showed a tendency to lose water on distillation, b.p. 104–106° (0.02 mm.), $n^{21}{}_{D}$ 1.5708; selected infrared maxima: 3530 and 1152 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.85; H, 8.77.

URBANA, ILLINOIS

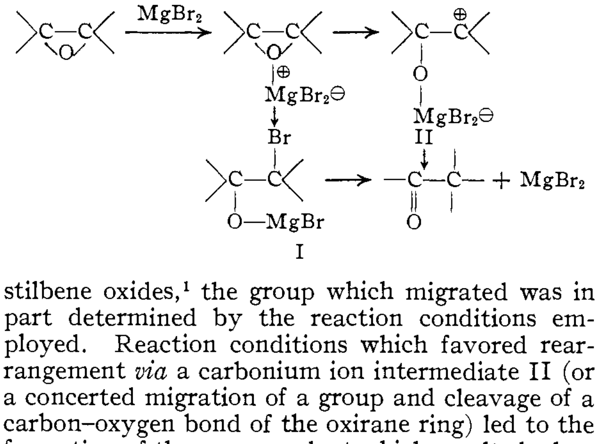
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of Aliphatic Ethylene Oxides

BY HERBERT O. HOUSE

RECEIVED MAY 2, 1955

cis- and *trans*-2,3-epoxybutane have been isomerized to 2-butanone by the action of magnesium bromide. In the presence of boron trifluoride etherate the *cis*-oxide gave only 2-butanone whereas a mixture of 2-butanone and isobutyraldehyde was obtained from the *trans* isomer under the same conditions. The bromomagnesium salts of both *erythro*- and *threo*-3-bromo-2-butanol isomerized to 2-butanone. Similarly, the bromomagnesium salt of 1-bromo-2-methyl-2-propanol was converted to isobutyraldehyde, the salt of 2-bromo-3-pentanol to 3-pentanone containing 5% of the 2-isomer and the salt of 3-bromo-2-pentanol to 2-pentanone containing 20% of the 3-isomer.



The isomerization of a substituted oxirane to a carbonyl compound in the presence of magnesium bromide or a Grignard reagent may follow two different reaction paths as shown in the accompanying equations. In a study of the isomerization of the stilbene oxides,[1] the group which migrated was in part determined by the reaction conditions employed. Reaction conditions which favored rearrangement *via* a carbonium ion intermediate II (or a concerted migration of a group and cleavage of a carbon–oxygen bond of the oxirane ring) led to the formation of the same product which resulted when the related bromohydrins and glycols underwent the pinacol rearrangement. The product was the same regardless of the stereochemistry of the epoxide. However, the products obtained under conditions which favored the formation of the salt of the bromo alcohol I were dependent on the stereochemistry of the epoxide and differed from the products of analogous pinacol rearrangements in certain cases. The group which migrated when an intermediate of the type I was involved was the one predicted by the hypothesis that isomerization occurs by way of a cyclic transition state in which the oxymagnesium bromide group bonded to one carbon atom and the largest group bonded to the adjacent carbon atom are oriented *trans* to one another.[1–3] It was of interest to learn whether the above generalizations based on 1,2-diarylethylene oxide systems would be applicable to isomerizations involving 1,2-dialkylethylene oxides.[4] Since this question is of particular importance in any preparative sequence which uses such rearrangements, either independently or as the first step in the reaction of an oxirane ring with a Grignard reagent, the investigation of several aliphatic epoxides was undertaken. The results obtained with the 2,3-epoxybutanes III and IV and 1,2-epoxy-2-methylpropane (XIII) are reported here.

Both *cis*- (III) and *trans*-2,3-epoxybutane (IV)[5] have been reported[6] to yield 3-methyl-3-pentanol on treatment with ethylmagnesium bromide. The formation of this alcohol could be explained by the isomerization of each oxide to 2-butanone (V) followed by the addition of ethylmagnesium bromide. Such an explanation is consistent with our results. Treatment with magnesium bromide either in benzene or in a benzene–ether mixture converted each of the isomeric oxides III and IV to the ketone V (Table II). Similarly, both *threo*-(VI)[5] and *erythro*-3-bromo-2-butanol (VII)[5] were converted to 2-butanone (V) by treatment with one equivalent of ethylmagnesium bromide (Table I). Since magnesium bromide failed to convert the bromo alcohols VI and VII to carbonyl compounds, the rearrangement of the bromohydrins VI and VII necessarily involves either the bromomagnesium salts of the alcohols (*i.e.*, intermediates of type I) or the epoxides III and IV. Evidence bearing on this point was gained from an investigation of the 2-pentene bromohydrins VIII and IX.

Tiffeneau and Tchoubar have reported the conversion of 2,3-epoxypentane (X) to mixture of 2-pentene bromohydrins VIII and IX by the action of a cold solution of magnesium bromide.[7] 3-Bromo-2-pentanol (IX) was the predominant product in this mixture. When the oxide X was heated with magnesium bromide a mixture of pentanones XI and XII was formed in which 2-pentanone (XII) was the major product.[7] The paucity of experimental detail in this report coupled with the ab-

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(1) H. O. House, THIS JOURNAL, **77**, 3070 (1955).

(2) D. Y. Curtin and E. K. Meislich, *ibid.*, **74**, 5905 (1952).

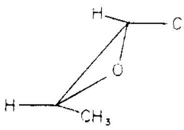
(3) F. Bergmann and A. Kalmus, *ibid.*, **76**, 4137 (1954).

(4) It seems probable that similar generalizations apply to 1,2-disubstituted ethylene oxides where one of both of the substituents are vinyl groups rather than aryl groups. The following references report cases where the treatment of such epoxides with magnesium bromide led to the migration of a vinyl group rather than a hydrogen atom. The stereochemistry of the epoxides was not stated. (a) Y. Deux, *Compt. rend.*, **207**, 920 (1938); **211**, 441 (1940). (b) M. Tiffeneau and P. K. Kuriaki, *ibid.*, **209**, 465 (1939).

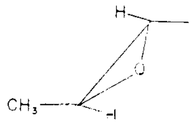
(5) Only one of the enantiomorphic structures of the racemate employed has been pictured.

(6) F. H. Norton and H. B. Hass, THIS JOURNAL, **58**, 2147 (1936).

(7) M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **207**, 918 (1938). The stereochemistry of the 2,3-epoxypentane was not stated.



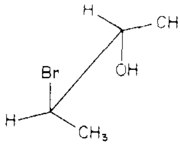
III



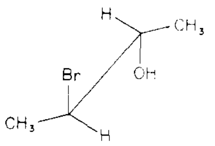
IV

$CH_3COCH_2CH_3$

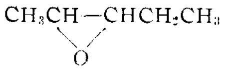
V



VI

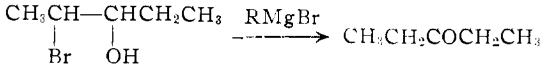


VII



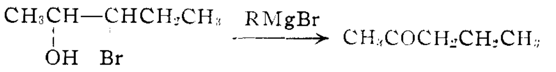
X

$CH_3CH{-}CHCH_2CH_3$ (epoxide, –O– bridging C-2 and C-3)



VIII XI

$CH_3CH(Br){-}CH(OH)CH_2CH_3 \xrightarrow{RMgBr} CH_3CH_2COCH_2CH_3$

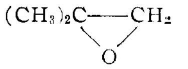


IX XII

$CH_3CH(OH){-}CH(Br)CH_2CH_3 \xrightarrow{RMgBr} CH_3COCH_2CH_2CH_3$

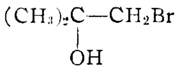
sence of direct evidence for the conversion of each bromo alcohol VIII or IX to the corresponding ketone XI or XII prompted us to study the isomerization of the bromomagnesium salt of each alcohol. The required bromohydrins were prepared by the reduction of the appropriate bromoketones with sodium borohydride. No attempt was made to separate the mixture of diastereoisomers produced in each case. 2-Bromo-3-pentanol when treated with one equivalent of ethylmagnesium bromide was converted to 3-pentanone (XI) containing 5% of the 2-pentanone (XII). Similarly, 3-bromo-2-pentanol yielded 2-pentanone (XII) which contained 20% of the 3-pentanone. These results like those obtained with the *trans-p*-chlorostilbene bromohydrins[1] suggest that the bromomagnesium salts of bromo alcohols derived from 1,2-disubstituted ethylene oxides rearrange more rapidly than they equilibrate with the corresponding epoxides.

Huston and Brault have reported the conversion of 1,2-epoxy-2-methylpropane (XIII) to 1-bromo-2-methyl-2-propanol (XIV) in the presence of magnesium bromide.[8] When treated with various proportions of several Grignard reagents, the oxide XIII was converted to mixtures of the bromohydrin XIV, isobutyraldehyde (XV) and carbinols of the types XVI and XVII.[8a] As the proportion of the Grignard reagent in the reaction mixture was increased the amount of the carbinol XVII, the product which would result from the addition of the Grignard reagent to isobutyraldehyde (XV), increased at the expense of the other products. These results imply that the bromomagnesium salt of the bromo alcohol XIV rearranges to yield isobutyraldehyde (XV), a change which cannot



XIII

$(CH_3)_2C{-}CH_2$ (epoxide, –O– bridging)

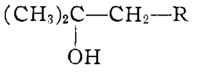


XIV

$(CH_3)_2C(OH){-}CH_2Br$

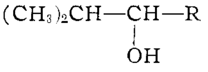
$(CH_3)_2CHCHO$

XV



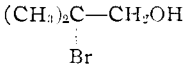
XVI

$(CH_3)_2C(OH){-}CH_2{-}R$



XVII

$(CH_3)_2CH{-}CH(OH){-}R$



XVIII

$(CH_3)_2C(Br){-}CH_2OH$

reasonably be explained other than by a preliminary conversion of the bromo alcohol derivative to the oxide XIII. The isomerization of the epoxide XIII to isobutyraldehyde (XV) may involve the intermediate formation of the bromomagnesium salt of 2-bromo-2-methyl-1-propanol (XVIII). The preparation and properties of this isomeric isobutylene bromohydrin XVIII have not been reported.

The bromohydrin XIV was prepared by the addition of hypobromous acid to isobutylene as described by Suter and Zook.[9] In order to establish the structure of the bromo alcohol as XIV rather than the isomeric 2-bromo-2-methyl-1-propanol (XVIII) a sample of the bromo alcohol prepared from isobutylene was treated with chromium trioxide. Under conditions which permitted the rapid oxidation of isobutyl alcohol neither *t*-butyl alcohol nor the alcohol in question was attacked. The bromo alcohol could be converted to a single crystalline phenylurethan and to a single 3,5-dinitrobenzoate whose melting point agreed with the reported value.[8a] The infrared spectrum of 1-chloro-2-methyl-2-propanol, prepared by the hydration of methallyl chloride,[10] resembled closely the infrared spectrum of the bromohydrin XIV. Only a small amount (1.8%) of isobutyraldehyde (XV) was produced by treatment of the bromohydrin XIV with silver nitrate in aqueous ethanol.

Treatment with one equivalent of ethylmagnesium bromide converted the 1-bromo-2-methyl-2-propanol (XIV) to isobutyraldehyde (XV) in yields ranging from 14 to 26% (Table I). 1,2-Epoxy-2-methylpropane (XIII), the probable intermediate in the isomerization of the bromomagnesium salt of the bromo alcohol XIV, was readily converted to isobutyraldehyde (XV) in the presence of either magnesium bromide or boron trifluoride etherate (Table II). Unlike the isomerization of 1,2-disubstituted ethylene oxide derivatives discussed previously, the isomerization of the bromomagnesium salt of 1-bromo-2-methyl-2-propanol (XIV) provides an example in which the salt of a bromohydrin is isomerized more slowly than it is converted to an epoxide.

It is of interest to compare the behavior of the 2,3-epoxybutanes III and IV in the presence of magnesium bromide with the results obtained from pinacol rearrangements involving related systems. *meso*-2,3-Butanediol has isomerized to a mixture of 2-butanone (V, 71–79% of the mixture) and isobutyraldehyde (XV, 29–21% of the mixture) by the action of aqueous phosphoric acid.[11] With *racemic*-2,3-butanediol the proportion of the aldehyde XV in the product was appreciably lower

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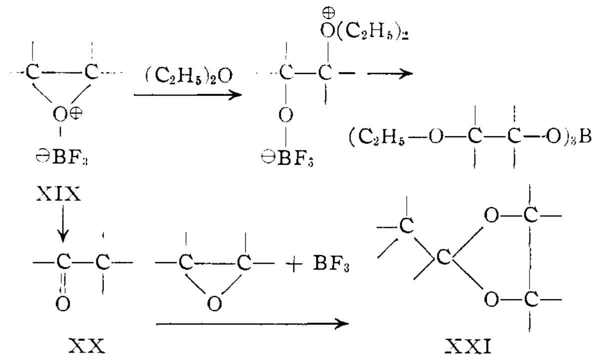
[8] (a) R. C. Huston and R. G. Brault, *J. Org. Chem.*, **15**, 1211 (1950). (b) The opening of an epoxide derived from a terminal olefin in the presence of magnesium bromide to yield a primary bromide reported by these authors is in agreement with the work of R. E. Buckles and J. E. Maurer [*ibid.*, **18**, 1585 (1953)], but conflicts with the reports of M. Tiffeneau, P. Weill and B. Tchoubar (*Compt. rend.*, **205**, 54, 144 (1937)) and M. Tiffeneau and B. Tchoubar (ref. 7).

[9] C. M. Suter and H. D. Zook, THIS JOURNAL, **66**, 738 (1944).

[10] J. Burgin, G. Hearne and F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

[11] E. R. Alexander and D. C. Dittmer, THIS JOURNAL, **73**, 1665 (1951).

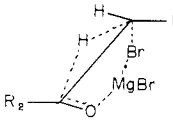
(1–6%). Similarly aqueous acid converted *trans*-2,3-epoxybutane (IV) to a mixture of 2-butanone (V, 75% of the mixture) and isobutyraldehyde (XV, 25% of the mixture) while the product obtained from the *cis*-oxide (III) contained only 7% of the aldehyde XV.[11] In agreement with these findings *trans*-2,3-epoxybutane (IV) was converted to a mixture of 2-butanone (V, 84% of the mixture) and isobutyraldehyde (XV, 16% of the mixture) by action of boron trifluoride in ether; when the *cis*-oxide (III) was subjected to the same conditions only the ketone V could be isolated (Table II). The yields (12–13%) obtained when the oxides III and IV were isomerized in the presence of boron trifluoride etherate were markedly lower than the yields (53–75%) obtained when the isomerizations were effected in the presence of magnesium bromide. The low yields obtained in the boron trifluoride-catalyzed rearrangement of ethylene oxides might be attributed to at least two possible side reactions. The conjugate acid XIX of the oxirane may be attacked by ether to yield a borate ester (or a β-ethoxy alcohol after hydrolysis).[12] This side reaction would be expected to be more serious with 1,2-dialkylethylene oxides than with epoxides which have an aryl or vinyl group or two alkyl groups bonded to one of the carbon atoms of the oxirane ring. Rearrangement involving the prior or simultaneous cleavage of a carbon–oxygen bond of the conjugate acid of a 1,2-dialkylethylene oxide without participation of an ether molecule would require the formation of a secondary rather than a tertiary or allylic carbonium ion.



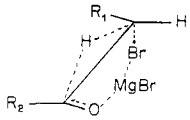
A second side reaction which might be expected is the condensation of the initial isomerization product XX with an additional molecule of the oxide to yield a dioxolane XXI.[13] In order to establish that the isomerization products V and XV, isolated as their 2,4-dinitrophenylhydrazones, derived from the butene oxides III and IV (Table II) represented both the free carbonyl components XX and their dioxolane derivatives XXI present in the reaction mixtures, the reaction mixture derived from each oxide III and IV was boiled with an ethanolic solution of 2,4-dinitrophenylhydrazine and hydrochloric acid for two hours; the relative proportions of the products from each oxide remained unchanged and the yields of the products were somewhat reduced. Since similar reaction conditions are known to cleave both of the expected dioxolanes,[14] the yields reported for the isomerization products V and XV are presumed to represent the total amounts of V and XV and their dioxolanes present in the reaction mixtures.

Since both the *cis*(III)- and *trans*(IV)-oxides yielded only 2-butanone (V) on treatment with magnesium bromide, these isomerizations would appear to involve the bromomagnesium salts of the corresponding bromohydrins VI and VII as intermediates in a process of the type I. However, it must be noted that treatment of either the 3-chloro-2-butanols[11] or the 3-bromo-2-butanols (VI and VII, Table I) with aqueous silver nitrate produced 2-butanone (V) containing little or no isobutyraldehyde (XV). Control experiments performed by Alexander and Dittmer[11] indicated that the absence of isobutyraldehyde in the product cannot be explained by the assumption that the nitric acid produced in the reaction mixture destroyed the aldehyde by oxidation.

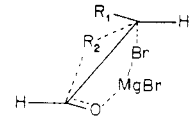
The fact that the stereochemistry of the epoxides III and IV (or the bromohydrins VI and VII) did not influence the structure of the products obtained from isomerization in the presence of magnesium bromide does not invalidate the hypothesis that both the oxides III and IV and the bromohydrins VI and VII isomerize *via* cyclic transition states such as XXII (from the *cis*-oxide or *threo*-bromohydrin, $R_1 = R_2 = CH_3$) or XXIII (from the *trans*-oxide or *erythro*-bromohydrin, $R_1 = R_2 = CH_3$). In cases where the group represented by R_1 is small the difference in energy between transition states in which the group R_1 and the oxymagnesium bromide group are oriented *cis* (as in XXII) rather than *trans* (as in XIII or the analogous transition state XXIV derived from the *cis*-oxide III which would yield the aldehyde XV) would be expected to be slight.[15] In such instances the tendency for a hydrogen atom to migrate (or be eliminated) in preference to the migration of an alkyl group[16] may control the course of the reaction.



XXII



XXIII



XXIV

If this hypothesis concerning the isomerization of the bromomagnesium salts of bromohydrins is correct 1,2-dialkylethylene oxides, when treated with magnesium bromide, may be expected to yield ketones rather than aldehydes except in cases where a transition state of the type XXII (derived from a *cis*-epoxide) is especially unfavorable. Such excep-

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[12] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning and E. Pfeil, *J. prakt. Chem.*, **147**, 257 (1936); H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *ibid.*, **154**, 83 (1939).

[13] M. T. Bogert and R. O. Roblin, Jr., THIS JOURNAL, **55**, 3741 (1933); T. Bersin and G. Willfang, *Ber.*, **70**, 2167 (1937); G. Willfang, *ibid.*, **74**, 145 (1941); A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 981 (1940); *C. A.*, **35**, 3603 (1941).

[14] H. J. Backer, *Rec. trav. chem.*, **55**, 1036 (1936); A. N. Bourns and R. V. V. Nicholls, *Can. J. Research*, **25B**, 80 (1947); A. C. Neish and F. J. Macdonald, *ibid.*, **25B**, 70 (1947).

[15] D. Y. Curtin, *Record of Chemical Progress*, **15**, 111 (1954).

[16] For examples see (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 473–523; (b) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 451–534; (c) D. J. Cram, THIS JOURNAL, **74**, 2137 (1952).

tions might be predicted in cases where the group R_1 is very bulky or where the bromohydrin derivative has been formed from a *cis*-oxide which is part of a cyclic system. An example of the latter type is found with cyclohexene oxide which has been converted to cyclopentanecarboxaldehyde by the action of magnesium bromide; the bromomagnesium salt of cyclohexene chlorohydrin gave the same product.[17] In this case a transition state of the type XXIV would be expected to be operative since a transition state of the type XXII, which would yield cyclohexanone, would be particularly unfavorable sterically. In cases where epoxides derived from five- and six-membered cyclic olefins have been isomerized in the presence of magnesium bromide to yield cyclic ketones with the same ring size[18] the formation of a bromohydrin derivative as the first step in the rearrangement would appear doubtful.

Experimental[19]

The 3-Bromo-2-butanols.—*erythro*-3-Bromo-2-butanol (VII), b.p. 52.5–53.5° (13 mm.), $n^{25}\mathrm{D}$ 1.4769 (lit.[20] b.p. 53.1° (13 mm.), $n^{25}\mathrm{D}$ 1.4767), and *threo*-3-bromo-2-butanol (VI), b.p. 50–50.5° (13 mm.), $n^{20}\mathrm{D}$ 1.4771 (lit.[20] b.p. 50.5° (13 mm.), $n^{25}\mathrm{D}$ 1.4756), were prepared from the corresponding olefins by the method of Winstein and Lucas.[20]

1-Bromo-2-methyl-2-propanol (XIV).—Isobutylene was converted to 1-bromo-2-methyl-2-propanol, b.p. 61–62° (31 mm.), $n^{25}\mathrm{D}$ 1.4708 (lit.[9] b.p. 49.5° (16 mm.), $n^{25}\mathrm{D}$ 1.4710), according to the procedure of Suter and Zook.[9] The compound formed a 3,5-dinitrobenzoate which crystallized from hexane as white plates, m.p. 118–119° (lit.[8a] 120°). The phenylurethan of 1-bromo-2-methyl-2-propanol crystallized from pentane as flat needles, m.p. 75.5–76.5°.

Anal. Calcd. for $C_{11}H_{14}BrNO_2$: C, 48.53; H, 5.18; Br, 29.36; N, 5.14. Found: C, 48.69; H, 5.05; Br, 29.13; N, 5.18.

The infrared spectrum[21] of the bromo alcohol exhibits bands at 3330 and 3450 cm.$^{-1}$ attributable to associated and unassociated hydroxyl functions as well as a strong band at 1120 cm.$^{-1}$ attributable to the oxygen–hydrogen deformation vibration (or carbon–oxygen stretching vibration) of a tertiary alcohol.[22]

A mixture of 1.53 g. (0.01 mole) of the bromo alcohol, 1.33 g. (1 equivalent) of chromium trioxide and 27 ml. of water was allowed to stand with occasional stirring for 6 hours. As control experiments 0.74 g. (0.01 mole) samples of isobutyl alcohol and *t*-butyl alcohol were subjected to the same conditions. Although isobutyl alcohol was rapidly attached by the oxidant no reaction was evident with either *t*-butyl alcohol or the bromo alcohol. The reaction mixture containing the bromo alcohol was extracted with two 50-ml. portions of ether. The combined extracts were dried over magnesium sulfate and the solvent was removed. The infrared spectrum[21] of the residual oil (1.21 g., 79% recovery) is essentially identical with the spectrum of the pure bromo alcohol. In particular no band is present in the 6 μ region attributable to a carbonyl function.

1-Chloro-2-methyl-2-propanol.—Methallyl chloride was converted to 1-chloro-2-methyl-2-propanol, b.p. 126–129°, $n^{24}\mathrm{D}$ 1.4380 (lit.[10] b.p. 126.7°) as described by Burgin, Hearne and Rust.[10] The infrared spectrum[21] of this chloro alcohol closely resembles the spectrum of 1-bromo-2-methyl-2-propanol, absorption bands being found at 3350 cm.$^{-1}$ (associated O–H), at 3480 cm.$^{-1}$ (unassociated O–H) and at 1130 cm.$^{-1}$ (O–H deformation or C–O stretching).

The 2,3-Epoxybutanes.—*cis*-2,3-Epoxybutane (III), b.p. 59–61°, $n^{25}\mathrm{D}$ 1.3792 (lit. b.p. 59.7°,[20] 61.5–62.8°,[11] $n^{20}\mathrm{D}$ 1.3825,[11] 1.3828,[20] $n^{25}\mathrm{D}$ 1.3802[20]), and *trans*-2,3-epoxybutane (IV), b.p. 53.5–54.5°, $n^{24}\mathrm{D}$ 1.3708 (lit. b.p. 53.5°,[20] 56.5–56.7°,[11] $n^{20}\mathrm{D}$ 1.3739,[11] 1.3736,[20] $n^{25}\mathrm{D}$ 1.3705[20]), were prepared from the corresponding 3-bromo-2-butanols as described by Wilson and Lucas.[23] The lack of absorption in the 6 μ region of the infrared[21] indicated that neither of the isomeric oxides contained appreciable quantities of an impurity possessing a carbonyl group.

1,2-Epoxy-2-methylpropane (XIII).—The treatment of 1-bromo-2-methyl-2-propanol with aqueous potassium hydroxide according to the method of Wilson and Lucas,[23] produced 1,2-epoxy-2-methylpropane, b.p. 51° (758 mm.), $n^{21.8}\mathrm{D}$ 1.3713, in 58% yield. Similarly, 1-chloro-2-methyl-2-propanol was converted to 1,2-epoxy-2-methylpropane, b.p. 50–51°, $n^{25}\mathrm{D}$ 1.3695, in 72% yield. The infrared spectra[21] of the two samples are identical in every respect; no bands are present which may be attributed to the stretching vibration of either an oxygen–hydrogen bond or a carbon–oxygen double bond. Negative Beilstein tests indicated that both samples were free from halogen-containing impurities. An analytical sample, prepared by distillation of the oxide from metallic sodium, was collected at 51.5°, $n^{25}\mathrm{D}$ 1.3697.

Anal. Calcd. for C_4H_8O: C, 66.63; H, 11.19. Found: C, 66.30; H, 11.29.

The reason for the discrepancy between the physical constants cited here and the constants previously reported (b.p. 57–58°, $n^{20}\mathrm{D}$ 1.3894)[24] is not known, the previous sample of the oxide also having been prepared from 1-chloro-2-methyl-2-propanol.

2-Bromo-3-pentanol (VIII).—To a solution of 33 g. (0.20 mole) of 2-bromo-3-pentanone, b.p. 51–52° (12 mm.), $n^{24.5}\mathrm{D}$ 1.4547 (lit.[25] b.p. 62–64° (28 mm.)) (prepared by the bromination of 3-pentanone according to the directions of Catch and co-workers[26]), in 75 ml. of methanol was added dropwise and with stirring, a solution of 2.00 g. (0.053 mole) of sodium borohydride in 40 ml. of water, the temperature of the reaction mixture being kept below 20° throughout the addition by means of an ice–salt bath. After the addition was complete the mixture was stirred for 2 minutes and then neutralized by the addition of cold, dilute sulfuric acid. The reaction mixture was diluted with water to a volume of 400 ml. and the heavy organic layer separated. The aqueous phase was extracted with three 75-ml. portions of ether. The combined organic layers were dried over magnesium sulfate and the ether was distilled from the mixture through a Vigreux column. No attempt was made to isolate the 2,3-epoxypentanes and 3-pentanone which were probably present. The residual oil was fractionally distilled through a 25-cm. Fenske column, the following fractions being collected (wt., b.p. (11 mm.), $n^{25.3}\mathrm{D}$): (1) 2.0 g., below 57.5°, 1.4590; (2) 5.9 g., 57.5–58.5°, 1.4698; (3) 3.8 g., 58.5°, 1.4720; (4) 5.3 g., 58.5–59°, 1.4728; (5) 2.1 g., 59°, 1.4728. The infrared spectra[21] of fractions two to five, which exhibited no absorption in the 6 μ region, indicated that no unchanged bromo ketone was present. The spectra of the four fractions were identical, each spectrum exhibiting a band at 3400 cm.$^{-1}$ (unassociated O–H). The total yield of the mixture[27] of *erythro*- and *threo*-2-bromo-3-pentanols was 17.1 g. (51%). Fractions three, four and five were combined and redistilled, a sample, b.p. 74° (23 mm.), $n^{24.5}\mathrm{D}$ 1.4732, being collected for analysis.

Anal. Calcd. for $C_5H_{11}BrO$: C, 35.94; H, 6.63; Br, 47.85. Found: C, 35.84; H, 6.61; Br, 47.58.

3-Bromo-2-pentanol (IX).—In the same manner 3-bromo-2-pentanone, b.p. 77–79° (50 mm.), $n^{23.5}\mathrm{D}$ 1.4568–1.4574 (lit.[26] b.p. 78.0–78.5°, $n^{22}\mathrm{D}$ 1.4563), was reduced with so-

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(17) P. Bedos, *Compt. rend.*, **189**, 255 (1929).

(18) B. Tchoubar, *ibid.*, **214**, 117 (1942).

(19) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with a Baird double beam infrared recording spectrophotometer, model B, fitted with a sodium chloride prism. The microanalyses were performed by Dr. S. M. Nagy and his associates.

(20) S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1576 (1939).

(21) Determined in carbon tetrachloride solution.

(22) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 94–97.

(23) C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936).

(24) W. T. Somerville and P. E. Spoerri, *ibid.*, **72**, 2185 (1950).

(25) E. Venus-Daniloff, *Bull. soc. chim. France*, [4] **43**, 582 (1928).

(26) J. R. Catch, D. H. Hey, E. R. H. Jones and W. Wilson, *J. Chem. Soc.*, 276 (1948).

(27) H. J. Lucas, M. J. Schlatter and R. C. Jones [THIS JOURNAL, **63**, 22 (1941)] have reported the following physical constants for mixtures of the 2-bromo-3-pentanols and the 3-bromo-2-pentanols: the mixed *erythro* isomers, b.p. 59° (10 mm.), $n^{20}\mathrm{D}$ 1.4717; the mixed *threo* isomers, b.p. 53° (10 mm.), $n^{20}\mathrm{D}$ 1.4758.

dium borohydride. From the subsequent fractional distillation the following fractions were collected (wt., b.p. (12 mm.), $n^{24.6}_{\text{D}}$): (1) 3.8 g., below 57°; (2) 4.1 g., 57–58.5° 1.4683; (3) 5.0 g., 58.5–60°, 1.4718; (4) 6.9 g., 60–61.5°, 1.4733. Although the infrared spectra[21] of fractions three and four exhibit no absorption in the 6 μ region, the spectrum of fraction two has a weak band at 1710 cm.$^{-1}$ probably attributable to the carbonyl group of some unchanged 3-bromo-2-pentanone present in the fraction. Each of the spectra exhibits bands at 3350 cm.$^{-1}$ (associated O–H) and at 3480 cm.$^{-1}$ (unassociated O–H). The yield of the mixture[27] of *erythro-* and *threo*-3-bromo-2-pentanol based only on the two pure fractions was 11.9 g. (36%). A sample from fraction 3 was taken for analysis.

Anal. Calcd. for $C_5H_{11}BrO$: C, 35.94; H, 6.63; Br, 47.85. Found: C, 35.72; H, 6.66; Br, 47.58.

Preparation of the 2,4-Dinitrophenylhydrazones.—An authentic sample of isobutyraldehyde was treated with a solution of 1.0 g. of 2,4-dinitrophenylhydrazine and 5 ml. of concentrated hydrochloric acid in 50 to 75 ml. of ethanol. After the mixture had been boiled for 5 minutes sufficient boiling ethanol was added to give a clear solution. The cold solution deposited yellow needles which were dissolved in benzene and passed through an 8-g. column of neutral alumina. The column was eluted with benzene until a colorless eluate was obtained, any 2,4-dinitrophenylhydrazine (and its hydrochloride) being retained on the column. After the benzene eluate had been concentrated to dryness, the residue was recrystallized from ethanol to give the dinitrophenylhydrazone of isobutyraldehyde as yellow needles, m.p. 182–184° (lit.[28] 182°). Similarly the 2,4-dinitrophenylhydrazone of 2-butanone separated as orange needles, m.p. 108–111°. However, repeated recrystallization of the ketone derivative from excess ethanol permitted the isolation of a high melting form as yellow needles, m.p. 117.5–118.5°. Further recrystallization from ethanol did not alter this melting point. The infrared spectra[29] of the two forms of the dinitrophenylhydrazone are identical in every respect. When the form melting at 117.5–118.5° was recrystallized from ethanol containing a few drops of concentrated hydrochloric acid, the compound separated as orange needles, m.p. 111–113°. The melting point values reported for the 2,4-dinitrophenylhydrazone of 2-butanone range from 110–111°[30] to 116–117°.[31] Our data suggest the initial formation of a mixture of the *syn* and *anti* forms of the derivative (m.p. 108–111°) from which one form (m.p. 117.5–118.5°) may be separated by recrystallization. Although the separation of the *syn* and *anti* forms of 2-butanone 2,4-dinitrophenylhydrazone has been reported,[28] the melting points of the two forms were not stated. In this report all yields are based on the mixture of forms, m.p. 108–111°, which was obtained initially.

Since mixtures of the 2,4-dinitrophenylhydrazones of isobutyraldehyde and 2-butanone were anticipated, a means was required for estimating the composition of such mixtures. Since the infrared spectra[29] of the two materials differed only in the relative intensities of three bands an additional method was desirable. Therefore, a series of mixtures of 2-butanone 2,4-dinitrophenylhydrazone (m.p. 108–111°) and isobutyraldehyde 2,4-dinitrophenylhydrazone (m.p. 182–184°) of known composition were prepared and the temperature at which each of these mixtures became completely molten was determined. A plot of these clearing temperatures against the per cent. of isobutyraldehyde 2,4-dinitrophenylhydrazone in the mixture is given in Fig. 1. The mixtures containing low and high concentrations of isobutyraldehyde were recrystallized from minimum quantities of ethanol. In no case did the change in the clearing temperature indicate a change in composition which exceeded 3%.

To avoid losses in the experiments involving the rearrangement of the 2-butene and 2-methylpropene derivatives the reaction mixtures obtained in each case were treated directly with 2,4-dinitrophenylhydrazine without preliminary purification. Consequently, each of the compounds whose rearrangement was studied was treated with 2,4-dinitrophenylhydrazone, hydrochloric acid and ethanol as described above. The appropriate quantity of benzene was also added in cases where the reaction mixture contained this solvent. In all cases where benzene was present, it was necessary to boil the solution for an additional 5 to 15 minutes in order to remove the bulk of the benzene. In only two instances were 2,4-dinitrophenylhydrazones isolated from these blank determinations; from 0.37 g. of 1,2-epoxy-2-methylpropane was obtained 19 mg. (1.5%) of isobutyraldehyde 2,4-dinitrophenylhydrazone. *threo*-3-Bromo-2-butanol (0.78 g.) yielded 64–100 mg. (5–8.8%) of 2-butanone 2,4-dinitrophenylhydrazone. The relatively large amount of the 2-butanone derivative isolated from the experiment involving *threo*-3-bromo-2-butanol cannot be ascribed to the presence of this ketone as an impurity in the bromo alcohol since the infrared spectrum[21] of the alcohol exhibits no absorption in the 6 μ region attributable to a carbonyl group. Likewise, the outcome of the determination was not altered by the use of a freshly distilled sample of *threo*-3-bromo-2-butanol. The corrected yields for rearrangements involving *threo*-3-bromo-2-butanol (Table I) and 1,2-epoxy-2-methylpropane (Table II), based on the maximum amounts of the 2,4-dinitrophenylhydrazones obtained in the blank determinations, are indicated in footnotes at the bottom of the tables.

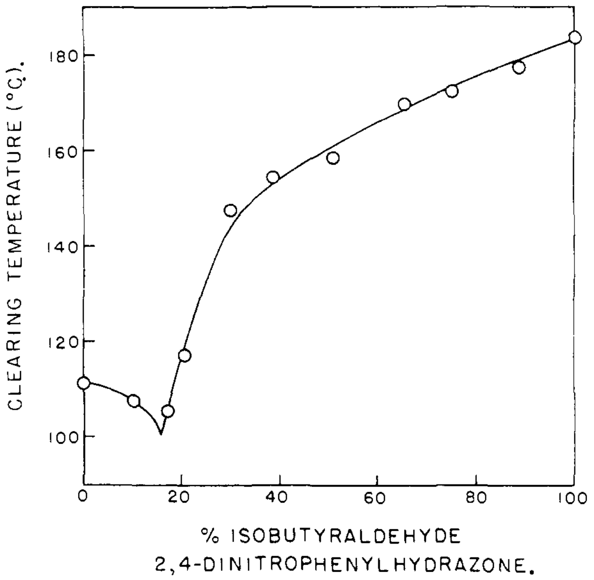

Fig. 1.—The clearing temperature for mixtures of 2-butanone 2,4-dinitrophenylhydrazone and isobutyraldehyde 2,4-dinitrophenylhydrazone.

The 2,4-dinitrophenylhydrazone of 3-pentanone separated from ethanol as flat, orange needles, m.p. 154.5–156° (lit.[32] 156°). The 2,4-dinitrophenylhydrazone of 2-pentanone crystallized from ethanol as orange plates, m.p. 137–139°. Four additional crystallizations from ethanol raised the melting point of the dinitrophenylhydrazone to 141–142.5° (lit. 141°,[32] 143–144°[30]). When the higher melting form (m.p. 141–142.5°) was recrystallized from ethanol containing a few drops of concentrated hydrochloric acid the dinitrophenylhydrazone crystallized as orange plates, m.p. 135–137°. The infrared spectra[29] of the three 2-pentanone 2,4-dinitrophenylhydrazone samples are identical. Concentration of the mother liquor obtained from the initial recrystallization of the 2-pentanone 2,4-dinitrophenylhydrazone (m.p. 137–139°) permitted the isolation of a small quantity of yellow needles which melted over the range 130–137°.

Anal. Calcd. for $C_{11}H_{14}N_4O_4$: C, 49.61; H, 5.30; N, 21.04. Found: C, 49.72; H, 5.54; N, 21.13.

The infrared spectrum[33] of this low-melting material (m.p. 130–137°) is identical with the spectrum[33] of a sample of 2-pentanone 2,4-dinitrophenylhydrazone which melts at 137–139°. It is therefore suggested that 2-pentanone, like 2-butanone, reacts with 2,4-dinitrophenylhydrazine to yield

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(28) B. E. Gordon, F. Wopat, Jr., H. D. Burnham and L. C. Jones, Jr., *Anal. Chem.*, **23**, 1754 (1951).

(29) Determined in chloroform solution.

(30) N. R. Campbell, *Analyst*, **61**, 391 (1936).

(31) W. Dirscherl and H. Nahm, *Ber.*, **73B**, 448 (1940).

(32) C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

(33) Determined as a suspension in a potassium bromide pellet.

TABLE I

REARRANGEMENTS INVOLVING THE BROMOHYDRINS OF THE 2-BUTENES AND 2-METHYLPROPENE

Compd.	Reaction conditions	Reaction time, minutes	Yield of isobutyraldehyde 2,4-dinitrophenylhydrazone,[a] %	Yield of 2-butanone 2,4-dinitrophenylhydrazone,[b] %
1-Bromo-2-methyl-2-propanol	EtMgBr, boiling benzene	5	13.9	None
		30	21.6	None
		40	25.5	None
		90	20.5	None
		240	13.5	None
	$AgNO_3$, heated on steam-bath	5	1.8	None
	$MgBr_2$, boiling benzene	10	None	None
erythro-3-Bromo-2-butanol	EtMgBr, boiling benzene	45	None	64.6
	$AgNO_3$, room temp.	60	None	18.8
	$MgBr_2$, boiling benzene	30	None	None
threo-3-Bromo-2-butanol	EtMgBr, boiling benzene	45	None	60[c]
	$AgNO_3$, room temp.	60	None	39.2[d]
	$MgBr_2$, boiling benzene	30	None	1.1

[a] In every case the melting point of the product was within the range 178.5–183.5°. The lowest temperature at which any of the products melted completely was 181.5°. [b] In every case the melting point of the product was within the range 108 112°. The lowest temperature at which any of the products melted completely was 111°. [c] Yield after correction 52.3%. [d] Yield after correction 31.4%.

a mixture of the *syn* and *anti* forms of the 2,4-dinitrophenylhydrazone.

Attempts to separate the 2,4-dinitrophenylhydrazones of 2-pentanone and 3-pentanone by chromatography on silica gel[28] were unsuccessful. Fractional crystallization and mixed melting point determinations were of no value as methods for estimating the composition of mixtures of the two ketone derivatives; a mixture of equal weights of the two 2,4-dinitrophenylhydrazones crystallized from ethanol as orange plates, m.p. 137–140°. The infrared spectra[29] of 2-pentanone 2,4-dinitrophenylhydrazone and 3-pentanone 2,4-dinitrophenylhydrazone differ slightly in the intensities of the bands at 1070 and 1045 cm.$^{-1}$. In addition the spectrum of the 3-pentanone derivative possesses a weak band at 1455 cm.$^{-1}$ which is present only as a shoulder in the spectrum of 2-pentanone 2,4-dinitrophenylhydrazone.

Rearrangements Involving the Bromohydrins of the 2-Butenes and 2-Methylpropene.—The results of these rearrangements are summarized in Table I. In each case the identity of the product was confirmed by means of a mixed melting point determination with an authentic sample.

The bromomagnesium salts of the bromohydrins were prepared and rearranged in the following manner. A solution of 0.78 g. (0.0051 mole) of the bromo alcohol in 15 ml. of benzene was treated with 5 ml. (0.0051 mole) of a standard solution of ethylmagnesium bromide in equal volumes of benzene and ether. The resulting mixture was boiled under reflux for the specified time and then treated with 1.2 g. of 2,4-dinitrophenylhydrazine; the product was isolated as described previously.

The rearrangements catalyzed by silver ion were effected by treatment of a solution of 0.61 g. (0.0040 mole) of the bromo alcohol in 15 ml. of ethanol with 0.72 g. (0.0042 mole) of silver nitrate dissolved in 10 ml. of water. After the resulting mixture had been warmed or allowed to stand for the specified time, the silver bromide was removed by filtration and washed with ethanol. The combined filtrates were treated with 1.0 g. of 2,4-dinitrophenylhydrazine and worked up in the usual way.

Each of the bromohydrins (0.46 g., 0.0030 mole) was treated with 25 ml. of a solution of magnesium bromide etherate in benzene.[34] After the resulting solution had been refluxed for the specified time, it was treated with 0.70 g. of 2,4-dinitrophenylhydrazine and then worked up as described previously.

Rearrangements Involving the Epoxides of the 2-Butenes and 2-Methylpropene.—The results of these rearrangements are summarized in Table II. In all cases where one product was formed the identity of the material was confirmed by means of a mixed melting point determination with an authentic sample.

The rearrangements catalyzed by boron trifluoride etherate were effected by the treatment of a solution of 0.37 g. (0.0051 mole) of the epoxide in 15 ml. of ether with 1.0 ml. of boron trifluoride etherate. The resulting solution was stirred for the specified time and then treated with 1.2 g. of 2,4-dinitrophenylhydrazone in the usual fashion.

Alternatively, the oxide (0.22 g., 0.0031 mole) was treated with 25 ml. of a solution of magnesium bromide etherate in benzene[34] accompanied in some cases by additional amounts of benzene and by ether. The resulting mixture was refluxed or was allowed to stand for the specified time and was then treated with 0.70 g. of 2,4-dinitrophenylhydrazine in the usual fashion.

In one instance, the reaction of *trans*-2,3-epoxybutane with boron trifluoride etherate, a mixture of dinitrophenylhydrazones, m.p. 90–100°, was obtained. The melting point of the mixture suggests the presence of 16% of isobutyraldehyde 2,4-dinitrophenylhydrazone in the mixture (Fig. 1); calculations based on the infrared spectrum[29] of the mixture indicate the presence of 13% of the aldehyde derivative. A 109-mg. portion of the sample was partially fractionated by chromatography on a silica gel–Celite mixture.[35] The first fractions, eluted with a 4% solution of ether in benzene, were recrystallized from ethanol to give 41 mg. of orange crystals, m.p. 99–108°. This melting point was not altered when the material was mixed with a synthetic mixture, m.p. 100–108.5°, prepared from 7 mg. of isobutyraldehyde 2,4-dinitrophenylhydrazone and 93 mg. of 2-butanone 2,4-dinitrophenylhydrazone (see Fig. 1). The remaining fractions, eluted from the column with a 25% solution of ether in benzene, separated from ethanol as yellow-orange crystals (16 mg., m.p. 100–134°). No depression was obtained in a mixed melting point determination with a mixture, m.p. 100–134°, prepared from 24 mg. of isobutyraldehyde 2,4-dinitrophenylhydrazone and 76 mg. of 2-butanone 2,4-dinitrophenylhydrazone. The reaction mixtures obtained from the boron trifluoride-catalyzed isomerizations of *cis*- and *trans*-2,3-epoxybutane were also treated with an ethanolic solution of 2,4-dinitrophenylhydrazine and hydrochloric acid as described above except that each resulting mixture was boiled under reflux for 2 hours. From the *cis*-oxide 2-butanone 2,4-dinitrophenylhydrazone, m.p. 106–111°, was isolated in 11% yield; from the *trans*-oxide a mixture (m.p. 86–100°, Fig. 1) of isobutyraldehyde 2,4-dinitrophenylhydrazone and 2-butanone 2,4-dinitrophenylhydrazone was obtained in 10% yield.

Rearrangement of 2-Bromo-3-pentanol.—2-Bromo-3-pentanol (2.56 g., 0.0153 mole) was treated with 15 ml. (0.0153 mole) of a standard solution of ethylmagnesium bromide in equal volumes of benzene and ether. The mixture was boiled under reflux for 30 minutes and then poured into a saturated solution of ammonium chloride. The organic

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(34) This solution was prepared from 0.0092 mole of bromine as described in a previous report (ref. 1).

(35) J. D. Roberts and C. Green, *Ind. Eng. Chem., Anal. Ed.*, **18**, 335 (1946).

TABLE II

REARRANGEMENTS INVOLVING THE EPOXIDES OF THE 2-BUTENES AND 2-METHYLPROPENE

Compd.	Reaction conditions	Reaction time, min.	Yield of isobutyraldehyde 2,4-dinitrophenylhydrazone,[a] %	Yield of 2-butanone 2,4-dinitrophenylhydrazone,[b] %
1,2-Epoxy-2-methylpropane	$BF_3 \cdot Et_2O$ room temp. in ether	6	74.6[c]	None
	$MgBr_2$, boiling benzene	10	40.5[d]	None
		30	46.6[e]	None
	$MgBr_2$, boiling mixture of 40 ml. of benzene and 25 ml. of ether	10	38[f]	None
	$MgBr_2$, room temp. 40 ml. of benzene and 50 ml. of ether	120	74.7[g]	None
	$MgBr_2$, 1:1 benzene–ether mixture (by vol.) room temp.	180	78.7[h]	None
cis-2,3-Epoxybutane	$MgBr_2$, boiling benzene	30	None	74.7
	$MgBr_2$, 1:1 benzene–ether mixture (by vol.), room temp.	240	None	52.8
	$BF_3 \cdot Et_2O$, ether, room temp.	6	None	13.2
trans-2,3-Epoxybutane	$MgBr_2$, boiling benzene	30	None	61.7
	$MgBr_2$, 1:1 benzene–ether mixture (by vol.), room temp.	240	None	64
	$BF_3 \cdot Et_2O$, ether, room temp.	6	1.8[i]	10[i]

[a] In every case where only one product was obtained the melting point of the product was within the range 176.5–184°. The lowest temperature at which any of these products melted completely was 180°. [b] In every case where only one product was obtained the melting point of the product was within the range 107–112°. The lowest temperature at which any of these products melted completely was 111°. [c] Yield after correction 73.3%. [d] Yield after correction 39.1%. [e] Yield after correction 45.1%. [f] Yield after correction 36.5%. [g] Yield after correction 73.3%. [h] Yield after correction 77.3%. [i] Calculated values (see Experimental). The total yield of mixed 2,4-dinitrophenylhydrazones was 152 mg. (11.8%), m.p. 90–100°.

layer was separated and the aqueous layer extracted with ether. The combined organic layers were dried over magnesium sulfate and then distilled through a Holtzman column. After the ether had been removed from the mixture, the remaining benzene–ketone mixture was collected in two fractions. A 1.00-g. aliquot of fraction one (total weight 3.32 g.) was treated with 1 g. of 2,4-dinitrophenylhydrazine; 219 mg. of 3-pentanone 2,4-dinitrophenylhydrazone, m.p. 154.5–156°, was isolated. Likewise, a 0.40-g. aliquot of fraction two (total weight 1.20 g.) yielded 371 mg. of 3-pentanone 2,4-dinitrophenylhydrazone, m.p. 154.5–156°. The melting points of mixtures of the two dinitrophenylhydrazones with authentic samples of 3-pentanone 2,4-dinitrophenylhydrazone were not depressed. Thus, the total yield of 3-pentanone amounted to 45.3%. The infrared spectrum[36] of fraction two was compared with the spectra of benzene solutions of 3-pentanone and a mixture composed of 90% (by weight) 3-pentanone and 10% 2-pentanone. Calculations based on the relative optical densities of bands at 1415, 1170, 1120 and 1095 cm.$^{-1}$ indicated that the 3-pentanone portion of fraction two contained 5% of 2-pentanone.

Rearrangement of 3-Bromo-2-pentanol.—3-Bromo-2-pentanol (2.56 g., 0.0153 mole) was treated with one equivalent of ethylmagnesium bromide as described above. A 2.00-g. aliquot of the first fraction from the distillation of the product (total weight 3.00 g.) gave 73 mg. of a 2,4-dinitrophenylhydrazone, m.p. 132–134°. A 0.50-g. aliquot of the second fraction (total weight 1.93 g.) yielded 228 mg. of a 2,4-dinitrophenylhydrazone, m.p. 133–135°. The total yield of the pentanone mixture was 24.4%. The infrared spectrum[36] of fraction two was compared with the spectra of benzene solutions of 2-pentanone and a mixture composed of 60% (by weight) 2-pentanone and 40% 3-pentanone. Calculations based on the relative optical densities of bands at 1170 and 1120 cm.$^{-1}$ in the infrared spectrum[36] indicated that the 2-pentanone portion of fraction two contained 20% of 3-pentanone. The infrared spectrum[29] of the 2,4-dinitrophenylhydrazone mixture was identical with the spectrum of 2-pentanone 2,4-dinitrophenylhydrazone except for a slight difference in the intensity of the band at 1070 cm.$^{-1}$. This difference in intensity is in the direction which would be predicted by the presence of 3-pentanone 2,4-dinitrophenylhydrazone in the mixture.

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(36) Determined as a pure liquid.