g. (61%). Recrystallization of the first crop from absolute ethanol-dry ether yielded two crops totalling 11.5 g. (39%) and both melting at 212-213° (sealed tube).

Anal. Calcd. for $C_9H_{13}ClN_2O_4$: C, 43.47; H, 5.27. Found: C, 43.57; H, 5.10.

Oxidation of 2-Amino-2-*p*-nitrophenyl-1,3-propanediol Hydrochloride (VI).—Oxidation of 0.52 g. (0.0021 mole) of the analytically pure hydrochloride with alkaline permanganate according to the procedure described by Shriner and Fuson[5] gave a 70% yield of the nitrobenzoic acid. Recrystallization from water and ether-petroleum ether and precipitation from an ammonia solution by addition of hydrochloric acid raised the melting point to 240.5° (cor.). The acid was identified as the para isomer by mixed melting point with an authentic sample (no depression) and by a mixed melt of the *p*-bromophenacyl esters (no depression). The esters were prepared by the procedure described in Shriner and Fuson.[6]

2-Amino-2-*p*-nitrophenyl-1,3-propanediol (VII).—To a solution of 2.48 g. (0.01 mole) of 2-amino-2-*p*-nitrophenyl-1,3-propanediol hydrochloride in 40 ml. of water was added 0.92 g. (0.01 mole plus 10%) of sodium bicarbonate. Shortly after evolution of carbon dioxide had subsided, crystals began to separate. The product was washed liberally with cold water and dried one and one-quarter hours at room temperature at <1 mm., yield 1.90 g. (*ca.* 90%), m. p. 114.5-115°. One recrystallization from ethyl acetate raised the melting point to 137.5-138°.

Anal. Calcd. for $C_9H_{12}N_2O_4$: C, 50.94; H, 5.70. Found: C, 50.97; H, 5.63.

It seems probable that the original crystals (m. p. 114.5-115°) described above were a hydrate. Further drying of these crystals at room temperature at <1 mm. for one and one-half hours raised the melting point to 135-138°. An attempt to "rehydrate" a bit of the sample used for analysis by dissolving it in dilute hydrochloric acid and reprecipitating with sodium bicarbonate resulting in crystals which, when dried at room temperature at <1 mm. for one and one-half hours, melted at 135-136°. A second preparation of the free base was carried out in the same way as above except that a more concentrated water solution was employed. After being dried for five hours at room temperature at <1 mm. the product melted partially at 115° and partially at 130-132°. A very rapid determination of the melting point gave a value of *ca.* 120°. When this material was further dried in a drying pistol for five hours at 100° at <1 mm. it melted at 136-138°.

2-Dichloroacetamido-2-*p*-nitrophenyl-1,3-propanediol (VIII).—A mixture of 1.65 g. (*ca.* 0.008 mole) of 2-amino-2-*p*-nitrophenyl-1,3-propanediol (m. p. partially at 115° and partially at 132°), 1.14 g. (0.008 mole) of methyl dichloroacetate and 10 ml. of absolute ethanol was heated to solution and the solution refluxed for eight and one-half hours in a calcium chloride protected system. The solvent was evaporated on the steam-bath and the residual liquid dried at room temperature at < 1 mm. to remove unreacted ester. The last traces of unreacted ester were removed at 100° at <1 mm. No crystals could be obtained from the yellow sirup. A solution of the sirup in 75 ml. of ice-cold ethyl acetate was extracted with 10 ml. of ice-cold dilute hydrochloric acid and washed with 5 ml. of saturated sodium bicarbonate solution followed by two 5-ml. water washes. The ethyl acetate layer was evaporated to a gum on the steam-bath and the gum dried by dissolving it in absolute ethanol, treating with charcoal, filtering, and evaporating to dryness. The partially solid residue was taken up in acetone, diluted with benzene, concentrated to cloudiness typical of incipient crystallization, and the milky solution decanted from a fairly large quantity of precipitated gelatinous material. On being allowed to cool slowly overnight the decantate produced 1.2 g. (46%) of white needle rosettes, m. p. 123-128°. After being recrystallized from chloroform-ligroin and acetone-benzene it amounted to 0.9 g. (35%) and melted at 130.5-132.5°. A constant melting point of 132.5-133° was obtained by further recrystallizations from acetone-benzene and chloroform-ligroin.

Anal. Calcd. for $C_{11}H_{12}Cl_2N_2O_5$: C, 40.88; H, 3.74. Found: C, 41.23; H, 3.85.

DEPARTMENT OF CHEMISTRY
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A Safe Method for the Isolation of Acetyl Peroxide

BY E. S. SHANLEY

Acetyl peroxide is a versatile reagent useful in various connections where free radicals are desired. The preparation of acetyl peroxide is straightforward[1] but isolation of the product is very hazardous because the dry crystals detonate upon the slightest mechanical disturbance; serious accidents have been reported from this cause.[2]

This note reports upon a relatively safe way to isolate acetyl peroxide from the commercially available 25% solution in dimethyl phthalate.[3]

The rather high vapor pressure of acetyl peroxide suggested that it might be possible to volatilize the material from the DMP solution. This was successfully accomplished in a still consisting of an 18-mm. test-tube supported inside a 24-mm. side-arm test-tube by means of a tightly fitting rubber stopper. An outlet tube with stopcock was fused to the bottom of the outer test-tube.

With this stopcock closed, a 2-ml. charge of 25% acetyl peroxide in DMP was placed in the outer tube, after which the inner tube with stopper was inserted and adjusted to about a 5-mm. clearance above the liquid level. A mixture of hydrochloric acid and ice was then placed in the open inner tube, after which the still was evacuated through the side arm to a pressure of about 1 or 2 mm. The outer tube was not heated. After about an hour, the lower end of the inner "condenser" tube was covered with white crystalline material. The crystals were found to melt at about 30° and to detonate when struck but not when merely touched. The active oxygen content was found by iodometric titration to be almost 11%. It was concluded that the distillate contained about 80% acetyl peroxide with dimethyl phthalate as the most likely impurity.

It was found possible to estimate the amount of acetyl peroxide on the condenser by measuring the active oxygen loss from the DMP solution during distillation. The bottom drain was used to draw off the spent solution, and to admit any desired solvent or reaction mixture which could then be drawn up far enough to dissolve the acetyl peroxide from the condenser. This procedure constitutes a safe way to obtain a known small weight of fairly pure acetyl peroxide in any desired reaction mixture.

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(1) S. Gambarjan, *Ber.*, **42**, 4010 (1909).

(2) L. P. Kuhn, *Chem. Eng. News*, **26**, 3197 (1948); E. S. Shanley, *ibid.*, **27**, 175 (1949).

(3) Product of Buffalo Electro-Chemical Company, Inc., Buffalo, N. Y.

RESEARCH DEPARTMENT
BUFFALO ELECTRO-CHEMICAL COMPANY, INC.
BUFFALO, N. Y.
RECEIVED SEPTEMBER 6, 1949

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m-Trifluoromethylphenyl Substituted Alcohols

BY H. HARRY SZMANT, JOSEPH F. ANZENBERGER AND ROBERT HARTLE[1]

By allowing *m*-trifluoromethylphenylmagnesium bromide to react with formaldehyde, ethyl-

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TABLE I

m-TRIFLUOROMETHYLPHENYL SUBSTITUTED ALCOHOLS (m-$F_3CC_6H_4$ = R)

ROH	Yield, %	B. p., °C.	Mm.	$n^{25}D$	d^{25}_4	MR_D Obs.	MR_D Calcd.	Carbon,[a] % Calcd.	Carbon,[a] % Found	Hydrogen, % Calcd.	Hydrogen, % Found
RCH_2OH	38, 48[b]	100	10	1.4574	1.2850	37.38	37.27	54.55	54.67	4.00	4.26
RCH_2CH_2OH[c]	70	86	4	1.4628	1.2608	41.49	41.90	...	...	..	..
$RCH_2CH(OH)CH_3$ $R—CH(CH_3)CH_2OH$	43	84–94	3	1.4584	....	...	...	58.84	58.42	5.39	5.23
$RCH_2CH(OH)CH_2Cl$[d]	70	120	13	1.4802	1.3298	51.21	51.37	50.32	50.04	4.22	4.28

[a] Analyses by Mr. S. L. Stragand of the Micro-Analytical Laboratory, University of Pittsburgh. [b] Yield by the Cannizzaro method based on the aldehyde. [c] Reported by Bachman and Lewis, THIS JOURNAL, 69, 2022 (1947). [d] Structure postulated on the basis of the formation of secondary alcohols by the opening of the oxirane ring of epichlorohydrin; *cf.* Swern, *et al.*, *ibid.*, 71, 1152 (1949); Gilman, *et al.*, *ibid.*, 71, 1478 (1949); Kharasch, *et al.*, *J. Org. Chem.*, 8, 189 (1943).

ene oxide, propylene oxide, and epichlorohydrin there were prepared the expected m-trifluoromethylphenyl substituted alcohols listed in Table I. The reaction product obtained using propylene oxide boiled over a ten degree range and was shown to consist of two products which were partially separated by fractional distillation. The lower boiling fractions gave a positive haloform test, while the higher boiling fractions gave either slight or negative haloform tests. Thus the lower and higher boiling products consist predominately of 1-(m-trifluoromethylphenyl)-2-propanol and 2-(m-trifluoromethylphenyl)-1-propanol, respectively. The isomeric alcohols were subjected to an Oppenauer oxidation and m-trifluoromethylphenylacetone was isolated as the 2,4-dinitrophenylhydrazone (*Anal.* Calcd. for $C_{16}H_{13}O_4N_4F_3$: C, 50.28; H, 3.42. Found: C, 50.31; H, 3.45).

m-Trifluoromethylbenzyl alcohol was also prepared by the Cannizzaro reaction of m-trifluoromethylbenzaldehyde.[2]

(2) Gilman, THIS JOURNAL, 68, 427 (1946).

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Exchange Studies between Sodium Trimetaphosphate and Sodium Hexametaphosphate,[1] Using Radioactive Phosphorus

BY RICHARD C. VOGEL[2] AND HAROLD PODALL[3]

Hull[4] found that no appreciable exchange took place between ortho and meta, ortho and pyro or between pyro and metaphosphoric acids. His method of preparation of the metaphosphoric acid probably gave a polymeric acid of indefinite composition. It has been found that[5] at least two metaphosphate species coexist in yeast suspended in orthophosphate media. One form exchanges radioactive phosphorus readily with the media while the other does not. It is of interest to verify independently the implication that there are no exchanges of phosphorus between the various metaphosphates. This study has been made within the limitations imposed by the dearth of separation methods for the metaphosphates.

Experimental

$NaH_2P^*O_4$.—Twelve grams of C.P. NaH_2PO_4 was dissolved in 20 ml. of distilled water, and 0.2 ml. of phosphoric acid solution[6] containing 0.2 millicurie of P^{32} was added. The solution was evaporated to the first appearance of crystals, poured into a beaker and stirred until completely crystallized. The resulting salt was powdered and dried at 100° for two hours.

$(NaP^*O_3)_3$.—Ten grams of $NaH_2P^*O_4$ was placed in a covered platinum crucible and heated in a muffle furnace at 300° for one hour. The temperature was increased to 610° and kept there for three hours, slowly decreased to 390° and kept there for fourteen hours. The resulting solid was powdered and preserved in a desiccator. Analysis by the method of Jones[7] indicated 100 ± 1% trimetaphosphate.

$(NaPO_3)_6$.—Ten grams of C.P. NaH_2PO_4 was heated at 900° for three hours, then quickly poured into a stainless steel beaker, the resulting glass was powdered and preserved in a desiccator. Analysis by the method of Jones[7] gave 90.4% hexameta and 9.6% trimetaphosphate.

The temperature of the furnace used for preparing the metaphosphates was controlled to ±1° up to 650° by an iron–constantan thermocouple and up to 900° by a platinum–rhodium thermocouple, the thermocouples being connected to a Leeds and Northrup Micromax recorder and temperature control.

A solution of 0.5 M $(NH_4)_2MoO_4$ was prepared according to Jones'[7] procedure and 3% collodion solution was made by mixing collodion with equal volumes of anhydrous ethyl alcohol and anhydrous ether.

Method.—Equal volumes of 0.06 F sodium hexametaphosphate and 0.01 M radioactive sodium trimetaphosphate were mixed. The solutions were thermostated at various temperatures and 5-ml. aliquots periodically removed and transferred to 15-ml. centrifuge tubes. The solution was made just acid to methyl orange with hydrochloric acid or sodium hydroxide and 2 ml. of 0.1 M barium chloride was added to precipitate the hexametaphosphate. This is the precipitation method of Jones.[7] The precipitate was separated by centrifuging. The supernatant trimetaphosphate solution was transferred to another centrifuge tube. The precipitate was washed with three 1-ml. portions of barium chloride solution and the washings added to the trimetaphosphate solution. The hexametaphosphate precipitate was dissolved by the addition of 2 ml. of 6 N nitric acid and converted to the orthophosphate by boiling for twenty minutes with an addi-

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(1) Sodium hexametaphosphate (Graham's salt) is a polymeric metaphosphate glass whose molecular weight and structure have not been completely determined. The concentrations of this substance will thus be given in formalities and based on a formula weight of 102.06.

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(3) Present address: Edwal Laboratories Inc., Chicago, Illinois.

(4) D. E. Hull, THIS JOURNAL, 63, 1269 (1941).

(5) E. Juni, M. D. Kamen, S. Spiegelman and J. M. Wiame, *Nature*, 160, 717 (1947).

(6) One millicurie P^{32} in the form of phosphoric acid was obtained with the coöperation of the Atomic Energy Commission from the Oak Ridge National Laboratory.

(7) L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, 14, 536 (1942).