A yellow zone on the column was removed by elution with benzene–alcohol, and a crystalline yellow product obtained after concentrating the solution gave on sublimation 240 mg. of material, m. p. 167–168.5°, and 70 mg., m. p. 160–165°. The total product was converted to the **trinitrobenzene derivative,** which crystallized from benzene–alcohol in bright orange needles, m. p. 239–240°. Decomposition of the derivative in benzene–alcohol with stannous chloride and hydrochloric acid afforded colorless plates. On recrystallization from alcohol 250 mg. (26%) of colorless blades were obtained, m. p. 167.5–168.5°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.95; H, 5.96.

The substance dissolves only with difficulty in hot, dilute alkali. The sample darkened on storage and the melting point was depressed. The **picrate** crystallized from benzene–alcohol in bright red needles, m. p. 210.5–211.5°.

Addition of Maleic Anhydride to 1-Propenylnaphthalene.—A mixture of 14 g. of the hydrocarbon[17] and 35 g. of the anhydride was heated on the steam-bath for five hours, during which time the addition product crystallized from the melt. After washing with ether, 17.2 g. (77.5%) of white product, m. p. 261–263°, was obtained. Crystallization from acetic acid, ethyl acetate, and benzene–acetone afforded colorless needles, m. p. 271.8–272°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.28. Found: C, 76.33; H, 5.30.

Since the substance was not isomerized by being refluxed for five hours in acetic acid–anhydride saturated with hydrogen chloride,[18] it probably is **3-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride.**

(17) Fieser and Hershberg, THIS JOURNAL, **60**, 1658 (1938).
(18) Cook and Warren, *J. Chem. Soc.*, 1318 (1937).

3-Methylphenanthrene-1,2-dicarboxylic anhydride was obtained in small amounts (10%) by heating the above product with two equivalents of sulfur. The tarry reaction mixture was extracted with acetic acid and the product sublimed and crystallized from chlorobenzene and from benzene, giving orange-yellow needles, m. p. 332–333°.

Anal. Calcd. for $C_{17}H_{10}O_3$: C, 77.85; H, 3.84. Found: C, 77.86; H, 4.11.

Summary

dl-α,β-Dimethylsuccinic anhydride condenses smoothly with the Grignard reagents from α- and β-bromonaphthalene and 9-bromophenanthrene to give the respective α,β-dimethyl-β-aroylpropionic acids in 66–74% yields. These keto acids were reduced to the γ-arylbutyric acids in excellent yield by hydrogenation over copper chromite catalyst in neutral aqueous solution. Cyclization gave intermediates from which the following new hydrocarbons were synthesized: 1,2,3-trimethylphenanthrene, 2,3,4-trimethylphenanthrene, 2,3-dimethyltriphenylene, and 1,2,3-trimethyltriphenylene. The first two substances were desired as possible models of carcinogenic hydrocarbons of the 1,2-benzanthracene and 3,4-benzphenanthrene series.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED JANUARY 10, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. X. The Vapor Phase Fluorination of Acetone

BY NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

In recent papers,[1] we have discussed the vapor phase fluorination of organic gases over a copper gauze catalyst. It seemed very desirable, however, to extend the scope of this successful process, and to make it applicable to volatile organic liquids as well. This paper will deal with the results obtained by the fluorination of acetone, when the liquid sample was introduced into a heated reaction chamber, through a calibrated capillary.

Apparatus and Operation.—The new apparatus is illustrated to approximate scale in Fig. 1. The organic liquid A, under air pressure measured by B, entered the vertical electrically heated brass reaction chamber C through glass capillary D, which was connected by a mercury sealed slip-joint E. The sample volatilized at once, and the gas passed into the copper gauze packing at G, while the fluorine was led in through H, and entered the packing at I below G. The reaction took place smoothly, and the gaseous products passed out above, through J, while less volatile material was collected simultaneously below in K. The gases passed through two heated tubes filled with sodium fluoride, L and L′ and were condensed by liquid air or dry-ice in the trap M, which was protected from air and moisture at all times, by passing nitrogen either through O or the bubble counter P. In operation, with acetone, the reaction chamber was first heated to 60°, but the temperature rose considerably as the fluorination progressed. The sodium fluoride tubes were maintained at 95° continuously.

A number of runs were made under different conditions, and the lower boiling products from M separated into empirical cuts by distillation, using the Booth–Podbielniak fractionating unit. The results, expressed in liquid volume per cent. of the total condensate, and rounded off

(1) Paper IX, THIS JOURNAL, **62**, 3302 (1940); see also VII, *ibid.*, **62**, 267 (1940).

to the nearest 5%, are shown in Table I. Corresponding to a fluorine flow of closely 1800 cc. per hour (5 amp. through the generator) the liquid volume of the total condensate was always approximately equal to the liquid volume of acetone used. The latter value was also employed to calculate the corresponding gas volume of acetone at 25° and 760 mm. as given in Table I.

TABLE I

THE EMPIRICAL CUTS OBTAINED BY FRACTIONATING FLUORINATED ACETONE

Liquid volume % of material boiling	Gas volume ratio of fluorine to acetone to nitrogen 6:1:18	4:1:12	4:1:8	3:1:6	2:1:4
(1) All < −105° (mostly CF_4)	20	10	15	5	5
(2) −105 to −61°	20	10	15	10	5
(3) − 61 to −35°	10	10	5	5	5
(4) − 35 to −15°	10	5	5	5	10
(5) All > −15°	40	65	55	75	80

This tabulation shows that when the fluorination ratio (fluorine to acetone) was increased, or the dilution ratio (fluorine to nitrogen) was decreased, the lower boiling products were favored consistently, and *vice versa*. However, no particular fraction was greatly favored under any of the conditions studied. The material boiling above −15° was not divided into cuts in this manner. The fractions were accumulated, and then rectified separately, with the following results.

Separation of the Products

Fraction (2).—This material (b. p. −105 to −61°) almost certainly consisted of a mixture of carbon dioxide, silicon tetrafluoride and carbonyl fluoride, COF_2. The distillation curve showed three distinct plateaus, (a) b. p. −92°, mol. wt. 84 (probably $SiF_4 + CO_2 + COF_2$), (b) b. p. −88°, mol. wt. 62 (presumably $CO_2 + COF_2$), (c) pure carbonyl fluoride, COF_2, b. p. −83° (−83°[2]), mol. wt. 66 (calcd. 66). Both (a) and (b) contained subliming components. For certain identification, the pure fluorophosgene was passed into ethyl alcohol and completely absorbed. On rectification in a high temperature Podbielniak still, pure diethyl carbonate was obtained, b. p. 127° (126.7–127.2°[3]).

Fraction (3).—This portion (b. p. −61 to −35°) consisted for the most part of an azeotrope, b. p. −59°, mol. wt. 102. In one case the mol. wt. rose to 116 at the end, which led us to believe that the mixture contained trifluoroacetyl fluoride, CF_3COF (b. p. −59°,[4] mol. wt. calcd. 116), and it also was passed into alcohol and completely absorbed. On rectification there came over an azeotrope, b. p. 56°, consisting in all probability of ethyl trifluoroacetate and alcohol, which was dissolved in liquid ammonia. After evaporation of the solvent a solid remained, which, on crystallization from chloroform, yielded large white plates of pure trifluoroacetamide, CF_3CONH_2, m. p. 74–75° (74.8°[4]), confirming the presence of trifluoroacetyl fluoride as one component of the azeotrope, b. p. −59°. The other component may have been O_2F_2, b. p. −57°,[5] but this was not proved.

(2) Ruff, *Z. anorg. allgem. Chem.*, **221**, 154 (1934).
(3) Perkin, *J. Chem. Soc.*, **65**, 421 (1894).
(4) Swarts, *Bull. Sci. Acad. Roy. Belg.*, **8**, 343 (1932).
(5) Ruff, *Z. anorg. allgem. Chem.*, **217**, 85 (1934).

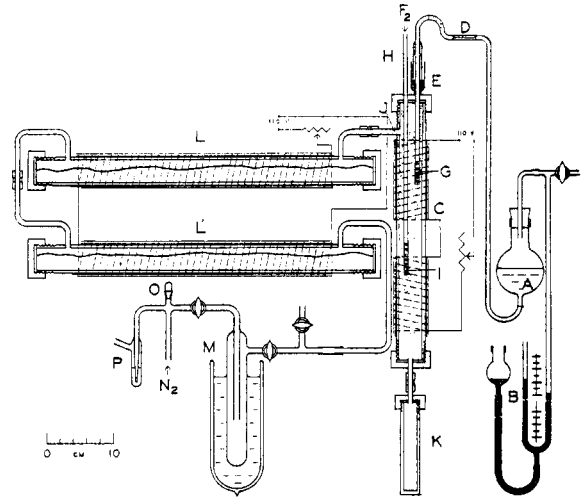


Fig. 1.—Apparatus for vapor phase fluorination of volatile organic liquids.

Fraction (4).—This product consisted mostly of pure colorless hexafluoroacetone, CF_3COCF_3, b. p. −28°, m. p. −129°, which has not been prepared heretofore.

Anal. Calcd. for C_3OF_6: F, 68.7; mol. wt., 166. Found: F, 68.6, 68.8; mol. wt., 165.

This interesting compound resembled acetone. It was soluble in water without decomposition, and readily yielded a white crystalline semicarbazone which separated from water as the monohydrate, m. p. 153° (decompn.).

Anal. Calcd. for $C_4H_5N_3OF_6 \cdot H_2O$: F, 47.3. Found: F, 47.4.

When the crystals were boiled with chloroform, however, the anhydrous compound was formed, also m. p. 153° (decompn.).

Anal. Calcd. for $C_4H_5N_3OF_6$: F, 51.1. Found: F, 50.8.

The hexafluoroacetone gave some evidence of hydrate formation, but the aqueous solution was completely volatile at low pressures, and the distillate yielded the semicarbazone. The ketone was completely decomposed by dilute alkali, however, with the apparent formation of trifluoroacetic acid.

Fraction (5).—The accumulated residues from the low temperature distillation (b. p. > −15°) contained unreacted acetone, as well as high boiling products, some of which were probably formed by the condensing action of hydrogen fluoride. Upon rectification, this material yielded two pure compounds, oxalyl fluoride $(COF)_2$ and monofluoroacetone CH_2FCOCH_3, which together comprised perhaps a fifth of the whole. The remaining mixture has not yet been separated, but gave evidence of containing penta- and tetrafluoroacetone.

The oxalyl fluoride, which is new, was a colorless, highly reactive liquid, b. p. 26°.

Anal. Calcd. for $C_2O_2F_2$: F, 40.4; mol. wt., 94. Found (Parr bomb): F, 40.4, 40.6; mol. wt., 94.

For further identification, the product was treated with methyl alcohol, and the mixture dissolved in liquid ammonia. Upon evaporation of the solvent, a white solid remained, which sublimed at 160–170° in an open

tube, and melted with decomposition at a high temperature in a closed tube. These properties correspond to those of the expected oxamide. Curiously enough, the isomeric difluoroacetones, $C_3H_4OF_2$, have exactly the same molecular weight and fluorine content as oxalyl fluoride, and it was necessary therefore to eliminate the possibility that the new substance was one of these. It was known that when pentafluoroethane, containing less than 1% of hydrogen, was burned over silica,[1] the deposit of moisture on the cooler portion of the clear silica tube was plainly visible, whereas no deposit whatever appeared when the compound analyzed contained no hydrogen. The combustion of the oxalyl fluoride in this manner yielded no trace of deposit, indicating definitely that the sample contained no hydrogen, while the difluoroacetones have more than 4% of this element. However, this method for the analysis of oxalyl fluoride did not give satisfactory values for fluorine, as the sample reacted with the stopcock lubricant. To obtain correct values, a portion was distilled directly into a bulblet, sealed off, weighed and burned in a Parr bomb.

The monofluoroacetone was a slightly yellowish liquid, very similar to acetone, but not fully miscible with water, b. p. 78° (72.5[6]). No pungent odor could be detected, contrary to the observation of the earlier investigators.

Anal. Calcd. for C_3H_5OF: F, 25.0; mol. wt., 76. Found: F, 24.8, 25.0; mol. wt. (Victor Meyer), 74.77.

The ketone readily yielded a white crystalline semicarbazone, m. p. 132° (decomp.) (132° (decomp.)[6]).

Discussion

From the foregoing results it is seen that the vapor phase fluorination of acetone yielded carbon tetrafluoride, CF_4, carbonyl fluoride, COF_2, trifluoroacetyl fluoride, CF_3COF, hexafluoroacetone, CF_3COCF_3, oxalyl fluoride $(COF)_2$ and monofluoroacetone, CH_2FCOCH_3, in the order of their boiling points.

These findings may be explained conveniently by means of the free radical, chain mechanism postulated[1] for vapor phase fluorination, as illustrated by the equations

$$F_2 \longrightarrow 2F\cdot \text{ (catalytic or thermal)} \quad (1)$$

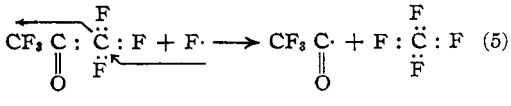
$$CH_3COCH_3 + F\cdot \longrightarrow CH_3COCH_2\cdot + HF \quad (2)$$

$$CH_3COCH_2\cdot + F_2 \longrightarrow CH_3COCH_2F + F\cdot \quad (3)$$

and so on until fully fluorinated CF_3COCF_3 is formed. Then

$$CF_3COCF_3 + F\cdot \longrightarrow CF_3CO\cdot + CF_4 \quad (4)$$

or, more explicitly



(5)

There are several possible points of attack for the fluorine atom, (a) the fluorine or oxygen atoms in the ketone, (b) the central carbon atom or (c) one of the end carbon atoms. Postulate (a) is unlikely, since these elements are strongly electronegative, and their octets are presumably even more stable than those surrounding the carbon atoms. The possibility (b) appears doubtful because it would involve (1) the action of *two* fluorine atoms, accompanied by the displacement of oxygen and the production of octafluoropropane, which was not formed, or (2) the action of one fluorine atom, with the corresponding displacement of a $\cdot CF_3$ radical and the subsequent production of hexafluoroethane, which was not isolated, or (3) the action of one fluorine atom, with the rupture of the double bond, and the ultimate formation of an oxygen–fluorine link or a peroxide, neither of which would be expected to be very stable. The final suggestion (c) seems best and has been adopted because (1) it accounts readily for the products actually formed, and (2) the primary product, carbon tetrafluoride, is a highly stable, resonating[7] molecule, with a very low energy content. This interpretation assumes that when the fluorine atom approaches the halogenated ketone, the unpaired electron enters the octet surrounding one of the end carbon atoms in order to form a pair and thus complete the highly stable octet around the fluorine atom. The result is an unstable complex,[8] of short life, which then loses the trifluoroacetyl radical, and forms the highly stable carbon tetrafluoride. Then we have

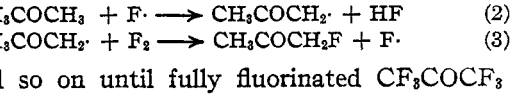
$$CF_3CO\cdot + F_2 \longrightarrow CF_3COF + F\cdot \quad (6)$$

followed by

$$CF_3COF + F\cdot \longrightarrow COF\cdot + CF_4 \quad (7)$$

The radical $COF\cdot$, being of relatively low molecular weight, can become stabilized easily either by reacting with another fluorine molecule, or by dimerization

$$COF\cdot + F_2 \longrightarrow COF_2 + F\cdot \text{ or} \quad (8)$$



(9)

In support of this portion of the interpretation, it should be noted that the temporary existence of the analogous $COCl\cdot$ radical has been postulated[9] to explain the results obtained by the photolysis of oxalyl chloride; and very recently Kharasch and co-workers[8] have obtained chemical evidence for the existence of the $COCl\cdot$ radical, among others, in organic reactions.

(6) Ray, *J. Ind. Chem. Soc.*, **12**, 93 (1935).

(7) Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(8) See, for example, Brown, Kharasch and Chao, THIS JOURNAL, **62**, 3435 (1940).

(9) Krauskopf and Rollefson, *ibid.*, **58**, 443 (1936).

If equation (9) is valid, it follows that the radical formed in equation (5) should be able to dimerize also

$$2CF_3CO\cdot \longrightarrow CF_3COCOCF_3 \qquad (10)$$

This compound has not yet been isolated, but it is significant that in the distillations a portion was always obtained boiling around $-9°$ the molecular weight of which was *higher* than that of hexafluoroacetone. There are only two presumably low boiling possibilities here, hexafluorodiacetyl and octafluoropropane. The latter, however, boils at $-36°$ and so is eliminated as a possibility.

From all these considerations it becomes increasingly clear that vapor phase fluorinations in all probability proceed by a free radical, non-ionic mechanism.

Summary

The simple and convenient apparatus previously used for the direct fluorination of organic gases has been adapted to the vapor phase fluorination of volatile organic liquids, thereby greatly increasing its usefulness.

Acetone has been fluorinated without difficulty. The principal products were hexafluoroacetone CF_3COCF_3, monofluoroacetone CH_2FCOCH_3, trifluoroacetyl fluoride CF_3COF, oxalyl fluoride $(COF)_2$, carbonyl fluoride COF_2 and carbon tetrafluoride.

The results have been explained on the basis of a free radical, non-ionic mechanism.

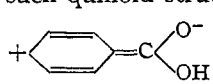
DURHAM, NORTH CAROLINA
RECEIVED NOVEMBER 23, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Dissociation Constants in the Cinnamic Acid Series[1]

BY R. D. KLEENE, F. H. WESTHEIMER AND G. W. WHELAND

It has been known for some time that the acid strength of benzoic acid is increased by practically any substituent ortho to the carboxyl group, regardless of the effect which that substituent exerts when in the meta or para position. To explain this "ortho effect," the suggestion[2] has been made that the ortho substituent inhibits resonance with such quinoid structures as



This suggestion seemed reasonable since such resonance would be expected to stabilize the acid more than it would the corresponding negative ion. A similar explanation can be offered for the fact that *cis* cinnamic acid, for which a completely planar configuration is not possible, is appreciably stronger than the *trans* isomer.

In an investigation of the above hypothesis, the strengths of a series of substituted cinnamic acids have been determined. On account of the insolubility in water of some of the compounds studied, the measurements were made in an acetone–water mixture containing 40% acetone by volume. This had the effect of making the measured dissociation constants more or less uniformly lower than in pure water.[3] The experimental results, which are summarized in the accompanying table, leave something to be desired in the way of precision, but they are sufficiently accurate to show that the strengths of the acids in question can*not* be accounted for on the basis of an inhibition of resonance. Thus *trans*-2,4,6-trimethyl cinnamic acid is stronger than the *cis* isomer by a factor of about $2^1/_2$, even though the former is probably, and the latter is certainly not entirely planar. The fact that the dissociation constants of *cis* and *trans*-α-methylcinnamic acids are in the ratio of approximately 10:1 is even more difficult to explain since it seems quite probable that neither of these acids can achieve planarity. This failure of the theory of inhibition of resonance to account for the strengths of the cinnamic

(1) Part of a thesis presented by R. D. Kleene to the faculty of the Division of Physical Sciences of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy, December, 1940.

(2) Baddeley, *Nature*, **144**, 444 (1939). See also Allan, Oxford, Robinson and Smith, *J. Chem. Soc.*, 401 (1926), and Ives, Linstead and Riley, *ibid.*, 561 (1933). A further suggestion, involving the idea of steric hindrance, has been made by Flürscheim (*ibid.*, **95**, 718 (1909)). This will not be considered here since its theoretical basis seems questionable. The chelation theory of Dippy, Evans, Gordon, Lewis and Watson (*ibid.*, 1421 (1937)) and of Smith (THIS JOURNAL, **61**, 1176 (1939)) will also not be considered here, since, in its application to the acids discussed below, it requires the formation of a hydrogen bond between an oxygen and a carbon atom. The supposition that such a hydrogen bond can exist in cases like the present ones, in which the carbon atom does not carry negative substituents, requires independent confirmation. *Cf.* Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).

(3) See, for example, Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921).