TABLE I

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

ROH	Yield, %	B. p., °C.	Mm.	$n^{25}D$	d^{25}_4	*M*RD Obs.	*M*RD 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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(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).

tional 2 ml. of concentrated nitric acid. The trimetaphosphate portion was similarly converted to orthophosphate. The two solutions were neutralized with ammonium hydroxide until just acid to methyl red. Two ml. of the ammonium molybdate reagent was added to each portion to precipitate ammonium phosphomolybdate. These precipitates were separated by centrifuging, slurried with distilled water, and quantitatively transferred to aluminum pans (1 inch diameter, $^1/_8$ inch deep). They were carefully evaporated to smooth surfaces with an infrared lamp and coated with 3 drops of the 3% collodion solution. The activities of the samples were determined by using a thin-walled self-quenching Geiger–Müller counter and a scale of 64 scaling unit. The samples were counted for ten minutes and the resulting activities corrected for background and decay of the P^{32}. The background was consistently 0.29 ± 0.01 count per second for a counting time of 100 minutes. The activity of the trimetaphosphate portion was within 10% of 8.0×10^5 counts per second per mole. The exchange data are given in Table I.

TABLE I

EXCHANGE DATA OF 0.005 *M* SODIUM TRIMETA- AND 0.03 *F* SODIUM HEXAMETAPHOSPHATE

Temp., °C.	Initial *p*H	Time, hours	Activity hexameta, counts/sec.
0	2.0	25	0.02 ± 0.04
	5.0	2	0.04
		20	.05
		40	.02
		90	.01
	10.0	26	.05
25	2.0	25	.00
	5.0	20	.02
	10.0	26	.05
100	2.0	0.17[a]	
	5.0	0.17	.08
	10.0	0.25	.02

[a] Hexametaphosphate completely hydrolyzed—no precipitate.

Discussion of Results

It is known that the various metaphosphates hydrolyze through a number of phosphate species ultimately to orthophosphate. Kinetic studies[8] indicate that sodium hexametaphosphate hydrolyzes to ortho and trimetaphosphate. The latter hydrolyzes to ortho and triphosphate, triphosphate going to pyro which then hydrolyzes to orthophosphate. Under the conditions of our experiments the trimetaphosphate was not appreciably hydrolyzed. However, the hexametaphosphate was slowly hydrolyzing to trimetaphosphate as the experiment proceeded, and thus one could not make the hexametaphosphate radioactive. When the trimetaphosphate is radioactive and the hexametaphosphate not, the latter will become radioactive only if an exchange mechanism is operating.

The 0.9 statistical error of the activities of the hexametaphosphate precipitates was about ±0.04 count per second. Thus, the observed activities of the hexametaphosphate precipitate are of the order of magnitude of this error. If complete exchange had occurred the activity of the precipitate would be about 13 counts per second.

In one further experiment a solution was made 0.03 *F* $(NaPO_3)_6$, 0.005 *M* $(NaP^*O_3)_3$ and 0.015 *M* $NaH_2P^*O_4$. After twenty-five hours at 25° the activity of the barium hexametaphosphate precipitate was 0.07 count per second.

Thus, we may conclude that the phosphorus of trimetaphosphate or orthophosphate will not exchange with that of hexametaphosphate under these experimental conditions. The reaction in which trimetaphosphate is formed from hexametaphosphate is therefore irreversible. These experiments also show that barium hexametaphosphate may be precipitated by the method of Jones[7] without appreciable co-precipitation of ortho and trimetaphosphate.

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[8] R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947).

The Identity of β-Longilobine with Retrorsine

BY FRANK LOUIS WARREN, MEYER KROPMAN,[1] ROGER ADAMS, T. R. GOVINDACHARI AND J. H. LOOKER

In a recent paper Adams and Govindachari[1a] have described the separation of longilobine, obtained by Manske[2,3] from *Senecio longilobus*, into α-longilobine, $C_{18}H_{23}O_5N$, and β-longilobine, $C_{18}H_{25}O_6N$.

In two publications[4] it has been shown that both retrorsine and isatidine give on hydrolysis either retronecic or isatinecic acids according to the method employed. In fact, following the designation by Leisegang and Warren[5] of the structure of isatinecine as retreonecine N-oxide, it has been shown that isatidine is retrorsine N-oxide. Retronecic and isatinecic acids are geometrical isomers and their structures have been elucidated.[4a]

β-Longilobine has the characters of retrorsine[3,6] and gives on hydrolysis retronecine and β-longinecic acid, $C_{10}H_{16}O_6$, which seemed to be identical with the known isatinecic acid, $C_{10}H_{16}O_6$.[7]

	M. p., °C.	$[\alpha]_D$	CH_3I Cpd.
β-Longilobine[1]	207–208	−48.6°	256°
Retrorsine[6]	212		260°
Retrorsine[3]	214–215	−17.6°	266°
β-Longinecic acid[1]	146–147	− 9.06°	
Isatinecic acid[7]	148.5		

Furthermore, β-longilobine on reduction[1] takes up two moles of hydrogen to give the tetrahydro compound as an amorphous powder which, hydrolyzed with barium hydroxide, gave retronecanol

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[1] C. S. I. R. Bursar.

[1a] Adams and Govindachari, THIS JOURNAL, **71**, 1180 (1949).

[2] Manske, *Can. J. Res.*, **17B**, 1 (1939).

[3] Manske, *ibid.*, **5**, 651 (1931).

[4] Christie, Kropman, Leisegang and Warren, *J. Chem. Soc.*, 1700 (1949); (a) Christie, Kropman, Novellie and Warren, *ibid.*, 1703 (1949).

[5] Leisegang and Warren, *ibid.*, 486 (1949).

[6] Barger, Seshadri, Watt and Yabnta, *ibid.*, 11 (1935).

[7] de Waal, *Onderstepoort J. Vet. Sci. Animal Husb.*, **14**, 442 (1940).