quency factors with the former effect dominating. Since the effect of stabilization of the S· species would be expected to influence only the activation energy through weakening the carbon–hydrogen bond, the increase in frequency factor with more active solvents would also tend to decrease the sensitivity of the chain transfer reaction to the S· reorganization energy.

At 70°, the chain transfer constant of triphenylsilane is greater than that of triethylsilane by a factor of 13.7. At 80°, the ratio is more uncertain, but it probably lies between 14 and 28. These ratios point to a definitely lower free energy of activation for the triphenylsilane chain transfer process than for the triethylsilane transfer. The higher rate of the triphenylsilane transfer could be attributed to greater resonance stabilization of the triphenylsilyl radical with respect to the triethylsilyl radical, or to the inductive influence of the phenyl groups on the Si–H bond strength. Uncertainty[6] as to the relative importance of the frequency factors and activation energies of the process preclude any possibility of estimating a reliable value of the resonance stabilization, if any, of the triphenylsilyl radical.

The chain transfer constants of both the silanes tested show a high degree of reactivity relative to the hydrocarbon solvents in Table IV. Triethylsilane lies between diphenylmethane and triphenylmethane and triphenylsilane is a more efficient transfer agent than triphenylmethane, approaching carbon tetrachloride in reactivity. The silicon–hydrogen bond energy at 298°K. has been calculated from critically evaluated data at 79 kcal./mole, while carbon–hydrogen bonds have an energy of 88 kcal./mole on the same scale.[19] The lower silicon–hydrogen bond energy is most probably responsible for the increased efficiency of silicon–hydrogen compounds over hydrocarbons in the chain transfer reactions.

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[CONTRIBUTION FROM THE CHEMICAL CORPS, CHEMICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Esterification of Carboxylic Acids by Dialkyl Phosphonates

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Aliphatic and aromatic carboxylic acids have been converted to alkyl esters in excellent yields by heating with dialkyl phosphonates.

The dealkylation of alkyl esters of phosphorous acid by hydrogen halides has been studied extensively in the past by Gerrard and co-workers.[2] The rates of this reaction for a given phosphite ester with respect to the hydrogen halide were found to decrease in the order: HI > HBr >> HCl, and with respect to a given hydrogen halide in the order: $(RO)_3P >> (RO)_2P(O)H > ROP(OH)_2$.[2b] The dealkylation of phosphites with hydrogen halides which proceeds according to the reaction sequence: $(RO)_3P + HX \rightarrow (RO)_2P(OH) + RX$; $(RO)_2P(O)H + HX \rightarrow ROP(OH)_2 + RX$; $ROP(OH)_2 + HX \rightarrow H_3PO_3 + RX$, can be used conveniently for the preparation of alkyl halides as well as mono- or dialkyl phosphites.[2a,c]

The acidolysis of the alkyl phosphites is not restricted to the hydrogen halides but was found in our study to occur also with the weakly acidic aliphatic and aromatic carboxylic acids. However, while the reaction with hydrogen halides proceeds at room temperature or below,[2a,c,3] the dealkylation by carboxylic acids requires higher reaction temperatures and is, in general, for preparative purposes best carried out by heating the mixture of alkyl phosphite and acid to temperatures above 100°. As in the reaction of an alkyl phosphite with a hydrogen halide, an alkyl group of the phosphite is replaced by hydrogen and transferred to the acid anion with the formation of the corresponding carboxylic acid ester. Although the rate of the acidolysis of a trialkyl phosphite is considerably faster than that of a dialkyl phosphonate (phosphite), the latter esters are of greater practical value as reactants for a rapid esterification of a carboxylic acid because of their ready availability from alcohols and phosphorus trichloride.[4] Since the acidolysis of an alkyl phosphite with excess acid results in the formation of phosphorous acid, each one of the alkyl groups of a dialkyl phosphonate can be utilized for esterification under the proper reaction conditions. By heating a carboxylic acid with 0.5 to 1 mole equivalent of a dialkyl phosphonate, esterification of an acid can be achieved readily in excellent yields without the use of a solvent or of excess alcohol as reaction medium as in most conventional esterifications. The resulting carboxylic acid esters can be separated easily from the acidolysis products of the phosphite by several simple manipulations, such as direct distillation, extraction or steam distillation. A similar method for the esterification of organic acids has been described recently by Sumrell and Ham,[5] who utilized the acidolysis of several alkyl orthosilicates by carboxylic acids for the preparation of the corresponding alkyl esters of the organic acids.

As the cleavage of alkyl phosphites by carboxylic

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[2] (a) M. C. Berlak and W. Gerrard, *J. Chem. Soc.*, 2309 (1949); (b) W. Gerrard and E. G. G. Whitbread, *ibid.*, 914 (1952); (c) V. F. Cooke and W. Gerrard, *ibid.*, 1978 (1955).

[3] C. H. Campbell and D. H. Chadwick, THIS JOURNAL, **77**, 3379 (1955).

[4] H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

[5] G. Sumrell and G. E. Ham, THIS JOURNAL, **78**, 5573 (1956).

TABLE I

PREPARATION OF ALKYL ESTERS OF CARBOXYLIC ACIDS

Acid	Mole ratio of reactants[a]	Maximum reaction temp., °C.	Heating period in hr.	Method of isolation	Yield of ester, %	B.p., °C.	B.p., °C. lit.[b]	n^{25}D	n^tD lit.[b]
Methyl esters									
Acetic[c]	0.5	150	3	A	90	55–58	57.1	1.3595	1.36170 (20°)
[c]	1	150	3	A	100	54–57			
Propionic	0.5	130	10 min.[d]	A	98	78–80	79.9	1.3742	1.3779 (25°)
Caproic	0.5	176	40 min.[d]	A	71.5[e]	149–150	151.2	1.4021	1.40699[g]
	1	164	2	A	78[f]	149.5–150.5			
Benzoic[c]	1	200	2	C[h]	75	193–196	199.6	1.5146	1.5164 (20°)
Salicylic	1	200	6	B	80	98–100(200 mm.)	224	1.5352	1.5369 (20°)
Succinic	1	195	4	C	79	193.5–195.5	196.0	1.4199 (20°)	1.41965 (20°)
Adipic	0.5	197	5	C[h]	68	121–123(20 mm.)	107.6(11 mm.)	1.4292 (20°)	1.42835 (20°)
Phthalic	1[i]	220	6	B	20.5	[k]	283.8°	1.5123	1.5138 (20°)
Perfluorobutyric	1	142	0.5[d]	A	80	81.5–82	79(737 mm.)[l]	....	1.293 (20°)[l]
Ethyl esters									
Formic	0.5	111	7	A[m]	85	54–55	54.2	1.3583	1.35975 (20°)
	1	124	4	A[n]	99	54.5		1.3573	
Acetic	1	153	3.5	A[o]	95	77–78	77.2	1.3704	1.3707 (20°)
Propionic	0.5	143	10 min.[d]	A	94	97–99	99.1	1.3879 (20°)	1.3853 (20°)
o-Toluic	1	204	2.5	C	88	113(18 mm.)	227	1.5023	1.507 (21.6°)
Salicylic	0.5	200	6	B	79	58(0.4 mm.)[p]	234	1.5253	1.52542 (20°)
	1	200	6	B	76	[k]		1.5222	
Succinic	0.5	160	4	A	92	101–102(14 mm.)	217.7	1.4200 (20°)	1.41975 (20°)
	1	145	6	B	91	[k]		1.4183	
Adipic	1	205	6	A	74	75–76(5 mm.)	245	1.4260	1.4265 (20°)
Perfluorobutyric	0.5	121	0.5[d]	A[q]	80	95.5–9.65	95(744 mm.)[l]	1.3006	1.3032 (20°)[l]
Propyl esters									
Acetic[c]	0.5	160	2	A	93	100–101.5	101.6	1.3835 (20°)	1.3847 (20°)
[c]	1	160	2	A	95.5	100–101.5		1.3835 (20°)	
Propionic	1	160	5	C	83	58–59(100 mm.)	123.4	1.3920	1.3932 (20°)
Benzoic	1	200	4	C	88	60(0.50 mm.)	231.2	1.4952	1.4959 (25°)
Salicylic	1	200	4	C	84.5	75(0.50 mm.)	249–251	1.5161	1.5161
Succinic	1	200	8	C	87	99–101(0.50 mm.)	248.0	1.4247	1.4252 (20°)
Perfluorobutyric	1	160	2.5	C	95.5	103–104[r]	...	....	....
Butyl esters									
Acetic	1	150	4	C	95	55(100 mm.)	126	1.3929	1.3961 (15°)
Propionic	1	160	4	C	97	144–145	146.8	1.4000	1.4038 (15°)
Caproic	0.5	165	4	A	95	95–96.5(20 mm.)[s]	207.7	....	
Benzoic	1	200	4	C	80	81(1 mm.)	250.3	1.4955	
Salicylic	1	200	3	C	88	80(0.30 mm.)	270	1.5099	1.5095
Succinic	1	200	7	A	86	96(0.05 mm.)	274.5	1.4290	1.4298 (20°)
Perfluorobutyric	0.5	142	0.5[d]	A	74	132.5–133.5	132(740 mm.)[l]	1.3242	1.3249[l]
Hexyl esters									
Acetic	1	170	3.5	C	95.5	57–59(5 mm.)[t]	178.1	1.4090	1.4112[g]
Propionic	0.5	160	3	A	84	185–186	190	1.4067	1.4162[g]
Benzoic	1	200	8.5	C	85	101(0.10 mm.)[u]	200–202 (100 mm.)	1.4559	
Adipic	1	178	6	C	79	182.5(4 mm.)[v]		1.4397	
Perfluorobutyric	0.5	160	5	A	95	169–170[w]		1.3486	

[a] Molar ratio of dialkyl phosphonate to carboxyl group. [b] Except where stated otherwise, the literature data were taken from Huntress and Mulliken, "Identification of Pure Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941. [c] The authors greatly appreciate the help of W. G. Gall who performed this run. [d] After the indicated reflux period, the resulting ester was distilled from the reaction mixture at the rate of its formation. [e] *Anal.* Calcd.: C, 64.63; H, 10.77. Found: C, 64.8; H, 10.8. [f] *Anal.* Calcd.: C, 64.63; H, 10.77. Found: C, 64.3; H, 10.6. [g] n^{15}He. [h] Without neutralizing the reaction mixture before extraction. [i] A similar run with a reactant ratio of 1.5 did not give any ester at all. [k] Steam distilled material. [l] Minnesota Mining & Manufacturing Co., St. Paul, Minn., Data Sheet "Heptafluorobutyric acid." [m] The colorless viscous distillation residue, degassed for 3 hr. at 0.8 mm. pressure, contained 94.4% H_3PO_4,

1.9% $C_2H_5OP(OH)_2$ and 1.1% $(C_2H_5O)_2P(O)H$. [n] The colorless distillation residue contained approximately 18.9% H_3PO_4, 56% $C_2H_5OP(OH)_2$ and 21.9% $(C_2H_5O)_2P(O)H$ after degassing for 2 hr. at 0.5 mm. pressure. [o] The colorless viscous distillation residue contained approximately 36% H_3PO_4, 16% $(C_2H_5O)_2P(O)H$ and 48% $C_2H_5OP(OH)_2$. [p] *Anal.* Calcd.: C, 65.05; H, 6.07. Found: C, 65.05; H, 6.1. [q] The lower layer (separated from the crude ester layer) contained 73.9% H_3PO_4, 17.5% $C_2H_5OP(OH)_2$ and less than 0.5% $(C_2H_5O)_2P(O)H$. [r] *Anal.* Calcd.: C, 32.82; H, 2.75. Found: C, 32.5; H, 2.8. [s] *Anal.* Calcd.: C, 69.72; H, 11.70. Found: C, 69.5; H, 11.3. [t] *Anal.* Calcd.: C, 66.68; H, 11.11. Found: C, 66.5; H, 11.3. [u] *Anal.* Calcd.: C, 75.69; H, 8.80. Found: C, 75.3; H, 8.6. [v] *Anal.* Calcd.: C, 68.75; H, 10.90. Found: C, 68.5; H, 10.8. [w] *Anal.* Calcd.: C, 40.28; H, 4.39; C, 40.26; H, 4.39; $d^{25}{}_4$ 1.2266.

acids appeared to show promise as a preparative method for organic esters, we investigated this reaction using a number of organic acids and dimethyl, diethyl, di-*n*-propyl, di-*n*-butyl and di-*n*-hexyl phosphonate. The results of this study are presented in Table I.

The susceptibility of both alkoxy groups of a dialkyl phosphonate to acidolysis by carboxylic acid groups was demonstrated by a number of runs using a molar ratio of 1:2 of phosphite ester to carboxylic acid group (all runs of Table I with a reactant ratio of 0.5). In most of these runs the yields of the resulting organic esters were above 90%. The yields of the once-distilled esters listed in the table were obtained from single runs and by no means represent optima. That the lower yields of some of the runs can be improved by a proper adjustment of the reaction conditions is demonstrated clearly by the analysis of the phosphorous acid layer of the run with perfluorobutyric acid and diethyl phosphonate (see footnote *q* of table). The presence of 17.5% of monoethyl phosphite in the distillation residue shows the incompleteness of the acidolysis reaction suggesting that a longer reflux period will improve the yield of ethyl perfluorobutyrate considerably. Almost complete acidolysis of the phosphonate was observed in the esterification of formic acid with diethyl phosphonate using a mole ratio of the reactants of 0.5 (see footnote *m* of table). The relatively low yield of 85% of ethyl formate in this run is mainly the result of a loss of product in the distillation forerun. It is interesting to note that a similar run with a reactant ratio of 1 (99% yield of ethyl formate) left a distillation residue, the analysis of which clearly proves that the ratio of the rates of dealkylation by formic acid of the di- and monoalkyl phosphite at the relatively high reaction temperature is approximately 2.5:1. Cook and Gerrard[2c] had found this ratio for the dealkylation by hydrogen iodide to be 13.1:1. A similar approximate dealkylation ratio of about 3:1 was observed in a 1:1-mole run with acetic acid and diethyl phosphonate. These results show that, in contrast to the reaction with anhydrous HI, the dealkylation of a dialkyl phosphonate by a carboxylic acid at higher temperatures, although useful for the esterification of an organic acid, is not suitable for the preparation of monoalkyl phosphites.

Experimental

Materials.—Commercial diethyl phosphonate (Virginia Carolina Chemical Corp.) was used without further purification. Dimethyl phosphonate, b.p. 60° (12 mm.), $n^{25}D$ 1.4015, d_{20} 1.195; di-*n*-propyl phosphonate, b.p. 50° (0.30 mm.), $n^{25}D$ 1.4150, d_{25} 1.0098; di-*n*-butyl phosphonate, b.p. 71° (0.20 mm.), $n^{25}D$ 1.4242, d_{25} 0.9829; and di-*n*-hexyl phosphonate, b.p. 104–105° (0.10 mm.), $n^{25}D$ 1.4331, d_{25} 0.9442, were prepared by the method of McCombie, *et al.*,[4] in 82, 79, 73 and 69% yield, respectively, from the corresponding alcohols and phosphorus trichloride. The carboxylic acids were all commercial products.

General Procedure for the Esterification of Carboxylic Acids with Dialkyl Phosphonates.—A mixture of the appropriate aliphatic or aromatic carboxylic acid with 0.5 to 1.0 mole equivalent of the dialkyl phosphonate was heated in a Pyrex round-bottom flask, equipped with reflux condenser, for varying periods of time depending on the nature of the alkyl phosphonate and the carboxylic acid. The pot temperature ranged, in general, between 100 and 200°. The esterification was complete in runs using a reactant ratio of 0.5, when the insoluble phosphorous acid layer did not increase further in volume, and in runs with a reactant ratio of 1, when no further changes of vapor and pot temperatures were noted. However, in runs in which the boiling point of the resulting ester was higher than the temperature of the reaction mixture, the mixture was maintained at temperatures between approximately 150 and 200° for periods of 4–8 hr.

Low boiling alkyl esters were distilled directly from the reaction mixture (method A). Higher boiling esters were isolated by diluting the entire reaction mixture with two to three volumes of water, neutralizing with aqueous alkali or saturated aqueous sodium or potassium carbonate to litmus and steam distilling (method B) or extracting with diethyl ether (method C).

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