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

CONDENSATIONS OF CHLORAL AND BROMAL WITH PHENOLIC ETHERS IN THE PRESENCE OF ANHYDROUS ALUMINUM CHLORIDE

BY E. E. HARRIS[1] WITH G. B. FRANKFORTER

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The use of concd. sulfuric acid as an agent to bring about a condensation between an aldehyde and aromatic hydrocarbons is well known as the Baeyer reaction.[2] By this reaction formaldehyde, acetaldehyde and chloral were caused to react with benzene, phenyl bromide, mesitylene and phenol. Goldschmiedt[3] extended the reaction to include bromal, Weiler[4] included the acetals. The reaction is represented as follows.

$$RCHO + 2C_6H_6 \xrightarrow{H_2SO_4} RCH(C_6H_5)_2 + H_2O$$

Later the reactions of dichloro-acetaldehyde and chloro-acetal[5] were included in the above reactions

A number of other catalysts have been used to bring about this reaction including hydrochloric acid,[6] zinc chloride and aluminum chloride. Two early workers[7] found that the last mentioned substance acted as a Friedel-Crafts reagent when used with halogen-substituted aldehydes. Another worker[8] found that an aldol condensation took place. While studying this reaction of aluminum chloride, Frankforter and Kritchevsky[9] found that, at low temperatures, no halogen was substituted for and no aldol condensation took place but, instead, the condensation proceeded as the Baeyer reaction. This same reaction was found to take place between chloral and pinene,[10] trioxymethylene and benzene or its homologs,[11] and between butyl chloral with benzene or its homologs.[12] In the reactions using aluminum chloride, the products of the reaction were separated only with difficulty and very low yields were obtained.

In this communication is described the condensation of halogen-substituted aldehydes, alcoholates and acetals with aromatic hydrocarbons

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[1] This communication is an abstract of a thesis submitted by Elwin E. Harris in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Minnesota.

[2] Baeyer, *Ber.*, (a) **5**, 25, 200, (b) 1094 (1872); (c) **7**, 1180, (d) 1190 (1874).

[3] Goldschmiedt, *Ber.*, **6**, (a) 985, (b) 1504 (1873).

[4] Weiler, *Ber.*, **7**, 1181 (1874).

[5] Fritsch, *Ann.*, **279**, 319 (1894). Buttenberg, *Ann.*, **279**, 324 (1894).

[6] Baekeland and Bender, *Ind. Eng. Chem.*, **17**, 225 (1925).

[7] Combs, *Bull. soc. chim.*, **45**, 226 (1886). Blitz, *Ber.*, **26**, 1952 (1893).

[8] Dienesmann, *Compt. rend.*, **141**, 201 (1905).

[9] Frankforter and Kritchevsky, THIS JOURNAL, **36**, 1511 (1914).

[10] Frankforter and Poppe, paper read before the International Congress of Applied Chemistry, New York, **1912**.

[11] Frankforter and Kokatnur, THIS JOURNAL, **36**, 1529 (1914).

[12] Frankforter and Daniels, Doctor's *Dissertation* (unpublished).

and aromatic ethers in the presence of aluminum chloride. The plan of work corresponds to that of Kritchevsky, with an improvement of the method to obtain larger yields and purer products in less time and with fewer recrystallizations, an extension of the application of the reaction, and also the study of the properties of the condensation products.

The following condensations were studied: chloral with benzene, toluene, anisole, phenetole, cresol methyl ether, and *p*-cresol ethyl ether; bromal with the above aromatic compounds; dibromo-acetaldehyde with anisole, phenetole, *p*-cresol methyl ether, and *p*-cresol ethyl ether, bromo-acetal with anisole and phenetole; and chloral alcoholate with phenetole. Only a few condensations were run with the latter aldehydes but very likely other aromatic ethers would condense in an analogous manner.

By the action of alcoholic potassium hydroxide these halogen-substituted condensations were converted into ethylenic compounds by the loss of a molecule of halogen acid. This reaction was easily accomplished in the case of the benzene, toluene, anisole and phenetole condensation products but very difficultly in the case of the cresol ether compounds.

Heating in a sealed tube with sodium alcoholate converts the phenyltolyldichloro and dibromomethylene derived as indicated above into diphenyl- and ditolylacetic acid, respectively. Dianisyl and diphenetyl dihalogen ethylenes give the corresponding tolanes. Dianisyl- and diphenetylmonobromo-ethylenes give tolanes when heated with sodium alcoholate on the water-bath.

Attempts to hydrolyze the substituted trichloro-ethanes by heating with silver oxide resulted in the oxidation of the compound and the formation of the substituted benzoic acid.

When the trihalogen ethane compounds are heated for several hours with sodium powder in purified benzene, they are converted into the corresponding stilbenes. Dihalogen ethylene compounds give tolanes.

Oxidation of the substituted ethanes and ethylenes gave substituted benzophenones.

The following chart gives an outline of the reactions just mentioned.

$$2C_6H_6 + CHOCCl_3 \xrightarrow{AlCl_3} (C_6H_5)_2CH.CCl_3 \xrightarrow{KOH} (C_6H_5)_2C{=}CCl_2$$

$$(C_6H_5)_2CH.CCl_3 \xrightarrow[\text{Benzene}]{Na} C_6H_5CH{=}CHC_6H_5$$

$$(C_6H_5)_2C{=}CCl_2 \xrightarrow[\text{Benzene}]{Na} C_6H_5C{\equiv}CC_6H_5$$

$$(C_6H_5)_2C{=}CCl_2 \xrightarrow[180^\circ]{NaOC_2H_5} (C_6H_5)_2CHCOOH$$

$$(C_6H_5)_2C{=}CCl_2 \xrightarrow{AgOH} C_6H_5COOH$$

$$(C_6H_5)_2C{=}CCl_2 \xrightarrow[Cr_2O_3]{} (C_6H_5)_2C{=}O$$

In the case of substituted compounds the reactions are the same as indicated above except

$$(CH_3OC_6H_4)_2C{=}CCl_2 \xrightarrow[180°]{NaOC_2H_5} CH_3O.C_6H_4C{\equiv}CC_6H_4.OCH_3$$

Experimental Part

General Procedure for the Condensation of Substituted Aldehydes with Aromatic Hydrocarbons and Phenolic Ethers.—A 1-liter, three-necked, round-bottomed flask was equipped with a mercury-sealed mechanical stirrer through its central neck; one side neck was fitted with a reflux condenser and the third was stoppered. To the upper end of the

TABLE I

CONDENSATION OF SUBSTITUTED ALDEHYDES WITH PHENOLIC ETHERS

Ethane	Formula	M. p., °C.	Solvent for crystallization	Yield, %	Halogen, %	
					Calcd.	Found
Diphenyltrichloro[a]	$(C_6H_5)_2CHCCl_3$	64	Alcohol	80	37.26	37.27
Ditolyltrichloro[b]	$(CH_3C_6H_4)_2CHCCl_3$	89	Alcohol	80	33.86	33.9
Dianisyltrichloro[b,c]	$(CH_3OC_6H_4)_2CHCCl_3$	94	Alcohol-chloroform	94	30.84	30.71
Diphenetyltrichloro[d]	$(C_2H_5OC_6H_4)_2CHCCl_3$	105.5	Alcohol-chloroform	91	28.51	28.60
3,3-Dimethyl-6,6-dimethoxydiphenyltrichloro	$[CH_3(CH_3O)C_6H_3]_2CHCCl_3$	159	Chloroform	93	28.52	28.49 28.50
3,3-Dimethyl-6,6-diethoxydiphenyltrichloro	$[CH_3(C_2H_5O)C_6H_3]_2CHCCl_3$	128	Alcohol-chloroform	80	26.52	26.66
Diphenyltribromo[e]	$(C_6H_5)_2CHCBr_3$	76	Alcohol-ether	50	57.28	57.17
Ditolyltribromo	$(CH_3C_6H_4)_2CHCBr_3$	104	Alcohol-ether	85	53.7	53.8
Dianisyltribromo	$(CH_3OC_6H_4)_2CHCBr_3$	115	Alcohol-ether	90	50.1	50.2
Diphenetyltribromo[f]	$(C_2H_5OC_6H_4)_2CHCBr_3$	118	Alcohol-ether	85	47.33	47.8
3,3-Dimethyl-6,6-dimethoxydiphenyltribromo	$[CH_3(CH_3O)C_6H_3]_2CHCBr_3$	192	Alcohol-chloroform	75	47.34	47.4
3,3-Dimethyl-6,6-diethoxydiphenyltribromo	$[CH_3(C_2H_5O)C_6H_3]_2CHCBr_3$	171	Alcohol-chloroform	75	44.86	44.98
Dianisyldibromo[g]	$(CH_3OC_6H_4)_2CHCHBr_2$	122	Ether	80	40.00	40.09
Diphenetyldibromo	$(C_2H_5OC_6H_4)_2CHCHBr_2$	104	Ether	70	37.4	37.5
3,3-Dimethyl-6,6-dimethoxydiphenyldibromo	$[CH_3(CH_3O)C_6H_3]_2CHCHBr_2$	152	Alcohol-chloroform	90	37.4	37.39
3,3-Dimethyl-6,6-diethoxydiphenyldibromo	$[CH_3(C_2H_5O)C_6H_3]_2CHCHBr_2$	131	Alcohol	70	35.08	35.10
Dianisylbromo[h,i,j]	$(CH_3OC_6H_4)_2CHCH_2Br$	(Oil)		50	25.29	25.06
Diphenetylbromo	$(C_2H_5OC_6H_4)_2CHCH_2Br$	(Oil)		50	22.92	23.36

[a] Ref. 2 b, p. 1098.

[b] Ref. 2 d.

[c] "Studies in Physical Science and Mathematics," University of Minnesota, February, **1914**.

[d] Fritsch and Feldmann, *Ann.*, **306,** 72 (1899).

[e] Goldschmiedt found his sample to melt at 89° (Ref. 3 a, p. 990).

[f] Ref. 9, p. 1524.

[g] Prepared according to Mylo [*Ber.*, **45,** 647 (1912)].

[h] Weiler found that acetals could be used in the Baeyer reaction (Ref. 4).

[i] Bromo-acetal was prepared according to Fischer and Landsteiner [*Ber.*, **25,** 2551 (1892)].

[j] Corresponding experiments were performed with chloro-acetal in the Baeyer reaction [Hepp, *Ber.*, **6,** 1439 (1873)].

condenser was attached a drying tube with a tube leading into a flask of water to catch the hydrogen chloride evolved; this tube should not touch the water. Two equivalents of the hydrocarbon[13] or the phenol ether was dissolved in about ten times its weight of purified carbon disulfide[14] and the solution cooled in a freezing mixture of ice and calcium chloride until the temperature was 0° or below; then 1.2 equivalents of the aldehyde, acetal or alcoholate was added. While stirring was continued, anhydrous aluminum chloride (0.1 to 0.2 equivalent) was added in small portions to the cooled solution through the stoppered opening. About three hours was required for the addition of the chloride. During the reaction the color changes to a dark green or purple. After all of the chloride has been added, the stirring is continued for one-half hour to one hour. Then, while the mixture was stirred, chipped ice was added until the color of the condensate had been destroyed, at which time hydrolysis was considered complete. A few cubic centimeters of dil. hydrochloric acid was added to dissolve any colloidal aluminum salts. The mixture was then poured into a separatory funnel and allowed to stand until the carbon disulfide layer separated. This was then removed, dried over anhydrous calcium chloride, decanted and allowed to evaporate spontaneously. After the liquid had stood overnight, crystallization was usually complete. The remaining oil, if there was any, was decanted and the crystals were dissolved in a small amount of chloroform; alcohol was then added to decrease the solubility. Two or three crystallizations usually were sufficient. The solvent for final crystallization varied with the solubility of the individual substance.

General Procedure for Conversion to the Ethylenic Derivative

The pure, substituted diphenyl halogen ethane was treated with pure potassium hydroxide dissolved in absolute alcohol freshly distilled from lime and potassium hydroxide. The mixture was heated for two to three hours under a reflux condenser. On cooling, crystals of the ethylenic compound separated. These were recrystallized from boiling absolute alcohol in which they were quite soluble. With some of the compounds it was found necessary to change the solvent. A small amount of ether mixed with the alcohol in some cases aided in the purification.

The Action of Sodium Alcoholate in Alcohol

General Procedure.—When the unsubstituted diphenyltrichloroethane or diphenyltribromo-ethane compound is heated on a water-bath

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[13] All reagents were purified and analyzed before use regardless of the description on the container.

[14] The carbon disulfide was dried over fused calcium chloride, decanted and distilled, then placed over anhydrous aluminum chloride from which it was distilled for each experiment.

TABLE II

ACTION OF ALCOHOLIC POTASSIUM HYDROXIDE ON SUBSTITUTED DIPHENYL-HALOGEN-ETHANES

Ethylene	Formula	M. p., °C.	Solvent for crystallization	Halogen, % Calcd.	Halogen, % Found
Diphenyldichloro[a]	$(C_6H_5)_2C{=}CCl_2$	80	Alcohol	28.52	28.32
Ditolyldichloro[b]	$(CH_3C_6H_4)_2C{=}CCl_2$	85	Alcohol	25.63	25.70
Dianisyldichloro[c,d]	$(CH_3O.C_6H_4)_2C{=}CCl_2$	109	Alcohol	22.98	22.72
Diphenetyldichloro[c]	$(C_2H_5O.C_6H_4)_2C{=}CCl_2$	105	Alcohol	21.07	20.90
Diphenyldibromo	$(C_6H_5)_2C{=}CBr_2$	84	Alcohol-ether	47.34	47.42
Ditolyldibromo	$(CH_3C_6H_4)_2C{=}CBr_2$	118	Alcohol	43.72	43.86
Dianisyldibromo	$(CH_3O.C_6H_4)_2C{=}CBr_2$	91	Alcohol	40.20	40.12
Diphenetyldibromo	$(C_2H_5O.C_6H_4)_2C{=}CBr_2$	...	Alcohol	37.3	37.3
Dianisylmonobromo	$(CH_3O.C_6H_4)_2C{=}CHBr$	85	Alcohol-ether	25.08	25.19
Diphenetylmonobromo	$(C_2H_5O.C_6H_4)_2C{=}CHBr$	64	Alcohol-ether	23.06	23.28
3,3-Dimethyl-6,6-dimethoxymonobromo	$[CH_3(CH_3O)C_6H_3]_2{=}CHBr$	105	Alcohol-ether	21.33	21.21
Dianisyl[e] (*unsym.*)	$(CH_3O.C_6H_4)_2C{=}CH_2$	142	Benzene-alcohol	C 80.00 H 6.7	79.7 79.5 7.0 6.8
Diphenetyl (*unsym.*)	$(C_2H_5O.C_6H_4)_2C{=}CH_2$	138	Benzene-alcohol	C 80.06 H 7.4	80.2 80.1 7.16 7.22

[a] Elbs, *J. prakt. Chem.*, New Folge, **47,** 44 (1893).

[b] Ref. 2 d.

[c] Ref. *d* of Table I, p. 75.

[d] Ref. 9, p. 1526.

[e] Ludwig and Gattermann, *Ber.*, **22,** 1132 (1888).

with sodium alcoholate for 10–12 hours the principal product is the unsaturated dihalogen compound. There is also an offensive aromatic odor which suggests that there is a secondary reaction. When the mother liquor left from the crystallization of the dihalogen compounds was acidified, a small amount of oil separated. This was treated with concd. hydrochloric acid for about four hours and then was soluble in an aqueous solution of sodium hydroxide. This alkaline solution was filtered and acidified; a crystalline substance formed. This was found to recrystallize from 50% acetic acid solution. To raise the temperature of the reaction the experiment was conducted in a sealed tube in a bomb furnace at 180–200°; this increased the yield of the product to about 80%.

	Formula	M. p., °C.		Anal. Calcd., %	Found, %	
Diphenylacetic acid	$(C_6H_5)_2CHCOOH$	146	C	79.3	79.17	79.16
			H	5.6	5.55	5.54
Ditolylacetic acid	$(CH_3C_6H_4)_2CHCOOH$	145	C	80.0	80.3	80.05
			H	6.7	6.74	6.73

When the substituted trihalogen ethanes, dihalogen ethylenes or monohalogen ethylenes were treated in the sealed tube with sodium alcoholate, yields of about 80% of disubstituted tolanes were obtained; about 20%

of the dihalogen ethylene compound remained unchanged. No disubstituted acetic acid could be isolated from the mixture.[15]

	Formula	M. p., °C.	Anal. Calcd., %		Found, %	
Dimethoxytolane[16]	$CH_3O.C_6H_4C\equiv CC_6H_4.OCH_3$	141	C	80.7	80.5	80.85
			H	5.9	5.92	5.8
Diethoxytolane	$C_2H_5O.C_6H_4C\equiv CC_6H_4.OCH_3$	160	C	81.2	81.5	81.25
				6.7	6.5	6.77

The Action of Moist Silver Oxide on Dianisyl and Diphenetyltribromo-ethanes

The tribromo-ethanes were boiled with silver oxide in water for 36 hours. The excess of silver oxide was dissolved in dil. nitric acid. There remained an insoluble substance which was treated with boiling, dil. hydrochloric acid and filtered. On cooling, white crystals separated from the filtrate. These proved to be *para*-substituted benzoic acids.

	Formula	M. p., °C.	Anal. Calcd., %		Found, %		Yield
Anisic acid	$CH_3O.C_6H_4COOH$	185	C	63.2	62.95	63.7	16
			H	5.2	5.9	5.09	
p-Ethoxybenzoic acid[17]	$C_2H_5OC_6H_4COOH$	194	C	65.1	64.95	65.0	18
			H	5.89	5.89	5.78	

Action of Metallic Sodium on Dianisyl- and Diphenetyltrihalogen Ethanes

When an attempt was made to condense two molecules of the trihalogen compound by metallic sodium in dry ether, nothing had happened after 100 hours of boiling, so purified dry benzene was substituted for the ether; sodium powder was used. After boiling the halogen compound for 10 to 12 hours, the solution was filtered and the benzene solution evaporated to about half; then alcohol was added. Crystals representing a 95% yield of the substituted stilbene separated. When the mother liquor from these was evaporated, crystals of substituted tolane crystallized from the solution in about a 2% yield. When substituted diphenyl dihalogen or monohalogen ethylenes were treated, only substituted tolanes were formed.

Oxidation of the Trihalogen Ethanes with Chromic Acid in Glacial Acetic Acid

The oxidation was carried out in boiling acetic acid to which the chromic acid solution in acetic acid was added drop by drop. The compounds, in each case, were found to oxidize to the ketones, some of which were converted to the oximes for identification.

[15] Ref. *d*, Table I.

[16] Wiechell, *Ann.*, **279**, 338 (1894).

[17] Griess, *Ber.*, **21**, 980 (1887). Gattermann, *Ann.*, **244**, 63 (1888).

Ethane	Product	M. p., °C.	M. p. of oxime, °C.
Diphenyltribromo	Benzophenone	45	139
Ditolyltribromo	*p*-Dimethylbenzophenone	94[18]	162
Dianisyltribromo	*p*-Dimethoxybenzophenone	144[19]	
Diphenetyltribromo	Diethoxybenzophenone	130[20]	

Summary

1. Halogen-substituted aldehydes can be made to condense almost quantitatively with aromatic hydrocarbon or phenolic ethers in the presence of anhydrous aluminum chloride.

2. These condensation products in the presence of alcoholic potassium-hydroxide lose a molecule of halogen acid to form the ethylenic compound.

3. When the hydrocarbon-substituted dihalogen ethylene compounds are heated with sodium alcoholate in a sealed tube they are converted to disubstituted acetic acids.

Dianisyl- and diphenetyl-ethylenic compounds give substituted tolanes.

4. Moist silver oxide oxidizes the condensation products to benzoic acid or substituted benzoic acids.

5. Metallic sodium in boiling benzene converts the trihalogen condensation products into stilbenes and the ethylenic derivatives into tolanes.

6. Chromic acid oxidizes all compounds of this series to benzophenone or its derivatives.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

THE HIGHLY UNSATURATED FATTY ACIDS OF FISH OILS. II THE LIMIT OF UNSATURATION IN MENHADEN OIL[1]

BY ROB ROY McGREGOR WITH GEORGE D. BEAL

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Introduction

Although the study of unsaturated fatty acids has interested investigators with many different ends in view, there has always been a difficulty in definitely characterizing the unsaturated acids present in a mixture. This difficulty becomes more and more marked as the unsaturation increases. The mutual solubilities of these acids, one in the other, and the similarity of chemical properties make them difficult, or impossible, of

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[18] Weiler, *Ber.*, **7,** 1183 (1874). Odor, *Ber.*, **12,** 2303 (1878). Goldschmidt, *Ber.*, **23,** 2747 (1889).

[19] Bösler, *Ber.*, **14,** 328 (1880).

[20] Gattermann, *Ber.*, **28,** 2871 (1894).

[1] Abstracted from a thesis presented by Rob Roy McGregor in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois, **1926.**