The reaction was carried out by heating 5.0 g. (0.03 mole) of the carbinol with 22.0 g. (0.15 mole) of crude triethylammonium formate in a distilling flask which was equipped with a receiver and water-cooled condenser. The heating was carried out at a temperature of 120–125° for two hours; then it was raised to 130–135° and allowed to run overnight. During the heating period droplets of oil could be observed throughout the reaction mixture and the odor of triethylamine could be detected. A few drops of oil and water collected on the receiver.

On cooling and rinsing the entire apparatus with water into a beaker, a gummy mass separated. This mixture was extracted with ether, evaporated to dryness and stirred thoroughly with three small portions of low-boiling petroleum ether. This solution was again evaporated to dryness and the residue steam distilled. From the distillate a small amount of oil was obtained by extraction with ether and evaporation of the excess solvent. It was characterized by warming with excess methyl iodide and recrystallizing the yellow quaternary salt formed from a mixture of alcohol and ether. After three recrystallizations 0.6 g. (6%) of a very faintly yellow material was obtained, m. p. 219–220° (dec.).[10] A mixed melting point of this material showed no depression with the methiodide of a sample of *p*-dimethylaminoethylbenzene prepared by the high pressure reduction of *p*-dimethylaminophenylmethylcarbinol over Raney nickel.[11]

Reduction of Benzalaniline with Triethylammonium Formate.—Benzalaniline (5.0 g., 0.0276 mole) and triethylammonium formate (13.0 g., 0.0884 mole) were heated with a small flame until the temperature of the reaction mixture reached about 140°. At this point a mild exothermic reaction took place; triethylamine was evolved and the reaction proceeded without further heating. In a very short time the reaction subsided and heating was continued at 140–160° for two hours.

After cooling the reaction mixture was poured into water, an oil separated, and the aqueous layer extracted with two small portions of benzene. The oil and the benzene extracts were then combined and heated with 10 ml. of concentrated hydrochloric acid in such a way that the benzene was allowed to evaporate. The residual oil was hydrolyzed in about ten minutes and the resulting solution was completely homogeneous. On cooling, the hydrolysis mixture completely solidified. It was broken up with a spatula, sucked as dry as possible on a Büchner funnel and rinsed with ice water and ether. After drying thoroughly, 6.9 g. (97.5%) of benzylaniline hydrochloride, m. p. 214–215°[12] was obtained. A second recrystallization from water did not improve the melting point. On regeneration with alkali, the free amine gave a benzamide, m. p. 107–108°, and a benzenesulfonamide, m. p. 118–119°.[13]

Summary

At 120–130° in diethylene glycol solution, acetophenone has been found to undergo the Leuckart reaction with ammonium formate but not with formamide. This indicates that at this temperature ammonium formate and not formamide is the essential reactant for the transformation.

Benzalaniline and *p*-dimethylaminophenylmethylcarbinol were reduced to N-benzylaniline (97%) and *p*-dimethylaminoethylbenzene (6%) by heating with triethylammonium formate at temperatures ranging from 130 to 160°. These compounds are analogous to the intermediates which were postulated by Wallach and by Crossley and Moore for the Leuckart reaction.

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[10] Davies and Hulbert, *J. Soc. Chem. Ind.*, **57**, 349 (1938).

[11] The decomposition point of a quaternary salt depends somewhat upon the rate of heating. For the mixed melting point, therefore, samples of the material prepared in each way were included in the heating bath to serve as controls.

[12] Brand, *Ber.*, **42**, 3462 (1909).

[13] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 195.

URBANA, ILLINOIS RECEIVED AUGUST 2, 1947

[CONTRIBUTION FROM THE GROSVENOR LABORATORY]

Preparation of Acetonechloroform and its Homologs

BY CH. WEIZMANN, E. BERGMANN AND M. SULZBACHER

For an investigation which is reported in the preceding paper, acetonechloroform ((trichloromethyl)-dimethylcarbinol) was needed in considerable quantities. Fishburn and Watson[1] concluded from a systematic investigation that the best method for its preparation was the condensation of acetone and chloroform by means of potassium hydroxide in excess acetone as solvent, and reported a yield of 25% under these conditions. Sodamide in anhydrous ether gives a yield of about 75%[2] but it has to be used in 50% excess and under strictly anhydrous conditions.

It has now been found that chloroform will condense with acetone and certain other ketones (see Experimental Part) in solutions of acetals containing potassium hydroxide to yield trichloromethyl carbinols. The yields are quite satisfactory, although some of the chloroform and/or the trichloromethyl carbinol formed reacts with the alkali to give potassium chloride, a side reaction which is the more pronounced the higher the water content of the potassium hydroxide used. The extent to which this side reaction occurs can be further reduced if one does not allow the reaction to go quite to the end.

The reaction can be extended to aldehydes, but only to those which are branched in α-position to the carbonyl group such as 2-ethylhexanal and isobutyraldehyde; straight-chain aldehydes undergo self-condensation more readily than condensation with chloroform. Benzaldehyde condenses with chloroform,[3] benzophenone does not.

While chloroform and bromoform condensed with the carbonyl compounds specified, methylene chloride failed to react at all, and 1,1,1,2,2,3,3-heptachloropropane was simply dehydrohalogenated to hexachloropropylene, even at low tem-

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[1] Fishburn and Watson, *J. Am. Pharm. Assoc.*, **28**, 491 (1939); see Taffe, *Chem. Zentr.*, **95**, II, 304 (1924).

[2] Schwyzer, "Fabrikation pharmazeutischer und chemisch-technischer Produkte," Berlin, 1931, p. 112.

[3] Rapson and co-workers, *J. Chem. Soc.*, **74** (1944).

TABLE I

Carbonyl compound	Solvent	T,[a] °C.	Carb. cpd. rec., %	% Chloroform		Product	Yield,[b] %	Characteristics B. p., °C. (mm.)
				Rec.	Dec.			
Acetone[c]	Acetal	−1	..	26	13	Acetone-chloroform	80	.....
Acetone[c]	Acetal	−1	..	20	16	Acetone-chloroform	77	.....
Methyl ethyl ketone	Methylal	−5	..	23	24	T[d]-Methylmethylethylcarbinol	67	98–99 (29)[e]
Methyl ethyl ketone	Methylal[f]	−5	..	33	8	T[d]-Methylmethylethylcarbinol	85	.....
Methyl ethyl ketone	Acetal[f]	−5	20	36	7	T[d]-Methylmethylethylcarbinol	89	.....
Cyclohexanone	Methylal	−5	53	20	28	1-T-Methylcyclohexanol	64	120–123[e] (20)[g]
Cyclohexanone	Acetal	−5	51	37	10	1-T-Methylcyclohexanol	85	.....
Acetophenone	Methylal	−5	83	67	16	T-Methylphenylmethylcarbinol	41	[e,h]
Methyl isobutyl ketone	Methylal	−5	90	79	11	1,1,1-T-2,4-Dimethyl-2-pentanol	89	98–100 (22)
2-Ethylhexanal[i]	Methylal	−3	43	34	12	1,1,1-T-3-Ethyl-2-heptanol	82	135–140 (16)[j]
Isobutyraldehyde	Methylal	−4	..	..	..	1,1,1-T-3-Methyl-2-butanol	13	125–130 (760)[k,l]

[a] Temperature of the reaction. [b] Calculated on chloroform entered into reaction. [c] Double quantities used here. [d] T = trichloro-. [e] This condensation has been achieved by means of sodamide by *Chem. Fabrik. Wiernik*, German Patent 515,539 (1931). For the condensation of methyl ethyl ketone and chloroform by means of potassium hydroxide, see the unsuccessful attempts by Ekeley and Klemme, THIS JOURNAL, **46**, 1252 (1924). [f] 51 g. of freshly molten, pure potassium hydroxide. [g] M. p. 50–52°. [h] Colorless oil; *Anal.* Calcd. for $C_9H_9OCl_3$: C, 45.0; H, 3.8; Cl, 44.6 Found: C, 44.7; H, 4.0; Cl, 44.6. [i] B. p. 80° (16 mm.). [j] *Anal.* Calcd. for $C_9H_{17}OCl_3$: C, 43.6; H, 6.9; Cl, 43.0. Found: C, 43.9; H, 7.0; Cl, 42.8. [k] This substance was prepared by Howard, THIS JOURNAL, **49**, 1068 (1927), from chloral and isopropylmagnesium bromide; b. p. 105° (674 mm.). See also Jozicz, *Chem. Zentr.*, **68**, I, 1013 (1897). [l] Considerable quantities (40 g.) of relatively high boiling range (170–230°) were formed.

perature. It had been chosen for these experiments as it contains, according to Rebek and Mandrino, a mobile hydrogen atom.[4]

Experimental

Acetone and Chloroform. (a) **In Methylal** (Formaldehydedimethylacetal).—At −4°, 120 g. of powdered technical potassium hydroxide (102 g. KOH; 1.8 moles) was added to 500 cc. of dry methylal, with vigorous agitation. At about the same temperature (not higher than −1°), a mixture of 215 g. (1.8 moles) of chloroform and 116 g. (2.0 moles) of acetone was added in the course of two hours and the agitation continued for two hours. The pale yellow reaction product was then run into a mixture of crushed ice and dilute sulfuric acid, the top layer separated and the aqueous bottom layer extracted with methylal. Distillation removed the solvent and any unchanged chloroform. The residue, which crystallized at once, was steam-distilled; needles, melting at 91° (after drying). In two parallel experiments, 41.0 and 40.0 g. of chloroform (19.1 and 18.6% of the total quantity employed) were recovered and 175.0 and 177.0 g. of trichloromethyldimethylcarbinol were isolated, corresponding to 67.7 and 68.1% of the chloroform entered into reaction. Titration of the aqueous layer showed that 98 g. of potassium chloride had formed which accounts for 24.3% of the chloroform employed.

When the amount of potassium hydroxide was halved, 108.0 g. (50.2% of the initial) of chloroform was recovered and 130.0 g. of the chlorinated alcohol and 32 g. of potassium chloride were formed, amounting to 81.7 and 8.0%, respectively, of the chloroform entered into reaction. The yield was, therefore, better (the decomposition very much reduced), but the conversion was unsatisfactorily low. If on the other hand the amount of potassium hydroxide was doubled, only 24.0 g. (11.2% of the initial) of chloroform was recovered, but the yield of acetonechloroform was very much reduced.

As already pointed out, freshly molten potassium hydroxide gives considerably better results. In two parallel experiments, conducted as described above, but using 102 g. of freshly molten potassium hydroxide, 82.0 and 80.0 g. of chloroform (38.1 and 37.2% of the total) were recovered and 170.0 and 175.0 g. of acetonechloroform formed (86.0 and 87.2%, calculated on chloroform entered into reaction). Only 7.0 and 6.2% of the chloroform decomposed.

(b) **In Butyraldehydedibutylacetal.**—A suspension of 60 g. of potassium hydroxide flakes (51 g., 0.9 mole KOH) was heated in 300 cc. of butyraldehydedibutylacetal[5] (b. p. 218°; 100–103° (15 mm.)) at 150° until two liquid layers had formed. The mixture was then slowly cooled to −2° with violent agitation which produced a very fine suspension. At this temperature, a mixture of 107.5 g. (0.9 mole) of chloroform and 58 g. (1 mole) of acetone was added slowly, the agitation continued for two more hours, and the product poured into a mixture of cracked ice and dilute sulfuric acid; 32.5 g. (30.2% of the initial) of chloroform were recovered and 97.5 g. of acetonechloroform isolated. This corresponds to 87.5% of the chloroform consumed in the reaction.

All the other experiments are summarized in Table I. It refers to the reaction between 1 mole of carbonyl compound, 10.9 mole of chloroform and if not otherwise stated 60 g. of powdered potassium hydroxide of 85% KOH content.

Acetone and Bromoform.—A mixture of 227.5 g. of bromoform and 58 g. of acetone was slowly added to the suspension of 60 g. of potassium hydroxide (51 g. KOH) in 250 cc. of acetal at −2°. The reaction was extremely violent, and the temperature rose temporarily to +9°; 71.4% of the bromoform used was recovered, but only 10.5 g. of acetonebromoform (from petroleum ether, fine needles, m. p. 168–170°)[6] could be isolated, which corresponds to 13.1% of the bromoform consumed. The balance was decomposed to potassium bromide.

Summary

Good yields of acetonechloroform are obtained when the components are condensed by means of potassium hydroxide in acetals as solvent.

Methyl ethyl ketone, methyl isobutyl ketone, acetophenone, cyclohexanone and α-branched aldehydes (isobutyraldehyde, 2-ethylhexanal) condense with chloroform smoothly under the same

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[4] Rebek and Mandrino, *Chem. Zentr.*, **109**, II, 1204 (1938). See, however, *C. A.*, **33**, 1266 (1939).

[5] Adkins and co-workers, THIS JOURNAL, **55**, 299 (1933); **56**, 442 (1934).

[6] Aldrich, *ibid.*, **33**, 386 (1911).

conditions. Benzophenone does not react. Straight-chain aldehydes undergo self-condensation.

Acetone could not be condensed with methylene chloride or 1,1,1,2,2,3,3-heptachloropropane.

LONDON, S. W. 1, ENGLAND RECEIVED APRIL 29, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Orienting Effect of Negatively Substituted Vinyl Groups in Aromatic Substitution

BY F. G. BORDWELL AND KENNETH ROHDE[1]

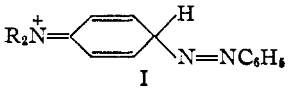
The orienting influence of groups on the course of aromatic substitution reactions was one of the first problems attacked in the development of the "English theory."[2] The directive properties of negatively substituted vinyl groups attracted attention during the early growth of the theory,[3,4] but groups of this nature have since been largely ignored in discussions and reviews. Baker and Wilson in their study of the nitration of ω-nitrostyrene found that the *p*- and *o*-isomers were formed almost exclusively. At that time they believed that the electron attracting effect of the nitro group was "damped out" by the electrons available in the olefinic bond, and that the substituted vinyl group was analogous to a methyl group in its directive properties. Since this early study, additional data concerning the orienting effect of substituted vinyl groups have become available, and the theory has also progressed.

The literature contains no mention of *m*-isomers from the nitration of such negatively substituted vinylbenzenes as α-methoxystyrene,[3] β-bromostyrene,[5] ω-nitrostyrene,[4] cinnamic acid,[6] α-chlorocinnamic acid,[7] α,β-dibromocinnamic acid[7] or 2-phenylethenesulfonyl chloride.[8,9] By careful analysis Baker and Wilson[4] found that the amount of *m*-isomer formed in the nitration of ω-nitrostyrene was less than 2%. Using a similar procedure, we have found that nitration in the *m*-positions of 2-phenylethenesulfonyl chloride also occurs to the extent of less than 2%. These data clearly illustrate the powerful *o*-*p*-directing effect of substituted vinyl groups.

In order to describe completely the orienting effect of a substituent on the course of aromatic substitution, it is necessary to know not only the positions taken by incoming groups under its direction, but also whether the substituent activates or deactivates the benzene nucleus. To determine the latter property for substituted vinyl groups, competitive nitration experiments were carried out by the method developed by Ingold, *et al.*[10] The competitive nitration of 2-phenylethenesulfonyl chloride and benzene was first studied, but the results obtained were not precise. Much better data were obtained from a study of the competitive nitration of cinnamic acid and benzene. The rates of nitration of 2-phenylethenesulfonyl chloride and of cinnamic acid were found to be appreciably lower than that of benzene, and of the same order as that of chlorobenzene. Negatively substituted vinyl groups, therefore, appear to belong with the halogen atoms in the class of strong *o*-*p*-directing groups which deactivate the benzene nucleus toward electrophilic substitution reactions.

Discussion

According to the most recent concepts of the role of orienting groups in aromatic substitution, the ability of a group to produce a more rapid reaction at *o*-*p*- than at *m*-positions is accounted for by assuming a resonance stabilization of the transition state for *o*-*p*- but not *m*-substitution.[11] Thus in the coupling of the benzenediazonium ion with dialkylaminobenzenes, Hughes and Ingold[11] attribute the *o*-*p*-directing influence of the dialkylamino groups to its ability to enhance the stability of the transition state by virtue of the contribution of structure I.



I

This concept of the role of orienting groups can be applied to all common *o*-*p*-directing groups, assuming a hyperconjugation effect for alkyl groups.[11] It is useful in explaining the fact that halogen atoms are strong *o*-*p*-directing groups despite their deactivating effect on the benzene nucleus. Al-

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[1] Abstracted from the M. S. thesis of Kenneth Rohde, August 1947.

[2] See, for example, Allan, Oxford, Robinson and Smith, *J. Chem. Soc.*, 401 (1926); Ingold and Ingold, *ibid.*, 1310 (1926); and subsequent papers by Robinson and Ingold and their collaborators.

[3] Ingold and Ingold, *J. Chem. Soc.*, **127**, 870 (1925).

[4] Baker and Wilson, *ibid.*, 842 (1926).

[5] Flürscheim, *J. prakt. Chem.*, **66**, 19 (1902).

[6] Müller, *Ann.*, **212**, 124 (1882); Underwood and Kochman, THIS JOURNAL, **48**, 254 (1926).

[7] Pfeiffer, *Ber.*, **47B**, 1755 (1914).

[8] Bordwell, Colbert and Alan, THIS JOURNAL, **68**, 1778 (1946).

[9] However, nitration of 1-phenyl-1-nitro-2-(*p*-nitrophenyl)-ethene gave 21% of the *meta* isomer,[4] and Moore and Tucker, THIS JOURNAL, **49**, 258 (1927), isolated about 17% of *m*-sulfocinnamic acid from the sulfonation of cinnamic acid.

[10] Bird and Ingold, *J. Chem. Soc.*, 918 (1938), and previous papers.

[11] (a) Hughes and Ingold, *ibid.*, 608 (1941); (b) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 470; (c) Wheland, THIS JOURNAL, **64**, 900 (1942); Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 256.