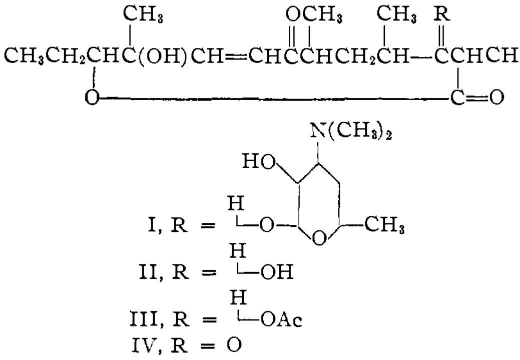
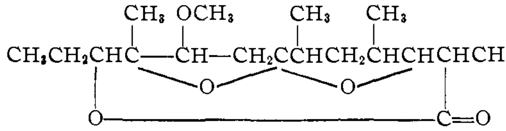
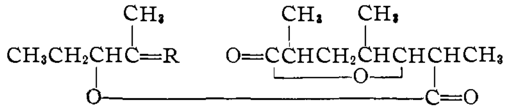
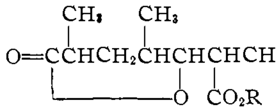
$[\alpha]_D$ +38°, λ_{max}^{KBr} 3.05 (broad), 5.68 and 5.76 μ; Found: C, 59.91; H, 8.05; neut. equiv., 199 (immediate titration), 100 (after standing for 2 hours in excess base)). Lead tetraacetate oxidation of the hydroxy acid VI gave the methyl ketone VII (positive iodoform test), which in turn upon alkaline saponification led to the lactone acid VIIIa and 3-hydroxy-2-pentanone (isolated and identified as the bis-2,4-dinitrophenylhydrazone of pentane-2,3-dione).[7]


I, R = ; II, R = H —OH; III, R = H —OAc; IV, R = O

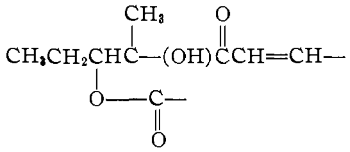

V


VI, R = OH —CO₂H

VII, R = O


VIIIa, R = H

b, R = CH_3


IX

It is clear that 2,4,6-trimethylcyclohex-2-en-1-one, isolated[6b] from the alkali fusion of methymycin (I), must have arisen by a cyclization process involving a fragment containing the carbon sequence of VIIIa. Since methymycin cannot contain the partial structure IX[8] (which would also have led to the oxidation products VI, VII and VIII), the trimethylcyclohexenone precursor can, for all practical purposes, be attached only in the manner shown in II and this in turn would lead to formulation VIIIa for the lactone acid. This acid (as well as its methyl ester VIIIb, m.p. 79–81°) proved to be identical with a specimen isolated by Prof. V. Prelog and colleagues[9] from some related antibiotics. Since the Swiss investigators[9] have shown that decarboxylation of VIIIa followed by oxidation yields acetaldehyde and meso-α,α'-dimethylglutaric acid, this fully confirms structures VI and VII and consequently also II.

The placement of the desosamine fragment as shown in I rather than attaching it to the tertiary hydroxyl function follows from three lines of evidence: (a) methymycin amide[6a] is recovered unchanged under conditions where II is oxidized to the ketone IV in good yield; (b) since the lithium aluminum hydride reduction product of methymycin[6b,8] was processed under non-acidic conditions prior to periodate oxidation, a glycosidic linkage involving desosamine and the tertiary hydroxyl group would almost certainly not have been cleaved and consequently no periodate would have been consumed; (c) the alternative structure would not explain the resistance[6b] to periodate of the lithium aluminum hydride reduction product of tetrahydrodesoxymethymycin.[6a]

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USE OF GAS PHASE CHROMATOGRAPHY FOR THE SEPARATION OF MIXTURES OF CARRIER FREE RADIOACTIVE SUBSTANCES: PRODUCTS OF CHEMICAL REACTIONS ACTIVATED BY NUCLEAR PROCESSES

Sir:

When organic bromides are irradiated with neutrons, the Br^{82}(36 hr.) formed with high kinetic energy by the $Br^{81}(n,\gamma)Br^{82}$ process ruptures the parent bond and reënters combination as a variety of compounds.[1] Such compounds are present at mole fractions of the order of 10^{-12}. By gas–liquid partition chromatography we have separated over twenty different radioactive organic compounds from a drop of neutron irradiated *n*-propyl bromide and detected their presence with the aid of a scintillation counter (curve A, Fig. 1), thus demonstrating that: (1) the gas chromatographic technique is as effective for materials at tracer concentrations as at macro concentrations; (2) the number of products from the (n,γ) reaction in n-C_3H_7Br is at least twice as great as formerly suspected. Curve B, Fig. 1, shows a similar chromatogram of the organic products containing Br^{80}

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[7] Comparison with an authentic sample (P. F. Wiley, K. Gerzon, E. H. Flynn, M. V. Sigal and U. C. Quarck, THIS JOURNAL, **77**, 3676 (1955)) was kindly carried out by Dr. K. Gerzon.

[8] Lithium aluminum hydride reduction of methymycin (ref. 6b) or of II followed by periodate oxidation results in consumption of only one equivalent of reagent and formation of propionaldehyde which is only compatible with structures I and II. Furthermore, IX is also excluded by the formation of the spiroketal V.

[9] We are greatly indebted to Prof. V. Prelog (E. T. H., Zurich) for carrying out the direct comparison and for informing us of his results prior to publication.

[10] Squibb Postdoctorate Research Fellow at Wayne University, 1955–1956.

[1] For a discussion of chemical reactions activated by nuclear processes see J. E. Willard, *Ann. Rev. of Nuc. Sci.*, **3**, 193 (1953).

(18 min.) formed when 5 mole% Br_2 undergoing the Br^{80m}(4.4 hr.) $\xrightarrow{I.T.}$ Br^{80} (18 min.) reaction was dissolved in n-C_3H_7Br.

For the (n,γ) activation experiments highly purified n-C_3H_7Br containing 5 mole% Br_2 was irradiated in the Argonne National Laboratory CP5 reactor for 30 min. at 10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$ and subsequently extracted with aqueous sulfite. The total "organic yield"[1] was 24%. Fifty microliters was placed on the gas chromatography column. Nitrogen flowed through at 40 ml./min. The column consisted of 6 ft. of 4 mm. i.d. glass tubing, bent in a U. The most satisfactory packing tried was crushed Johns-Manville C-22 insulating brick, sieved to 40–60 mesh, washed with water, dried and coated with 40% of its weight of General Electric SF-96(40) silicone oil. During a 30-min. separation run, the temperature of the oil-bath in which the column was immersed was raised from 60 to 200°, which allowed components of successively higher boiling point to move through the column at a desirable rate. The effluent gas passed to the bottom of a thin-walled 1-ml. glass thimble which fit in the well of a NaI(Tl) scintillation crystal. The scintillation crystal fed through a photomultiplier tube, preamplifier, linear amplifier and rate meter to a chart recorder. The first peak of each chromatogram in Fig. 1 was caused by about 10^5 dis./min., *i.e.*, about 10^{-13} g. of CH_3Br^{82}(36 hr.) or 10^{-15} g. of CH_3Br^{80}(18 min.).

With 6-ft. columns packed with insulating brick, the pressure required to maintain a 40 ml./min. flow rose from 3 lb. gage at 60° to 6 lb. at 200°. With Celite 545 packing, the required pressure rose to over 30 lb. after several runs. The two packings gave equally good resolution. Overlapping peaks were more completely resolved in the same time by use of a 12-ft. column of C-22 brick with a 60 ml./min. flow maintained by a 12 to 19 lb. pressure. Di-(2-ethylhexyl) phthalate ("Octoil") coatings gave resolution which was inferior to the silicone oil and also showed signs of decomposition at the higher temperatures.

Previous investigations[2,3] of the organic products of the $Br^{81}(n,\gamma)Br^{82}$ process in n-C_3H_7Br containing 5 mole% Br_2, made by fractional distillation with added carriers, have identified ten compounds with the following relative percentages[3]: CH_3Br (5.8%), C_2H_5Br (1.4%), i-C_3H_7Br (3.4%), n-C_3H_7Br (35.7%), CH_2Br_2 (4.6%), $C_2H_4Br_2$ (6.5%), 1,2-$C_3H_6Br_2$ (10.5%), n-$C_6H_{13}Br$ (1.4%), 1,3-$C_3H_6Br_2$ (10.4%), 1,1,2-$C_2H_3Br_3$ (4.4%), higher boiling (15.7%). Many of these can be correlated with peak heights of Fig. 1. Definite assignment of all the peaks should be possible by calibration with known compounds, using a thermal conductivity detector.

Curves A and B of Fig. 1 are consistent with the conclusion that the product distributions from activation by the (n,γ) and isomeric transition processes are identical,[4,5] although they do not exclude small quantitative differences.

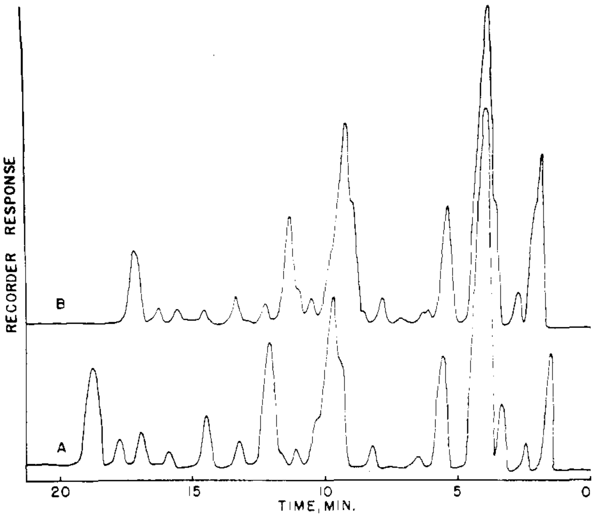

Fig. 1.—Gas chromatogram of trace compounds in n-C_3H_7Cr obtained with 6-ft. Celite 545-silicone oil column: Curve A, activated by (n, γ) process, monitored with scintillation counter; curve B, activated by isomeric transition, monitored with Geiger tube. Curves are not corrected for radioactive decay. The shorter retention time in Curve B was caused by a slightly faster heating rate.

Among the places where the techniques reported here should be valuable is in the separation of radioactive products formed by the photolysis or radiolysis of radioactive compounds or compounds containing dissolved radioactive halogens to scavenge free radicals.

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RECEIVED APRIL 27, 1956

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(2) M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

(3) J. C. W. Chien, Ph.D. Thesis, University of Wisconsin, 1954.

(4) J. F. Hornig and J. E. Willard, THIS JOURNAL, **75**, 461 (1953).

(5) G. Levey and J. E. Willard, *ibid.*, in press (1956).

TERNARY OXIDES OF TETRAVALENT MOLYBDENUM

Sir:

We have prepared ternary oxides of tetravalent molybdenum containing divalent magnesium, zinc, cobalt and iron which are of an apparently new structural type. The general formula is $A_4Mo_6O_{16}$ (A = Mg^{+2}, Zn^{+2}, Co^{+2}, Fe^{+2}). We have also prepared a ternary oxide with calcium having the composition $CaMoO_3$.

Recently, Scholder and Brixner[1,2] reported the preparation of several ternary oxides of molybdenum, among them $CaMoO_3$ and $MgMoO_3$. However no chemical analyses or X-ray data were given for these compounds. Our results are in agreement with their findings for $CaMoO_3$ but in contrast to their work we have been unable to prepare a compound of composition $MgMoO_3$. All attempts to prepare this compound led to the formation of $Mg_4Mo_6O_{16}$.

All preparations were made by heating appropriate mixtures of the constituents in evacuated, sealed, silica capsules for 48 hours at 1150°. The

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(1) R. Scholder, *Angew. Chem.*, **66**, 467 (1954).

(2) R. Scholder and L. Brixner, *Z. Naturforschg.*, **10b**, 178 (1955).