modifying the method of Livak, *et al.*[1] The over-all yield was increased and the method simplified when the α-amino-γ-hydroxybutyric acid needed for the preparation of the 5-(β-bromoethyl)-hydantoin was not isolated.

α-Bromo-γ-butyrolactone (462 g., 2.8 moles) was added, at such a rate that the temperature did not exceed 25°, with stirring to 985 ml. of concentrated ammonia water. After standing overnight at room temperature, a solution of 157 g. of potassium hydroxide in 2575 ml. of water was added. The solution was concentrated to a volume of *ca.* one liter. A solution of 174 g. (2.15 moles) of potassium cyanate in 334 ml. of water was added to the hot solution and the clear reddish-brown solution which resulted was heated at an internal temperature of 65° for two hours. Fourteen hundred ml. of 48% hydrobromic acid was then added to the chilled solution, which was then heated in a steam-bath (internal temperature was 93°) for two hours. After distilling to dryness *in vacuo*, the residue was suspended in two liters of boiling acetone. The mixture was filtered and the insoluble salts were washed well with hot acetone. The solvent was removed from the filtrate by distillation and the residue was heated with 1350 ml. of 48% hydrobromic acid in a steam-bath for two hours. The solution was taken to dryness *in vacuo* and the crude product remaining was dissolved in 400–500 ml. of boiling water. On chilling in an ice-bath, a tan precipitate appeared. This was filtered, washed with ice-water, and recrystallized from one liter of water. The product melted at 139–141° (uncor.) and weighed 142 g. (24.5%). Livak, *et al.*,[1] obtained their 5-(β-bromoethyl)-hydantoin in an 18.6% over-all yield and reported a melting point of 141.5–142°.

A solution of 41.4 g. (0.2 mole) of 5-(β-bromoethyl)-hydantoin and 16.8 g. (0.22 mole) of thiourea in 75 ml. of absolute ethanol was refluxed for 28.5 hours. After chilling in an ice-bath, the precipitate was separated and washed with ethanol followed by ether. The tan solid melted with decomposition at 191–192° (cor.) and weighed 51.5 g. (91%). When the volume of ethanol was decreased to 50 ml., the yield was increased to 95% but the product then melted at 186.5–189.5°.

Anal. Calcd. for $C_6H_{11}BrN_4O_2S$: C, 25.45; H, 3.92. Found: C, 25.79; H, 3.98.

DEPARTMENT OF CHEMISTRY
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RECEIVED MAY 12, 1951

N-(*p*-Dimethaminobenzyl)-aminoethanol

A warm solution of 74.6 g. (0.5 mole) of *p*-dimethylaminobenzaldehyde and 40 g. (0.66 mole) of ethanolamine in 100 ml. of absolute ethanol was hydrogenated at an initial pressure of 58 lb. in the presence of 250 mg. of platinum oxide. About ten hours was required for the reduction. The catalyst and solvent were removed and the residue vacuum distilled. The product, a pale yellow viscous liquid, weighed 139.2 g. (76%), b.p. 157–158° (1.5 mm.).

Anal. Calcd. for $C_{11}H_{18}N_2O$: N, 14.30. Found: N, 14.28.

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COMMUNICATIONS TO THE EDITOR

ON THE MECHANISM OF THE *IN VIVO* SYNTHESIS OF D-RIBOSE[1]

Sir:

The *in vivo* synthesis of D-ribose in the chick has been studied to determine whether the major pathway is by direct conversion from hexose.[2] Such a conversion would be expected to yield ribose labeled similarly to glycogen after feeding a C^{14}-labeled compound.

In a representative experiment, 7 chicks 1 month old were fasted for 48 hours and fed 6 mM. of sodium acetate containing 72×10^6 counts/minute/mg. of carboxyl carbon and 15 g. of chick mash per 100 g. body weight. After 18 hours, the animals were sacrificed. Glycogen was isolated from a cold trichloroacetic acid extract of the pooled internal organs and muscle and degraded by the method of Wood, *et al.*[3] Ribose was obtained from the purine nucleotide fraction of the trichloroacetic acid insoluble residue. The sodium nucleates were isolated,[4] the pentose and desoxypentose nucleic acids separated[5] and the purine ribonucleotides hydrolyzed with dilute acid. Ribose was purified by two filter paper chromatographic separations using ethyl acetate–acetic acid–water (3:1:3)[6] and *n*-butanol–ethanol–water (4.5:0.5:5) as solvents. A portion of the pentose was fermented with *Lactobacillus pentosus* 124-2 to acetate and lactate followed by further degradation to give the individual carbons as carbon dioxide. The remainder of the ribose was converted to potassium ribonate[7] and the salt oxidized with periodate as a check on the fermentation results. The work of Lampen, *et al.*,[8] has indicated that in this fermentation the α and carboxyl carbons of the acetate arise from pentose carbons 1 and 2, respectively; the carboxyl, α and β carbons of the lactate, from carbons 3, 4 and 5. The data being reported are in agreement with this interpretation.

The values,[9] in counts/minute/mg. carbon, obtained in this experiment for glycogen and ribose by fermentation were

	C_1	C_2	C_3	C_4	C_5	C_6
Glycogen	39	21	2460	2460	21	39
	C_1	C_2	C_3	C_4	C_5	
Ribose		45	52	338	10	0

(1) Sponsored in part by a grant of the American Cancer Society. The C^{14} used was obtained on allocation from the Atomic Energy Commission.

(2) F. Dickens, *Biochem. J.*, **32**, 1626, 1645 (1938); F. Dickens and G. E. Glock, *Nature*, **166**, 33 (1950); B. L. Horecker and P. Z. Smyrniotis, *Arch. Biochem.*, **29**, 232 (1950); D. B. McNair Scott and S. S. Cohen, *J. Biol. Chem.*, **188**, 509 (1951).

(3) H. G. Wood, N. Lifson and V. Lorber, *ibid.*, **159**, 475 (1945).

(4) J. N. Davidson and C. Waymouth, *Biochem. J.*, **38**, 375 (1944).

(5) G. Schmidt and S. J. Thannhauser, *J. Biol. Chem.*, **161**, 83 (1945).

(6) M. A. Jermyn and F. A. Isherwood, *Biochem. J.*, **44**, 402 (1949).

(7) S. Moore and K. P. Link, *J. Biol. Chem.*, **133**, 293 (1940).

(8) J. O. Lampen, H. Gest and J. C. Sowden, *J. Bact.*, **61**, 97 (1951).

(9) Values have been corrected for addition of carrier during degradation. Radioactivity measurements were made on $BaCO_3$ with an end-window Geiger–Müller counter. Measurements on ribose and ribonate were checked with a gas phase counter at the Brookhaven National Laboratory by Dr. Robert Steele whose assistance is greatly appreciated.

Periodate oxidation of ribonate indicated the following activities[9]: 41 in carbon 1, 125 as average for carbons 2, 3 and 4 and 0 in carbon 5. The activity[9] obtained by total combustion of ribonate was 80.

These data show that the C^{14} patterns in glycogen and ribose are markedly different and that, therefore, the direct conversion of hexose to ribose is probably not a major, although it may be a contributing, pathway in the synthesis of this pentose under these conditions. It would appear from this experiment that ribose might be synthesized by combination of two and three carbon units.

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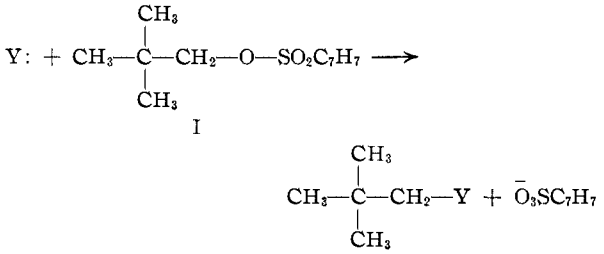
RECEIVED AUGUST 10, 1951

(10) Predoctoral Fellow, National Cancer Institute of the National Institutes of Health, Public Health Service, Federal Security Agency. The author gratefully acknowledges the guidance of Dr. Harland G. Wood and the assistance of Mr. Kenneth Lentz.

DISPLACEMENT REACTIONS IN NEOPENTYL-TYPE SYSTEMS[1]

Sir:

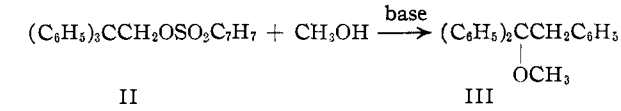
In a recent communication Sommer, Blankman and Miller[2] described what they believed to be "the first unequivocal examples of reactions of the neopentyl–oxygen bond proceeding without rearrangement." The authors apparently overlooked our preliminary report[3] of displacement reactions of neopentyl *p*-toluenesulfonate (I) with morpholine, thiourea, sodium phenyl mercaptide, sodium benzyl mercaptide or sodium iodide to give good yields of *unrearranged* products.



Y: = OC_4H_8NH, $S{=}C(NH_2)_2$, $C_6H_5S^-$, $C_6H_5CH_2S^-$, or I^-

The authors[2] point out that their work makes neopentyl bromide as available (47% from the alcohol) as other aliphatic bromides. It should be noted that the more reactive neopentyl *p*-toluenesulfonate (I) (95% from the alcohol) is an alternative starting material for many displacement reactions (see above). For example, we have now obtained neopentyl mercaptan in 64% yield (together with neopentyl sulfide) by the reaction of sodium hydrogen sulfide with I in refluxing methyl cellosolve solution for 2.5 hours.[4] With sodium methoxide and I, however, attack occurs at sulfur rather than at carbon and the ultimate products are neopentyl alcohol, sodium *p*-toluenesulfonate, and methyl ether (not isolated).[5]

Turning to a system more susceptible to rearrangement we have investigated the reactions with basic reagents of 2,2,2-triphenylethyl *p*-toluenesulfonate (II), which is known to undergo solvolytic-type rearrangement reactions with particular ease.[6] Recently the structurally analogous tritylmethyl chloride was reported to exhibit very marked steric hindrance in bimolecular nucleophilic displacements, and to form triphenylethylene in hydroxylic solvents at rates unaffected by added alkali.[7] We have noted that in refluxing methanol, II also gave triphenylethylene, but when the solution was kept from becoming acid during the reaction by the presence of added bases (sodium methoxide, potassium carbonate or sodium phenyl mercaptide), the major product was 1,1,2-triphenylethyl methyl ether (III). In methanol solution III was cleaved by dilute acid to triphenylethylene.



II III

Further examples of rearrangement under basic conditions were observed in the reaction of II with methylmagnesium iodide in ether to yield 35% of 1,2,2-triphenylpropane, with lithium aluminum hydride in ether to yield 35% of 1,1,2-triphenylethane, and with excess morpholine to yield 20% of a basic product assumed to be N-(1,1,2-triphenylethyl)-morpholine by analogy with the above reactions, and by its non-identity with an isomeric amine obtained from triphenylacetomorpholide and lithium aluminum hydride.

These results can perhaps best be rationalized by assuming the formation of an intermediate ion similar to that suggested by Cram.[8]

(1) This investigation was supported by the American Petroleum Institute as part of Project 48B.

(2) L. H. Sommer, H. D. Blankman and P. C. Miller, THIS JOURNAL, **73**, 3542 (1951).

(3) F. G. Bordwell, M. Knell and B. M. Pitt, paper presented at the American Chemical Society Meeting in Philadelphia, Pa., April 1950, p. 67L of abstracts.

(4) This experiment was carried out by Mr. Harry M. Andersen.

(5) Similar results were reported by J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912), for phenyl *p*-toluenesulfonate and sodium ethoxide.

(6) S. Winstein, paper presented at the 11th National Organic Symposium, Madison, Wisconsin, June 21, 1948, p. 65; S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2705 (1951).

(7) J. C. Charlton, I. Dostrovsky and E. D. Hughes, *Nature*, **167**, 986 (1951).

(8) D. J. Cram, THIS JOURNAL, **71**, 3863 (1949).

DEPARTMENT OF CHEMISTRY F. G. BORDWELL
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EVANSTON, ILLINOIS MARTIN KNELL

RECEIVED AUGUST 13, 1951

PANTOTHENIC ACID INVOLVEMENT IN FATTY ACID OXIDATION[1]

Sir:

The observations by Stern and Ochoa[2] and by Novelli and Lipmann[3] that Coenzyme A is involved in the incorporation of a C_2 unit (at the oxidation level of acetate) into the citric acid cycle, together

(1) Paper No. 11 of a series on pantothenic acid studies. This work was supported by grants from the Nutrition Foundation, Inc., the General Research Council of Oregon State College, and the Division of Research Grants and Fellowships of the National Institutes of Health, U. S. Public Health Service. Published with the approval of the Monographs Publications Committee, Oregon State College, Research Paper No. 183, School of Science, Department of Chemistry.

(2) J. R. Stern and S. Ochoa, *J. Biol. Chem.*, **179**, 491 (1949).

(3) G. D. Novelli and F. Lipmann, *ibid.*, **182**, 213 (1950).