[Contribution from the Research Department of Union Carbide Chemicals Co.]

Preparation of Aliphatic Peroxyacids

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Received June 9, 1958

Convenient procedures are described for preparing peracetic and perpropionic acids as anhydrous solutions in solvents of negligible acidity. The method is based on the reaction of carboxylic acids with hydrogen peroxide and employs azeotropic removal of water to drive the reaction to completion. Conditions for safe operation are chosen on the basis of measurements of the detonability of peracid solutions.

Aliphatic peroxyacids are growing in importance as reagents for the conversion of olefinic compounds into alpha-epoxides and of cyclic ketones into lactones.[1] For these uses the peroxyacid solutions should preferably be free of water, hydrogen peroxide, diacyl peroxides, carboxylic acids, strong acids, and salts.[1-4]

The recently described synthesis of peracetic acid from acetaldehyde[5] is an economical route to water-free solutions of this peroxyacid in solvents of negligible acidity; however, it requires specialized equipment and accordingly is not a convenient laboratory method for the occasional user. Water-free solutions can also be obtained by addition of the appropriate solvents to distilled, highly concentrated peracetic acid, prepared by known methods,[2,6-8] but the explosive nature of concentrated peracetic acid makes this hazardous.

We have developed an improved method for preparing water-free solutions of peracetic and perpropionic acids in solvents of negligible acidity and have studied the detonability of peroxyacid solutions in order to delineate the hazards involved. This method is based on the synthesis of peracetic acid from hydrogen peroxide and acetic acid.[6]

$$CH_3\overset{O}{\underset{\|}{C}}-OH + H_2O_2 \rightleftharpoons CH_3\overset{O}{\underset{\|}{C}}-OOH + H_2O$$
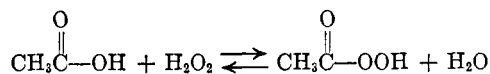
Approximately stoichiometric amounts of the two starting materials are used, along with an inert solvent and an acidic catalyst. The solvent serves not only as a diluent but also as an azeotroping agent for continuous removal of water from the reaction mixture and thus provides a way of driving the reaction to completion. In this respect the procedure resembles well known esterification methods, but a complicating factor is the fact that peracetic acid itself not only forms a minimum boiling azeotrope with water[9] but also forms, with many water-immiscible solvents, heterogeneous ternary azeotropes having high concentrations of peracetic acid in the aqueous layers. We have found that these difficulties may be avoided by using the lower aliphatic esters, particularly ethyl, isopropyl, and n-propyl acetates, as solvents and azeotroping agents. Table I summarizes the results from typical runs. Yields of peracetic acid ranged from 74 to 93%.

(1) B. Phillips and D. L. MacPeek, *Peracetic Acid*, in First Supplement Volume, *Encyclopedia of Chemical Technology*, edited by R. E. Kirk and D. F. Othmer, The Interscience Encyclopedia, Inc., New York, N. Y., 1957, pp. 622–642.

(2) B. A. Arbuzow and B. M. Michailow, *J. prakt. Chem.*, 127, 1, 92 (1930).

(3) S. Winstein and R. B. Henderson, *Ethylene and Trimethylene Oxides*, in *Heterocyclic Compounds*, edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 1–60.

(4) P. S. Starcher and B. Phillips, *J. Am. Chem. Soc.*, 80, 4079 (1958).

(5) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, 79, 5982 (1957).

(6) J. D'Ans and W. Frey, *Ber.*, 45, 1845 (1912).

(7) British Patent 745,594 (1956).

(8) H. Krimm, U. S. Patent 2,813,896 (1957).

(9) Homogeneous azeotrope: 56.5% peracetic acid, 43.6% water. Boiling point 34° at a pressure of 45 mm.[1]

TABLE I

SYNTHESIS OF PERACIDS FROM CARBOXYLIC ACIDS AND HYDROGEN PEROXIDE

Carboxylic Acid Compound	Moles	Aq. H_2O_2 Conc.	Aq. H_2O_2 Moles	Mole Ratio Acid/H_2O_2	Catalyst Kind	Catalyst Conc. %	Solvent Kind	Solvent Wt. Grams	Temp, °C[d]	Time, Hours	Product Wt. of Solution, Grams	Product Wt. % Peracid	Product Wt. % H_2O_2	Product Yield of Peracid, %	Product Peroxide in Distillate, Moles	Total Peroxide Recovery, %
Acetic acid	3.90	53.4	3.0	1.30	H_2SO_4	1.0	EtOAc	550	50	13.7	521	31.5	0.25	72	0.005	74
	3.90	90.5	3.0	1.30	H_2SO_4	1.0	EtOAc	660	50	7.5	853	23.4	0.44	87.5	Nil	91
	1.95	90.5	1.5	1.30	None		EtOAc	310	50[a], 60, 70	3.0[e], 4.7[e], 6.8[e]	375	3.8	11.0	12.5		96
	3.90	53.4	3.0	1.30	I.E.R.[b]	3.0[c]	EtOAc	550	50	12.8	343	6.0	6.9	18.0		64
	3.90	53.4	3.0	1.30	I.E.R.[b]	15.0[c]	EtOAc	550	50	15.5	464	37.3	0.29	76[g]	Nil	79[f]
	1.95	53.4	1.5	1.30	H_2SO_4	1.0	i-PrOAc	300	40	4.0	374	26.2	3.0	86	Nil	86
	2.0	35	2.0	1.00	H_2SO_4	0.31	i-PrOAc	688	50	7.5	709	17.3	0.0	80	Nil	86
	1.95	53.4	1.5	1.30	H_2SO_4	1.0	PrOAc	300	50	3.0	378	25.2	0.5	84		90
	1.95	53.4	1.5	1.30	I.E.R.[b]	1.5[c]	PrOAc	300	40	3.7	349	24.7	0.04	76	0.087	87[f]
	1.48	35	1.48	1.00	H_2SO_4	0.17	$CHCl_3$	1200	40	11.0	1211	6.7	0.09	72	0.15	
Propionic acid	2.0	34	1.0	2.00	H_2SO_4	1.0	$CHCl_3$	400	40	14.0	533	13.7	0.01	81	0.01	74
	5.0	55.6	4.0	1.25	H_2SO_4	0.6	EtCOOEt	720	40	10.5	660	42.0	0.04	77		77

[a] Temperature was increased periodically during this run. [b] Ion exchange resin, Amberlite IR-120 in the acid form. [c] Based on dry resin. [d] Approximate system pressures required for these temperatures were as follows: EtOAc: 50°, 190 mm.; 60°, 300 mm.; 70°, 450 mm. i-PrOAc: 40°, 70 mm.; 50°, 100 mm. EtCOOEt: 40°, 50 mm. CHCl₃: 40°, 50 mm.; 50°, 80 mm. CHCl₃: 40°, 250 mm. Benzene: 40°, 200 mm. [e] Times at each temperature. [f] Includes small amount of peroxide in ion exchange resin. [g] Water in distillate corresponded to only 87% conversion.

Reaction conditions are dictated largely by the desirability of avoiding shock-sensitive solutions. A series of safety tests carried out with ethyl acetate and acetic acid solutions of peracetic acid gave the results plotted in Fig. 1. It can be seen that if the reaction temperature is held at 50°, the final peracetic acid concentration should be less than 55% to avoid the detonable range.

Although removal of water and completion of the reaction can be accomplished more quickly by using highly concentrated hydrogen peroxide as the starting material, we prefer to use 50% aqueous hydrogen peroxide to minimize the danger of forming explosive mixtures.[10]

The reaction proved to be impractically slow at 50° in the absence of a catalyst, but with 1% of sulfuric acid could be completed in less than three hours. The resulting peracetic acid solutions were then freed of sulfuric acid by continuous flash distillation under reduced pressure.

Ion exchange resins of the polystyrene–sulfonic acid type were known to be good catalysts for the reaction of acetic acid with hydrogen peroxide,[11–13] and it was found that they gave good results in the present process. With 3% of Amberlite IR-120[14] in its acid form, the reaction could be completed in about 4 hours under optimum conditions. The Amberlite IR-120 was easily removed from the product by decantation or filtration. Increasing the concentration of the ion exchange resin to 15% actually gave a much slower rate.

In order to avoid peracid loss due to decomposition catalyzed by traces of heavy metal ions it was found desirable to carry out the reaction in the presence of a sequestering agent. The one generally employed was "Victawet 35B," the sodium salt of a partially-esterified polyphosphate.[15]

The procedure was found to be very satisfactory for the preparation of perpropionic acid, and it appears reasonable that it could be used for making still higher peracids, including those of the aromatic series. Modification of the solvent system would be necessary in these cases, however, since the higher acids and peracids are very insoluble in water and hydrogen peroxide. For example, an attempt to prepare peroxy-2-ethylhexanoic acid
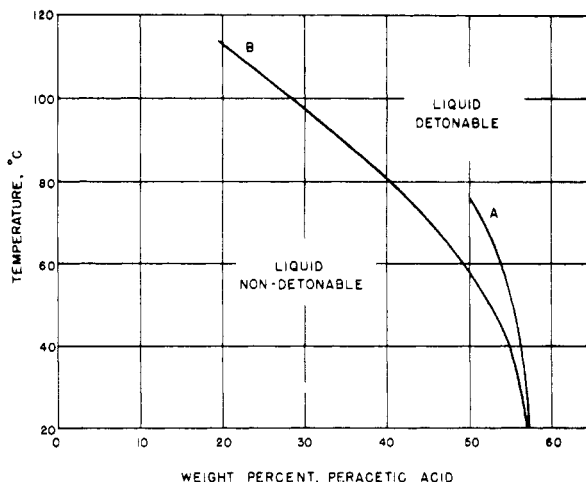

Fig. 1. Detonability of peracetic acid solutions. (A) peracetic acid in ethyl acetate. (B) peracetic acid in acetic acid

was unsuccessful when sulfuric acid was used as the catalyst and chloroform as the solvent and azeotroping agent. In this experiment 87% of the hydrogen peroxide appeared unchanged in the aqueous layer of the distillate.

Acknowledgment. We are indebted to J. P. Leinroth, R. S. Leithiser, D. H. Way, and H. L. Cobb, Jr., who collaborated with us in planning and carrying out the safety tests.

EXPERIMENTAL

Preparation of peracetic and perpropionic acids. All of the experiments listed in Table I were carried out in an all-glass still having a fractionating column (1 in. in diameter and 36 in. long) packed with triple-turn $^3/_{16}$-in. glass helices. The still head had a down-draft condenser which directed the condensate to a decanter where the aqueous layer was collected. The nonaqueous layer of the condensate was returned to the top of the fractionating column. Circulating brine at approximately −10° was used as coolant in the condenser.

In a typical experiment (Table I, No. 8) 96 g. (1.5 moles) of 53.4% aqueous hydrogen peroxide was first added to 117 g. (1.95 moles) of acetic acid containing 5.0 g. of sulfuric acid and 0.21 g. of Victawet 35B.[15] This was diluted with 300 g. of n-propyl acetate, and the mixture was heated in the above-described still using an electric heating mantle. The system was partially evacuated, and the pressure (approximately 80 mm. of Hg, absolute) was adjusted so as to maintain the reaction mixture at 50° under reflux. Minor adjustments to slightly lower pressures were necessary from time to time during the experiment. Water was continuously removed at the lower layer of the distillate and was collected in the decanter. After 3 hr. 82 g. of aqueous layer had been collected, and the separation of additional water from the condensate had substantially ceased. The flask was allowed to cool, and its contents (378 g.) were analyzed for hydrogen peroxide by titration with potassium permanganate solution[6] and for peracetic acid by subsequent iodimetric titration[5] of the same sample. It was found to contain 0.04% of hydrogen peroxide (0.15 g.) and 25.2% of peracetic acid (95 g.). The yield of peracetic acid was 84% of the theoretical. In addition, peroxide corresponding to 7.4 g. of peracetic acid was shown by iodimetric analysis to be present in the two layers drained from the decanter at the end of the experi-

(10) E. S. Shanley and F. P. Greenspan, Ind. Eng. Chem., 39, 1536 (1947).

(11) F. P. Greenspan, Belgian Patent 540,412 (1955).

(12) E. I. du Pont de Nemours & Co., Peroxygen Products Bulletin P 61-454 (1954).

(13) A. T. Hawkinson and W. R. Schmitz, British Patent 776,758 (1957).

(14) Amberlite IR-120 is described by the manufacturer (Rohm & Haas Co.) as being a cross-linked polystyrene nuclear sulfonic acid having, in the sodium form, 4.25 milliequivalents of sulfonate groups per gram of dry resin. See Rohm & Haas Bulletin IE-4-54 (1954).

(15) According to the manufacturer, Victor Chemical Works, "Victawet 35B" has the formula $Na_5R_6(P_3O_{10})_2$, where R = 2-ethylhexyl. See Chemical Materials Catalog 9, 512 (1958), Reinhold Publishing Corp., New York, N. Y.

ment. The total peroxide recovery was accordingly 90%. Elimination of the sulfuric acid catalyst from the product was best effected by flash distillation as described in the next section.

When the ion exchange resin (Amberlite IR-120) was used as the catalyst, it was first converted to its acid form by the standard treatment, in a tower, with aqueous hydrochloric acid. The resin was washed with water till free of chloride ion and then with acetic acid to displace the water. The resin was employed in the acetic acid–wet form, but the quantity of resin used was based on the calculated dry resin content. At the end of the experiment the ion exchange resin was readily removed by filtration.

Flash distillation of peroxyacid solutions to eliminate sulfuric acid. A 2000-ml., round-bottomed, 3-necked flask was fitted with a dropping funnel, a thermometer, and a short offset Claisen-type distillation head that led to the side of a Friedrich condenser which in turn drained into an ice-cooled receiver. The flask was heated by a Wood's metal bath maintained at 195 to 205°, and the pressure in the system was lowered to 175 mm. The peracetic acid solution was then fed slowly through the dropping funnel at such a rate that immediate distillation took place and no significant build-up of liquid in the flask occurred. There was negligible loss of peracetic acid when distillation was carried out under these conditions. Because of the danger of a vapor-phase detonation, however, this procedure was used only for dilute (25%) peracetic acid solutions. Although no detonations were encountered in this work, safety glass shields were always placed in front of equipment in which peracetic acid solutions were being distilled. Fresh stabilizer was always added to the distilled peracid since the original stabilizer remained with the residue.

Detonability of peroxyacid solutions. The explosion tests with peracid solutions were carried out behind a protective wall of steel and concrete. An open-top 14-gage stainless steel tube, 1.5 in. in diameter and 6 in. long, was mounted in a water bath. The solution to be tested (25 ml.) was poured into the tube, and a No. 6 blasting cap was submerged and centered in the liquid. When the blasting cap was set off, a bulging of the tube occurred. This increase in diameter was taken as a measure of the severity of the detonation. Control experiments carried out with acetic acid or ethyl acetate resulted in increases in diameter of about 0.12 in. at the point of maximum bulge. With detonable solutions the explosions were often severe enough to rupture the tubes.

Fig. 1. summarizes the results of detonation tests conducted with solutions of peracetic acid at various temperatures. The curves—one for acetic acid solutions and one for ethyl acetate solutions—mark the boundaries between the detonable and nondetonable regions. Explosions were more severe the deeper the point in the detonable region.

Solutions of perpropionic acid in ethyl propionate were tested at 25°, and it was shown that they were unstable to the shock and fire of No. 6 blasting caps at peracid concentrations above 60% by weight.

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Synthesis of Some New Triarylethylene Glycols and Attempts to Oxidize These to α-Arylbenzoins
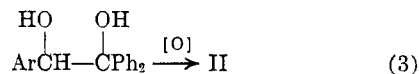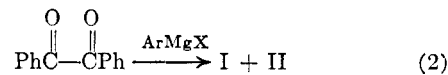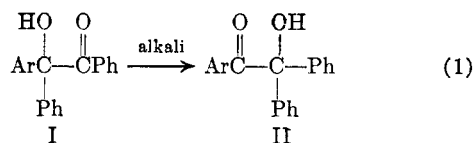
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In an attempt to develop a general synthetic route to α-arylbenzoins several 1,1-diphenyl-2-arylethylene glycols have been prepared and oxidized with various reagents. This and one other route investigated for the same purpose met only partial success. In the course of the work an example of the addition of an organocadmium reagent to a carbonyl group was found and a new product from the reaction of a Grignard reagent with an aroyl cyanide was isolated.

α-Arylbenzoins (I) undergo molecular rearrangement when treated with alkali (1).[1,2] Further, the obvious synthesis of this type of compound, inverse addition of a Grignard reagent to benzil, also may proceed with rearrangement (2).[1] Because of these rearrangements associated with the α-arylbenzoin system, a general unequivocal synthesis of the system would be desirable. Reported in this paper are two methods attempted for such a synthesis.[3]

(1) J. F. Eastham, J. E. Huffaker, V. F. Raaen, and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4232 (1956).

(2) W. von E. Doering and R. S. Urban, *J. Am. Chem. Soc.*, **78**, 5938 (1956). The tentative conclusion of these authors that α-arylbenzoin rearrangement (1) occurs only when steric strain is released is incorrect. With C-14-labeled α-anisylanisoin it was shown[1] that rearrangement occurs with the only change being a mixing of the position of labeling.

(3) Previous methods of synthesis, other than that of equation 2, have yielded only three crystalline α-arylbenzoins. H. Biltz [*Ber.*, **32**, 655 (1899)] obtained α-phenyl-

$$\underset{\substack{\text{I}}}{\underset{\substack{|\\\text{Ph}}}{\text{Ar}\overset{\text{HO}}{\underset{|}{\text{C}}}\text{—}\overset{\text{O}}{\underset{\|}{\text{C}}}\text{Ph}}} \xrightarrow{\text{alkali}} \underset{\substack{\text{II}}}{\underset{\substack{|\\\text{Ph}}}{\text{Ar}\overset{\text{O}}{\underset{\|}{\text{C}}}\text{—}\overset{\text{OH}}{\underset{|}{\text{C}}}\text{—Ph}}} \qquad (1)$$

$$\text{Ph}\overset{\text{O}}{\underset{\|}{\text{C}}}\text{—}\overset{\text{O}}{\underset{\|}{\text{C}}}\text{Ph} \xrightarrow{\text{ArMgX}} \text{I} + \text{II} \qquad (2)$$

$$\text{Ar}\overset{\text{HO}}{\underset{|}{\text{C}}}\text{H—}\overset{\text{OH}}{\underset{|}{\text{C}}}\text{Ph}_2 \xrightarrow{[\text{O}]} \text{II} \qquad (3)$$

The first method attempted (Equation 3) was oxidation of α-aryldihydrobenzoins, *i.e.*, 1,1,2-tri-

benzoin by oxidation of α-phenyldesoxybenzoin with nitric acid; W. E. Bachmann [*J. Am. Chem. Soc.*, **54**, 2112 (1932)] obtained 2-methyl-α-phenylbenzoin by addition of o-tolylmagnesium bromide to methyl benzilate; and D. Y. Curtin and S. Leskowitz [*J. Am. Chem. Soc.*, **73**, 2633 (1951)] obtained α-benzhydrylbenzoin by a molecular rearrangement of benzhydryl desyl ether. None of these methods of synthesis seems general.