TABLE I

EXPERIMENTAL DATA AND RESULTS OF DIPOLE MOMENT MEASUREMENT[a]

| Soln. | $N_1$ | $N_2$ | $\epsilon_{12}$ | $D$ | $P_2$ | $_n$D | $_E$P |
|---|---|---|---|---|---|---|---|
| 0 | 1.0000 | 0.0000 | 2.2741 | 0.8724 | ...... | 1.4962 | .. |
| 1 | 0.9507 | .0493 | 2.2967 | .8843 | 158 ± 10 | .... | .. |
| 2 | .8994 | .1006 | 2.3113 | .8963 | 162 ± 5 | 1.5003 | 143 |
| 3 | .8708 | .1292 | 2.3338 | .9038 | 155 ± 3 | 1.5040 | 146 |

[a] $N_1$ = mole fraction benzene, $N_2$ = mole fraction of compound, $\epsilon_{12}$ = dielectric constant of solutions, $D$ = density of solution, $P_2$ = calculated total molar polarization of compound, $n_D$ = refractive index of solution at 27°, $_EP$ = electronic polarization of solute calculated from $n_D$. Solution 1 was too dilute for an accurate measurement of $n_D$. All measurements were made at 27 ± 1°.

(5893 Å.) is not too far removed from the absorption band at 5000 Å. with $\epsilon$ 2.5 × $10^3$. It is therefore possible that, due to the dispersion of the refractive index through this absorption band, the value of $n_D$ is higher than the true $n$ measured well away from any absorption band. Thus 144 must be taken as an upper limit of $_EP$. One can attempt to estimate $_EP$ by consideration of the values in other carbonyl molecules. Weiss[10] reports $_EP$ values for $Fe(CO)_5$, $Co(CO)_3$-(NO) and $Fe(CO)_2(NO)_2$ of 42, 35 and 40 cc., respectively. If we then assume a contribution of ~35 cc. per $Co(CO)_3$ group and a contribution of ~10 cc. from the $C_2H_2$ portion of the molecule, we estimate $_EP$ for II as ~115 cc. If $_EP$ is actually this low, then, allowing ~20 cc. for $_AP$, one calculates $\mu \simeq 1.6$ D. Thus we feel it reasonable to conclude that the dipole moment is less than 1.6 D. and quite possibly zero.

**Acknowledgment.**—We are indebted to Mr. J. R. Leto of M. I. T. for measuring the proton resonance spectrum and to Dr. William Westphal of the Laboratory for Insulation Research, M. I. T., for help in measuring the dielectric constants.

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[CONTRIBUTION FROM THE RESEARCH & DEVELOPMENT DEPARTMENT, PENNSALT CHEMICALS CORP.]

# Reactions of Perchloryl Fluoride with Organic Compounds. II. Fluorination of Certain Active Methylene Compounds[1]

BY C. E. INMAN, R. E. OESTERLING AND E. A. TYCZKOWSKI

RECEIVED JANUARY 27, 1958

Direct methods for replacement of the acidic hydrogen atoms of active methylene compounds by fluorine have not been previously reported. The reaction of perchloryl fluoride with the sodium salts of active methylene compounds constitutes a novel procedure for such fluorinations and is believed to be generally applicable. Several new fluorinated compounds have been prepared and are described.

Previous studies of perchloryl fluoride have shown it to be a surprisingly stable molecule, possessing a $C_{3v}$ tetrahedral symmetry and essentially no electrical dipole moment.[2] In a previous paper the authors have described the heterolysis of this compound in the presence of strongly electrophilic reagents such as aluminum chloride to give the $ClO_3^+$ ion and bring about the novel perchlorylation reaction with aromatic hydrocarbons.[3] Perchloryl fluoride has also been shown to undergo nucleophilic attack in the presence of alkaline inorganic reagents, such as ammonia, to give fluoride ion and the $ClO_3^+$ ion.[4]

In the present investigation, it was found that perchloryl fluoride also reacts with strong organic bases. Moreover, in the case of the sodium salts of active methylene compounds, the reaction was found to introduce fluorine into the organic molecule. For example, when perchloryl fluoride was passed into an alcoholic solution of the sodium salt of diethyl malonate, diethyl difluoromalonate was produced. The reaction tends to replace all hydrogens of the active methylene group. Thus in the case of diethyl malonate, if an insufficiency of sodium ethylate was used to neutralize each acidic hydrogen successively, the product was diethyl difluoromalonate with unchanged diethyl malonate. When a two-to-one mole ratio was used, the reaction was essentially quantitative, and only the difluorinated product was obtained. No monofluorinated diethyl malonate was found in any case, although it was undoubtedly formed as an intermediate. The monofluoro compound, as a stronger acid than diethyl malonate, competes effectively for the available base and undergoes reaction with perchloryl fluoride a second time to form the difluoro compound before further monofluoro intermediate may be formed.

The anticipated reaction products were obtained from diethyl malonate, diethyl ethylmalonate, diethyl phenylmalonate, ethyl acetoacetate and 2,4-pentanedione. Product yields in general were high. In the case of the ethyl acetoacetate however, yields of only 30 to 40% of the fluorinated product were originally obtained, complicating the purification of the product. It was found, however, that by lowering the reaction temperature and by addition of the base in small increments to form the sodium salt, the yield could be substantially increased. By limiting the excesses of strong base present in the reaction media, this procedure is believed to avoid the possibility of cleavage of the fluorinated product at the carbonyl group. Cleavage of this type with carbonyl compounds bearing negative constituents on the $\alpha$-carbon is well known.[5] This improved procedure

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(1) Presented in part before the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb. 5, 1958.

(2) (a) R. P. Madden and W. S. Benedict, *J. Chem. Phys.*, **25**, 594 (1956); (b) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **25**, 595 (1956); (c) **25**, 1128 (1956); (d) A. A. Maryott and S. J. Kryder, *ibid.*, **27**, 1221 (1957).

(3) C. E. Inman, R. E. Oesterling and E. A. Tyczkowski, THIS JOURNAL, **80**, 5286 (1958).

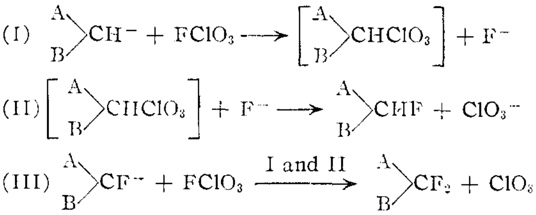
(4) (a) A. Englebrecht and H. Atzwanger, *J. Inorg. Nuclear Chem.*, **2**, 348 (1956); (b) A. Englebrecht and H. Atzwanger, *Monatsh. Chem.*, **83**, 1087 (1952); (c) G. Barth-Wehrenalp and H. C. Mandell, Jr., to be published.

(5) E. Bergmann, *J. Org. Chem.*, **23**, 476 (1958).

was adopted for the succeeding preparations described. The reaction techniques are believed to be generally applicable to many such active methylene compounds. This relatively simple, one-step preparation makes available for the first time many fluorinated compounds which have been impossible or impractical to prepare in the past or obtainable only through very indirect syntheses.

Secondary derivatives of the initial fluorinated products also were prepared and are described. The malonamides were prepared from diethyl 2,2-difluoromalonate and diethyl 2-fluoro-2-phenylmalonate. Diethyl 2-ethyl-2-fluoromalonate gave the corresponding barbituric acid derivative; and from ethyl 2,2-difluoroacetoacetate and 3,3-difluoro-2,4-pentanedione the 2,4-dinitrophenylhydrazone derivatives were obtained.

The mechanism of the fluorination reaction is not fully understood. However, if one assumes a direct heterolysis of perchloryl fluoride similar to that which takes place with inorganic reagents the sequence can be postulated

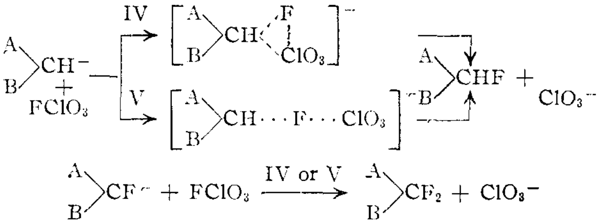


$$\text{(I)}\quad {}^{A}_{B}\!>\!\mathrm{CH^-} + \mathrm{FClO_3} \longrightarrow \left[{}^{A}_{B}\!>\!\mathrm{CHClO_3}\right] + \mathrm{F^-}$$

$$\text{(II)}\quad \left[{}^{A}_{B}\!>\!\mathrm{CHClO_3}\right] + \mathrm{F^-} \longrightarrow {}^{A}_{B}\!>\!\mathrm{CHF} + \mathrm{ClO_3^-}$$

$$\text{(III)}\quad {}^{A}_{B}\!>\!\mathrm{CF^-} + \mathrm{FClO_3} \xrightarrow{\text{I and II}} {}^{A}_{B}\!>\!\mathrm{CF_2} + \mathrm{ClO_3^-}$$

This appears unlikely, however, as reactions carried out in the presence of bases more nucleophilic toward carbon[6] than fluoride, *e.g.*, ethoxide or chloride, showed none of the anticipated competition with reaction II. There remains the possibility therefore, that the reaction is essentially a one-step displacement on halogen. Whether or not the transition state involves the interhalogen bond in the manner indicated in mode IV or only one of the bond termini as in mode V cannot be predicted from present knowledge. Decision between these two modes of reaction on basis of the physical structure of perchloryl fluoride is not possible because of the non-polar nature of the molecule.[2]



$${}^{A}_{B}\!>\!\mathrm{CH^-} + \mathrm{FClO_3} \xrightarrow{\text{IV}} \left[{}^{A}_{B}\!>\!\mathrm{CH}\begin{smallmatrix}\mathrm{F}\\ \vdots\\ \mathrm{ClO_3}\end{smallmatrix}\right]^- \longrightarrow {}^{A}_{B}\!>\!\mathrm{CHF} + \mathrm{ClO_3^-}$$

$${}^{A}_{B}\!>\!\mathrm{CH^-} + \mathrm{FClO_3} \xrightarrow{\text{V}} \left[{}^{A}_{B}\!>\!\mathrm{CH\cdots F\cdots ClO_3}\right]^- \longrightarrow {}^{A}_{B}\!>\!\mathrm{CHF} + \mathrm{ClO_3^-}$$

$${}^{A}_{B}\!>\!\mathrm{CF^-} + \mathrm{FClO_3} \xrightarrow{\text{IV or V}} {}^{A}_{B}\!>\!\mathrm{CF_2} + \mathrm{ClO_3^-}$$

## Experimental[7]

**Diethyl 2,2-Difluoromalonate.**—Diethyl malonate (32 g., 0.2 mole), was added to a solution of 0.4 mole of sodium ethylate in 150 ml. of absolute ethanol. The solution was cooled externally and efficiently stirred. Perchloryl fluoride gas was passed into the mixture by mean of a subsurface addition tube. Reaction was rapid and some heat of reaction was evident. The reaction temperature was controlled at 10 to 15° by the rate of addition of the perchloryl fluoride as well as by the external cooling. As the reaction progressed, solid sodium chlorate precipitated from the reaction medium. When the solution showed no further alkalinity, the addition of perchloryl fluoride was discontinued.

The reaction mixture was poured into three times its volume of water and stirred to dissolve all inorganic salts. The aqueous solution was extracted with several portions of diethyl ether. The ether extract, in turn, was washed with several small portions of water and dried over anhydrous magnesium sulfate. The solution was distilled and diethyl 2,2-difluoromalonate, 33 g. (84% yield), was obtained as a colorless liquid, b.p. 184°, 53° (1 mm.), $n^{20}\text{D}$ 1.3800, $d^{25}_{4}$ 1.162.

*Anal.* Calcd. for $C_7H_{10}F_2O_4$: C, 42.86; H, 5.14. Found: C, 43.13; H, 5.27.

The infrared spectrum showed absorption characteristic of the carbonyl group at 5.61 and 5.68 $\mu$. This is a shift to a lower wave length compared to the carbonyl absorption in diethyl malonate (5.75 and 5.70 $\mu$) and is evidence of the introduction of fluorine into the molecule. A strong band in the 8.7 $\mu$ region may be associated with a carbon–fluorine stretching frequency.

The ester was dissolved in anhydrous ether and anhydrous ammonia was passed through the solution to precipitate difluoromalonamide as a white solid. Recrystallization from ethanol gave colorless needles, m.p. 200–201° uncor. Henne and DeWitt[8] reported 205°, corrected. The infrared spectrum was found to be identical to that of an authentic sample of difluoromalonamide.[9]

**5-Ethyl-5-fluorobarbituric Acid.**—Using the above procedure 60 g. of diethyl 2-ethylmalonate (0.32 mole) was treated with perchloryl fluoride in the presence of 0.34 mole of sodium ethylate in 200 ml. of absolute ethanol; 53 g. of a colorless liquid was obtained, b.p. 48° (0.2 mm.). Vapor chromatography showed both the fluorinated product as well as the starting malonate to consist of two components.

The products were separated by reaction with urea in the presence of sodium ethylate and absolute alcohol in an autoclave at 122–128° for 7 hours. The reaction mixture was evaporated to dryness on a water-bath and the residues leached with dilute hydrochloric acid. The insoluble portions were dissolved in sodium carbonate solution and reprecipitated with dilute hydrochloric acid. The product was 5-ethyl-5-fluorobarbituric acid, a pure white solid, m.p. 204–205.5°.

*Anal.* Calcd. for $C_6H_7FN_2O_3$: N, 16.1; F, 10.9. Found: N, 16.25; F, 10.75.

**Ethyl 2,2-Difluoroacetoacetate.**—Ethyl acetoacetate (130 g., 1.0 mole) was dissolved in 500 ml. of absolute ethanol. The procedure was modified by addition of solid sodium methylate (54 g. 1.0 mole) and passing in perchloryl fluoride gas as before while maintaining the reaction temperature at −10 to 0°. When sufficient perchloryl fluoride had been passed into the mixture to react with all the base present, additional sodium methylate was added in progressively smaller portions, bringing the reaction medium to the neutral point with perchloryl fluoride before the addition of each succeeding portion. A total of 114 g. (2.1 moles) of sodium methylate was added. The reaction mixture was treated as before to give 98 g. (59% yield) of ethyl 2,2-difluoroacetate, a colorless liquid, b.p. 75° (41 mm.), $n^{26}\text{D}$ 1.3709. The infrared spectrum showed absorption at 5.61 and 5.76 $\mu$ characteristic of the carbonyl group. This compares to 5.75 and 5.82 $\mu$ for the unfluorinated ester. A strong band at 8.8 $\mu$ can be attributed to a carbon–fluorine stretching vibration.

*Anal.* Calcd. for $C_6H_8F_2O_3$: C, 43.38; H, 4.85. Found: C, 43.46; H, 4.80.

The 2,4-dinitrophenylhydrazone derivative of the fluorinated ester, ethyl 2,2-difluoroacetoacetate, was prepared in the usual manner in ethanol with 2,4-dinitrophenylhydrazine and recrystallized from ethanol to give pale yellow plates, m.p. 106–107°.

*Anal.* Calcd. for $C_{12}H_{12}O_6N_4F_2$: C, 41.62; H, 3.49; N, 16.18. Found: C, 41.89; H, 3.48; N, 16.62.

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(6) A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956).

(7) Perchloryl fluoride itself is a stable compound quite safe to handle. It is, however, a powerful oxidizing agent, and all mixtures with oxidizable substances should be considered potentially dangerous and handled accordingly. The details of handling and safety are described in Booklet DC-1819, "Perchloryl Fluoride," Commercial Development Dept., Pennsalt Chemicals Corp., 3 Penn Center, Philadelphia 2, Pa.

(8) A. L. Henne and E. G. DeWitt, This Journal, **70**, 1548 (1948).

(9) R. N. Haszeldine, private communication.

**3,3-Difluoro-2,4-pentanedione.**—2,4-Pentanedione (89 g., 0.89 mole) in 500 ml. of absolute ethanol was treated with perchloryl fluoride while adding 102 g. (1.9 moles) of sodium methylate portionwise as described in the previous experiment. The product, isolated as before, was 94 g. (77% yield) of 3,3-difluoro-2,4-pentanedione, a colorless liquid, b.p. 114° with slow decomposition; 61° (102 mm.), $n^{27}D$ 1.3680.

*Anal.* Calcd. for $C_5H_6F_2O_2$: C, 44.12; H, 4.45. Found: C, 44.33; H, 4.93.

The infrared spectrum showed absorption at 5.71 $\mu$ characteristic of the carbonyl linkage. The starting material, 2,4-pentanedione, shows little or no normal carbonyl absorption because of almost complete enolization of the compound.[10] A strong band at 8.93 $\mu$ may be associated with the carbon–fluorine stretching frequency.

The 2,4-dinitrophenylhydrazone derivative was prepared in aqueous ethanol from the fluorinated pentanedione and 2,4-dinitrophenylhydrazine in dilute sulfuric acid to give yellow plates from benzene–light petroleum ether, m.p. 124–125°.

*Anal.* Calcd. for $C_{11}H_{10}F_2N_4O_5$: N, 17.72. Found: N, 17.92.

**Diethyl 2-Fluoro-2-phenylmalonate.**—Using the procedures described in the previous two experiments, diethyl 2-phenylmalonate (87 g., 0.37 mole) in 300 ml. of absolute ethanol was treated with perchloryl fluoride while adding 24 g. (0.44 mole) of sodium methylate portionwise. The product, isolated as before, was 88 g. (93% yield) of diethyl 2-fluoro-2-phenylmalonate, a colorless oil, b.p. 124° (0.3 mm.), $n_D^{28}$ 1.4792. Absorption in the infrared spectrum characteristic of the carbonyl linkage appears at 5.69 $\mu$. This compares with absorption at 5.76 $\mu$ in the starting material, diethyl phenylmalonate.

*Anal.* Calcd. for $C_{13}H_{15}FO_4$: C, 61.41; H, 5.95; F, 7.47. Found: C, 61.59; H, 5.88; F, 7.27.

2-Fluoro-2-phenylmalonamide was prepared by reaction of the diethyl ester with liquid ammonia containing sodium to give white needle crystals from 95% ethanol, m.p. 204–205°.

*Anal.* Calcd. for $C_9H_9FN_2O_2$: C, 55.10; H, 4.62; N, 14.29. Found: C, 55.42; H, 5.19; N, 14.45.

**Acknowledgments.**—The authors wish to express their gratitude to Miss Ruth Kossatz and Dr. R. N Haszeldine for their valuable assistance in supplying and interpreting infrared data, to Dr. H. Q Smith for contributing the fluorobarbiturate synthesis, and to Mr. Howard Francis and co-workers for the microanalysis herein reported.

WYNDMOOR, PENNA.

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[10] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

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[CONTRIBUTION NO. 4 FROM THE EXPLORATORY RESEARCH LABORATORY OF DOW CHEMICAL OF CANADA, LTD.]

# Aromatic Substitution. IV.[1a] Protonated and Deuterated Alkylbenzene Tetrafluoroborate Complexes[1b]

BY G. A. OLAH AND S. J. KUHN

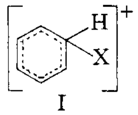
RECEIVED JULY 7, 1958

As a preparative proof of H. C. Brown's "$\sigma$-complex" theory, onium salt (or $\sigma$-complex) intermediates of alkylbenzenes with HF + $BF_3$ and DF + $BF_3$, with molecular composition of 1:1:1 were isolated. Silver tetrafluoroborate with HCl and HBr or DCl and DBr was also found to be a suitable reagent for preparing the intermediate complexes.

**Theoretical Considerations.**—During the study of the mechanism of the electrophilic aromatic substitutions the SE1 reaction type was found to be objectionable by Dewar[2] for theoretical and kinetic reasons. Even if a dissociation equilibrium in benzene exists, this has to occur so slowly and to such a small extent that this cannot serve as a basis for the substitution process.

In connection with the results of the kinetic measurements a mechanism following the second order has to be taken into account.

The pure SE2 reaction would be expected to be the simplest mechanism when the substitution proceeds in one step, without the precipitation of the $\pi$-electrons of the benzene ring, though as a consequence of the positive charge that should be present in a polarized state. In this case the intermediate complex can be formulated[3] as (the entering electrophilic substituent is represented by X)



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The substitution takes place on a sp²-bonded carbon atom. There is no possibility of inversion occurring as in the case of aliphatic substitutions since this causes an increase of the potential energy. After Hammett this intermediate may be considered as the most probable. since the investment of the orbit-delocalizating (resonance) energy of the aromatic system becomes superfluous for the process of the substitution.

Recently published investigations on aromatics containing hydrogen isotopes, however, excluded the possibility of the pure SE2 mechanism, although its relative simpleness may appear convenient. Melander's[4] investigations with tritium labeled aromatics led first of all to this result. In the case of the electrophilic substitution of benzene, derivatives substituted by tritium should show a significantly different value of the substitution ratio of protium:tritium, primarily because of the differences of the zero point energies. Since kinetic investigations did not show such a difference in the case of the investigated nitration and halogenation,

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[1] (a) Part III, *J. Chem. Soc.*, 2174 (1957). (b) The work was started in the authors' earlier laboratory, the Chemical Central Research Institute of the Hungarian Academy of Sciences, Budapest (Hungary). Partly delivered as a paper at the XVI International Congress of the International Union of Pure and Applied Chemistry in Paris, July 18, 1957, and in a lecture before the Hungarian Academy of Sciences, June 15, 1956, in Budapest; preliminary communication appeared *Nature*, **178**, 694 (1956).

[2] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 162.

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 309.

[4] L. Melander, *Acta Chem. Scand.*, **3**, 95 (1949); *Nature*, **163**, 599 (1949); *Arkiv. Kemi*, **2**, 213 (1950).