hyde, was introduced in a manner described previously.[7] The material was stirred for 10 hr. and then hydrolyzed. The organic layer was washed with water and dried, the solvent was removed, and the residue was distilled. The product decolorized permanganate rapidly.

Diethyl α-(Diphenylmethylene)benzylphosphonate (VIII).—Benzophenone (18.2 g., 0.1 mole), dissolved in 250 ml. of ether, was added dropwise to a stirred suspension of I. The mixture was stirred and refluxed for 1 hr., stirred for 12 hr., and hydrolyzed. The solvent was removed from the dried organic layer. The oily residue solidified when it was triturated with petroleum ether (b.p. 30–40°). It was triturated again with petroleum ether (b.p. 90–100°).

Diethyl α-(Benzohydryl)benzylphosphonate (X).—A mixture of 2.0 g. of VIII, dissolved in 100 ml. of warm absolute ethanol, and 0.2 g. of 5% palladium on carbon was hydrogenated for 18 hr. under an initial pressure of 40 lb. After filtration, with the use of Celite, water was added to the hot filtrate until it became turbid. The product separated from the cold mixture.

α-(Benzohydryl)benzylphosphonic Acid (XI).—A mixture of 1.0 g. of X and 20 ml. of concentrated hydrochloric acid was refluxed for 24 hr., and the inorganic acid was then removed in a stream of air. The residue was treated with aqueous sodium bicarbonate, and the mixture was extracted with benzene. The alkaline layer was acidified and extracted with benzene. After removal of the solvent from the dried benzene layer, the residue was recrystallized.

Diethyl Cinnamylphosphonate (XII).—To a stirred, refluxing suspension of 11.5 g. (0.5 g.-atom) of sodium and 500 ml. of xylene there was added dropwise 72.5 g. (0.52 mole) of diethyl phosphite.[8] The mixture was refluxed for 5 hr. and 76.0 g. (0.5 mole) of cinnamyl chloride[9] was added dropwise to the stirred refluxing mixture. After the material had been refluxed for 8 hr., it was cooled, the liquid was decanted from the sodium chloride, and the salt was washed with xylene. The solvent was removed and the residue was distilled. The product decolorized permanganate.

Diethyl α-Carboxycinnamylphosphonate (XIII) and Diethyl α-Carbomethoxycinnamylphosphonate (XIV).—The Ivanov-like reagent was prepared, in the usual manner, from 12.7 g. (0.05 mole) of diethyl cinnamylphosphonate dissolved in 25 ml. of benzene. After the addition of about 25 g. of Dry Ice, the mixture was stirred for 3 hr. and then hydrolyzed with dilute hydrochloric acid. The organic layer was shaken with aqueous sodium bicarbonate whereupon three layers were obtained. The alkaline layer and the oil were separated and the mixture was acidified with dilute hydrochloric acid. After extraction with benzene, the solvent was removed from the dried extract and the oily product XIII (6 g., 40%), which decolorized permanganate instantly, was treated with diazomethane to yield XIV.

Acknowledgment.—This investigation was supported by grants from The Wm. S. Merrell Company and from the American Foundation or Pharmaceutical Education.

[7] F. F. Blicke, H. Raffelson, and B. Barna, *J. Am. Chem. Soc.*, **74**, 253 (1952).

[8] Purchased from the Victor Chemical Works.

[9] J. F. Norris, M. Watt, and R. Thomas, *J. Am. Chem. Soc.*, **38**, 1078 (1916).

Preparation of Acyl Halides and Esters from Salts of Perfluoroalkanoic Acids[1]

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Contribution No. 281 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota

Received October 28, 1963

It is quite well known that perfluoroacyl chlorides,[2] fluorides,[3] and esters[4] may be prepared from the corresponding free perfluoroalkanoic acids. While acyl chlorides have been prepared from salts by means of inorganic chlorides,[5] the use of organic acyl chlorides[5c] normally produces mixed anhydrides; in certain cases, partially fluorinated acyl chlorides have been obtained by the latter procedure,[6] albeit only in fair yield.

The use of benzenesulfonyl fluoride to convert sodium benzoate to benzoyl fluoride (plus benzoic anhydride) has been reported,[7] though the reaction was not offered as a useful synthetic procedure.

The purpose of this Note is to call attention to several synthetic advantages which may be gained by the use of the salts, rather than the free perfluoroalkanoic acids, in exchange reactions with certain acyl halides and esters. These are (1) high yields, (2) simplicity of procedure, (3) applicability to small scale, (4) freedom from evolution of hydrogen chloride or other volatile species, (5) as a corollary, fractional distillation of the product in good purity directly from the reaction mixture. For large-scale preparations the procedure is somewhat inconvenient owing to the formation of a caked solid phase, and to the relatively high reaction temperatures usually required to achieve a suitable rate of production. In certain cases, as for example perfluorocyclohexanecarboxylic acid,[8] the salt is too unstable to permit such procedures, but this is not the usual case.[9]

It is probable that the greatest value of the salt reactions lies in small-scale analytical applications, as for example in the characterization of fluorocarbon materials by alkaline cleavage or by permanganate oxidation. Normally the sodium or potassium salts are separated from inorganic contaminants by virtue of the relative insolubility of the latter in warm absolute ethanol. Acyl halides and methyl esters are especially desired for nuclear magnetic resonance spectroscopy and for retention time measurement by gas–liquid chromatography, as well as for molecular weight and saponification number determinations. Analytical purity of product is often obtained on a 1- to 5-g. scale without recourse to refractionation.

Experimental

The reactions were conveniently carried out by treating the powdered well-dried salt (usually the sodium salt) with a two- to threefold excess (*i.e.*, about an equal weight) of the organic exchange agent, in a flask of such size as to be about half filled therewith, and which was fitted with a short fractionating column of perhaps five to ten theoretical plates. An intermittent take-off head was desirable for boiling point determination, as well as

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[1] Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., 1955, p. 27M.

[2] (a) CF_3COCl *via* PCl_5: R. G. Jones, *J. Am. Chem. Soc.*, **70**, 143 (1948); and A. L. Henne, R. M. Alm, and M. Smook, *ibid.*, **70**, 1968 (1948). (b) C_3F_7COCl and higher homologs *via* PCl_5: M. Hauptschein, J. F. O'Brien, C. S. Stokes, and R. Filler, *ibid.*, **75**, 87 (1953); J. H. Simons, W. T. Black, and R. F. Clark, *ibid.*, **75**, 5621 (1953); and R. Filler, J. F. O'Brien, J. V. Fenner, and M. Hauptschein, *ibid.*, **75**, 966 (1953); (c) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 549.

[3] G. Olah, I. Kuhn, and I. Beke, *Chem. Ber.*, **89**, 862 (1956).

[4] (a) F. Swarts, *Bull. classe sci. acad. roy. Belg.*, **6**, 300 (1920); (b) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 480.

[5] (a) J. H. Simons and E. O. Ramler, *J. Am. Chem. Soc.*, **65**, 389 (1943); (b) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 547; (c) p. 559.

[6] (a) M. Prober, *J. Am. Chem. Soc.*, **75**, 968 (1953); (b) **77**, 910 (1955).

[7] W. Steinkopf and P. Jaeger, *J. prakt. Chem.*, [2]**128**, 65 (1930).

[8] T. J. Brice and J. H. Simons, *J. Am. Chem. Soc.*, **73**, 4017 (1951).

[9] L. J. Hals, T. S. Reid, and G. H. Smith, *ibid.*, **75**, 4595 (1953).

to prevent contamination of the product by the organic exchange agent when the reaction proceeds slowly despite high pot temperatures. While the reactions begin around 150° (much lower in the case of dimethyl sulfate), it is sometimes necessary to heat the mixture as high as 250° to collect the last of the product. Yields and physical properties are given in Table I.

TABLE I

REACTIONS OF SALTS OF PERFLUOROALKANOIC ACIDS

Product[a]	Exchange agent	Yield, %	B.p., °C.	n^{25}_{D}[b]
n-C_3F_7COCl	C_6H_5COCl	88	39	1.2852
n-C_3F_7COCl	$C_6H_5CCl_3$	92	39	1.2854
n-C_3F_7COCl	p-$CH_3C_6H_4SO_2Cl$	80	39	1.2851
n-C_3F_7COCl[c]	$C_6H_5CCl_3$	87	39	1.2851
n-$C_7F_{15}COCl$	o-$C_6H_4(COCl)_2$	76	136	1.3035
(n-$C_9F_{19}COCl$)[d]	C_6H_5COCl	(–)[d]	(163)[d]	(1.3150)[d]
n-$C_9F_{19}COCl$	o-$C_6H_4(COCl)_2$	88	173	1.3087
n-$C_5F_{11}COF$	p-$CH_3C_6H_4SO_2F$	68	59	1.2625
n-$C_7F_{15}COF$	p-$C_2H_5C_6H_4SO_2F$	80	104	1.2764
n-$C_3F_7CO_2CH_3$	p-$CH_3C_6H_4SO_3CH_3$	98	81	1.2901
n-$C_3F_7CO_2CH_3$	$(CH_3)_2SO_4$	98	81	1.2922

[a] The sodium salt was used in all cases but one. Amounts used varied from 5 to 50 g. The structure of the salt used corresponds to the structure of the product. [b] This is the refractive index of the "crude" product; it agrees closely with the reported value. [c] The calcium salt was used. [d] The product was contaminated with benzoyl chloride, which codistilled.

The organic exchange agent should be chosen to boil far above the desired product, as otherwise it may become a serious contaminant owing to codistillation; this results from partial immiscibility with the fluorinated product and *cannot* be overcome by increasing the efficiency of the fractionating column. Benzoyl chloride, or benzotrichloride (which forms benzoyl chloride during the reaction), may be used for synthesis of up to six-carbon perfluoroacyl chlorides, but higher ones require phthalyl chloride. In special cases, dimethyl sulfate may be used for the synthesis of close-boiling esters by the expedient of using slightly *less than equimolar* amounts; it is thereby completely converted to the salt of methylsulfuric acid, and thus does not contaminate the product.

The identity and purity of the products was well established by comparison of physical properties with literature values, and also by infrared spectroscopy; in addition, the following analytical data were secured on the "crude" products of Table I in order to lend further support to the claims of purity. The n-C_3F_7COCl,[2b,10] from the sodium salt *via* $C_6H_5CCl_3$, had a strong infrared band due to C═O at 5.52 μ.

Anal. Calcd. for C_4ClF_7O: Cl, 15.25. Found: Cl (hydr.), 15.2.

For n-$C_7F_{15}COCl$[2b] also, the C═O band was at 5.52 μ.

Anal. Calcd. for $C_8ClF_{15}O$: C, 22.2; Cl, 8.25; F, 65.9. Found: C, 22.3; Cl (hydr.), 8.3; F, 65.1.

Similarly, n-$C_9F_{19}COCl$[2b] had its C═O band at 5.53 μ.

Anal. Calcd. for $C_{10}ClF_{19}O$: C, 22.6; Cl, 6.66; F, 67.9. Found: C, 22.7; Cl (hydr.), 6.7; F, 67.2.

The sample of n-$C_5F_{11}COF$ had its C═O band at 5.32 μ.

Anal. Calcd. for $C_6F_{12}O$: C, 22.8; F(hydr.), 6.02. Found: C, 23.0; F (hydr.), 6.0.

The n-$C_7F_{15}COF$ showed its C═O band at 5.31 μ, and was, therefore, not further analyzed. There was no question as to the identity of the $C_3F_7CO_2CH_3$,[11] which is a well-known compound.

Acknowledgment.—The author thanks Dr. W. E. Keiser and Dr. J. J. McBrady for the infrared spectral analysis.

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Alkaline Hydrolysis of Ethyl Benzoate in Aqueous Dimethyl Sulfoxide

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Received November 26, 1963

The data presented in the recent review article of Parker[1] very clearly demonstrate the marked rate-enhancing ability of dipolar aprotic solvents such as dimethyl sulfoxide upon bimolecular displacement reactions effected with anions. Thus Friedman and Shechter[2] reported the greatly accelerated displacement of halide by cyanide, azide, thiocyanate, and halide ions; Smiley and Arnold[3] observed the facile interconversion of primary and secondary halides to nitriles by the action of cyanide ion in dimethyl sulfoxide; and Cram and co-workers[4] found that use of dimethyl sulfoxide as a solvent allows both the Wolff–Kishner reduction and the Cope elimination reaction to be run at room temperature.

In accordance with these findings and his own excellent work with S_NAr-type reactions, Parker[5a] postulated that any bimolecular reaction of a small anion passing through a large polarizable transition state will be considerably accelerated in the change from protic to dipolar aprotic solvents.

Such a reaction that has yet to be investigated kinetically in dipolar aprotic solvents is the alkaline hydrolysis of esters.[5b] In consideration of the large amount of work that has been carried out towards elucidating the mechanism of ester saponification (BAc^2),[6,7] a quantitative study of the effect of an aprotic solvent upon this reaction should be of interest. To this end, the present paper deals with the alkaline hydrolysis of ethyl benzoate in aqueous dimethyl sulfoxide. This ester was selected for study because a similar investigation carried out with ethyl benzoate in aqueous ethanol permits a comparison with a typical protic solvent system.

Table I presents the kinetic findings of this work. It is readily apparent from this table that alkaline hydrolysis of ethyl benzoate in aqueous dimethyl sulfoxide is accelerated relative to aqueous ethanol. Since the mechanism of the base-catalyzed hydrolysis of a normal ester[6,7] involves the production of a large polarizable transition state *via* the rate-determining addition of hydroxide ion to the carbonyl carbon atom of the ester, the data reported in Table I are in accord with Parker's postulate. Change from aqueous ethanol to aqueous dimethyl sulfoxide leads to a diminishment in hydroxide ion solvation[1,8] and an increase in transition state

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