanol (50 ml.) were refluxed for 5 min., then diethylamine (1 ml.) was added. A clear yellow solution resulted after 5 min. and refluxing was continued for 45 min. Cooling in a freezing mixture gave a gum which was dissolved in methanol; evaporation gave a white *adduct*, m. p. 149—155°. Crystallisation from ethyl acetate gave a *hydrate* (0·27 g., 16%), m. p. 179—180° (Found: C, 71·7; H, 5·8; N, 5·3. $C_{34}H_{32}O_6,\frac{1}{4}H_2O$ requires C, 71·7; H, 5·7; N, 5·0%).

(ii) "*p*-Dichalcone" (1·7 g., 0·005 mole) and diethylamine (2 ml.) were shaken with ethyl

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[13] Kohler, *Amer. Chem. J.*, 1907, **37**, 385.

[14] Thiele and Falk, *Annalen*, 1906, **347**, 120.

[15] Robinson and Shah, *J.*, 1933, 610.

cyanoacetate (3·35 g., 0·025 mole) in dry ethanol (100 ml.) at room temperature for 24 hr. Crystallisation of the solid adduct from ethyl acetate gave white crystals (0·79 g., 28%), m. p. and mixed m. p. with product from (i) 179°.

Heterocyclic *analogues* were prepared by the methods described above and are listed in the Table.

Heterocyclic compounds.

Heterocyclic radical	Yield (%)	M. p.	Formula	Found (%)				Required (%)			
				C	H	N	S	C	H	N	S
1,1′-*Disubstituted* 3,3′-p-*phenylenedi*(*prop*-2-*en*-1-*ones*) (I)											
2-Furyl	51·0	230·5°	$C_{20}H_{14}O_4$	75·3	4·7	—	—	75·5	4·4	—	—
2-Thienyl	75·5	225—225·5	$C_{20}H_{14}O_2S_2,\frac{1}{4}H_2O$	67·4	3·8	—	16·6	67·8	4·1	—	18·1
2-Pyridyl	67·5	194 *	$C_{22}H_{16}N_2O_2,\frac{1}{2}H_2O$	75·8	4·9	8·8	—	75·7	5·1	8·0	—
4-Pyridyl	33·0	235—236 *	$C_{22}H_{16}N_2O_2,\frac{1}{4}H_2O$	76·4	5·2	—	—	76·6	4·8	—	—
1,1′-*Disubstituted* 3,3′-m-*phenylenedi*(*prop*-2-*en*-1-*ones*) (II)											
2-Furyl	57·0	164·5	$C_{20}H_{14}O_4$	75·2	4·7	—	—	75·5	4·4	—	—
2-Thienyl	80·0	197—198	$C_{20}H_{14}O_2S_2,\frac{1}{4}H_2O$	67·9	4·0	—	18·7	67·8	4·1	—	18·1
2-Pyridyl	58·0	180—180·5	$C_{22}H_{16}N_2O_2$	77·3	4·7	8·1	—	77·6	4·7	8·2	—
4,4′-*Disubstituted diethyl* 6,6′-p-*phenylenedi*-(2-*oxocyclohex*-3-*enecarboxylates*) (III)											
2-Thienyl	49·4	212—214	$C_{32}H_{32}O_6S_2$	—	—	—	9·6	—	—	—	9·5
2-Furyl	98·7	227—228	$C_{32}H_{32}O_8$	70·1	6·1	—	—	70·5	5·9	—	—
2-Pyridyl	27·6	199—203 *	$C_{34}H_{30}N_2O_6$	72·2	5·8	4·6	—	72·5	5·8	4·8	—
3,3′-*Disubstituted* 5,5′-p-*phenylenedi*(*cyclohex*-2-*enones*) (IV)											
2-Thienyl	—	270—272 *	$C_{26}H_{22}O_2S_2,2H_2O$	—	—	—	13·8	—	—	—	13·8
2-Furyl	—	281—282 *	$C_{26}H_{22}O_4,\frac{1}{2}H_2O$	76·7	5·8	—	—	76·7	5·7	—	—

* With decomp.

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