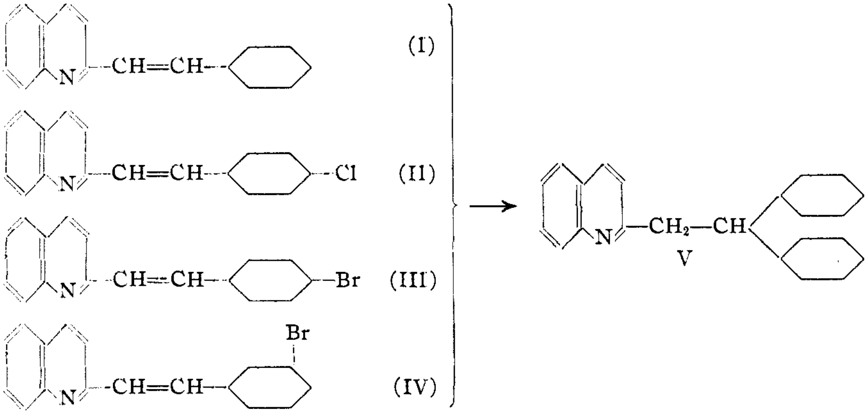
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reversible Addition of Aromatic Compounds to Conjugated Systems

BY REYNOLD C. FUSON, A. P. KOZACIK AND J. T. EATON

In a study of ring–chain conjugation in the quinoline series[1] it has recently been shown that benzalquinaldine (I) reacts with benzene in the presence of aluminum chloride to give α-benzohydrylquinaldine (V). This condensation is analogous to the addition under similar conditions of aromatic hydrocarbons to α,β-unsaturated carbonyl compounds—a reaction which has been observed by a number of investigators.[2]



However, with *p*-chlorobenzalquinaldine the reaction appeared to take a different course, for the product was not the expected α-(*p*-chlorobenzohydryl)-quinaldine but the chlorine-free α-benzohydrylquinaldine (V). This anomalous result has been subsequently investigated and the results are being reported in the present paper.

An early suggestion was that the removal of the chlorine might be due to the action of aluminum chloride alone; experiment showed, however, that *p*-chlorobenzalquinaldine was unaffected by long contact with aluminum chloride.

That the nature of the halogen atom or its position on the benzene ring might have a bearing on the result was also considered. It was found, however, that both *p*-bromobenzalquinaldine (III) and its meta isomer (IV) reacted smoothly to give α-benzohydrylquinaldine (V).

It now became apparent that the reaction involved not merely the

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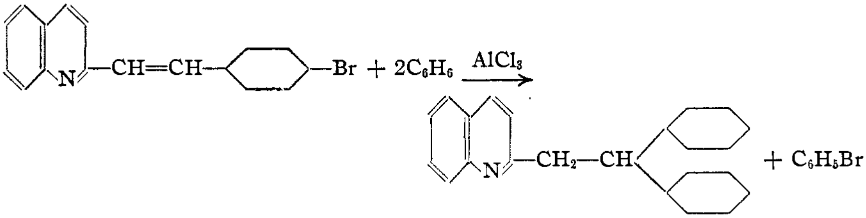
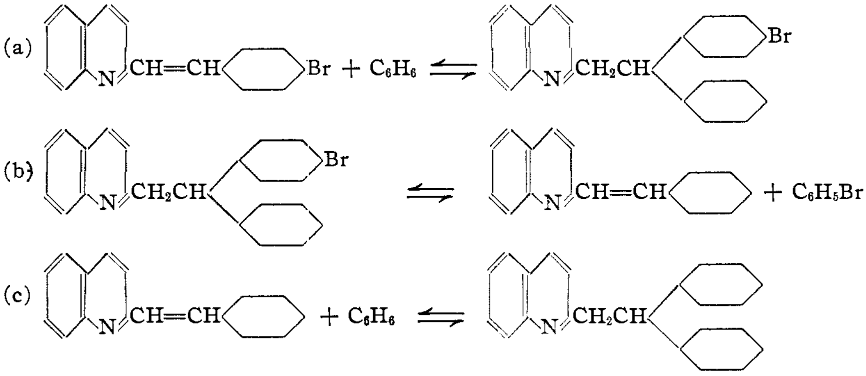
(1) Hoffman, Farlow and Fuson, THIS JOURNAL, **55**, 2000 (1933).

(2) (a) Eijkman, *Chem. Weekblad*, **4**, 727 (1907); **5**, 662 (1908); (b) Kohler, *Am. Chem. J.*, **42**, 375 (1909); Kohler, Heritage and Burnley, *ibid.*, **44**, 60 (1910); (c) Pummerer and Prell, *Ber.*, **55B**, 3105 (1922); Pummerer and Fiedler, *ibid.*, **60B**, 1439 (1927); Pummerer and Huppmann, *ibid.*, **60B**, 1445 (1927); (d) Vorländer and Friedberg, *Ber.*, **56B**, 1144 (1923); (e) Browning and Adams, THIS JOURNAL, **52**, 4098 (1930); Shildneck and Adams, *ibid.*, **53**, 343 (1931); (f) Rice, *ibid.*, **53**, 3153 (1931).

replacement of the halogen atom but that of the entire halophenyl radical. Experiments with *p*-bromobenzalquinaldine confirmed this deduction; it was found that *bromobenzene was produced in the reaction.* The reaction therefore is to be represented by the equation

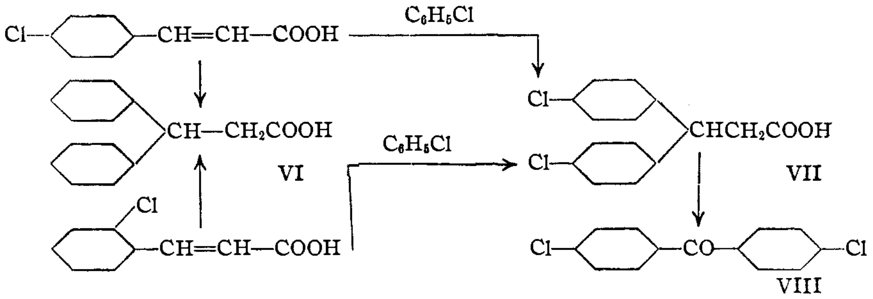


A possible explanation of these results is that the condensation is *reversible.* The reaction could then be resolved into the following three phases.



In a search for further evidence for the proposed mechanism it was found that the quinaldine derivatives were frequently difficult to handle, and efforts were made to determine whether the reaction was general for systems of the α,β-unsaturated carbonyl type. Nuclear halogen derivatives of cinnamic acid were found to behave in a manner entirely analogous to that observed with the halobenzalquinaldines and, consequently, subsequent studies have been carried out with the simpler system.

The Addition of Benzene and Chlorobenzene to *o*- and *p*-Chlorocinnamic Acids.—In the work with the chlorocinnamic acids it was first shown that both the *ortho* and the *para* chloro derivatives reacted with benzene in the presence of aluminum chloride to yield β,β-diphenylpropionic acid (VI). A crucial test of the theory was afforded by the addition of chlorobenzene to the two chlorocinnamic acids. It was found *that the addition products in the two cases were identical.* The product was β,β-di-(*p*-chlorophenyl)-propionic acid (VII). The positions of the chlorine atoms were established by degradation of the acid to the known p,p'-dichlorobenzophenone (VIII).



The mechanism suggested provides a satisfactory explanation of the result. Obviously, in the case of the *o*-chlorocinnamic acid the primary addition product is β-(*p*-chlorophenyl)-β-(*o*-chlorophenyl)-propionic acid, from which the *o*-chlorophenyl group is eliminated as chlorobenzene; the latter then condenses with the *p*-chlorocinnamic acid simultaneously produced. When chlorobenzene adds to the unsaturated acid, however, it reacts preferentially at the *para* position. It is evident that all of the facts obtained thus far are in agreement with the predictions based on the theory that the condensation is reversible.

Similar results have been obtained in work with α,β-unsaturated ketones. These will be reported separately but it may be said here that the later results furnish even more striking evidence in favor of the theory that the condensation takes place reversibly.

Experimental

***p*-Chlorobenzalquinaldine.**—The treatment of *p*-chlorobenzalquinaldine with aluminum chloride and benzene described in the preceding paper[1] was repeated except that the benzene was replaced by carbon disulfide and no hydrogen chloride was introduced. The yellow addition compound formed immediately but no further reaction took place; at the end of twelve hours the original base was recovered.

***m*-Bromobenzalquinaldine.**—This compound was prepared from *m*-bromobenzaldehyde and quinaldine by a procedure similar to that already described for the *p*-chlorobenzalquinaldine.[1] After recrystallization from alcohol the crystals melted at 96°.

Anal. Calcd. for $C_{17}H_{12}NBr$: Br, 25.8. Found: Br, 25.5.

The dibromide melted at 185–186°.

Anal. Calcd. for $C_{17}H_{12}NBr_3$: Br, 51.1. Found: Br, 51.3.

The action of benzene, aluminum chloride and hydrogen chloride on *m*-bromobenzalquinaldine was tested in the manner described for *p*-chlorobenzalquinaldine.[1] Here also the product was α-benzohydrylquinaldine.

***p*-Bromobenzalquinaldine.**—This base, prepared by the method already described for *p*-chlorobenzalquinaldine, melted at 137–138°.

Anal. Calcd. for $C_{17}H_{12}NBr$: Br, 25.8. Found: Br, 26.1.

The dibromide melted at 194–195°.

Anal. Calcd. for $C_{17}H_{12}NBr_3$: Br, 51.1. Found: Br, 51.3.

The action of benzene, aluminum chloride and hydrogen chloride on *p*-bromobenzalquinaldine gave α-benzohydrylquinaldine.

The excess benzene was washed with dilute acid, then with dilute carbonate solution and finally with water. The greater part of the benzene was distilled; the residue contained halogen and gave a refractive index (n^{20}_{D} 1.5145) somewhat higher than that of pure benzene (n^{20}_{D} 1.5010). Calculations based on the refractive index indicated that the residual liquid contained about 3 g. of bromobenzene, or 60% of the theoretical amount. This residual liquid (15 cc.) was placed in the usual Grignard apparatus and was treated with 0.5 g. of magnesium and 100 cc. of dry ether. When most of the magnesium had dissolved, 0.5 g. of phenyl isocyanate was added in small portions. There was a vigorous reaction. The mixture was heated under reflux for two hours after the addition was complete and then poured upon a mixture of 50 cc. of concentrated hydrochloric acid and 200 g. of ice. The solid which remained when the ether and benzene were evaporated was recrystallized from alcohol; colorless leaflets, melting at 160°. A mixture of these crystals with a sample of benzanilide also melted at 160°. The yield of benzanilide was 20% of the theoretical amount.

p-**Chlorocinnamic Acid.**—This acid was prepared by the Perkin method, using potassium acetate in place of sodium acetate.[3] The yield was 66% of the theoretical amount; melting point, 246–247° (uncorr.).[4]

The action of benzene and aluminum chloride[5] on *p*-chlorocinnamic acid resulted in the formation of β,β-diphenylpropionic acid. To an ice-cold mixture of 20 g. of *p*-chlorocinnamic acid and 75 cc. of dry benzene was added 24 g. of pulverized anhydrous aluminum chloride. The flask containing the reaction mixture was kept in an ice-bath during the addition and was shaken frequently. When the evolution of hydrogen chloride had moderated the ice-bath was replaced by a water-bath maintained at a temperature of 35–40°. The shaking was continued and after an hour the mixture was decomposed by the addition of a mixture of 75 g. of ice, 75 g. of water and 24 g. of concentrated hydrochloric acid. The excess benzene was then removed by steam distillation and the product was extracted with ether. The solution was dried, the ether was distilled and the product was recrystallized from benzene. The β,β-diphenylpropionic acid melted at 153–154°. Eijkman[2a] gives the melting point as 154–155°.[6]

The action of chlorobenzene, aluminum chloride and hydrogen chloride was tested in the manner just described. In this case, however, the steam distillation was omitted and the product was separated from excess chlorobenzene by extraction with a solution of dilute alkali. The alkaline solution was then acidified and extracted with ether. Evaporation of the ether left the product as a viscous residue; recrystallization from alcohol gave crystals of β,β-di-(*p*-chlorophenyl)-propionic acid melting at 188–189°.

Anal. Calcd. for $C_{15}H_{12}O_2Cl_2$: Cl, 24.0. Found: Cl, 24.3.

o-**Chlorocinnamic Acid.**—This acid was prepared by the method of Lasch,[3,7] yield, 73% of the theoretical amount.

The action of benzene and aluminum chloride was determined by use of the procedure already outlined for the preparation of β,β-diphenylpropionic acid from *p*-chlorocinnamic acid. The product was identical with that obtained in the experiment with the para isomer.

The action of chlorobenzene, aluminum chloride and hydrogen chloride, as in the case of *p*-chlorocinnamic acid, gave an acid which melts at 188–189° and which was shown by the mixed melting point method to be β,β-di-(*p*-chlorophenyl)-propionic acid.

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(3) This is an adaptation of the method used by Lasch [*Monatsh.*, **34,** 1653 (1913)] in the preparation of the ortho compound.

(4) Reich, Araus, Potok and Tempel [*Helv. Chim. Acta*, **3,** 793 (1920)], who made the acid by a similar procedure, give the melting point as 245°.

(5) In this case the introduction of hydrogen chloride was not necessary.

(6) See also Henderson, *J. Chem. Soc.*, **59,** 734 (1891).

(7) A similar method was used by Stoermer, *Ber.*, **44,** 637 (1911).

Oxidation.—A 1-g. sample of β,β-di-(*p*-chlorophenyl)-propionic acid was oxidized by heating it for six hours with a solution of 4 g. of potassium permanganate in 80 cc. of water. The alkali-insoluble product was crystallized from alcohol; melting point, 144–145°. This is the melting point given by Dittrich[8] for *p*,*p*'-dichlorobenzophenone.

Summary

It has been shown that in the presence of aluminum chloride and hydrogen chloride benzene adds to halobenzalquinaldines and to chlorocinnamic acids. In all of these cases the halophenyl group is replaced by an unsubstituted phenyl group, giving a benzohydryl derivative in place of the halobenzohydryl derivative which was to be expected.

In the case of *p*-bromobenzalquinaldine it has been shown that bromobenzene is a product of the reaction.

Chlorobenzene adds to *o*- and *p*-chlorocinnamic acids in the presence of aluminum chloride to give, in both instances, β,β-di-(*p*-chlorophenyl)-propionic acid.

It has been suggested that the condensation of aromatic compounds with α,β-unsaturated carbonyl compounds and similarly constituted systems is a reversible process. An interpretation of the results, based on this assumption, has been given.

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(8) Dittrich, *Ann.*, **264**, 175 (1891). See also Norris and Green, *Am. Chem. J.*, **26**, 496 (1901).

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Preparation of Tetramethylmethane (Neopentane) and Determination of its Physical Constants[1]

BY FRANK C. WHITMORE AND GEO. H. FLEMING[2]

Tetramethylmethane has been prepared by relatively few workers and only its boiling point and freezing point have been reported. Because of the importance of the neopentyl system in rearrangements[3] the preparation and properties of the parent hydrocarbons have been studied.

This hydrocarbon has been obtained from petroleum,[4] also synthesized by the reaction of dimethylzinc with *tert*-butyl halides,[5] dimethyl sulfate with *tert*-butyl Grignard,[6] Grignards with halides,[7] and the hydrogenation of trimethylethylene in a silent electric discharge.[8] This formation is most interesting from the point of view of the current theory of rearrangements.[3]

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(1) THIS JOURNAL, **54**, 3460 (1932).

(2) Presented in partial fulfilment of the requirements for the Ph.D. degree.

(3) Whitmore and co-workers, THIS JOURNAL, **54**, 3279, 3431 (1932); **55**, 1106, 1528 (1933).

(4) Markownikoff, *Ber.*, **32**, 1449 (1899); Poni, *Ann. Sci. Univ. Jassy*, **1**, 205 (1901).

(5) Lwow, *Z. Chem.*, 520 (1870); dimethylzinc with 2,2-dichloropropane, *ibid.*, 257 (1871).

(6) Ferrario and Fagetti, *Gazz. chim. ital.*, **38**, [II], 630–634 (1908).

(7) Späth, *Monatsh.*, **34**, 1965–2014 (1913).

(8) Meneghini and Sargato, *Gazz. chim. ital.*, **62**, 621 (1932).