

formal-sorbitol, benzal-sorbitol and sorbitol hexaacetate are described.

Triacetone-sorbitol and the sorbitol pyridine compound are easily converted into triformal-sorbitol. This reaction provides a ready means for the identification of *d*-sorbitol and many of its

derivatives. The average values of the specific rotations of triformal-sorbitol determined in pyridine solution (about 1.5 g. per 100 ml. solution) were: 6678, -21.9° ; 5876, -28.6° ; 5780, -29.5° ; 5461, -33.0° ; 4358, -51.0° .

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Derivatives of Piperazine. II. Utilization in Identification of Fatty Acids

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Additional derivatives similar to that previously described with malonic acid¹ have now been prepared and data regarding them are given in Table I.

ether and recrystallized from the appropriate solvent. For qualitative organic analysis an excess of the acid is used. If immediate crystallization does not occur, this may be secured by

TABLE I
YIELDS, PROPERTIES AND COMPOSITION OF PIPERAZINE DERIVATIVES

Piperazonium	Yield, %	M. p., °C., corr.	Cryst. solv.	Neut. equiv. Calcd. Found		Analyses, %					
						C	Calcd. H	N	C	Found H	N
1-Acid oxalate	90	Not under 300	Water	176.1	178.1	40.88	6.87	15.91	40.98	6.94	15.82
1-Acid succinate	90	205 -206	(dec.) Alcohol (95%)	204.1	203.7	47.02	7.90	13.72	47.13	7.91	13.84
1-Acid adipate	83	244 -245	(dec.) Alcohol (50%)	232.1	229.4	51.69	8.62	12.07	51.77	8.74	12.17
1-Acid sebacate	82	166 -168	Water	288.2	284.3	58.27	9.79	9.72	58.10	9.92	9.72
1,4-Di-acid glutarate	77	152	Alcohol (95%)	116.7	117.0	47.97	7.48	8.00	47.72	7.86	8.29
1,4-Di-monochloroacetate	68	145 -146	Alcohol (95%)	275.1	275.1	Cl, 25.78		10.18	Cl, 25.48		10.16
1,4-Di-trichloroacetate	75	121 -121.5	Alcohol (95%)	412.8	411.5	Cl, 51.53		6.79	Cl, 51.34		6.83
1,4-Di-acetate	71	208.5-209	<i>n</i> -Butanol	206.1	203.1			13.59			13.43
1,4-Di-propionate	50	124 -125	Dioxane	234.2	232.9			11.96			12.07
1,4-Di-butyrate	88	121 -122	Dioxane	262.2	260.0			10.69			10.64
1,4-Di-valerate	85	112.5-113	Dioxane	290.2	293.4			9.65			9.80
1,4-Di-caproate	65	111 -111.5	Acetone	318.3	316.0			8.80			8.69
1,4-Di-heptoate	72	95 - 96	Acetone	346.3	343.2			8.09			8.09
1,4-Di-isobutyrate	90	89.5- 90	Dioxane	262.2	260.1			10.69			10.55
1,4-Di-isovalerate	67	139 -140	Acetone	290.2	290.9			9.65			9.68
1,4-Di-lactate	60	96 - 96.5	Cellosolve	266.2	266.6			10.52			10.65

All of these derivatives are hydrolyzed by refluxing in hydrochloric acid. The resulting piperazine dihydrochloride is identified by conversion into 1,4-dinitrosopiperazine.² The therapeutic properties of these compounds are being investigated.

The salts of piperazine hexahydrate have been found to be helpful for the identification of fatty acids. They are easily prepared and purified, the time required for the entire operation being less than an hour. They crystallize well, melt at convenient temperatures, and possess neutralization equivalents that can be easily determined. In preparing the salts for analytical purposes 0.05 mole of piperazine hexahydrate is added to 0.1 mole of the acid. Upon stirring, the entire solution solidifies. The solid mass is washed with

warming the solution or adding ether. After filtration, drying on a porous plate and washing with ether, the melting points of the salts thus obtained were within a few degrees of those of the highly purified products.

These derivatives are soluble in water, alcohol, hot acetone, hot cellosolve (monoethyl ether of ethylene glycol) and hot dioxane (diethylene oxide). They are insoluble in ether and hexane. Neutralization equivalent determinations yield values that indicate that one molecule of acid is hydrolyzed off of the 1,4-piperazonium compound. These have been determined on 0.3 to 0.5 g. samples of the highly purified products after drying over phosphorus pentoxide for a week. They are given in Table I. For qualitative organic analysis purposes, however, melting point and mixed melting point determinations suffice.

(1) Pollard and Adelson, *THIS JOURNAL*, **56**, 150 (1934).

(2) Ladenburg, *Ber.*, **24**, 2401 (1891).

A mixture of equal portions of 1,4-piperazonium di-propionate and 1,4-piperazonium di-butyrate melts at 100–110°; a mixture of equal portions of 1,4-piperazonium di-valerate and 1,4-piperazonium di-caproate melts at 100–106°. Thus these derivatives are highly satisfactory for utilization in identification of the aforementioned acids.

Summary

1. Additional derivatives of piperazine have been prepared.

2. The procedure for the preparation and use of piperazine salts for identification of fatty acids has been described.

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Ketene. I. Preparation and Reactions

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Since the discovery of this interesting substance in 1907 by Wilsmore, a considerable number of studies of its preparation and properties have been made, particularly in the last few years.¹ However, both in respect to its method of preparation and to its reactions, the literature is somewhat contradictory. In the original method of Wilsmore, liquid acetone or acetic anhydride was decomposed by a platinum wire immersed in the liquid and heated electrically. We have made some experiments using this method in this Laboratory, but met with considerable difficulty because of the ease with which the platinum wire broke; we found the method much less convenient² than that first developed by Schmidlin and Bergmann,^{1b} and later studied by Hurd and his co-workers,^{1c,d,k,l} of decomposing gaseous acetone. In this method acetone vapor is passed through a hard glass tube, which may be filled with pieces of baked clay, and which is heated in the range 500–700°. The yields from this method were good but far from quantitative. Hinshelwood and Hutchinson^{1e} studied the decomposition of acetone in a quartz static system and concluded that under these conditions the acetone decomposed according to the equation $\text{CH}_3\text{CO}-\text{CH}_3 \rightarrow \text{CO} + \text{CH}_2 + \text{CH}_3$, and that the two methyl groups then reacted to give methane, ethylene and hydrogen. The reaction was homo-

geneous, since partly filling the reaction bulb with broken quartz had no effect on the rate of decomposition; it followed a unimolecular law and had an activation energy of 68,000 cal. Later, Rice and Vollrath^{1f} showed that the decomposition in a quartz tube is the same as in hard glass and that quite high yields of ketene can be obtained in either case. We have since confirmed these experiments and have shown that the decomposition of acetone is homogeneous when either a quartz or a Pyrex reaction vessel is used.

Various claims have been made for solid catalysts that promote the decomposition of acetone into ketene and methane, but Hurd³ in a review of this in 1929 states that up to that time no effective catalyst for the production of ketene from acetone had been developed. Subsequent to this, further claims^{1h,i} have been made for catalysts, especially in a paper by Berl and Kullmann.¹ⁱ Hurd, Sweet and Thomas^{1k} have criticized the results of Berl and Kullmann and concluded that any catalytic effect was very small. Berl and Kullmann's conclusion as to the effect of catalysts and temperature must have been based on experiments in which less than 15% of the acetone was decomposed because all their other experiments (except two) show a yield of ketene of $55 \pm 12\%$; we have found that their method of analysis does not give reliable results for small percentage decompositions.

The literature on the chemistry of this compound is also somewhat contradictory; van Alphen⁴ concluded from a study of its reactivity with various substances that it is a somewhat weak acetylating agent; on the other hand,

(1) (a) Wilsmore, *J. Chem. Soc.*, **91**, 1938 (1907); (b) Schmidlin and Bergmann, *Ber.*, **43**, 2821 (1910); (c) Hurd and Cochran, *THIS JOURNAL*, **45**, 515 (1923); (d) Hurd and Tallyn, *ibid.*, **47**, 1427 (1925); (e) Hinshelwood and Hutchinson, *Proc. Roy. Soc. (London)*, **A111**, 245 (1926); (f) Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929); (g) Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929; (h) Al, *Z. angew. Chem.*, **45**, 545 (1932); (i) Berl and Kullmann, *Ber.*, **65**, 1114 (1932); (k) Hurd, Sweet and Thomas, *THIS JOURNAL*, **55**, 335 (1933); (l) Hurd and Dull, *ibid.*, **54**, 3428 (1932).

(2) See however Ott, Schröter and Packendorff, *J. prakt. Chem.*, **190**, 177 (1931), who used a tungsten filament instead of platinum.

(3) See Ref. 1g, p. 251.

(4) Van Alphen, *Rec. trav. chim.*, **43**, 823 (1924).