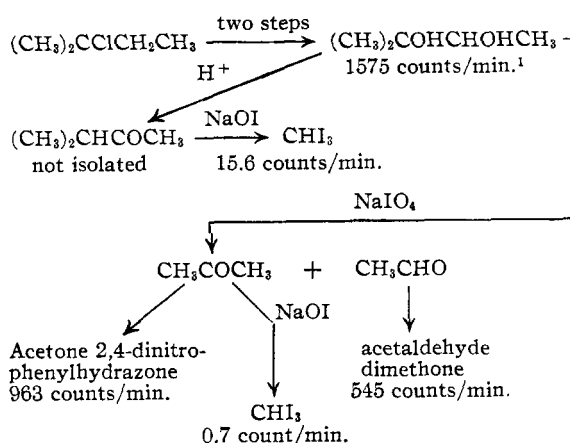The recovered chloride was degraded by the following scheme, the individual steps of which were shown to give no rearrangement of carbon atoms.

$$(CH_3)_2CClCH_2CH_3 \xrightarrow[H^+]{\text{two steps}} (CH_3)_2COHCHOHCH_3$$
1575 counts/min.[1]

$$(CH_3)_2CHCOCH_3 \xrightarrow{NaOI} CHI_3$$
not isolated   15.6 counts/min.

NaIO$_4$

$$CH_3COCH_3 \;+\; CH_3CHO$$

NaOI

Acetone 2,4-dinitrophenylhydrazone
963 counts/min.

acetaldehyde dimethone
545 counts/min.

CHI$_3$
0.7 count/min.

The results indicate that rearrangement of methyl groups may occur between the 2- and 3-positions of the *t*-amyl group but that the rate of interchange is very slow between the terminal carbon atoms and those in the middle of the chain.

Treatment of 2-methyl-2-chloropropane-2-C^{14} (I, X = Cl) with anhydrous aluminum chloride under conditions sufficiently drastic so that much of the starting material was converted to polymer gave a chloride (48% recovery) containing only 1–3% of II (X = Cl). The recovered chloride was degraded through isobutylene glycol by a procedure similar to that used for *t*-amyl chloride.

The most satisfactory interpretation of the present results (including the relative ease of isomerization of *t*-butyl and *t*-amyl chlorides) is on the basis of a series of rearrangements initiated by aluminum chloride involving carbonium-ion intermediates, with the relative rates of formation of the possible isomerization products being dependent on the relative stability of the ionic intermediates through which each is formed.

The behavior of tertiary alkyl chlorides under the influence of aluminum chloride appears to be strikingly different from that reported for the isomeric butanes with aluminum bromide.[2]

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(1) Activities are corrected for self-absorption and background. Values represent counts/min./mg. of barium carbonate and are corrected for dilution by the carbon atoms at the unlabeled positions.

(2) Otvos, Stevenson, Wagner and Beeck, *J. Chem. Phys.*, **16**, 745 (1948).

A SYNTHESIS OF D-*erythro*-2-DESOXYPENTOSE

Sir:

Although D-*erythro*-2-desoxypentose,[1] the sugar component of the "desoxyribose" nucleic acids, was isolated[2] in pure form twenty years ago and the synthesis of its enantiomorph[3] was accomplished even earlier, a satisfactory synthesis for the natural desoxy sugar has not yet appeared.

A synthesis of D-*arabo*-2-desoxyhexose was reported recently[4] via the corresponding acetylated C-nitroölefin. By an extension of this type of synthesis to the pentose series, D-*erythro*-2-desoxypentose has now been prepared: 4,6-Benzylidene D-glucose[5] was reduced with hydrogen and platinum to 4,6-benzylidenesorbitol (m. p. 132–133°; $[\alpha]^{22}$D −40.7° in water. Found: C, 57.8, H, 6.76; yield, 82%). Cleavage of the substituted sorbitol with sodium metaperiodate gave sirupy 2,4-benzylidene D-erythrose. Condensation of the latter with nitromethane gave, in 65% yield based on benzylidene sorbitol, a mixture of 3,5-benzylidene 1-nitro-1-desoxy-D-ribitol (m. p. 106–107°; $[\alpha]^{24}$D −38.8° in chloroform. Found: C, 53.6, H, 5.38) and 3,5-benzylidene 1-nitro-1-desoxy-D-arabitol (m. p. 145–146°; $[\alpha]^{24}$D −14.2° in ethanol. Found: C, 53.5, H, 5.60). Hydrolysis of the latter with dilute sulfuric acid gave, in 85% yield, 1-nitro-1-desoxy-D-arabitol (m. p. 147–148°; $[\alpha]^{18}$D −4.5° in water. Found: C, 33.1, H, 5.89). Acetylation gave the tetraacetate in 96% yield (m. p. 123–125°; $[\alpha]^{18}$D 36° in chloroform. Found: C, 44.8, H, 5.34). The nitroalcohol tetraacetate, when refluxed in benzene solution with sodium bicarbonate, gave, in 81% yield, D-*erythro*-triacetoxy-1-nitropentene-1 (m. p. 63–64°; $[\alpha]^{18}$D 5.3° in chloroform. Found: C, 45.7, H, 5.11). The double bond in the acetylated nitroölefin was hydrogenated in the presence of palladium black, and the sirupy product was dissolved in excess aqueous-alcoholic sodium hydroxide. The resultant solution was added to cold 60% sulfuric acid, and following neutralization, benzylphenylhydrazine was added. There resulted D-*erythro*-2-desoxypentose benzylphenylhydrazone (m. p. 126–127°; $[\alpha]^{20}$D −17.7° in pyridine)[2] in 60% yield. Cleavage of the hydrazone with benzaldehyde or formaldehyde in the usual manner gave D-*erythro*-2-desoxypentose (m. p. without recrystallization 80–83°; $[\alpha]^{22}$D −56° in water).

For preparative purposes, the isolation of intermediates as in the above synthesis is not necessary. Thus, 4,6-benzylidene glucose on cleavage with sodium metaperiodate followed by hydrolysis gives sirupy D-erythrose in nearly quantitative yield. Condensation with nitromethane, fol-

(1) The nomenclature used was proposed by Sowden, THIS JOURNAL, **69**, 1047 (1947).

(2) Levene and London, *J. Biol. Chem.*, **81**, 711; **83**, 793 (1929); Levene and Mori, *ibid.*, **83**, 803 (1929).

(3) Meisenheimer and Jung, *Ber.*, **60**, 1462 (1927).

(4) Sowden and Fischer, THIS JOURNAL, **69**, 1048 (1947).

(5) Zervas, *Ber.*, **64**, 2289 (1931).

lowed by acetylation and treatment with sodium bicarbonate then gives D-erythro-triacetoxy-1-nitropentene-1, the key compound for the desose synthesis, in 45% yield.

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REVISION OF THE PARACHOR

Sir:

The author[1] has recently advanced an interpretation of Sugden's parachor. In view of the observation of Ferguson and Kennedy[2] that the index of Macleod's equation[3] is sensibly different from 4, the need for a revision of the parachor[4] arises.

Sugden's method of testing Macleod's equation is misleading as large variations in C appear small by comparing the fourth roots of C. In attempting to show that $C^{1/4}$ is nearly constant over wide temperature intervals, Sugden[5] attributes deviations to experimental errors. A graphical or algebraic test would have shown that the experimental results are satisfactory, justifying the modification of Macleod's equation as suggested by Ferguson and Kennedy which is observed by the present author to be applicable right up to the critical temperature. Carbon dioxide, for instance, obeys it up to even 1° below the critical temperature. Further, the so-called associated liquids, methyl, ethyl and n-propyl alcohols and acetic acid obey this modified equation remarkably well at all temperatures. The substances ordinarily occurring as gases cited in Table I serve to supplement the observations of Ferguson and Kennedy, the data being taken from the "Int. Crit. Tables."[6]

Since p is not the same for all substances, $MC^{1/4} = P$ has no natural significance. Hence, Ferguson and Kennedy[2] proposed to express the parachor in the revised form $P_r = MC^{1/p}$. But, unfortunately, their paper has not attracted the attention which it deserves. Sugden[5] has stated that the parachors of lower alcohols and acids steadily increase with temperature. This anomaly disappears on taking the revised parachors. The theory postulated by Sidgwick[7] to account for the so-called parachor anomaly of associated liquids is, therefore, unnecessary.

(1) M. S. Telang, THIS JOURNAL, **71**, 1883 (1949).

(2) A. Ferguson and S. J. Kennedy, *Trans. Faraday Soc.*, **32**, 1474 (1936).

(3) D. B. Macleod, *ibid.*, **19**, 38 (1923).

(4) S. Sugden, "The Parachor and Valency," Routledge, London, 1930, p. 30.

(5) S. Sugden, *J. Chem. Soc.*, **125**, 32 (1924); "The Parachor and Valency," p. 26.

(6) In Sugden's paper,[5] for benzene at 280°, $(D - d)$ has been wrongly taken as 0.2305 instead of 0.2854; consequently, $C^{1/4}$ has suddenly shot up.

(7) N. V. Sidgwick and N. S. Bayliss, *J. Chem. Soc.*, 2033 (1930).

TABLE I

Substance	C	p
Acetic acid	23.28	3.716
Carbon dioxide	9.736	3.857
Carbon monoxide	24.85	4.343
Ethyl alcohol	55.69	3.774
Methyl alcohol	54.91	3.792
Nitrogen	20.31	3.887
Oxygen	7.683	4.053
n-Propyl alcohol	50.84	3.465

Further work on the investigation whether or not the revised parachor can eliminate the parachor anomalies is desirable, but it is too laborious and time-consuming for any individual worker. It would be a good idea to have a group of experts working on a coöperative basis and as such the forthcoming meeting of the International Union of Pure and Applied Chemistry should provide the necessary opportunity for taking up this work.

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INHIBITION OF UREASE

Sir:

In a recent publication Niemann and Harmon[1] showed that the enzyme urease is inhibited by phosphate ions, this inhibition being competitive with the substrate, urea. Following upon the finding of Lumry[2] that sulfite inhibits urease and that this inhibition is responsible for the "abnormal" temperature dependence of reaction rates in the urea-urease systems,[3] we have studied the inhibition by sulfite in detail.

Working with high concentrations of urea, at which the rate is zero order in urea, we find that this inhibition is first order in sulfite and in enzyme. It appears that both the sulfite and bisulfite ions are equally effective in causing inhibition, the equilibrium constant being inversely proportional, however, to hydrogen ion concentration. The data definitely do not fit the hypothesis that bisulfite ions alone are the cause of inhibition, as evidenced by Table I. The heat

TABLE I

Temperature 8.5°

pH	A_0 (original activity)	A (inhibited activity)	K $\dfrac{(A_0 - A)}{(A)(HSO_3^-)}$	K' $\dfrac{(A_0 - A)}{(A)\,(total\,sulfite)(H^+)}$
6.20	3.5	0.77	63	10.4×10^7
6.50	4.8	1.3	38	8.9×10^7
6.93	6.5	2.9	23	10.5×10^7
7.12	7.4	3.4	14	8.4×10^7
7.55	7.2	3.8	10	7.9×10^7

Av. 9.2×10^7

(1) Niemann and Harmon, *J. Biol. Chem.*, **177**, 601 (1949).

(2) Kistiakowsky and Lumry, THIS JOURNAL, **71**, in press (1949).

(3) Sizer, *J. Biol. Chem.*, **132**, 209 (1940).