sulfonyl chloride and 15 ml. of dry pyridine and a reaction time of 16 hours yielded 5.16 g. (87.5%) of *exo*-(B)-norbornyl *p*-bromobenzenesulfonate with the identical optical activity, $[\alpha]^{24}$D +1.85° (chloroform, *c* 10.21).

Relation of Configuration of *exo*- and *endo*-Norbornyl Enantiomorphs by Oxidation to Active Norcamphor.—1.93 g. of *ca.* 60–80% resolved *endo*-(A)-norbornyl acid phthalate[6] from middle fractions was saponified and steam distilled. The combined solid and *ca.* 20 ml. of aqueous distillate was treated with 8 ml. of acetic acid followed by 1.4 g. of potassium dichromate and 1.8 g. of concentrated sulfuric acid. After one hour standing with occasional warming to *ca.* 40°, excess sodium hydroxide was added and the norcamphor steam distilled. Only the 0.32 g. of solid norcamphor in the distillate was saved and dried *in vacuo* over potassium hydroxide, m.p. 95.5–96.2°, $[\alpha]^{24}$D −15.73° (chloroform, *c* 9.79).

Anal. Calcd. for $C_7H_{10}O$: C, 76.29; H, 9.16. Found: C, 76.08; H, 9.37.

In similar manner, 1.42 g. of optically pure *exo*-(B)-norborneol was oxidized and 0.68 g. of solid norcamphor separated by decantation from the steam distillate and dried, m.p. 107.1–109.3°, $[\alpha]^{24}$D +8.66 (chloroform, *c* 10.00).

Active (B) and Racemic *exo*-Norbornyl Acetates.—Optically pure *exo*-(B)-norborneol (1.00 g.) was dissolved in a mixture of 5 ml. of acetic anhydride and 20 ml. of dry glacial acetic acid in a 50-ml. volumetric flask and heated in a 75° bath for 10.0 hours. The solution was diluted with *ca.* five volumes of water, extracted four times with 50-ml. portions of pet. ether (b.p. 34–39°) and the extract washed in turn with water, aqueous sodium bicarbonate, and water. It was dried over anhydrous magnesium sulfate, and then concentrated to *ca.* 5 ml. through a fractionating column. The residue was carefully distilled *in vacuo* through a small all-glass apparatus to give 1.24 g. (90.2%) of *exo*-(B)-norbornyl acetate, α^{25}D +10.39° (1 dcm.), n^{25}D 1.4565.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.09; H, 9.15. Found: C, 69.95; H, 9.25.

The same procedure was used to prepare a sample of pure racemic *exo*-norbornyl acetate whose infrared spectrum was taken (Fig. 1).

Acetolysis of Active *exo*-(B)-Norbornyl *p*-Bromobenzenesulfonate in Glacial Acetic Acid.—Optically pure *exo*-(B)-norbornyl *p*-bromobenzenesulfonate (2.00 g.) was mixed with 2.00 g. of racemic *exo*-norbornyl *p*-bromobenzenesulfonate and the combined 4.00 g. dissolved in 120 ml. of dry glacial acetic acid (0.10 *M*) to which was added potassium acetate (0.085 *M* inadvertently insufficient) and the solution warmed in a 40° bath for 18 hours. The acetate was isolated as in the preparation from norborneol to yield 1.50 g. (80.5%) racemic *exo*-norbornyl acetate, α^{24}D +0.001° (1 dcm.), n^{25}D 1.4565, infrared spectrum in Fig. 1.

Actually, the amount of excess acid prevailing in this solvolysis because of the deficiency of potassium acetate employed in the run was insufficient to cause more than several per cent. racemization of the final acetate. This is clear from control experiments previously described[6] on the behavior of *exo*-acetate toward much more concentrated (0.76 *M*) toluenesulfonic acid at 75 and 25°, and also from the effect even at 75° of just this excess acid concentration on the surviving activity in the *exo*-acetate product from solvolysis of the *endo*-*p*-bromobenzenesulfonate.[6]

Kinetic and Polarimetric Measurements.—The general procedures for the titrimetric rate measurements were those previously employed.[4,6]

In most of the acetolysis runs, the solution aliquot was drained directly into at least an equal volume of pure pet. ether (b.p. 30–60°) which served to reduce the solvolysis rate very markedly. Cooling the pet. ether-diluted aliquot further slowed the solvolysis reaction so that titration could be postponed for at least an hour without error. Tests showed that the brom phenol blue indicator color and color change at the equivalence point were identical in 1:1 acetic acid–pet. ether and acetic acid.

In the case of the rapid solvolysis in 75% acetone, room temperature was kept close to 25° and the titrations concluded without delay. Time was taken at the titration end-point.

Routine polarimetric measurements were carried out with the Hilger instrument[6] in semimicro or micro 1 dcm. polarimeter tubes.

Polarimetric racemization rates of *exo*-(B)-norbornyl *p*-bromobenzenesulfonate in various solvents were carried out in a specially constructed 4-dcm. all-glass jacketed polarimeter tube of *ca.* 22-ml. capacity with sealed-on optically plane 1/4-inch Pyrex end pieces. Water from a 24.98 ± 0.01° thermostat was continuously circulated through the outer jacket during the course of the racemization rate runs. In each such rate run, solvent first brought to temperature in the thermostat was used to dissolve the weighed quantity of the active *p*-bromobenzenesulfonate to the mark in a 25-ml. volumetric flask. The resulting solution was then transferred as rapidly as possible to the polarimeter tube through the glass-stoppered opening at the center of the tube and then carefully located in place in the polarimeter trough. Readings were taken at appropriate intervals.

LOS ANGELES 24, CALIF. RECEIVED JUNE 11, 1951

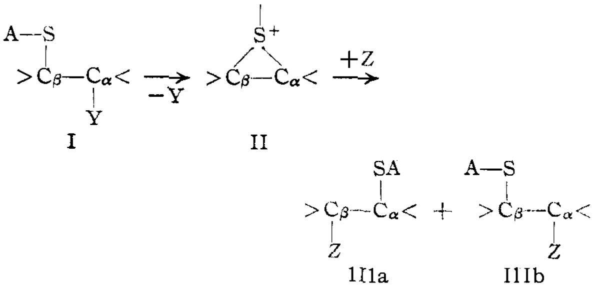
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Role of Neighboring Groups in Replacement Reactions. XVIII. Migration of the Methoxyl Group[1]

BY S. WINSTEIN AND L. L. INGRAHAM[2]

A simple recognizable result of participation of a functional neighboring group in a replacement process is migration of the neighboring group. Such a migration of a methoxyl group is shown to occur in solvolysis of 2-methyl-2-methoxy-3-bromobutane. This secondary bromide with a tertiary methoxyl group solvolyzes to give 3-methoxy-2-methyl-2-butanol, a tertiary alcohol containing a secondary methoxyl group.

Participation by functional neighboring groups in nucleophilic replacement processes, as in I → III, may control stereochemical results[3] and reactivity,[4] or give rise to the formation of unusual products, such as an orthoester[3c] in the case of the neighboring



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[1] Much of the material of this paper was presented in summary: (a) before the Organic Division of the American Chemical Society, St. Louis, September, 1948; (b) at the Eleventh National Organic Symposium, Madison, Wisconsin, June 21, 1949, page 65 of abstracts; (c) at Montpellier, France, April 26, 1950 [*Bull. soc. chim.*, [5] **18** 55C (1951)]. Paper XVII, THIS JOURNAL, **72**, 4669 (1950).

[2] From the Ph.D. Thesis of L. L. Ingraham, U. C. L. A., 1949.

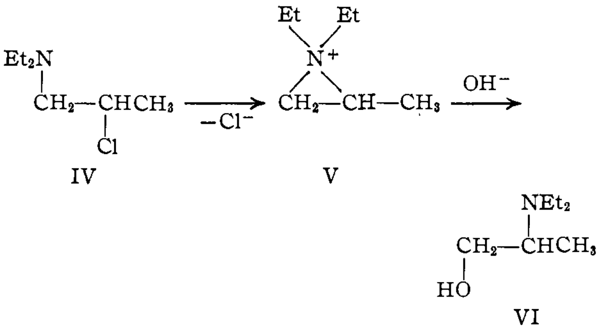
[3] *E.g.*, (a) S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1576, 2845 (1939); (b) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780 (1942); (c) S. Winstein and R. E. Buckles, *ibid.*, **65**, 613 (1943).

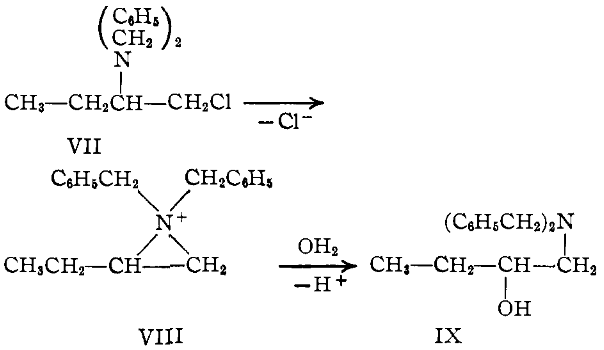
[4] S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

acetoxy group. As was pointed out previously,[3b] an even simpler recognizable result of importance is possible in the case of systems unsymmetrically substituted on C_α and C_β, for here it is possible to observe the migration of the neighboring group. If the intermediate II[5] opens largely in the sense which produces IIIa, fairly complete migration will be said to accompany the substitution process.

Examples of the above type of migration are known[1b] with so-called classical groups such as O^-, NH_2, NR_2 and SR. Two pertinent recent examples in the case of NR_2 involve the hydrolysis[6] of 1-diethylamino-2-propyl chloride (IV) to 2-diethylamino-1-propanol (VI) in basic solution and the hydrolysis[7] by bicarbonate solution of 2-dibenzylamino-1-chlorobutane (VII) to 1-dibenzylamino-2-butanol (IX). In this article we demonstrate migration of a so-called non-classical functional neighboring group[8] during substitution.

Because of the usual direction of opening of unsymmetrical intermediates such as II, it was clear that C_β needed to be more highly substituted than C_α to make the so-called rearranged product IIIa the predominant one from irreversible opening of II. This limits somewhat the choice of neighboring group S–A because ionization at the C_β–SA linkage may be more rapid than at the C_α–Y linkage. For this reason, neighboring groups with very low ionizing tendencies were considered, the methoxyl group fitting the requirements satisfactorily. The present study involved the silver ion assisted solvolysis of 2-methyl-2-methoxy-3-bromobutane (XI).





The bromo-ether (XI) was prepared from trimethylethylene (X) by the treatment with methanolic N-bromoacetamide and was assigned the indicated structure on the basis of Markownikow's rule. This structure was verified by catalytic reduction of XI to an ether XII, whose boiling point and refractive index agreed well (Table I) with those reported for methyl *t*-amyl ether (XII) and not with those for the isomeric 2-methyl-3-methoxybutane (Table I) which was prepared by the Williamson synthesis from methylisopropylcarbinol.

On addition of aqueous silver nitrate to a mixture of 2-methoxy-2-methyl-3-bromobutane (XI), calcium carbonate and water, XI was converted in *ca.* 60% yield to solvolysis product and *ca.* 15% yield to the pinacol type rearrangement product, methyl isopropyl ketone. For identification of the solvolysis product, samples of both trimethylethylene glycol monomethyl ethers XVII and XIV were prepared by other methods. Authentic tertiary carbinol XIV (Table I) was prepared through the action of the methyl Grignard reagent on methyl α-methoxypropionate. The same material was also obtained (Table I) from the methoxide ion-catalyzed opening of trimethylethylene oxide (XVIII) with methanol. The secondary carbinol, 3-methyl-3-methoxy-2-butanol (XVII) was obtained (Table I) from acid-catalyzed opening of trimethylethylene oxide XVIII with methanol. The tertiary alcohol XIV boils *ca.* 15° below the isomeric secondary material XVII, and the refractive indices also differ substantially, so that the two materials may be differentiated on the basis of physical properties.

The crude products of acid- and base-catalyzed opening of the oxide XVIII with methanol had small boiling ranges before refractionation, so it is not clear how perfectly free of the isomer each

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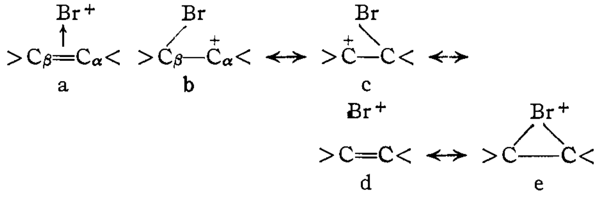
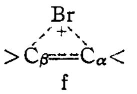
[5] Recently the π-complex notation has been suggested for certain of the intermediates II, for example the ethylene bromonium ion (a) [M. J. S. Dewar, *J. Chem. Soc.*, 406, 777 (1946)].



The symbol of the type a is designed for situations where three atoms (in this case C_α, C_β and Br), each with one atomic orbital, are bound by one pair of electrons. As one of us has remarked elsewhere [S. Winstein, *Bull. soc. chim.*, [5] **18**, C79 (1951)], the molecular orbital treatment on this basis gives rise to terms in the wave function corresponding to canonical structures b, c and d in the valence-bond language. Structure e of the resonance hybrid bromonium ion,[3a] which allows for the extra electrons on bromine, has no counterpart in the Dewar treatment. This same kind of difficulty arises with other neighboring groups with available electrons other than those involved in linking them to C_β, for example, neighboring phenyl [S. Winstein, Mary Brown, Kurt C. Schreiber and A. H. Schlesinger, THIS JOURNAL, **74**, 1140 (1952)].

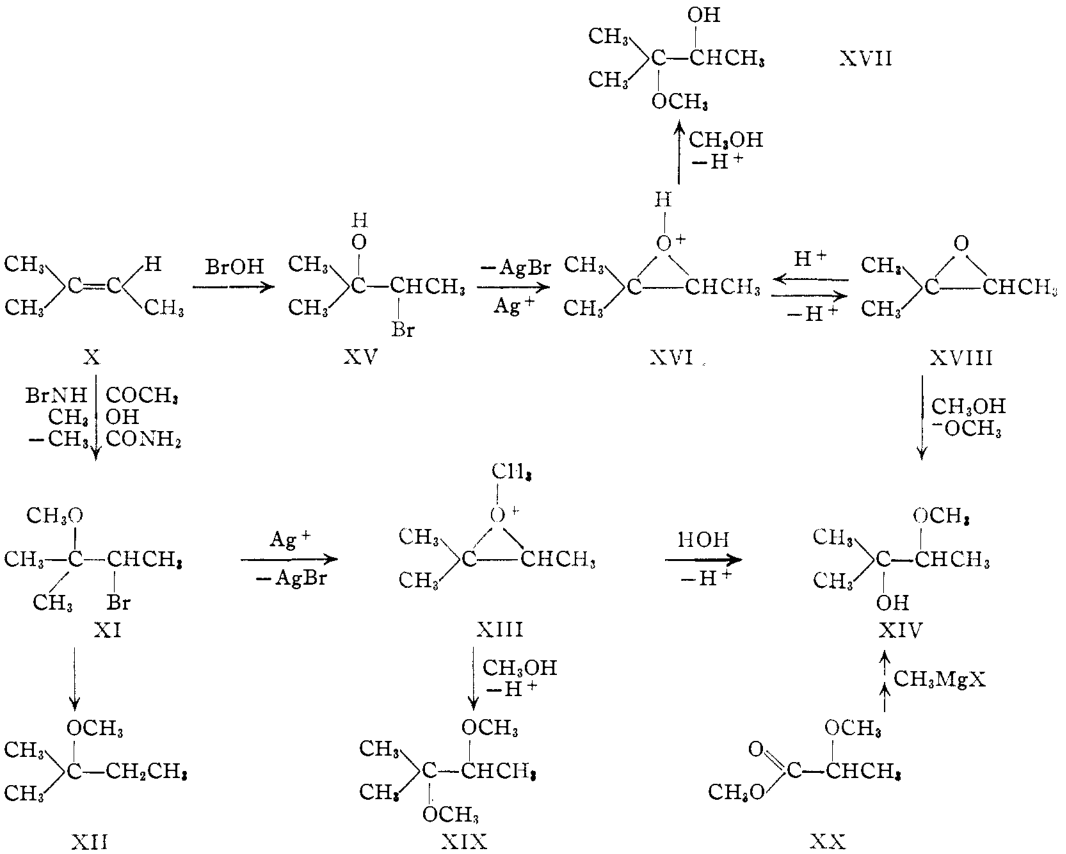
We have sometimes employed symbol e (or II) both to indicate the resonance hybrid or to indicate the one contributing structure e. A better symbol to employ, if one wishes to stress the resonance hybrid character, is f. This is the same type symbol we are employing for intermediates involving neighboring carbon [S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952)]. With this symbol, the linkages between the bridging atom and C_α or C_β may be less or more than half-bond in character, depending on the bridging atom (*e.g.*, H, R, Br, C_6H_5).



[6] S. D. Ross, *ibid.*, **69**, 2982 (1947).

[7] J. F. Kerwin, G. E. Ullyot, R. C. Fuson and C. L. Zirkle, *ibid.*, **69**, 2961 (1947).

[8] S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

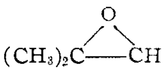


product is. However, the products are clearly very largely made up of the secondary and tertiary alcohols XVII and XIV, respectively. Similarly, the solvolysis product from the bromo-ether XI, judging by its properties (Table I), is at least very largely one isomer, namely, the tertiary carbinol XIV.

Thus, as was expected, the silver-ion assisted hydrolysis of the bromo-ether XI is attended by essentially complete migration of the methoxyl group. That this result is not due to prior formation of unrearranged secondary carbinol XVII which subsequently isomerizes to tertiary carbinol XIV is clear from a control experiment on XVII, which survives the reaction conditions perfectly without isomerization and also without formation of appreciable quantities of methyl isopropyl ketone.

TABLE I

PROPERTIES OF PURIFIED SAMPLES OF LIQUIDS

Compound		Source	B.p. °C.	Mm.	n^{25}_D	d^{25}_4	MR_D Calcd.	Found
$(CH_3)_2C(OCH_3)CHBrCH_3$	(XI)[a]	X	69.0–69.5	40	1.4553	1.2632	39.32	38.92
$(CH_3)_2CHCH(OCH_3)CH_3$			83.0–83.5	760	1.3812[d]	0.7542	31.85	31.99
$(CH_3)_2C(OCH_3)CH_2CH_3$	(XII)[b]	XI	85.0–86.5	760	1.3885[e]			
$(CH_3)_2C(OH)CH(OCH_3)CH_3$	(XIV)	XI	129.5–130	752	1.4100	.8877	33.07	32.98
		XX	129–130	760	1.4100			
		XVIII	129–130	760	1.4098			
		XI(AgOAc)	129.5–130	752	1.4100			
$(CH_3)_2C(OCH_3)CH(OH)CH_3$	(XVII)	XVIII	143–144	760	1.4193	.9151	33.07	32.67
 $(CH_3)_2\overset{O}{C{-}CHCH_3}$	(XVIII)[c]	XV (base)	73.0– 73.3	760	1.3822	.8000	24.73	25.07
		XV(Ag+)	72.0–73.0	760	1.3826			
$(CH_3)_2C(OCH_3)CH(OCH_3)CH_3$	(XIX)	XI	125.0–125.5	760	1.4026	.8571	37.80	37.61
		XVII	125.0–126.0	760	1.4018			
$(CH_3)_2C(OCH_3)CH(OAc)CH_3$		XVII	85	50	1.4122	.9456	42.32	42.18
$(CH_3)_2C(OAc)CH(OCH_3)CH_3$		XI	58.2–59.0	20	1.4100	.9410	42.32	42.19

[a] Reported[9] b.p. 41–43° (10 mm.), n^{20}_D 1.4549, d^{20}_4 1.2474. [b] Reported[10] b.p. 86.3° (760 mm.), n^{20}_D 1.3885. [c] Reported[11,12] d^{20}_4 0.8277, d^{0}_4 0.8288, n^{18}_D 1.3896. b.p. 74–78° (760 mm.), b.p. 73.0–74.2° (753 mm.). [d] n^{20}_D 1.3838. [e] This value at 20°.

Treatment of the bromo-ether XI with silver acetate in glacial acetic acid at 100° gave results analogous to those obtained with aqueous silver

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(9) E. Schmidt, W. Knilling and A. Ascherl, *Ber.*, **59B**, 1279 (1926).

(10) T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936).

(11) F. H. Norton and H. B. Haas, THIS JOURNAL, **58**, 2147 (1936).

(12) J. Read and W. G. Reid, *J. Chem. Soc.*, 1488 (1928).

nitrate, except that these conditions are too vigorous for complete survival of the product. There were obtained 25–47% yields of the rearranged acetate which yielded alcohol, at least very largely tertiary carbinol XIV, on saponification. Variable amounts of methyl isopropyl ketone accompanied the acetate product.

The use of methanol as a solvent for the solvolysis of XI (with added silver oxide) gave rise to the glycol dimethyl ether (XIX), which, by analogy with the products of the other solvolyses of XI, must have the original methoxyl group in the rearranged position.

Participation of neighboring methoxyl accounts nicely for its migration during solvolysis of the bromo-ether XI. The intermediate ethylene oxonium ion[13] XIII is opened by water, acetic acid, and presumably methanol at the most substituted carbon atom. This is analogous to the opening of the conjugate acid of trimethylethylene oxide XVI by methanol in the acid-catalyzed methanolysis of the oxide XVIII, or the opening of trimethylethylene bromonium ion by water or methanol. All of these cases represent structures favorable to displacement (or opening) at the carbon atom best able to tolerate cationic charge, namely, the most alkyl-substituted carbon atom.[14] The opening of the immonium ion VIII by water follows this same regularity. The contrasting behavior of the ethylene immonium ion V, which gives the primary alcohol, is probably to be correlated with the fact that the transformation V → VI is due to displacement by hydroxide ion and not water. Judging by the kinetic information available in cases of this kind,[15] the hydroxide ion concentration which preqailed[6] during the transformation IV→V→VI was sufficient to make hydroxide ion attack predominant. With this reagent, attack at the least substituted carbon atom is favored, but it is not unusual[14] for a change of nucleophilic agent to modify the effect of methyl substitution from rate-enhancing to rate-retarding.

The substitution of participating hydroxyl for participating methoxyl should give the conjugate acid of the oxide XVI instead of the ethylene oxonium ion XIII, and thus, in a buffered medium, oxide XVIII itself should be isolatable. Actually, when bromohydrin XV is treated with aqueous silver nitrate and sodium bicarbonate, a substantial yield of oxide XVIII and a small yield of methyl isopropyl ketone is obtained. However, the bromohydrin reacts slowly even with bicarbonate solution, and it is not yet clear how exclusively the oxide formation arises through the route XV→XVI→XVIII.

The formation of methyl isopropyl ketone which was produced in appreciable amount from the treatment of bromo-ether XI with aqueous silver nitrate does not arise from the tertiary alcohol XIV, for a control experiment showed it to be perfectly stable to the reaction conditions. It arises from competition with the outlined steps leading to substitution product, of others leading to pinacol rearrangement, but this competition is dealt with elsewhere.[1,2]

Experimental Part

All melting points are corrected. Properties of fractionated samples of liquid materials are summarized in Table I.

Trimethylethylene. Fractionation of the olefin from treatment of *t*-amyl alcohol with sulfuric acid yielded material, b.p. 38.7–38.9° (752 mm.), $n^{25}\text{D}$ 1.3845 [reported[16] b.p. 38.6° (760 mm.), $n^{25}\text{D}$ 1.3846 by extrapolation to 25° from $n^{20}\text{D}$ 1.3876 using Egloff's data[16] for the effect of temperature on refractive index].

2-Methoxy-3-bromo-2-methylbutane.—This material was prepared by essentially the method of Winstein and Henderson[13] used in preparing the 2-bromo-3-methoxybutanes. To a solution of 224 g. (1.62 moles) of N-bromoacetamide in 2000 ml. of methanol in a three-liter flask was added 175 ml. (1.62 moles) of trimethylethylene dropwise with stirring. The next day the reaction mixture was added to 2000 ml. of a saturated salt solution. The oil which separated was taken up in ether. The ether extract was washed with an equal volume of 0.5 *N* KOH and an equal volume of water. Then it was dried over potassium carbonate. Distillation through a 13″ glass spiral column yielded 227.0 g., 77%, of material, b.p. 69–70° (40 mm.) (Table I).

Anal. Calcd. for $C_6H_{13}OBr$: C, 39.79; H, 7.23. Found: C, 39.56; H, 7.07.

3-Methoxy-2-methylbutane.—A mixture of 26.4 g. (0.30 mole) of methylisopropylcarbinol, b.p. 111.8–111.9° (760 mm.), 6.9 g. (0.30 g. atom) of sodium and 250 ml. of ligroin (b.p. 150–190°) was refluxed until all of the sodium had dissolved. To this was added 42.5 g. (0.30 mole) of methyl iodide in 100 ml. of anhydrous ether and the solution was refluxed for an hour. The solution was washed with 25 ml. of water, dried over potassium carbonate and distilled through a 13″ centered rod column to yield 13.9 g., 45%, of the ether, b.p. 83–84° (760 mm.) (Table I).

Dehalogenation of 2-Methoxy-3-bromo-2-methylbutane.—A mixture of 36.2 g. (0.2 mole) of the bromide, 250 ml. of methanol containing 10 g. of palladium-on-calcium carbonate catalyst[17] and 17 g. (0.30 mole) of potassium hydroxide was shaken with hydrogen at one atmosphere for 24 hours. The solution was filtered, added to 250 ml. of water and extracted with ligroin (b.p. 150–190°). The extract was dried over potassium carbonate and refluxed with sodium. Distillation of the extract gave rise to 10.6 g., 52%, of a product, b.p. 82–89° (760 mm.), with a good plateau at 86.5°. Upon redistillation of the product all except a 2 ml. holdup in the column had a b.p. 85–86.5° (760 mm.) (Table I).

2,3-Epoxy-2-methylbutane.—To a solution of 270 g. (1.95 moles) of N-bromoacetamide in 2 liters of water, 230 ml. (2.10 moles) of trimethylethylene was added dropwise with stirring over a period of about 20 minutes. Stirring was continued for an hour. The next day the oil that separated was taken up in ether and the ether extract was dried over potassium carbonate. The ether was distilled off through a 13″ Vigreux column and the residue was added dropwise to a stirred solution of 400 g. of potassium hydroxide in 800 ml. of water at 90°, the oxide being distilled off as the bromohydrin was added. Redistillation through a 13″ glass spiral column yielded 81.1 g., 47.4%. of oxide, b.p. 72–75° (760 mm.) of which 34.7 g. had a b.p. 73.0–73.3° (760 mm.) (Table I).

2-Methyl-3-methoxy-2-butanol (a).—A 0.45 mole quantity of methyl α-methoxypropionate,[18] b.p. 129–130° (747 mm.) $n^{25}\text{D}$ 1.3957, $d^{25}{}_4$ 0.9948, *MR*D 28.54 (calcd. 28.59), was allowed to react with one mole of methyl Grignard reagent in the usual manner. The hydrolyzed mixture was extracted with ether and the ether was dried over potassium carbonate. Distillation through a 13″ centered rod column at atmospheric pressure gave 21.8 g., 41%, of 3-methoxy-2-hydroxy-2-methylbutane, b.p. 125–130° (760 mm.) with a good plateau at 129–130° (Table I).

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(13) S. Winstein and R. B. Henderson, THIS JOURNAL, **65**, 2196 (1943).

(14) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(15) P. D. Bartlett, S. D. Ross and C. G. Swain, *ibid.*, **69**, 2971 (1947).

(16) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, A. C. S. Monograph Series No. 78, Reinhold Publishing Corp., p. 179.

(17) M. Busch and H. Stove, *Ber.*, **49**, 1063 (1916).

(18) C. Niemann, A. A. Benson and J. F. Mead, *J. Org. Chem.*, **8**, 397 (1943).

Anal. Calcd. for $C_6H_{14}O_2$: C, 60.98; H, 11.94. Found: C, 60.79; H, 11.99.

(b).—A solution of 29 g. (0.33 mole) of 2,3-epoxy-2-methylbutane and 135 ml. of methanol in which 3 g. (0.15 g. atom) of sodium had been dissolved was refluxed for two hours. About half the methanol was distilled off through a 13″ Vigreux column and the remaining solution was added to an equal volume of water and extracted with ether. The ether extracted was dried over potassium carbonate. Distillation gave 20.9 g., 53%, of 3-methoxy-2-hydroxy-2-methylbutane, b.p. 126–133° (760 mm.), of which 12.6 g. boiled below 130° and had $n^{25}D$ 1.4097. The portion with b.p. 130–133° (760 mm.) had $n^{25}D$ 1.4100.

3-Methyl-3-methoxy-2-butanol.—When two drops of concd. sulfuric acid was added to 33.2 g. (0.385 mole) of trimethylethylene oxide in 155 g. of methanol, the solution began to boil and refluxed for a few minutes. After neutralization with methanolic potassium hydroxide to the brom thymol blue end-point, distillation through a 13″ centered glass rod column yielded 34.6 g., 76%, of product, b.p. 140–144° (760 mm.) of which 22.6 g. had a b.p. 143–144° (Table I). The portion with a b.p. 140–143° (760 mm.) had $n^{25}D$ 1.4190.

Treatment of 2-Methoxy-3-bromo-2-methylbutane with Aqueous Silver Nitrate.—To a mixture of 90.5 g. (0.5 mole) of the bromide, 30 g. (0.3 mole) of calcium carbonate and 400 ml. of water, 95 g. (0.55 mole) of silver nitrate was added dropwise with stirring over a period of about 20 minutes. The stirring was continued for four hours. The solution was filtered and extracted with ether. The ether extract was dried over potassium carbonate and distilled at atmospheric pressure through a 13″ centered rod column to give 35.3 g., 60% of 2-hydroxy-3-methoxy-2-methylbutane, b.p. 110–130° (760 mm.) [of which 28.1 g. had b.p. 129.5–130° (Table I)] and 6.4 g., 15% of a methyl isopropyl ketone fraction, b.p. 92–110° (760 mm.), of which 2.8 g. had b.p. 92–95° (760 mm.). The m.p. of the 2,4-dinitrophenylhydrazone was 122.0–122.5° and the same when mixed with the 2,4-dinitrophenylhydrazone of authentic methyl isopropyl ketone, m.p. 122.5–123.0° (reported[19] m.p. 117°).

Control Experiments.—To a mixture of 59 g. (0.5 mole) of 2-methoxy-3-hydroxy-2-methylbutane, 30 g. (0.30 mole) of calcium carbonate, 117.5 g. (0.5 mole) of silver iodide and 400 ml. of water, 0.5 mole of nitric acid in 100 ml. of water was added dropwise with stirring. The product was recovered as described above. Distillation through a 13″ centered rod column gave 47.1 g., 80% of recovered alcohol, b.p. 141–144° (760 mm.), $n^{25}D$ 1.4198. Less than 0.5 g. of material was in the boiling range 90–120° (760 mm.).

Identical treatment of 2-hydroxy-3-methoxy-2-methylbutane gave 47.6 g., 80.6%, of recovered alcohol, b.p. 126–130° (760 mm.) with a good plateau (about 90%) at 129–130° (760 mm.). Only 0.5 g. had a b.p. 85–100° (760 mm.).

Rearrangement of 2-Methoxy-3-bromo-2-methylbutane in Acetic Acid.—A mixture of 90.5 g. (0.5 mole) of 2-methoxy-3-bromo-2-methylbutane, 92 g. (0.55 mole) of silver acetate and 500 ml. of acetic acid was stirred at 90–110° for one hour. The silver salts were filtered out and the resulting solution was neutralized with 6 *N* potassium hydroxide under a layer of ether. The ether extract was dried over potassium carbonate and the ether was distilled off through a 13″ Vigreux column. The residue of crude ester was added to 100 ml. of ethanol and 100 ml. of 6 *N* potassium hydroxide and refluxed for two hours. The reaction mixture was continuously extracted with ether and the ether extract was dried over potassium carbonate. Distillation through a 13″ centered rod column yielded 20.8 g., 35%, of alcohol, b.p. 128–135° (752 mm.). Redistillation gave 16.8 g. of material, b.p. 129.5–130.0° (752 mm.) (Table I).

In some experiments the acetate was isolated by distilling the filtered acetic acid reaction at 50 mm. pressure. Yields of 25 to 47% of material, b.p. 58.2–59.0° (20 mm.), were obtained (Table I).

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.97; H, 10.07. Found: C, 59.89; H, 10.18.

Acetylation of 2-Methoxy-3-hydroxy-2-methylbutane.—A solution of 20 g. (0.17 mole) of acetic anhydride, 20 g. (0.17 mole) of 2-methoxy-3-hydroxy-2-methylbutane and 50 ml. of redistilled pyridine was refluxed for an hour. The solution was cooled and poured into 100 ml. of ice and 90 ml. of 6 *N* hydrochloric acid. An oil separated which was taken up in four 50-ml. portions of ether and the ether extract was dried over potassium carbonate. Distillation through a 13″ glass spiral column yielded 22 g., 73%, of the ester, b.p. largely at 85° (50 mm.) (Table I).

2,3-Dimethoxy-2-methylbutane.—A solution of 32.1 g. (0.272 mole) of 2-methoxy-3-hydroxy-2-methylbutane in 250 ml. of ligroin (b.p. 230–260°) was refluxed with 6.25 g. (0.272 atom) of sodium until all the sodium dissolved. To this solution was added 39 g. (0.272 mole) of methyl iodide in 100 ml. of ether and the resulting solution was refluxed for half an hour. The solution was washed with 100 ml. of water, dried over potassium carbonate and distilled through a 13″ centered rod column to give 17.3 g., 48%, of the dimethyl ether, b.p. 124–126° (760 mm.) (Table I).

Treatment of 2-Methoxy-3-bromo-2-methylbutane with Silver Oxide in Methanol.—A solution of 95.5 g. (0.5 mole) of the bromide in 500 ml. of methanol was refluxed with 70 g. (0.3 mole) of silver oxide with stirring for two hours. Filtration and distillation through a 13″ centered rod column yielded 44.8 g., 67.5%, of the dimethyl ether, b.p. 123–125° (760 mm.) (Table I).

Trimethylethylene Bromohydrin.—A mixture of 53 ml. (0.5 mole) of trimethylethylene, 89 g. (0.5 mole) of recrystallized N-bromosuccinimide and 1.5 l. of water was stirred together in a flask surrounded by an ice-bath for 1.5 hours. The reaction mixture was then saturated with salt and extracted with five 100-ml. portions of ether. The ether extract was dried over potassium carbonate. Distillation through a 9″ centered rod column yielded 67.33 g., 76%, of product, b.p. 48–51° (10 mm.) with a good flat at 49°; $n^{25}D$ 1.4712 (reported[20] b.p. 48° (10 mm.), $n^{25}D$ 1.4710).

Reaction of Trimethylethylene Bromohydrin with Silver Ion.—93.5 g. (0.55 mole) of silver nitrate in 200 ml. of water was added dropwise with stirring to 88.5 g. (0.5 mole) of trimethylethylene bromohydrin, 84 g. (1 mole) of sodium bicarbonate, and 300 ml. of water. The silver nitrate was added over a period of an hour and the stirring was continued for an hour more. The reaction mixture was extracted with five 100-ml. portions of ether and the ether extract was dried over potassium carbonate. The ether was partially distilled off and the residue was shaken with 42 g. (0.5 mole) of sodium bicarbonate and 47 g. (0.275 mole) of silver nitrate in 200 ml. of water to remove some remaining bromohydrin. The mixture was extracted with five 100-ml. portions of ether and the ether extract was dried over potassium carbonate. Distillation at atmospheric pressure through a 13″ centered rod yielded 21.90 g., 51%, of trimethylethylene oxide, b.p. 70–75° (760 mm.) which upon redistillation gave a pure center fraction 72–73° (760 mm.) (Table I) and 1.95 g., 4.5%, of methyl isopropyl ketone, b.p. 90–96° (760 mm.), 2,4-dinitrophenylhydrazone, m.p. 122.0–122.5°, m.p. 122.0–123.0° on admixture with authentic material.

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