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.

DEPARTMENT OF BIOCHEMISTRY
WESTERN RESERVE UNIVERSITY
CLEVELAND 6, OHIO
I. A. BERNSTEIN[10]

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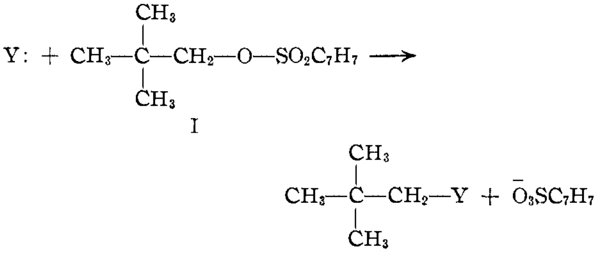
[10] Predoctoral Fellow, National Cancer Institute of the National Institutes of Health, Public Health Service, Federal Security Agency. The author gratefully acknowledges the guidance of Dr. Harland G. Wood and the assistance of Mr. Kenneth Lentz.

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.



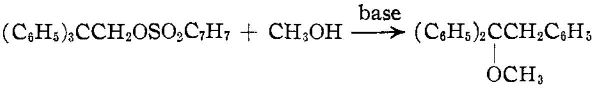
$$Y{:} + CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-O-SO_2C_7H_7 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-Y + \bar{O}_3SC_7H_7$$

I

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.



$$(C_6H_5)_3CCH_2OSO_2C_7H_7 + CH_3OH \xrightarrow{\text{base}} (C_6H_5)_2\underset{\displaystyle OCH_3}{C}CH_2C_6H_5$$

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]

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[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
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
F. G. BORDWELL
BURNETT M. PITT
MARTIN KNELL

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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

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[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).