the crude product produced recovered alcohol, 198 g. of 1,1,7-trihydroperfluoroheptyl benzoate, b.p. 155° (0.5 mm.), and 295 g. of 1,1,7-trihydroperfluoroheptyl orthobenzoate, b.p. 187° (0.1 mm.), 62% yield based on unrecovered alcohol.

Anal. Calcd. for $C_{28}H_{14}F_{36}O_3$: C, 31.05; H, 1.29. Found: C, 31.21; H, 1.36.

1,1,5-Trihydroperfluoropentyl Chlorocarbonate.—A solution of 69.6 g. (0.3 mole) of 1,1,5-trihydroperfluoropentanol and 5.4 g. (0.3 mole) of water was added intermittently over a period of 1.25 hr. to a mixture of 26.4 g. of ferric chloride in 60 ml. of carbon tetrachloride at 76°. Large amounts of phosgene and hydrogen chloride were evolved over a period of 5 hr. After the addition of 2.5 ml. more of water, the reaction was allowed to continue an additional 8 hr. After cooling, the entire reaction mixture was dissolved in ether, washed very quickly with cold water, dried, and distilled. The fractionation gave recovered alcohol, 40 g. (60%) of the chlorocarbonate, b.p. 53° (13 mm.), and 15 g. (21%) of the bis carbonate.

A part of the 1,1,5-trihydroperfluoropentyl chlorocarbonate (6.0 g., 0.02 mole) was added to excess methanol in ether at 50°. Distillation after work-up yielded 4.3 g. (70% of methyl 1,1,5-trihydroperfluoropentyl carbonate, b.p. 50° (0.15 mm.).

Methyl chlorocarbonate (10.4 g., 0.11 mole) was stirred with 23.2 g. (0.1 mole) of 1,1,5-trihydroperfluoropentanol in chloroform containing 0.02 mole of titanium tetrachloride for 5 hr. at 50°. After work-up similar to above experiments, fractionation of the product yielded 24.2 g. (80%) of the methyl fluoro alcohol carbonate, b.p. 46° (0.1 mm.).

The two methyl fluoro alcohol carbonates from these experiments were found to be identical by infrared and n.m.r. analyses and determination of the same retention times by g.l.p.c.

1,1,7-Trihydroperfluoroheptyl chlorocarbonate was prepared in a similar manner except the alcohol and water were added portionwise simultaneously. The chlorocarbonate was obtained in 40% yield, b.p. 73° (14 mm.).

Anal. Calcd. for $C_8H_3ClF_{12}O_2$: C, 27.70; H, 1.54. Found: C, 27.81; H, 1.44.

Phosgene was bubbled through a mixture of 22.7 g. (0.1 mole) of 1,1,5-trihydroperfluoropentanol and 8.1 g. (0.05 mole) of ferric chloride for 6 hr. at 50°. Less than 10% of chlorocarbonate was obtained.

Acknowledgment.—This paper is related to an observation by one of us (M. E. H.) at the U. S. Naval Ordnance Laboratory, Silver Spring, Maryland. The many stimulating discussions with Dr. D. V. Sickman and Dr. O. H. Johnson are gratefully acknowledged.

Modifications of the Hunsdiecker Reaction[1a]

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Received August 18, 1964

Bromodecarboxylation of organic acids by the Cristol–Firth modification of the Hundsiecker reaction using the free acid and red mercuric oxide was found to be much more effective than the modification using the acid chloride and silver oxide. A study has been made of the possible use of oxides other than mercuric oxide and of the effectiveness of various solvents.

Replacement of the carboxyl group in organic acids by a halogen atom, especially bromine, by treatment of the anhydrous silver salt of the acid with bromine, chlorine, or iodine in an inert solvent is commonly known as the Hunsdiecker reaction.[2-4] Yields are generally quite good (usually better than 60%), but the reaction is extremely sensitive to trace amounts of water, the presence of which leads to the recovery of unchanged acid. Unfortunately, the preparation of dry silver salts of carboxylic acids is frequently very difficult and, because such salts are usually quite sensitive to heat also, they are often quite hard to dry thoroughly.

Several years ago there appeared a report[5] that the acid chloride of penta-*O*-acetyl-D-gluconic acid undergoes smooth decarboxylation when heated with bromine and silver oxide in carbon tetrachloride, furnishing aldehydo-1-bromo-D-arabinose penta-*O*-acetate in an excellent yield. A second report[6] described the reactions of benzoyl chloride and three other aromatic acid chlorides with bromine and silver oxide in carbon tetrachloride.

An investigation of this modification of the Hunsdiecker reaction was started using the following acid chlorides: benzoyl chloride, *n*-butyryl chloride, phthaloyl chloride, *p*-nitrobenzoyl chloride, and *p*-chlorobenzoyl chloride.

The silver oxide was carefully dried as was all the glassware and the carbon tetrachloride, bromine, and acid chlorides were redistilled before use. Although numerous variations of the reaction conditions were tried, only trace amounts of the desired bromides were obtained by fractional distillation of the reaction mixtures. However, fair yields of bromobenzene were obtained from silver benzoate by the original Hunsdiecker reaction.

Fund, Cristol, and Firth have reported[7] that treatment of a slurry of excess red mercuric oxide in a refluxing solution of stearic acid in carbon tetrachloride with approximately an equivalent amount of bromine in the dark gave a 93% yield of crude heptadecyl bromide. The reaction also was reported to give poor yields with benzoic acid and glutaric acids, and fair to excellent yields with cyclopropanecarboxylic acid, 9,10-dihydro-9,10-ethane-9-anthronic acid, and lauric acid. As soon as we learned of the Cristol–Firth modification, its apparent convenience and simplicity in comparison to those procedures involving preparation of silver salts or acid chlorides immediately suggested a broad study of this modified procedure using different classes of carboxylic acids and the use of solvents other than carbon tetrachloride. Since mercuric oxide is relatively expensive and mercury compounds are toxic, a study also was made of the possibility of using other oxides for this reaction.

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(1) (a) This work was made possible by Grant #897-B from the Petroleum Research Fund, administered by the American Chemical Society; (b) American Chemical Society Petroleum Research Fund Scholar.

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TABLE I

PER CENT YIELDS BASED ON WEIGHT OF BROMIDE RECOVERED

Acid	Solvent	Product	Yield, %	B.p., °C.[a]	$n_D^{°C.}$[a]
Chloroacetic	$C_2H_2Cl_4$	Bromochloromethane	38	68–73 (68–69)[b]	1.4795^{25} (1.4832)[b]
n-Butyric	$C_2H_2Cl_4$	1-Bromopropane	53	70–74 (72)[c]	1.4351^{25} (1.4348)[c]
Isobutyric	$C_2H_2Cl_4$	2-Bromopropane	21	59–62 (59)	1.4250^{25} (1.4254)
2-Methylbutyric	$C_2H_2Cl_4$	2-Bromobutane	61	90–94 (91)	1.4301^{25} (1.4366)
Hexanoic	CCl_4	1-Bromopentane	31	125–130 (128)	1.4440^{31} (1.4450)
Heptanoic	CCl_4	1-Bromohexane	37	150–158 (159)	1.4470^{28} (1.4478)
Octanoic	CCl_4	1-Bromoheptane	31	175–180 (177.5)	1.4462^{31} (1.4505)
Dodecanoic	CCl_4	1-Bromoundecane	46	55–60 (114)[d]	1.4568^{25} (1.4569)

[a] Numbers in parentheses refer to literature values. Literature values of refractive index are given for 20°. [b] C. L. Stevens, T. K. Mukherjee, and V. J. Traynelis, *J. Am. Chem. Soc.*, **78**, 2264 (1956). [c] The literature values for 1-bromopropane and for all the compounds below it in the table are taken from A. I. Vogel, *J. Chem. Soc.*, 636 (1943). [d] Value given for 0.05 mm.; liturature value given for 5 mm.

TABLE II

PER CENT YIELDS BASED ON AMOUNT OF CARBON DIOXIDE PRODUCED[a]

Acids	CCl_4[b]	$C_2H_2Cl_4$[b]
Chloroacetic		71 (38)
Trichloroacetic		82 (13)
Propionic		94
n-Butyric		99 (53)
Isobutyric		90 (21)
2-Methylbutyric		77 (61)
2-Ethylbutyric	80	87 (17)
Trimethylacetic		85 (13)
Hexanoic	88 (31)	
Cyclohexanecarboxylic	88	
Heptanoic	90 (37)	
Octanoic	59 (31)	
2-Ethylhexanoic	76	92
Decanoic		69
Lauric	67 (46)	
Myristic	91	
Palmitic	90	81
Stearic	95	
Phenylacetic	41	71
Diphenylacetic	51	
Benzoic	48	83
p-Toluic	40	76
Anisic	54	
p-Nitrobenzoic	0	70
Phthalic		85
Terephthalic		20
Malonic	19	33
Glutaric	85	
Hexanedioic		53
Octanedioic	29	75
Decanedioic	66	79

[a] Using red mercuric oxide and either carbon tetrachloride or 1,1,2,2-tetrachloroethane as solvent. [b] Numbers in parentheses are per cent yields based upon the amount of organic bromide recovered by fractional distillation.

After trying a number of variations of the method, it was found that best yields were obtained when the acid, the red mercuric oxide, and the solvent were mixed and stirred with a magnetic stirrer. The mixture was then heated and a small fraction of the bromine was added. If a reaction did not occur spontaneously, heating was continued until the reaction started; then the remainder of the bromine was slowly added. The mixture was kept warm for 1 hr., then filtered and washed with 5% sodium hydroxide solution, then with water, and dried over anhydrous magnesium sulfate. It was then filtered and the bromide was separated by fractional distillation and identified by its boiling point and refractive index (see Table I).

As the isolation by fractional distillation of a small amount of liquid product from a relatively large volume of solvent is a time-consuming operation and normally is not quantitative, a large number of determinations was made in which the extent of reaction was determined by measuring the amount of carbon dioxide evolved. In these determinations 0.01 mole of acid was mixed with 5 g. (an excess) of red mercuric oxide (or an equivalent amount of other oxide) and 50 ml. of solvent. The mixture was warmed and 2 ml. of bromine was slowly added. The carbon dioxide was swept out of the apparatus with nitrogen and absorbed in a standard barium hydroxide solution. The barium carbonate precipitate was removed by filtration and the excess barium hydroxide was titrated with standard acid. See Table II for yields obtained when carbon tetrachloride and 1,1,2,2-tetrachloroethane were used as solvents.

Of the oxides that were tested as replacements for red mercuric oxide, only the five listed in Table III showed any reaction. Propionic acid dissolved in tetrachloroethane and treated with bromine in the presence of an oxide of each of the following gave no reaction: aluminum, antimony, barium, bismuth, calcium, cobaltic, cupric, cuprous, ferric, magnesium, nickelic, stannic, zinc, and sodium and titanium dioxides.

TABLE III

PER CENT YIELDS BASED ON AMOUNT OF CARBON DIOXIDE PRODUCED[a]

	Yield, %				
Acid	HgO (yellow)	Ag_2O	PbO	Pb_3O_4	CdO
Propionic	87	78	42	45	8
Palmitic	76	12		5 (CCl_4)	
Acid chlorides					
Benzoyl chloride		7 (CCl_4)			
Palmitoyl chloride		8 (CCl_4)			
Butyryl chloride		45			

[a] Using 1,1,2,2-tetrachloroethane as solvent and oxides other than red mercuric oxide.

For the effectiveness of solvents other than carbon tetrachloride and tetrachloroethane see Table IV.

Discussion

In this investigation it was found that the Cristol–Firth method using red mercuric oxide and the free acid gave much more decarboxylation than did the method

Table IV

Per Cent Yields Based on Amount of Carbon Dioxide Produced[a]

Acid	Yield, % Benzene	Nitrobenzene	Bromobenzene	Chlorobenzene	C_2Cl_4-F_2	C_2Cl_3-F_3	Hexane
Palmitic	69	82	76	67	71	58	40
Phthalic	0	0	32				
Terephthalic		26					
Propionic			79		61	2	40
Benzoic	6			48	41		0
Stearic						81	
2-Ethylbutyric					60	43	

[a] Using red mercuric oxide and different solvents.

using silver oxide and the acid chloride. The Cristol–Firth method is simpler than the original Hunsdiecker method in that it does not require the preparation of the dry silver salt. In many cases higher yields were obtained with tetrachloroethane as solvent than with carbon tetrachloride. This probably was due to the higher boiling point of the tetrachloroethane which permitted a higher reaction temperature. Bromobenzene and tetrachlorodifluoroethane seem to offer some promise as other solvents for this reaction. Yellow mercuric oxide was found to be almost as effective as red mercuric oxide. As a general rule aromatic and dicarboxylic acids underwent less bromodecarboxylation than did aliphatic monocarboxylic acids.

Experimental

For the preparation and isolation of the organic bromides, 0.1 mole of bromine was slowly added to a warm, stirred mixture of 0.1 mole of acid and 0.1 mole of red mercuric oxide in 150 to 200 ml. of solvent. The reaction mixture was then refluxed for at least 1 hr., then filtered, washed, and dried, and the organic bromide was separated by fractional distillation. The preparation of 1-bromohexane is typical of the method used.

Preparation of 1-Bromohexane from Heptanoic Acid.—A few drops of a solution containing 16 g. (0.1 mole) of bromine in 50 ml. of dry carbon tetrachloride produced an immediate reaction when added to a warm, stirred mixture of 13.0 g. (0.1 mole) of heptanoic acid and 22 g. of red mercuric oxide in 150 ml. of dry carbon tetrachloride. The remainder of the bromine solution was added slowly and the reaction mixture was refluxed for 1 hr. The mixture was then filtered, washed with 5% sodium hydroxide solution and then with water, and dried with anhydrous magnesium sulfate. Careful fractional distillation of the solution gave 6 g. of 1-bromohexane, b.p. 150–159°, n^{28}D 1.4470.

To determine the per cent yield based on the amount of carbon dioxide produced, 2 ml. of bromine was slowly added to a warm, stirred mixture containing 50 ml. of solvent, 0.01 mole of acid, and 5 g. of red mercuric oxide in a 500-ml., three-neck flask. The flask was fitted with a dry nitrogen inlet, separatory funnel for addition of the bromine, and a reflux condenser. The carbon dioxide produced was swept out of the flask by nitrogen and passed through three Dry Ice traps to remove all bromine vapor and then absorbed in standard barium hydroxide solution. The barium carbonate precipitate was filtered off and the excess barium hydroxide was titrated with standard acid. The following is typical of the method used.

Bromodecarboxylation of Palmitic Acid.—Bromine (2 ml.) was added slowly to a warm, stirred mixture containing 50 ml. of carbon tetrachloride, 2.564 g. (0.01 mole) of palmitic acid, and 5 g. of red mercuric oxide. The carbon dioxide produced was swept out of the flask by nitrogen and absorbed in 125.0 ml. of standard 0.2 *N* barium hydroxide solution. The barium carbonate precipitate was filtered off and the excess barium hydroxide titrated with standard hydrochloric acid, yielding 0.0090 (90%) mole of carbon dioxide.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the E. I. du Pont de Nemours and Company for furnishing samples of tetrachlorodifluoroethane and trichlorotrifluoroethane.

Synthesis and Reactions of Some Triphenylphosphazines. The Use of Long-Range P^{31}–H^1 Coupling for Structure Determination

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Received July 17, 1964

Some β-N-alkylidene- and -arylidenehydrazinotriphenylphosphonium bromides have been synthetized by reacting triphenylphosphine dibromide with appropriate hydrazones. Dehydrobromination of these phosphonium bromides with sodamide in liquid ammonia led to the corresponding triphenylphosphazines. These triphenylphosphazines are nucleophiles as is shown by their reactions with methyl and ethyl iodides to yield α-N-alkyl-β-N-alkylidene- and -arylidenehydrazinotriphenylphosphonium iodides. Thes tructures of these phosphonium iodides have been verified through n.m.r. spectroscopy. The ultraviolet and visible absorption data of triphenylphosphazines are compared with those of the corresponding hydrazones.

Recently we became interested in the synthesis and reactions of organophosphorus compounds containing a —N=P< linkage, such as triphenylphosphinalkylimines[2] and triphenylphosphin- and disubstituted aminoimines.[3,4] These compounds reacted readily with methyl and ethyl iodides to give dialkylaminotriphenylphosphonium iodides[2] and α-N-alkylhydrazino- and α-N-alkyl-β-N-disubstituted hydrazinotriphenylphosphonium iodides,[4] respectively. Hydrolysis of dialkylaminotriphenylphosphonium iodides and α-N-alkyl-β-N-disubstituted hydrazinotriphenylphosphonium iodides furnished the corresponding secondary amines and 1,1,2-trisubstituted hydrazines, respectively, in excellent yields. Thus, these compounds, containing a phosphorus–nitrogen double bond, represent a convenient tool for the synthesis of certain, especially sterically hindered, secondary amines and 1,1,2-trisubstituted hydrazines.

The structures of all organophosphorus compounds, mentioned above, were proved by elemental analyses, chemical behavior, and ultraviolet and n.m.r. spectroscopic studies. The latter method proved to be of

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