hydrofuran (1:1, 50 cc.) containing potassium bicarbonate (200 mg. in 5 cc. of water). Water was then added (50 cc.) and the solution was neutralized with acetic acid. Free 6α, 16α-dimethyl-"S" crystallized slowly overnight (23 mg.) from the aqueous solution as needles with m.p. 181–183°, $[\alpha]_D$ +84°, λ_{max} 240–242 mμ, log ε 4.19, ν_{max} 3550, 1715, 1660, 1610 cm.$^{-1}$ Extraction of the mother liquors with ethyl acetate furnished additional material. Total yield 78%. The analytical specimen was prepared by recrystallization from acetone-ether, m.p. 185–187°.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15%. Found: C, 74.29; H, 9.39%.

6α,16α-Dimethyl-4-pregnene-11β,17α,21-triol-3,20-dione (6α,16α-dimethyl- "hydrocortisone") (XIc). Incubation of free 6α,16α-dimethyl "Compound "S" (350 mg.) with fresh bovine adrenal glands[20] followed by extraction of the breis with acetone, concentration of the aqueous acetone solution *in vacuo*, extraction of the aqueous residue with methylene chloride, and removal of the solvent, provided a residue. This material was chromatographed directly, without previous removal of the fats, on silica gel (400 g.). The eluates obtained with ethyl acetate afforded 6α,16α-dimethylhydrocortisone as crystals purified from acetone-ether (80 mg.) m.p. 235–237°, $[\alpha]_D$ +98.4°, λ_{max} 242 mμ, log ε 4.15, ν_{max} 3500, 1720, 1660, 1610 cm.$^{-1}$.

Anal. Calcd. for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78; O, 20.48. Found: C, 71.09; 71.27; H, 8.87, 8.96; O, 20.18, 20.19. Yield 22% in purified material.

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[CONTRIBUTION NO. 32 FROM THE EXPLORATORY RESEARCH LABORATORY, DOW CHEMICAL OF CANADA, LIMITED]

Thermal Decomposition and Electrophilic Arylations with Aryldiazonium Tetrachloroborates and Tetrabromoborates. Remarks on the Mechanism of the Schiemann Reaction

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Thermal decomposition of aryldiazonium tetrachloroborates to aryl chlorides, boron trichloride, and nitrogen proceeds similarly to the Schiemann reaction of aryldiazonium tetrafluoroborates. Under similar conditions, aryldiazonium tetrabromoborates yield aryl bromides. Ring arylation was observed when the reactions were carried out in the presence of aromatic hydrocarbons. Quantitative investigation of the isomers formed in the case of arylation of fluorobenzene is in accordance with an electrophilic substitution mechanism. An ionic mechanism based on the experimental data for the thermal decomposition of all aryldiazonium tetrahaloborates investigated is suggested.

In 1927[1] Balz and Schiemann reported the thermal decomposition of aryldiazonium tetrafluoroborates to give aryl fluorides

$$ArN_2^+ BF_4^- \longrightarrow ArF + N_2 + BF_3$$

The Schiemann reaction has since gained widespread application for the preparation of aromatic fluorine compounds.[2] The mechanism of the Schiemann reaction has been investigated in some detail but only tentative mechanisms involving either a radical or ionic type reaction have been suggested.[2] Nesmeianov and his co-workers[3] investigated the decomposition reaction of aryldiazonium tetrafluoroborates in nitrobenzene and found that *m*-nitrobiphenyl was formed in the reaction in addition to fluorobenzene. They concluded that an ionic type of decomposition reaction involving the $C_6H_5^+$ ion takes place. Phenyldiazonium chloride under similar conditions gave a mixture of *o*-, *m*- and *p*-dinitrodiphenyl pointing, in this case, to a radical type phenylation reaction.

The preparation of aryldiazonium tetrachloroborates and tetrabromoborates[4] now makes it possible to investigate the thermal decomposition and arylation reactions of these new stable diazonium salts.

The solid aryldiazonium tetrachloroborates when heated above their decomposition point (with obvious care to exclude moisture) decompose very vigorously (sometimes explosively) with strong boron trichloride evolution. The thermal decomposition reaction can be carried out, however, under controlled conditions when the diazonium salt is heated in the presence of an inert diluent, such as a higher boiling aliphatic hydrocarbon. Under these conditions a smooth decomposition to aryl chlorides, nitrogen, and boron trichloride takes place.

(1) G. Balz and G. Schiemann, *Ber.*, **60-B**, 1186 (1927).
(2) A. Roe, *Org. Reactions*, V, 193 (1949).
(3) A. N. Nesmeianov and L. G. Makarova, *Bull. Akad. Sci. U.S.S.R., Div. Chem. Sci.*, 213 (1947); A. G. Makarova and M. K. Matveeva, *Bull. Akad. Sci. U.S.S.R., Div. Chem. Sci.*, 565 (1958); L. G. Makarova and E. A. Gribchenko, *Bull. Akad. Sci. U.S.S.R., Div. Chem. Sci.*, 693 (1958); L. G. Makarov, M. K. Matveeva, and E. A. Gribchenko, *Bull. Akad. Sci. U.S.S.R., Div. Chem. Sci.*, 1399 (1958).
(4) G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, in press.

$$ArN_2^+ BCl_4^- \longrightarrow ArCl + N_2 + BCl_3$$

Table I gives the data obtained in the thermal decomposition of aryldiazonium tetrachloroborates.

In all decomposition reactions a small amount of di- and polyphenyl derivatives was formed as by-products (less than 5%). In the thermal decomposition reaction of *o*-nitrophenyldiazonium tetrachloroborate, the product also contained about 2% *o*-dichlorobenzene and nitric oxide was evolved together with boron trichloride and nitrogen.

TABLE I

DECOMPOSITION OF ARYLDIAZONIUM TETRACHLOROBORATES

$ArN_2 BCl_4$	Dec. Point	ArCl Obtained	Yield, %
Phenyl	85–87	Chlorobenzene	79.0
o-Tolyl	35–37	*o*-Chlorotoluene	77.6
p-Tolyl	87	*p*-Chlorotoluene	48.1
p-Nitrophenyl	101	*p*-Nitrochlorobenzene	66.5
o-Nitrophenyl	90–92[a]	*o*-Nitrochlorobenzene	59.2
m-Bromophenyl	33–35	*m*-Bromochlorobenzene	75.4
p-Fluorophenyl	106	*p*-Fluorochlorobenzene	81.0

[a] Should be handled with care. The dry salt tends to explode spontaneously even during storage at room temperature.

Aryldiazonium tetrabromoborates when decomposed under similar conditions gave aryl bromides, nitrogen, and boron tribromide.

$$ArN_2^+ BBr_4^- \longrightarrow ArBr + N_2 + BBr_3$$

TABLE II

DECOMPOSITION OF ARYLDIAZONIUM TETRABROMOBORATES

$ArN_2 BBr_4$	Dec. Point	ArBr Obtained	Yield, %
Phenyl	82	Bromobenzene	71.0
p-Tolyl	90–91	*p*-Bromotoluene	80.0
o-Nitrophenyl	100	*o*-Bromonitrobenzene	51.5
p-Fluorophenyl	128–134	*p*-Bromofluorobenzene	96.5

When the decomposition reaction of aryldiazonium tetrachloro- and tetrabromoborates was investigated in an aromatic solvent, ring arylation was always observed. In order to get a better understanding of these arylations a quantitative investigation of the decomposition of the diazonium salts in fluorobenzene was carried out.

Thermal decomposition of aryldiazonium tetrafluoroborates in chloro- and bromobenzene were previously investigated by Nesmeianov[5] and found to give diphenylhalonium tetrafluoroborates

$$C_6H_5N_2^+BF_4^- + C_6H_5X \longrightarrow [C_6H_5{-}X^+{-}C_6H_5]BF_4^- + N_2$$

Aryldiazonium tetrachloroborates and tetrabromoborates under certain conditions are also able to react with halobenzenes to form diphenylhalonium tetrachloroborates.[6]

In the case of fluorobenzene, however, no trace of diphenyl halonium complex formation was found. This is easily understood when one considers the known inability of fluorine to form positive ions. Instead, besides halobenzene formation, ring arylation takes place. The diazonium salts were suspended in fluorobenzene and decomposed until almost no solid remained in the reaction mixture. Besides the corresponding halobenzene as the main products, 5–15% fluorobiphenyls were found. The reaction products were then analysed by a combined gas-liquid chromatography–infrared spectroscopy method. Comparative experiments were also carried out with phenyldiazonium chloride and phenyldiazonium tetrafluoroborate. The data obtained are summarized in Table III.

TABLE III

ARYLATION OF FLUOROBENZENE WITH ARYLDIAZONIUM SALTS

Arylating Agent	React. Temp.	React. Time, Hr.	% Fluorobiphenyl Isomers Obtained		
			ortho	*meta*	*para*
$C_6H_5N_2^+Cl^-$	25	8	26.2	46.7	27.1
$C_6H_5N_2^+BF_4^-$	85	48	45.0	—	55.0
$C_6H_5N_2^+BCl_4^-$	70–75	6	42.3	1.1	56.6
p-$FC_6H_4N_2^+BCl^-$	85	48	51.6	—	48.4
$C_6H_5N_2$ BBr_4	85	16	61.6	—	38.4

In the case of phenyldiazonium chloride, the isomer ratio obtained in the arylation of fluorobenzene points to a radical type substitution (with the formation of a large amount of *meta* isomer) and consequently to a radical type formation of chlorobenzene. (For data on the directing effect of fluorobenzene in electrophilic and radical type of halogenation see Ref. 7.)

In the case of aryldiazonium tetrahaloborates, including the diazonium tetrachloroborates and tetrabromoborates the formation of almost only *ortho* and *para* isomer biphenyls, the isomer ratios point to an electrophilic type arylation reaction and consequently to a similar ionic type of halobenzene formation.

We would like to point out however that our arylation experiments were carried out in an aromatic solvent at modest temperatures ($\angle$ 85°). Consequently our findings concerning an electrophilic arylation mechanism and that of the accompanying decomposition of the aryldiazonium salts to halobenzenes (Schiemann reaction) are valid only under the investigated reaction conditions. Decomposition of the diazonium salts at higher temperatures, or thermal decomposition of the solid salts in the absence of solvents, may take

(5) A. N. Nesmeianov, T. P. Tolstaia, and L. S. Issaieva, *Doklady Acad. Sci. U.S.S.R.*, 104, 872 (1955); A. N. Nesmeianov and T. P. Tolstaia, *Doklady Akad. Sci. U.S.S.R.*, 105, 95 (1955).

(6) G. A. Olah and W. S. Tolgyesi, unpublished results.

(7) G. Olah, A. Pavlath, and G. Varsanyi, *J. Chem. Soc.*, 1823 (1957).

place also through an other, preferable free radical mechanism.

EXPERIMENTAL

Thermal decomposition of aryldiazonium tetrachloroborates and tetrabromoborates. The diazonium complex (0.05 mole) was suspended in 80 g. of ligroin (b.p. 110–115°) in a 150 ml. flask equipped with a reflux condenser and closed with a calcium chloride tube to exclude atmospheric moisture. Decomposition of the material was carried out slowly by heating the flask to a temperature slightly above the decomposition point of diazonium complex. After complete decomposition was achieved, which could be noticed by the lack of evolution of boron halide on further heating, the dark solution was diluted with 120 ml. of benzene and poured on ice. The organic layer was isolated and washed with distilled water until neutral. The benzene-ligroin solution was dried with calcium chloride and fractionally distilled at atmospheric pressure.

Arylation of fluorobenzene with aryldiazonium tetrachloroborates and tetrabromoborates. Aryldiazonium tetrahaloborate (0.1 mole) was suspended in 200 ml. of fluorobenzene at room temperature in a 500-ml. flask, equipped with magnetic stirrer, thermometer, reflux condenser, and calcium chloride tube. With constant agitation the mixture was heated to a temperature 10–15° below the thermal decomposition point of the diazonium salt, or, in the case of more stable complexes (decomposition point above 95°), to the boiling point of fluorobenzene in the course of 1 hr. The mixture was then kept at that temperature with continuous agitation until all the solid material dissolved (6 to 48 hr.) yielding a clear brown-red solution. The solution was poured on ice, the organic layer washed with distilled water until it was neutral and dried with calcium chloride. After the removal of fluorobenzene by distillation at atmospheric pressure, the higher boiling reaction products were separated by fractionation at a reduced pressure and analysed by gas-liquid chromatography.

Arylation of fluorobenzene with phenyldiazonium chloride. Phenyldiazonium chloride (25 g.) was suspended in 200 g. of fluorobenzene at 10° in a 500-ml. flask equipped as in the previous experiment. The temperature of the mixture was allowed to rise to 25° in 0.5 hr. with constant agitation and kept at 25° until completion of the reaction (indicated by the disappearance of solid diazonium chloride). Further treatment of the solution was as previously described. Analysis of the fluorobiphenyl isomers was carried out by gas-liquid chromatography. A Perkin-Elmer, Model 154C Vapor Fractometer fitted with a 4 m. × 1/4-in. stainless steel column using polypropylene glycol (UCON LB 550-X) supported on diatomaceous earth was used at a temperature maintained at 195°. Hydrogen (or helium) flowing at 60 cc./min. was utilized as carrier gas.

From the areas of individual peaks mole % figures were calculated for each product after first determining relative response data obtained from pure fluorobiphenyls following the method of Messner, Rosie, and Argabright.[8] Individual peaks of the isomeric fluorobiphenyls were identified with the retention times determined on pure isomers used and also checked by their infrared spectra.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies of the Friedel Crafts Reaction on Unsaturated Azlactones

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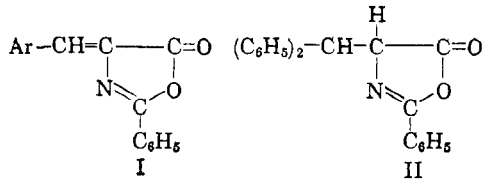
2-Phenyl-4-benzylidene-5(4H)-oxazolone reacts with benzene, toluene, *m*-xylene and chlorobenzene in the presence of anhydrous aluminum chloride to give ω-benzamidoacetophenone derivatives. 2-Benzamidoindenone and 2-acetamidoindenone are prepared by the action of anhydrous aluminum chloride on the corresponding benzylideneoxazolone in carbon tetrachloride. The constitution of the products is discussed.

On attempting to prepare 2-phenyl-4-diphenylmethyl-5-(4H)-oxazolone (II) (yellow crystals, m.p. 158–159°) by the action of anhydrous aluminum chloride on a mixture of benzene and 2-phenyl-4-benzylidene-5(4H)-oxazolone (Ia),[1] we obtained instead a colorless compound, m.p. 123–124°. The same compound was obtained when Ia was replaced by Ib.

This indicates that the reaction cannot take place by 1,4-addition of the benzene molecule as proposed by Filler and Hebron,[1] but by the elimination of the arylidene group.

The fact that when benzene was replaced by toluene, *m*-xylene, or chlorobenzene a different product was obtained indicates that the solvent is involved in the reaction. The similarity of the melting point of the products obtained from benzene and toluene with ω-benzamidoacetophenone (IVa), and ω-benzamino-4-methylacetophenone (IVb).[2–5] respectively, indicates that the reaction proceeds according to the following scheme.



I II

Ia. Ar = C_6H_5
Ib. Ar = *p*-Cl C_6H_4

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