cipitate purified in the usual manner. There was obtained an essentially quantitative yield of benzanilide, m. p. 160.5–162.0°. This was identified and distinguished from the azine and other possible products by mixture melting point experiments and hydrolysis to benzoic acid and aniline.

Extensions of an obvious nature are being carried out on the rearrangement of other hydrazones and of other hydrazine derivatives under these conditions.

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RECEIVED MARCH 31, 1949

THE DIELECTRIC CONSTANT OF WATER AT VERY HIGH TEMPERATURES

Sir:

A property of liquid water that is very important in modern solution theories is its dielectric constant. Since no data are available for temperatures above 100° we have made a number of measurements of the value of this constant at temperatures up to 375°. An all-platinum cell enclosed in a stainless steel bomb was used with a high frequency resonance measuring circuit for the range 70–250 megacycles. The temperature was determined with thermocouples calibrated against a platinum resistance thermometer. In Fig. 1 the dotted line represents values of the dielectric constant predicted from the equation of Akerlof (THIS JOURNAL, **54**, 4125 (1932))

$$\log D = 1.9461 - 0.00205t$$

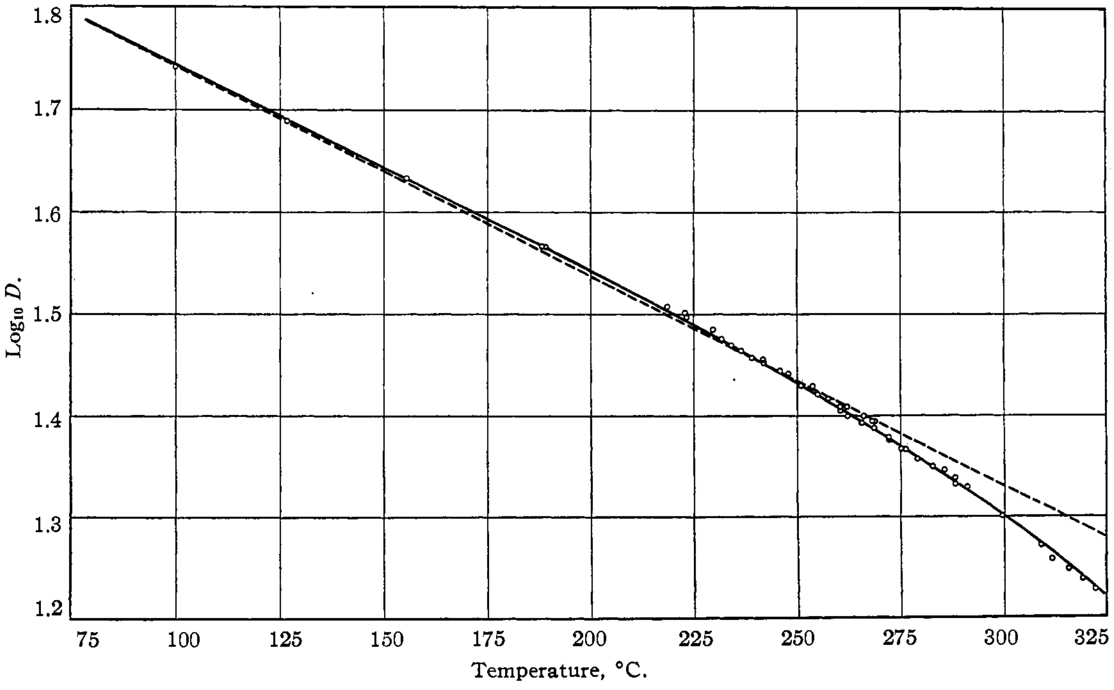

Fig. 1.

The full drawn curve represents our experimental values at temperatures up to 325°. The two curves practically coincide up to temperatures of about 250°.

We wish to express also in this place our sincere appreciation for the aid given us by Mr. Fred Denig, Vice President of the Koppers Company.

KOPPERS COMPANY, INC. H. I. OSHRY
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RECEIVED MARCH 7, 1949

REARRANGEMENT OF CARBON ATOMS IN ALKYL DERIVATIVES

Sir:

Carbon-14 has been used as a tracer to detect rearrangements of carbon atoms in *t*-butyl and *t*-amyl derivatives.

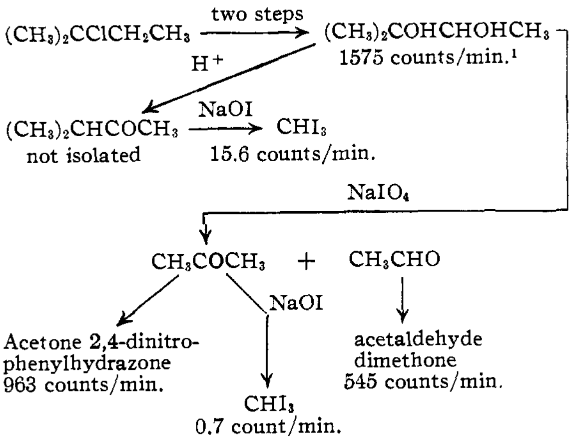
$$\underset{\text{I}}{(CH_3)_3C^{14}X} \rightleftarrows \underset{\text{II}}{(CH_3)_2(C^{14}H_3)CX}$$

$$\underset{\text{III}}{(CH_3)_2C^{14}XCH_2CH_3} \rightleftarrows \underset{\text{IV}}{(CH_3)_2CXC^{14}H_2CH_3} \rightleftarrows$$

$$\underset{\text{V}}{(CH_3)_2CXCH_2C^{14}H_3} \rightleftarrows \underset{\text{VI}}{C^{14}H_3(CH_3)CXCH_2CH_3}$$

Rearrangement of 2-methyl-2-chlorobutane-2-C^{14} (III, X = Cl) proceeded under the influence of aluminum chloride. Using conditions where 59% of the chloride was recovered the composition of the product was 64% of III (X = Cl), 35% of IV (X = Cl) and about 1% of V (X = Cl). Less than 0.1% of VI (X = Cl) was detected.

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



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]

This research was assisted by the joint program of the Office of Naval Research and the Atomic Energy Commission.

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RECEIVED APRIL 11, 1949

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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).