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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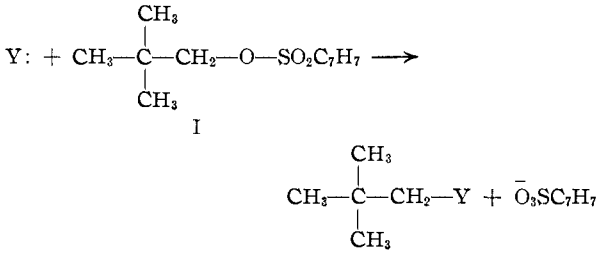
DISPLACEMENT REACTIONS IN NEOPENTYL-TYPE SYSTEMS[1]

Sir:

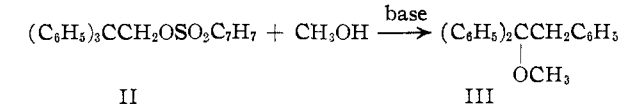
In a recent communication Sommer, Blankman and Miller[2] described what they believed to be "the first unequivocal examples of reactions of the neopentyl–oxygen bond proceeding without rearrangement." The authors apparently overlooked our preliminary report[3] of displacement reactions of neopentyl *p*-toluenesulfonate (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).

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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

(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).

with the finding by Lotspeich[4] that pantothenic acid deficiency symptoms in rats may be accentuated on a high-fat diet, have prompted us to investigate the effect of pantothenate upon fatty acid oxidation.

Wistar rats at 28 days of age were placed on a purified diet[5] containing 9% fat. During the first two weeks on the diet, pantothenic acid was removed from all animals. Thereafter a division was made into deficient and control groups, with the latter receiving 20 mg. of pantothenic acid per kg. of diet. After three to five additional weeks on the above regimen, the deficient animals weighed 50 to 75 grams (about 30–40%) less than the controls, and often exhibited bloody whiskers and "whisky noses."

In the various experiments, livers from three deficient or two normal animals were homogenized with an equal weight of 0.9% cold KCl for 45 to 90 seconds at *p*H 6.8, and examined for their ability to oxidize fatty acids.

As may be seen from Table I, the oxidation of caproate in the deficient samples was less than half of that observed for the controls. Statistical treatment of the data showed that the oxidation of caproate in the controls was not significantly different from 100%, whereas in the deficients the mean value lay between 12 and 40% (confidence coefficient = 0.95). The difference between the two groups was found to be significant beyond the 1% level ($F = 29.97$; a value of 8 plus or higher is needed at this level). Preliminary experiments with rat liver mitochondria (cyclophorase at the third residue state[6]) revealed similar trends to those observed for homogenates, although the differences became pronounced only when higher levels of caproate (40 μ moles) were used per flask. This is probably due to the much higher mitrochondrial density in the cyclophorase preparations, so that with less than 20 μ moles of caproate the latter becomes the limiting factor for oxidation.

Preliminary results with butyrate oxidation were similar to those described for caproate. Extension of these studies is being made to include the effect of pantothenate deficiency upon oxidation within the citric acid cycle. Details of this and other aspects of oxidation by rat liver systems will be presented elsewhere.

TABLE I

OXIDATION OF CAPROATE BY RAT LIVER HOMOGENATES

Each flask contained 1 ml. of liver homogenate, 0.1 ml. of 0.1 *M* caproate at *p*H 7.2, 0.2 ml. of 0.1 phosphate buffer of *p*H 7.2, 0.1 ml. of 0.1 *M* adenylic acid, 0.2 ml. of 0.02 *M* $MgCl_2$, 0.1 ml. of 7×10^{-3} *M* cytochrome C. Final volume 3 ml.; alkali in center well; oxygen in gas phase; temperature = 37°.

	Caproate oxidized,[a] %	
	Normal animals	
Expt.	1[b]	2[c]
1	82	128
2	115	90
3	23	124
4	74	67
	Pantothenate deficient animals	
1	18	46
2	0	10
3	39	4
4	0	21
5	18	74
6	13	59
7	26	10

[a] Theoretical oxygen consumption by caproate = 8 atoms per mole.[7] [b] In presence of 1 mol α-ketoglutarate per flask. [c] In presence of 2 mols α-ketoglutarate per flask.

(4) W. D. Lotspeich, *Proc. Soc. Exptl. Biol. Med.*, **73**, 85 (1950).

(5) T. E. King, F. M. Strong and V. H. Cheldelin, *J. Nutrition*, **42**, 195 (1950).

(6) D. E. Green, W. F. Loomis and V. Auerbach, *J. Biol. Chem.*, **172**, 389 (1948).

(7) V. H. Cheldelin, I. S. Mirviss and D. E. Green, Abstracts, 118th Meeting of Am. Chem. Soc., Atlantic City, 5C (1950).

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A NEW METHOD FOR THE CONVERSION OF NITRILES TO ALDEHYDES[1]

Sir:

In the course of an investigation of a synthesis of methionine-α-C^{14}, it was desired to prepare β-methylmercaptopropionaldehyde from cyanide-labeled β-methylmercaptopropionitrile. The Stephen reduction[2,7] and direct reduction with lithium aluminum hydride[3] gave unsatisfactory results. This aldehyde was prepared in good yield from the corresponding nitrile by a procedure involving a hitherto unreported reaction of lithium aluminum hydride, the reduction of an ortho ester to an acetal.

The methyl and ethyl esters of ortho-β-methylmercaptopropionic acid were obtained from β-methylmercaptopropionitrile[4] according to McElvain's procedure.[5] Methyl ester, 57.6% yield, b.p. 51–52° (1 mm.), (calcd. for $C_7H_{16}O_3S$: C, 46.59; H, 8.89. Found: C, 46.98; H, 8.68.). Ethyl ester, 65.5% yield, b.p. 71–72° (0.8 mm.), (calcd. for $C_{10}H_{22}O_3S$: C, 53.98; H, 9.90. Found: C, 54.35; H, 9.89). The following method was then used to reduce the ortho esters to the corresponding acetals: One quarter of a molar equivalent of lithium aluminum hydride (1 *M* ether solution) was added to a boiling solution (0.33 *M*) of the ortho ester in benzene. The mixture was refluxed four hours. The complex was decomposed with Rochelle salt solution (30%) and the benzene extract was dried and distilled.

Both the methyl and ethyl acetals of β-methylmercaptopropionaldehyde were obtained in good yield. Dimethyl acetal, 97% yield, b.p. 73° (0.9 mm.), (calcd. for $C_6H_{14}O_2S$: C, 46.98; H, 9.33. Found: C, 47.11; H, 8.95). Diethyl acetal, 73% yield, b.p. 68–74° (0.7 mm.), (calcd. for $C_8H_{18}O_2S$: C, 53.84; H, 10.12. Found: C, 54.13; H, 9.81). The acetals are readily hydrolyzed to β-methylmercaptopropionaldehyde.[6] The 2,4-di-

(1) This work was supported by Contract N6ori-126, Task VIII-B with the Office of Naval Research, United States Navy.

(2) H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

(3) L. Friedman, Abstracts, 116th Meeting American Chemical Society, Atlantic City, N. J., 1949, p. 5 M.

(4) S. Akabori, T. Kaneko and S. Matizuki, *J. Chem. Soc. Japan*, **59**, 1136 (1938).

(5) S. M. McElvain and J. W. Nelson, THIS JOURNAL, **64**, 1824 (1942).

(6) G. Barger and F. P. Coyne, *Biochem. J.*, **22**, 1417 (1928).