acetic acid which had been refluxed with 1% excess acetic anhydride. The disappearance of the yellow indicator color was taken as the end-point. Least squares slopes and their probable errors were calculated for plots of ln (% unreacted) against time; in all cases good straight lines were obtained for every run and at least one run for each compound was followed for three or more half-lives.

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CAMBRIDGE 38, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Studies of Configuration. VIII. Evidence for Methoxyl Migration in the Solvolysis of 4-Methoxycyclohexyl Tosylate by Tritium Labeling[1]

BY DONALD S. NOYCE AND BRUCE N. BASTIAN

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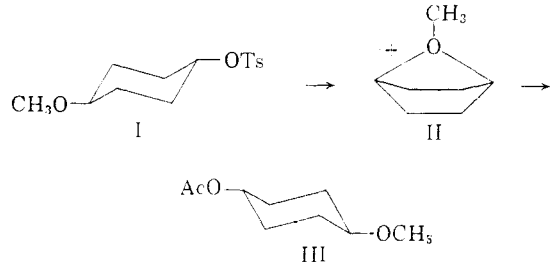
The preparation and solvolysis of *trans*-4-methoxycyclohexyl-1-*t* tosylate is reported. In acetic acid at 75° the solvolysis products are 66% 4-methoxycyclohexene, 9.6% *cis*-4-methoxycyclohexyl acetate and 24% *trans*-4-methoxycyclohexyl acetate. The tritium label is specifically in the 1-position in the olefin, demonstrating that none of the olefin arises from a symmetrical bicyclic oxonium ion intermediate II. The *cis*-4-methoxycyclohexyl acetate is likewise labeled only in the 1-position. The *trans*-4-methoxycyclohexyl acetate formed is nearly equally labeled in the 1- and 4-positions, demonstrating that it arises in large measure by an internally assisted pathway through the symmetrical ion II as an intermediate.

Introduction

In previous reports[2,3] from these laboratories we have demonstrated that the solvolysis of *trans*-4-methoxycyclohexyl tosylate (I) proceeds with some rate acceleration, and that the 4-methoxycyclohexyl acetate formed is largely of the *trans* configuration (III). It was concluded from the rate studies and the product studies that an internally assisted pathway was responsible for these results, with the symmetrical bicyclic oxonium ion (II) suggested as an intermediate. Winstein,



Allred, Heck and Glick[4] have shown that the solvolysis of 4-methoxypentyl *p*-bromobenzenesulfonate proceeds through a similar intermediate.

It is the purpose of the present study to examine further the reality of II as an intermediate in the solvolysis of I. For this purpose it was decided to use *trans*-4-methoxycyclohexanol labeled in the 1-position with tritium (IV). Tritium labeling appeared to be particularly suitable. At the end of the sequence of reactions summarized in Chart I, reoxidation to 4-methoxycyclohexanone would provide a simple means of determining the partitioning of the solvolysis product to 4-methoxycyclohexanol-1-*t* and 4-methoxycyclohexanol-4-*t*. Furthermore the use of tritium in tracer quantities has a distinct advantage over the use of deuterium in molar concentrations. In the oxidation of a mixture of 1-*d*- and 4-*d*-labeled cyclohexanol the well-known isotope effect might well provide spurious results, if the cyclohexanol-1-*d* were not completely oxidized.

Results

With these considerations in mind, we examined the preparation of 4-methoxycyclohexanol-1-*t*. Sodium borohydride in isopropyl alcohol afforded a mixture of the *cis*- and *trans*-4-methoxycyclohexanol containing about 77% of the *trans* isomer. Reduction with tritium labeled sodium borohydride afforded a similar mixture. The mixture was diluted with a large amount of inactive *trans*-4-methoxycyclohexanol. Oxidation of this alcohol with chromic acid in acetone gave 4-methoxycyclohexanone, with 99.97% of the activity removed. This experiment serves to verify the specific labeling introduced.

trans-4-Methoxycyclohexanol-1-*t* (IV) was converted to the tosylate V, further diluted with inactive tosylate, and crystallized several times. Pure V ($2.62 \pm 0.05 \times 10^6$ d.p.m./mmole) was used for the solvolytic experiments. Solvolysis in acetic acid at 75° afforded a mixture of acetates ($2.71 \pm 0.05 \times 10^6$; VI, VII, VIII), and olefin ($2.33 \pm 0.3 \times 10^6$) which were separated by distillation. Both the olefin and the acetates were separately examined for the position of labeling.

A diluted aliquot of the olefin (0.13×10^6 d.p.m./mmole) was oxidized to β-methoxyadipic acid. After several crystallizations from hexane, the acid showed no activity. These results establish clearly that none of the olefin arises from the symmetrical intermediate.

The acetates from the solvolysis were saponified to yield a mixture of *cis*- and *trans*-4-methoxycyclohexanol ($2.62 \pm 0.02 \times 10^6$ d.p.m./mmole; IX, X, XI). Infrared analysis of this mixture showed that 71% was the *trans* isomer.

A sample of the mixed alcohols was oxidized with chromic acid in acetone to 4-methoxycyclohexanone. The specific activity of the ketone XII,

(1) Supported in part by a grant from the National Science Foundation (NSF G-5921).

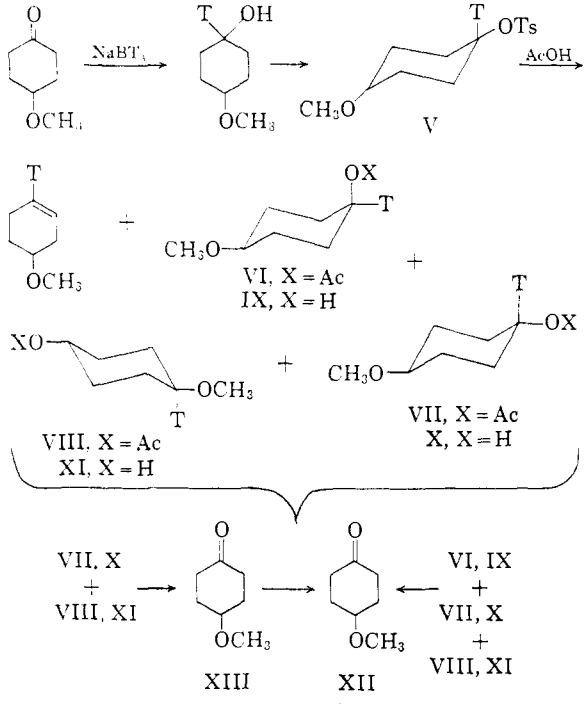
(2) D. S. Noyce and B. R. Thomas, THIS JOURNAL, **79**, 755 (1957).

(3) D. S. Noyce, B. R. Thomas and B. N. Bastian, *ibid.*, **82**, 885 (1960).

(4) S. Winstein, E. Allred, R. Heck and R. Glick, *Tetrahedron*, **3**, 1 (1958).

CHART I

FLOW SHEET FOR RADIOCHEMICAL SEQUENCES



$0.80 \pm 0.02 \times 10^6$ d.p.m./mmole, clearly shows that an appreciable fraction of the 4-methoxycyclohexanol arises by methoxyl migration.

Pure *trans*-4-methoxycyclohexanol (X, XI); $2.54 \pm 0.01 \times 10^6$ d.p.m./mmole) was isolated from the mixed alcohols *via* the hydrogen phthalate. When this alcohol was oxidized, 4-methoxycyclohexanone (XIII) having a specific activity of 1.13×10^6 d.p.m./mmole was obtained. To establish the radiochemical purity of this ketone and to establish that tritium had not migrated to the 2- or 6-positions a diluted aliquot of the ketone (0.224×10^6 d.p.m./mmole) was converted to the dibenzylidene derivative ($0.21 \pm 0.02 \times 10^6$ d.p.m./mmole). The error in this measurement was larger than usual due to the very low (2–4%) counting efficiency of the colored solutions. The specific activity of the dibenzylidene derivative did not vary outside of experimental error after further crystallization.

The radiochemical analyses of the ketones XII, XIII and the parent alcohols IX–XI permit the calculation of the composition of the acetates from solvolysis. For simplicity of calculation the original acetate mixture, and hence derived alcohol mixture, is considered to be composed of *cis*-4-methoxycyclohexyl-1-*t* acetate (VI), *trans*-4-methoxycyclohexyl-1-*t* (VII) and *trans*-4-methoxycyclohexyl-4-*t* acetate (VIII). The mixture is considered free of *cis*-4-methoxycyclohexyl-4-*t* acetate and isomers having tritium in the 2- or 6-positions. The validity of the first assumption follows from the radiochemical analysis. The validity of the second assumption was demonstrated above.

The ratio (0.80/2.62) of the specific activities of the ketone XII and the mixed alcohols IX-XI gives the fraction (0.3053) of *trans*-4-methoxycyclohexanol-4-*t* (XI) present in the mixture of alcohols. The fraction (0.4237) of *trans*-4-methoxycyclohexanol-1 (X) follows from the ratio (1.13/2.62) of ketone XIII to the sum of the specific activities of the parent *trans*-alcohols X, XI. The fraction (0.2795) of *cis*-4-methoxycyclohexanol-1-*t* (IX) must account for the difference if the original assumptions are correct. The fact that these assumptions are valid is shown by the close agreement of the radiochemical analysis which indicated 28% *cis*-4-methoxycyclohexanol and the infrared analysis of the alcohols (29% *cis*), and the vapor phase chromatographic analysis (29% *cis*) of the parent acetates.[3]

In earlier work[3] we established that 4-methoxycyclohexyl acetate comprises 33.6% of the reaction products. From these data the detailed product composition is derived and shown in Table I.

TABLE I

PRODUCTS OF ACETOLYSIS OF *trans*-4-METHOXYCYCLOHEXYL-1-*t* TOSYLATE

4-Methoxycyclohexene-1-*t*	66.4%
cis-4-Methoxycyclohexyl-1-*t* acetate	9.6%
trans-4-Methoxycyclohexyl-1-*t* acetate	13.8%
trans-4-Methoxycyclohexyl-4-*t* acetate	10.2%

Discussion

The results of the radiochemical investigation clearly demonstrate the intramolecular participation by the methoxyl group. This confirms the existence of a symmetrical oxonium ion intermediate II. The fact that *trans*-4-methoxycyclohexyl-4-*t* acetate accounts for 10.2% of the reaction product, while *trans*-4-methoxycyclohexyl-1-*t* acetate represents 13.8% of the reaction products requires further comment. To a first approximation these two species should have arisen in equal amount from the intermediate II. Two possibilities need to be considered. First, the magnitude of the α-isotope effect must be evaluated. The magnitude of this effect is unknown; in this case the central carbon atom at the transition state is visualized as being associated with both the methoxyl-group and solvent. In such a transition state containing both entering and leaving groups the wagging motion accounting for the isotope effect is impeded[5] and k_H/k_T would be expected to approach unity. Thus Shiner has found $k_H/k_D = 1$ for the S_{N2} displacement of 2-deuterio-2-bromopropane.[6] Therefore one would expect *trans*-4-methoxycyclohexyl-1-*t* acetate and *trans*-4-methoxycyclohexyl-4-*t* acetate to be present in equal quantities if acetate of retained configuration were derived only from the symmetrical intermediate.

Any change from this presumed pattern would be in the wrong direction; that is, *trans*-4-methoxycyclohexyl-4-*t* acetate should be favored slightly by any kinetic isotope effect.

An alternative source of excess *trans*-4-methoxycyclohexyl-1-*t* acetate from the normal solvolytic reaction does not appear likely. Winstein and Holness[7] find 98% inversion for the acetolysis of *trans*-4-*t*-butylcyclohexyl tosylate. We find no

(5) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, THIS JOURNAL, **80**, 2326 (1958).

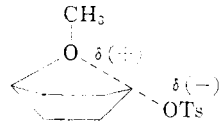
(6) V. J. Shiner, Jr., *ibid.*, **74**, 5285 (1952).

(7) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

evidence for any retained acetate in the solvolysis of *cis*-4-methoxycyclohexyl tosylate.[3]

The excess of *trans*-4-methoxycyclohexyl-1-*t* acetate over *trans*-4-methoxycyclohexyl-4-*t* acetate, coupled with the tritium labeling of the olefin which is formed, suggests that the complete reaction sequence involves a further intermediate *prior* to the bicyclic oxonium ion.

The conclusions[3] drawn from the rate data indicate that a significant proportion of the total reaction products arises from the assisted pathway. This requires that a substantial amount of the olefin be formed by the assisted pathway. One very reasonable fashion in which to accommodate this conclusion is by the inclusion of ion pair XIV in the total reaction scheme.



XIV

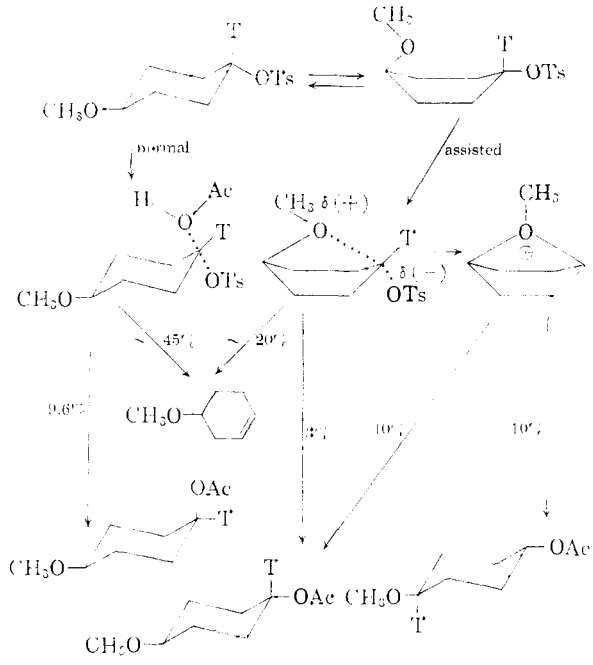
The validity of this suggestion is smoothly consistent with the radiochemical data. Three alternative reaction pathways are available to XIV, each of them supported by adequate analogy. Firstly, XIV may collapse to the bicyclic oxonium ion II (a process analogous to the completion act in normal solvolysis). Secondly, the tosylate group may be replaced by solvent acetic acid (a process analogous to reaction pathways leading to racemization in simpler solvolytic reactions). Finally, it is suggested that XIV may give rise to olefin (in a manner like the proposed "merged" mechanism suggested by Winstein, Darwish and Holness[8]).

An exact numerical breakdown for these various pathways is extremely difficult, since the data do not permit a precise evaluation of substitution to elimination ratios. If one assumes that the *trans*-4-methoxycyclohexyl tosylate would show an elimination:substitution ratio like the *cis* isomer (4.88:1), then a 20% yield of olefin comes from the assisted pathway, *via* the merged mechanism suggested above.

We finally conclude that the acetolysis of *trans*-4-methoxycyclohexyl-1-*t* tosylate proceeds nearly equally through a "normal solvolytic" pathway and an internally assisted pathway involving methoxyl participation. The total reaction scheme and the yield of products from each source are summarized in Chart II.

CHART II

MECHANISM OF ACETOLYSIS OF *trans*-4-METHOXYCYCLOHEXYL-1-*t* TOSYLATE



Experimental[9]

4-Methoxycyclohexanone.—The mixed *cis* and *trans* isomers of 4-methoxycyclohexanol were prepared by Raney nickel reduction of *p*-methoxyphenol. 4-Methoxycyclohexanol (34.8 g.) and acetone (125 ml.) were cooled in an ice-bath. Chromium trioxide (18.5 g.) and sulfuric acid (27.4 g.) in water (80 ml.) were added dropwise to the cooled stirred solution so that the temperature remained below 21°. After four hours the mixture was continuously extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and distilled at reduced pressure to afford 22.0 g. of 4-methoxy-cyclohexanone (65.9% yield), b.p. 97–99° (23 mm.), $n^{25}D$ 1.4542. **4-Methoxycyclohexanol-1-*t*.**—Sodium borohydride (95%, recrystallized from diglyme, 2.0 ml., 5.7 mg./ml.) in dry isopropyl alcohol was added to a stirred solution of 4-methoxycyclohexanone (1.64 g.) in dry isopropyl alcohol (10 ml.) under nitrogen. Twenty minutes later sodium borotriteride (10 mg., 11.2 millicuries, New England Nuclear Corp., Boston Mass.) in dry isopropyl alcohol (10 ml.) was added. The reaction mixture was stirred at room temperature for 12 hours under nitrogen and additional sodium borohydride (13 ml., 5.7 mg./ml.) in dry isopropyl alcohol was added. After 30 hours the solvent was removed under reduced pressure and the borate ester saponified with aqueous sodium hydroxide (10 ml., 1.3 *M*) for 7 hours at 80°. The reaction mixture was continuously extracted with ether. After drying over anhydrous sodium sulfate the ether was removed by distillation and the crude 4-methoxycyclohexanol-1-*t* purified by chromatography on Woelm 3 alumina. A center cut of pure 4-methoxycyclohexanol-1-*t* (0.517 g., 39.4%) whose infrared spectrum was identical with authentic material was diluted with pure non-radioactive *trans*-4-methoxycyclohexanol (10.298 g.) to yield alcohol having 6.028×10^7 d.p.m./mmole.[10]

Control Oxidation of 4-Methoxycyclohexanol-1-*t*.—4-Methoxycyclohexanol-1-*t* (1.0382 g., 6.028×10^7 d.p.m./mmole) in acetone (10 ml.) was oxidized with an equimolar quantity of chromium trioxide in aqueous sulfuric acid (3.4 ml., 2.5 *M*). Reaction conditions and work-up procedure were the same as described earlier. The 4-methoxycyclohexanone was purified by chromatography on Woelm 3 alumina being eluted with pure pentane. The ketone (0.553 g., 54.8%, 1.5×10^4 d.p.m./mmole, 0.025% of parent alcohol) had an infrared spectrum identical with authentic material.

trans-4-Methoxycyclohexyl-1-*t* tosylate prepared in the usual manner from *trans*-4-methoxycyclohexanol-1-*t* (9.234 g., 0.056 mole, 78.3%, m.p. 66°) was recrystallized six times from hexane. A portion of the tosylate (3.0079 g.) was mixed with 66.2 g. of inactive *trans*-4-methoxycyclohexyl tosylate and recrystallized again from hexane (m.p. 66.4–67.2°, specific activity, $2.62 \pm 0.05 \times 11^6$ d.p.m./mmole).

(8) S. Winstein, D. Darwish and N. J. Holness, THIS JOURNAL, **78**, 2915 (1956).

(9) All melting points are corrected, boiling points are uncorrected. Distillations were through a 2-foot modified Podbielniak column. Analyses are by the Microchemical Laboratory, Department of Chemistry, University of California.

(10) The 39% yield coupled with the calculation of radiochemical yield of 19.5% indicates a k_H/k_T for the sodium borohydride reduction of about 2.

Acetolysis of *trans*-4-Methoxycyclohexyl-1-*t* Tosylate.—*trans*-4-Methoxycyclohexyl-1-*t* tosylate (41.3 g., 0.145 mole, m.p. 66.4–67.2°, 2.62 ± 0.05 × 10^6 d.p.m./mmole) was solvolyzed in glacial acetic acid (500 ml., distilled from 10% acetic anhydride) containing sodium acetate (23.6 g.) and acetic anhydride (29.6 g.) at 74.98 ± 0.02° for 57.75 hours. The acetic acid was neutralized with aqueous sodium carbonate (1000 ml., 8.0 *M*) and sodium bicarbonate (81.4 g., 0.969 mole). The aqueous solution was continuously extracted with ether and the ethereal solution was dried over sodium sulfate–sodium carbonate. Distillation at reduced pressure yielded 4-methoxycyclohexene (b.p. 61–65° (77 mm.), 1.22 g., 7.5% yield, 2.33 ± 0.3 × 10^6 d.p.m./mmole) and 4-methoxycyclohexyl acetate (b.p. 85–86° (7 mm.), 7.52 g., 30.12% yield, 2.71 ± 0.05 × 10^6 d.p.m./mmole). The infrared spectra of these materials were identical with authentic samples.

Degradation of Solvolysis Products. (a) Oxidation of 4-Methoxycyclohexene-1-*t*.—4-Methoxycyclohexene-1-*t* (1.00 g., 1.30 × 10^5 d.p.m./mmole which was prepared by 20-fold dilution of the olefin above) in isoöctane (5 ml.) and water (25 ml.) was oxidized by dropwise addition of aqueous sodium permanganate (5.23 g., 30 ml.) below 18° under a carbon dioxide atmosphere. After one hour unreacted sodium permanganate was destroyed by addition of technical grade ether. Manganese dioxide was removed by filtration and washed with aqueous sodium hydroxide. The solution was adjusted to *p*H 1 and continuously extracted with ether. After removal of the ether under reduced pressure the crude β-methoxyadipic acid (1.00 g., 63%) was recrystallized seven times from hexane (m.p. 88.8–90.0°, Koefler hot-stage; 1850 d.p.m./mmole, 1.42% activity). After ten crystallizations the specific activity was zero; calcd. 88.09, found 88.60.

(b) Saponification of 4-Methoxycyclohexyl-1,4-*t* Acetate.—4-Methoxycyclohexyl-1,4-*t* acetate (6.35 g., 2.71 ± 0.05 × 10^6 d.p.m./mmole) from the acetolysis products was saponified with methanolic potassium hydroxide in the usual manner to yield a mixture of *cis*- and *trans*-4-methoxycyclohexanol-1,4 *t* (71% *trans* isomer by infrared analysis, b.p. 100.8–101.0° (13 mm.), 3.502 g., 72.9% yield, 2.63 ± 0.02 × 10^6 c.p.m./mmole).

(c) Oxidation of *cis–trans*-4-Methoxycyclohexanol-1,4-*t*.—The *cis–trans*-4-methoxycyclohexanol-1,4-*t* (0.913 g., 2.63 ± 0.02 × 10^6 d.p.m./mmole) was oxidized with chromium trioxide (14.92 meq.) in acetone (10 ml.) as before. The crude ketone was purified on Woelm 3 alumina. 4-Methoxycyclohexanone-4-*t* (0.591 g., 65.7%) was rechromatographed to afford material whose infrared spectrum was identical with authentic 4-methoxycyclohexanone. The specific activity was 0.80 ± 0.02 × 10^6 d.p.m./mmole.

(d) Separation of trans-4-Methoxycyclohexanol-1,4-*t*.—4-Methoxycyclohexanol-1,4-*t* (2.44 g., 2.63 ± 0.02 × 10^6 d.p.m./mmole) was converted to the hydrogen phthalate ester (3.4 g., 0.0122 mole, 65.2%) in the usual way. The ester was recrystallized three times from benzene (m.p. 149.8–150.4°) and saponified in aqueous sodium hydroxide. *trans*-4-Methoxy-cyclohexanol-1,4-*t* (0.888 g., 74.5%, b.p. 102° (13 mm.), 2.55 ± 0.01 × 10^6 c.p.m./mmole), having an infrared spectrum identical with authentic material, was isolated by fractional distillation.

(e) Oxidation of *trans*-4-Methoxycyclohexanol-1,4-*t*.—*trans*-4-Methoxycyclohexanol-1,4-*t* (0.664 g., 2.55 ± 0.10 × 10^6 d.p.m./mmole) was oxidized as before. The crude ketone was purified by chromatography and distillation through a short column at reduced pressure to yield 4-methoxycyclohexanone-4-*t* (0.477 g., 56.0%, 1.13 ± 0.01 × 10^6 d.p.m./mmole) having an infrared spectrum identical with authentic material.

(f) 2,6-Dibenzylidene-4-methoxycyclohexanone-4-*t*.—A diluted sample of 4-methoxycyclohexanone-4-*t* (0.116 g., 2.24 × 10^5 d.p.m./mmole), water (2 ml.), ethanol (0.5 ml., 95%), sodium hydroxide (0.15 g.), and freshly distilled benzaldehyde (0.36 g., 0.0034 mole, b.p. 90° (42 mm.)) was stirred at room temperature for 27 hours. Water (10 ml.) was added; the precipitate was collected and crystallized four times from aqueous ethanol to yield 2,6-dibenzylidene-4-methoxycyclo-hexanone-4-*t* (0.10 g., 36.4%, m.p. 118.4–118.8°). After seven crystallizations, m.p. 119.0–119.2°, the specific activity was 2.09 ± 0.20 × 10^5 d.p.m./mmole and after ten crystallizations, m.p. 119.2–119.3°, 2.13 ± 0.20 × 10^5 d.p.m./mmole. *Anal.* Calcd. for $C_{21}H_{18}O_2$: C, 82.86; H, 6.62. Found: C, 83.03; H, 6.47.

Radioassay.—The control oxidation product (4-methoxycyclohexanone) and its parent alcohol were counted with a Tracerlab model CE-1 liquid scintillation counter at the California Research Corporation. The remainder of the samples were counted on a locally fabricated liquid scintillation counter (using 2,5-diphenyloxazole) at Donner Laboratories. Samples were counted against background using both external and internal standards. Normal counting efficiencies of 20–35% were observed. Duplicate samples were counted in triplicate. The precision of these counts is indicated. The counting accuracy is the usual ±3%. Radioassay of 2,6-dibenzylidene-4-methoxycyclohexanone was made with added wave length shifter (1.2–1.8 mg./10 ml. of 2,2′-*p*-phenylenebis-[5-phenyloxazole]) and intensifier (523–543 mg./10 ml. of naphthalene). Counting efficiency was increased from 0.1 to 4% in these yellow solutions.

Acknowledgment.—We wish to express our appreciation to Mr. Irville M. Whittemore of the Donner Laboratory for his assistance with the counting procedures. We wish to thank Professor Melvin Calvin for making these facilities available to us. We wish also to thank Dr. Wm. A. Pryor and Dr. B. A. Fries of the California Research Corporation for their assistance with the early counting experiments.

BERKELEY 4, CALIF.

COMMUNICATIONS TO THE EDITOR

16-FLUORINATED CORTICOIDS. I. 16β-FLUOROHYDROCORTISONE ACETATE AND RELATED COMPOUNDS

Sir:

While 16β-bromo and 16β-chloro corticoids have been prepared by opening 16,17α-epoxy-20-keto steroids with hydrogen bromide[1] and hydrogen chloride,[2] efforts to prepare 16β-fluoro steroids by that route have been unsuccessful.[2] We now report the preparation of 16β-fluorohydrocortisone acetate and its Δ^1- and Δ^1-9α-fluoro derivatives by a different route. The reaction of 3β-hydroxy-5α-pregnane-11-20-dione[3] with diethyl oxalate in the presence of sodium methoxide gave the 21-ethoxyoxalyl derivative which was converted by means of bromination and Faworskii rearrangement with sodium methoxide[4] to methyl 3β-hydroxy-11-keto-5α-pregn-17(20)-[*cis*]-en-21-oate[5] (I), m.p.

(1) P. L. Julian, W. Cole, E. W. Meyer and B. M. Regan, THIS JOURNAL, **77**, 4601 (1955).

(2) R. E. Beyler and F. Hoffman, *J. Org. Chem.*, **21**, 572 (1956).

(3) G. Stork, J. Romo, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3546 (1951).

(4) J. A. Hogg, P. F. Beal, A. H. Nathan and F. H. Lincoln, U. S. Patent 2,790,814.

(5) This compound was prepared earlier in these laboratories by R. W. Jackson in connection with another problem.