198. *Chalcones and Related Compounds. Part III.* Addition of Benzene Analogues to the Chalcone System.*

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Addition of benzene to chalcone itself is well known, and the general method has also been used as a route to substituted ββ-diphenylpropiophenones. In the present work, adduct formation was by no means complete, and evidence is put forward for the isomerisation of the chalcones under these conditions.

ββ-DIPHENYLPROPIOPHENONE is readily prepared by addition of benzene to chalcone in the presence of aluminium chloride.[1] Substituents in a benzene nucleus are *generally* in the *para*-position in the corresponding adducts,[2,3] but, in view of possible uncertainty, substituted ββ-diphenylpropiophenones have been usually prepared from chalcones by other routes, particularly by way of the Grignard reaction[4,5] or other organometallic compound.[5,6] Such approaches have their limitations, particularly in preparing the nitro-compounds.

The optimum proportion of aluminium chloride was found experimentally to lie between two and three moles per mole of chalcone, in general agreement with the findings of Dippy and Palluel.[2] The presence of dry hydrogen chloride had no apparent effect, nor did the

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* Part II, preceding paper.

[1] *Org. Synth.*, Coll. Vol. II, p. 236.

[2] Dippy and Palluel, *J.*, 1951, 1415.

[3] Dippy and Young, *J.*, 1952, 1817.

[4] Kohler, *Amer. Chem. J.*, 1904, **31**, 642; 1907, **38**, 511.

[5] Cilman and Kirby, *J. Amer. Chem. Soc.*, 1941, **63**, 2046.

[6] Wittig and Bub, *Annalen*, 1950, **566**, 113.

rate or order of adding the components (cf. Perrier [7]). Increase in temperature led only to tar formation.

Results for the reaction of certain halogeno- and nitro-chalcones with typical benzenoid compounds are summarised in the accompanying Tables. The recovered products were found to consist, in general, of up to four components, as follows: (A) The expected adduct, in yields up to 36%; (B) unchanged chalcone, generally 60—70% (nitrochalcones); (C) the fraction of lowest m. p., in yields of up to 16% from the mother-liquors; (D) small yields (up to 3%) of ash-free material of high m. p. (255—285°).

EXPERIMENTAL

General Method (cf. ref. 1).—The chalcone (5 g.) was dissolved in the benzene analogue (150 ml.) and added to a mixture of aluminium chloride (6—8 g.) and further solvent (100 ml.). (In the reaction between 3-nitrochalcone and benzene, 350 ml. of the latter were required in all.) The mixture was then stirred at 20° until the components were virtually all in solution and then for a further hour. The mixture was filtered, the aluminium chloride addition compounds were decomposed in the usual way, and the solvent was evaporated slowly. The mother-liquors were finally steam-distilled and any residue was examined. Species of indefinite m. p. were further fractionated from alcohol.

Small amounts of material insoluble in the final reaction mixture generally consisted of unchanged chalcone. The insoluble fraction from the reaction between 4-nitrochalcone and chlorobenzene, however, contained 2·0% of chlorine. This was probably due only to strong adsorption of chlorobenzene since the chlorine content fell on washing with alcohol. The m. p. of this fraction was 160° (not sharp), unchanged on admixture with the original 4-nitrochalcone (m. p. 164°).

DISCUSSION

The yields of adduct, though low, are of the same order as those obtained by Dippy and Palluel,[2] and it seems that, with these particular chalcones and under these comparatively mild conditions, the reversible nature of the addition [8] has resulted in equilibrium at a fairly low concentration of adduct. Hence fractions A and B represent the relative proportions in the equilibrium mixture.

TABLE 1. *Products isolated from the reaction mixtures.*

		M. p. of fraction				Yield (%) of fraction			
Chalcone	Additive	A	B	C	D	A	B	C	D
3-NO_2	PhOMe	178°	146°	124°	280°	22	64	12	2
,,	C_6H_6	190	144	120	285	22	67	8	3
,,	PhCl	200	145	—	—	32	68	0	0
,,	PhMe	180	144	123	255	18	68	12	2
4-NO_2	PhCl	190	161	130	—	20	64	16	0
2′-NO_2	,,	—	124	107	—	0	99	1	0
3′-NO_2	,,	150	129	—	—	36	64	0	0
4′-Br	PhOMe	—	104	96	—	0	95	5	0
4′-I	PhMe	—	115	98	—	0	95	5	0

Material obtained as fraction C had the same analytical figures as the original chalcones but melting points were somewhat lower. The existence of more than one form has previously been reported for chalcone itself [9] and for certain nitro- and halogeno-chalcones.[10] Of the compounds now considered, Weygand and Schacher [11] had reported

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[7] Perrier, *Ber.*, 1900, **33**, 815.

[8] Eaton, Black, and Fuson, *J. Amer. Chem. Soc.*, 1934, **56**, 687.

[9] Le Fèvre, *J.*, 1937, 1037.

[10] Davey and Gwilt, Part I, *J.*, 1957, 1008.

[11] Weygand and Schacher, *Ber.*, 1923, **56**, 1144.

m. p.s of 120°, 145°, and 146° for 3-nitrochalcone and 150° and 163·5° for 4-nitrochalcone, and Brandstätter[12] reported 105°, 101°, and 97° for different forms of 4'-bromochalcone. In the latter instance, the stable form was cooled under controlled conditions, *i.e.*, truly polymorphic forms were obtained.

TABLE 2. *Analyses of adducts and isomers.*

		Adduct (A)			Isomer (C)		
Chalcone	Additive	Found N (%)	Formula	Reqd. N (%)	Found N (%)	Formula	Reqd. N (%)
3-NO_2	PhOMe	3·8	$C_{22}H_{19}O_4N$	3·9	5·5	$C_{15}H_{11}O_3N$	5·5
,,	C_6H_6	4·2	$C_{21}H_{17}O_3N$	4·2	5·4	,,	5·5
,,	PhCl	3·6	$C_{21}H_{16}O_3NCl$ [a]	3·8	—	—	—
,,	PhMe	4·0	$C_{22}H_{19}O_3N$	4·1	5·5	,,	5·5
4-NO_2	PhCl	3·6	$C_{21}H_{16}O_3NCl$ [b]	3·8	5·4	,,	5·5
2'-NO_2	,,	—	—	—	Trace	—	—
3'-NO_2	,,	3·8	,,	3·8	—	—	—
4'-Br	PhOMe	—	—	—	27·6 [d]	$C_{15}H_{11}OBr$	27·9 [d]
4'-I	PhMe	—	—	—	38·9 [d]	$C_{15}H_{11}OI$	38·0 [d]

[a] Found: Cl, 9·6%. [b] Found: Cl, 9·5%. [c] Found: Cl, 9·5% (Reqd. in all cases: Cl, 9·7%). [d] Halogen.

Price and Meister[13] suggest that the following four types of reaction are generally catalysed by the same compounds: (*a*) Friedel–Crafts reactions, (*b*) polymerisation of olefins, (*c*) condensation of olefins with aromatic compounds, and (*d*) *cis–trans*-isomerisation of olefins. They therefore consider that the same active intermediate is common to each of these reactions. It therefore seemed probable that isomerisation of the chalcones had occurred to some extent, and, coincidentally with the completion of our own experimental work, Dippy and his co-workers[14] reported the isomerisation of similar compounds under similar conditions.

In view of these and other more general observations (see, *e.g.*, ref. 15) it therefore appears that the material comprising fraction C (when present) is the *cis*-form of the chalcone while fraction B is the normal (*trans*-)form.

The materials in fraction D (from 3-nitrochalcone only) were insufficient for full analysis. Wittig and his co-workers[16] reported the dimerisation of chalcone. They also showed that further addition may occur between chalcone and certain adducts, and it seems likely that these high-melting compounds are of this type.

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[12] Brandstätter, *Monatsh.*, 1949, **80**, 1.
[13] Price and Meister, *J. Amer. Chem. Soc.*, 1939, **61**, 1595.
[14] Dippy, McGhie, and Young, *Chem. and Ind.*, 1952, 195.
[15] Kipping and Kipping, "Perkin and Kipping's Organic Chemistry," Chambers, London, 1939, p. 640.
[16] Wittig, Meyer, and Lange, *Annalen*, 1951, **571**, 167.