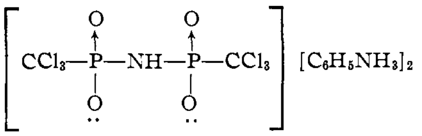
14. **Benzal Trichloromethylphosphonanilidic Hydrazide (XVI).**—The reaction solution of 2 g. of XIV, 100 ml. of ethanol and 22.2 g. of freshly distilled benzaldehyde was heated at reflux temperature for 3.5 hours. The reaction mixture was poured into 200 ml. of dilute sodium bisulfite solution and the insoluble product was filtered and warmed to 60° in 100 ml. of dilute sodium bisulfite solution. The insoluble product was again filtered and recrystallized from ethanol to afford a white fiber-like compound.

15. **N-[5-(Methylphenylamino)-2,4-pentadienylidene] P-Trichloromethylphosphonamidic Chloride Hydrochloride (XVII).**—In a 500-ml. erlenmeyer flask were placed 23.7 g. of I, 150 ml. of pyridine and 42.8 g. of redistilled N-methylaniline. The reaction was allowed to stand for four days, after which the contents of the flask were poured into cold dilute hydrochloric acid (100 ml. of concd. acid and 300 ml. of distilled water) with good stirring. The stirring was continued for 15 minutes and the solid was then filtered, washed with water and pressed down well on the filter paper. Since the compound was unstable to prolonged heating, it was dried in a vacuum desiccator for 24 hours. A pure sample was best prepared by one recrystallization each from chloroform, acetone and ethanol. The product was a dark red colored compound which formed glistening needles from ethanol.

16. **N-[5-(*p*-Chlorophenylmethylamino)-2,4-pentadienylidene] P-Trichloromethylphosphonamidic Chloride Hydrochloride (XVIII).**—The *p*-chloro-N-methylaniline used in this reaction was prepared by the reduction[13] of *p*-chloroformanilide[12] with lithium aluminum hydride according to the directions for similar compounds.

The preparation of this red compound was carried out in the same manner as described in 15. The reaction time in this case was 3.0 days.

17. **Imido Bis-(anilinium trichloromethylphosphonate).**—After filtration of XX in part 18, the filtrate was treated with charcoal and filtered until the solution was colorless. It was then acidified and evaporated under reduced pressure to about 75 ml. Aniline (3 g.) was added to the cooled solution and a gray solid precipitated. This was recrystallized from water to give a white compound. Apparently the phosphorus-containing half of the molecule coupled during the hydrolysis to form this compound.



$$\left[\mathrm{CCl_3{-}\underset{\underset{\cdot\cdot}{\overset{|}{O}}}{\overset{\overset{O}{\uparrow}}{P}}{-}NH{-}\underset{\underset{\cdot\cdot}{\overset{|}{O}}}{\overset{\overset{O}{\uparrow}}{P}}{-}CCl_3}\right]\mathrm{[C_6H_5NH_3]_2}$$

18. **5-(Methylphenylamino)-2,4-pentadienal (XX).**—In a 250-ml. erlenmeyer flask were placed 3 g. of XVII and 40 ml. of ethanol. Potassium hydroxide (1.2 g.) in 30 ml. of ethanol and 10 ml. of water was added slowly while swirling the reaction flask in an ice-bath. The color changed from red to yellow and became cloudy when 100 ml. of water was added. The flask was placed in the refrigerator for 2 hours. The yellow solid was filtered and recrystallized from ethanol.

19. **5-(*p*-Chlorophenylmethylamino)-2,4-pentadienal (XXI).**—This compound was prepared from XVIII in exactly the same way that XX was prepared from XVII. The compound was a yellow to orange colored solid when recrystallized from ethanol.

Acknowledgment.—The authors wish to thank Dr. H. Armin Pagel for his continued interest and aid in the problems of analysis. The authors also wish to express their appreciation to Parke, Davis and Company for financial aid.

LINCOLN 8, NEBRASKA

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(13) V. M. Micovic and M. Lj. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(12) *Org. Synthesis*, **20**, 66 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

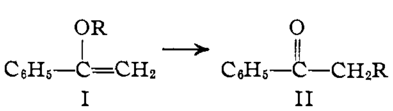
1,3-Shifts. II. The Stereochemistry of the Rearrangement of α-Alkoxystyrenes[1]

BY KENNETH B. WIBERG AND BERTRAM I. ROWLAND

RECEIVED AUGUST 16, 1954

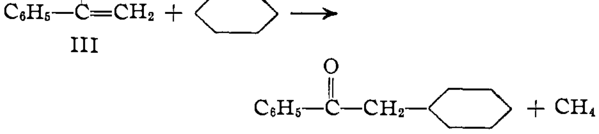
The thermal rearrangement of optically active α-2-butoxystyrene to β-methylvalerophenone was found to give over 95% racemization. The α-2-butoxystyrene and the product ketone were found to be configurationally stable under the conditions of the rearrangement. α-Neopentoxystyrene was found to rearrange to γ,γ-dimethylvalerophenone without rearrangement in the migrating group, indicating that a carbonium ion intermediate was unlikely. The reaction could be initiated by *t*-butyl peroxide, but the usual type of inhibition of a free radical chain reaction could not be realized. The kinetics of the rearrangement of α-2-butoxystyrene was found not to follow any simple rate law.

The rearrangement of α-alkoxy-styrenes (I) to the corresponding substituted acetophenone (II) was first reported by Claisen[2] in 1896. Subsequently, the rearrangement of α-methoxystyrene (III) received considerable study by Lauer, Spielman and Mortenson.[3] They found that the reaction was kinetically of the second order, and that the by-products, 1,2-dibenzoylpropane and methane, also were formed by a second-order process. Their data were however not very precise, and the kinetic order is still not certain. They observed that III would react with a hydrocarbon solvent to give methane and a substituted acetophenone having the substituent derived from the solvent as, for example, in the case of cyclohexane. It was noted also that III reacted with alkyl halides in a similar manner giving methyl halide and the substituted acetophenone.



$$\mathrm{C_6H_5{-}\overset{\overset{OR}{|}}{C}{=}CH_2 \longrightarrow C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}CH_2R}$$

I II



III

They suggested that the reaction involved a cyclic eight-membered transition state, in which the driving force was a "heteroenoid" system. This would explain the intermolecular nature of the re-

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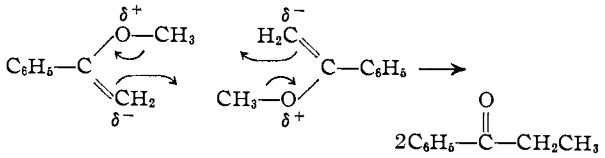
(1) Abstracted from part of a thesis submitted by Bertram I. Rowland to the University of Washington in partial fulfillment of the requirement for the degree of Doctor of Philosophy, 1954.

(2) L. Claisen, *Ber.*, **29**, 2931 (1896).

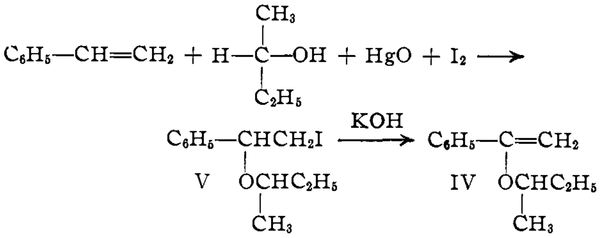
(3) E. H. MacDougall, W. M. Lauer and M. A. Spielman, THIS JOURNAL, **55**, 4089 (1933); W. M. Lauer and M. A. Spielman, *ibid.*, **55**, 4923 (1933); M. A. Spielman and C. W. Mortenson, *ibid.*, **61**, 666 (1939); **62**, 1609 (1940).

action and also second-order kinetics. It does not account for the reaction with alkanes and alkyl halides, nor does it account for the by-products which were observed.



It was our purpose to investigate some features of this reaction, particularly with a system which might rearrange at a lower temperature than III, and which would permit a stereochemical investigation of the reaction. α-2-Butoxystyrene (IV) appeared to meet both of these requirements.

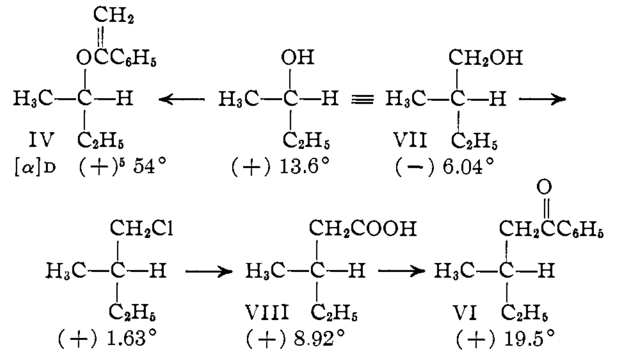
The α-2-butoxystyrene was prepared by the treatment of styrene with 2-butanol, iodine and mercuric oxide, giving α-2-butoxy-β-iodostyrene (V) which on treatment with alcoholic potassium hydroxide gave IV. This procedure was satisfactory for the preparation of optically active IV, although it was noted that the calculated maximum rotation of IV thus obtained varied from $[\alpha]^{25}\text{D}$ 37.7 to 54.0° in individual runs, indicating that some racemization had occurred in the formation of the alkoxystyrene.



$$C_6H_5{-}CH{=}CH_2 + H{-}\overset{CH_3}{\underset{C_2H_5}{C}}{-}OH + HgO + I_2 \longrightarrow$$

$$\underset{V}{C_6H_5{-}\underset{OCH(CH_3)C_2H_5}{CHCH_2I}} \xrightarrow{KOH} \underset{IV}{C_6H_5{-}\underset{OCH(CH_3)C_2H_5}{C}{=}CH_2}$$

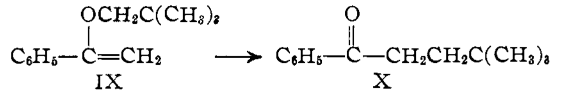
The product of rearrangement, β-methylvalerophenone (VI), was prepared in optically active form by a procedure which permitted the correlation of the configuration of the ketone with that of the vinyl ether. Active amyl alcohol (VII) was converted to the chloride and then to β-methylvaleric acid (VIII) *via* the Grignard reagent. A Friedel–Crafts acylation of benzene with the acid chloride of VIII give VI. Since the relative configuration of VI and 2-butanol is known,[4] it was apparent that (+)-VI and (+)-IV had the configurations



The rearrangement of α-2-butoxystyrene (IV) was found to give β-methylvalerophenone with over 95% racemization in the absence or presence of free radical inhibitors such as diphenylamine or hydroquinone. In one case, the reaction was run to one-half completion, and the unreacted IV was found to have 86% of its original rotation, whereas the ketone was at least 95% racemized, thus demonstrating that IV was not easily racemized under the reaction conditions. In another experiment, the optically active ketone VI was mixed with an equal weight of inactive IV, and the reaction was allowed to proceed to near completion. The ketone obtained from this reaction had over one-half of its original rotation. Since inactive ketone is formed in the reaction, this demonstrates that little or no racemization of VI occurred during the reaction.

The recent demonstration by Hart and Eleuterio[6] that α-phenethyl phenyl ether was rearranged thermally to *o*-α-phenethylphenol with 20% retention of configuration suggested the use of the α-phenethyl group in the present study since the two rearrangements appear analogous and proceed under essentially the same conditions. The α-phenethoxystyrene was prepared by the method described above, and the rearrangement was effected at 200°. The product, β-phenylbutyrophenone, was found to have no appreciable optical activity, and although the maximum rotation of the ketone is not known, it would appear that almost complete racemization occurred. It was thus apparent that the migrating group became sufficiently free from the rest of the molecule during the reaction for almost complete racemization to take place.

The most reasonable possibilities are that the migrating group existed as a carbonium ion or as a free radical. Of these, the latter is the more probable, since in the study of the rearrangement of α-methoxystyrene in *p*-methoxytoluene solution, it was found[3] that methane was formed, apparently by the removal of an α-hydrogen from the *p*-methoxytoluene. This is a type of reaction which is characteristic of a free radical, whereas a carbonium ion might be expected to attack the aromatic ring. In order to obtain further evidence concerning the nature of the migrating group, the rearrangement of α-neopentoxystyrene (IX) was studied. The preparation of IX was effected by the procedure used for IV. The product of the rearrangement was found to be γ,γ-dimethylvalerophenone (X), the normal rearrangement product. This was demonstrated by the identity of the infrared spectra of X and of a synthetic sample of X prepared by the hydrogenation of pivalacetophenone. The melting points of the 2,4-dinitrophenylhydrazones of the two samples of X also were identical and there was no depression of the melting point on admixture.



$$\underset{IX}{C_6H_5{-}\overset{OCH_2C(CH_3)_3}{C}{=}CH_2} \longrightarrow \underset{X}{C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2C(CH_3)_3}$$

The possibility of initiating the rearrangement of IV by the addition of one of the usual free radical catalysts was studied. A mixture of IV and 10% by

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[4] K. Freudenberg, "Stereochemie," Franz, Deuticke, Leipzig, 1933, pp. 677–679.

[5] The rotations given are the reported maximum rotations, or those calculated from the experimental data reported herein, if they are higher.

[6] H. Hart and H. S. Eleuterio, THIS JOURNAL, **76**, 521 (1954).

weight of di-*t*-butyl peroxide was heated at 135° and the infrared spectrum of the reaction solution was compared with that of a sample of IV which was heated under the same conditions in the absence of the catalyst. After nine hours, very little reaction was noted in the control, whereas the initiated reaction had gone to near completion (Fig. 1). This indicates that a free radical chain reaction giving VI is possible, even though it does not demonstrate that the thermal rearrangement involves this path. It might be noted that the main product derived from the peroxide was *t*-butyl alcohol, and not acetone.

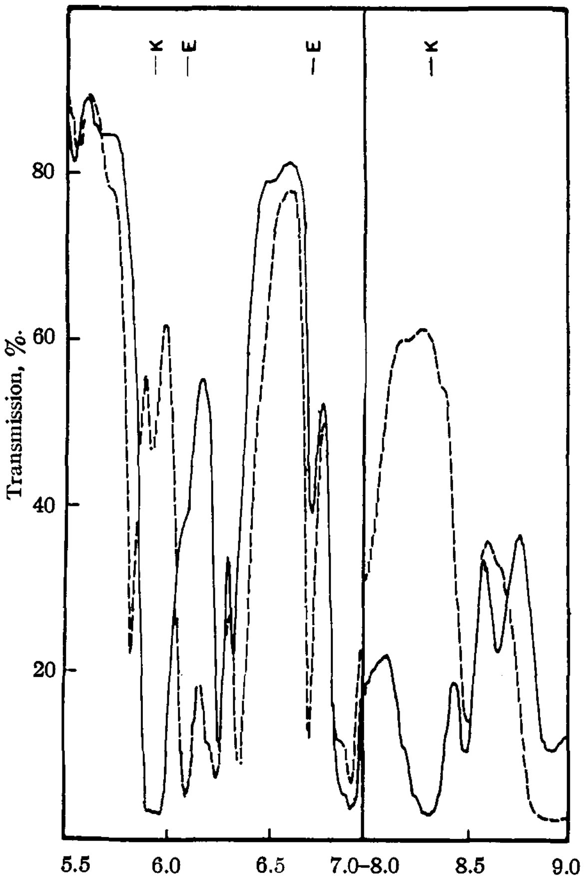

Fig. 1.—Infrared spectra of samples of α-2-butoxystyrene after heating for nine hours at 135°. The material containing di-*t*-butyl peroxide is represented by the solid line, and the control by the broken line. Characteristic peaks of the ether are marked E, those of the product ketone are marked K.

Since most radical chain reactions may be inhibited by the addition of compounds such as diphenylamine and chloranil, the effect of the addition of these substances was studied. An early qualitative study indicated that diphenylamine, hydroquinone and trinitrobenzene had little or no effect on the reaction. In a later experiment, 2% by weight of chloranil was added to IV and this sample and a control were heated under the same conditions for one hour at 200–210° giving somewhat over half-reaction. Distillation of the reaction mixtures under identical conditions gave essentially the same amount of product, and the infrared spectra of the two samples were nearly identical, indicating no significant inhibition.

Finally, the rate of the rearrangement of IV was determined at 178–179° in heptane solution using the log of the ratio of the transmission of the 8.33 μ band of IV and the 8.90 μ band of VI as a measure of the extent of reaction. A curve of percentage reaction against time is shown in Fig. 2. It was not possible to fit this result to any kinetic order because of the very fast initial reaction and the comparatively slow later reaction. This suggests that either a catalyst was present at the beginning of the reaction and that it had exhausted itself by about 30% reaction, or that a product of the reaction acted as an inhibitor, or both. This type of behavior was noted with a number of samples of IV, even those which had been distilled from sodium in an effort to remove any impurities which would initiate the reaction.

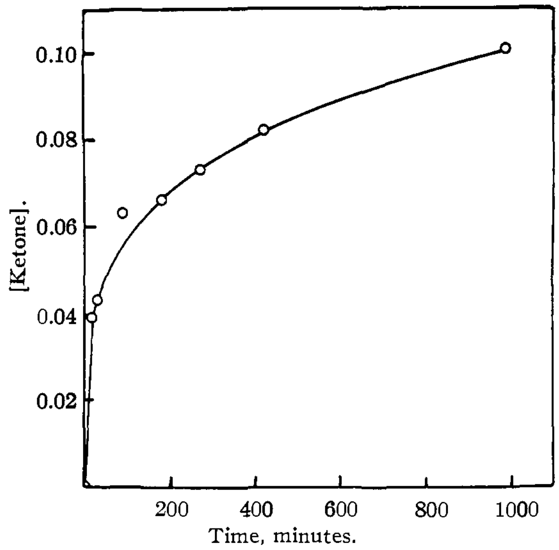

Fig. 2.—Rate of rearrangement of α-2-butoxystyrene in heptane solution at 178–179°.

From these results it would appear that a free radical mechanism is the most likely possibility for the reaction, even though inhibition was not noted. An attempt now is being made to determine whether the effect noted in the rate study is affected by exhaustive purification of the alkoxystyrene or by variations in the method of preparation. The effect of substituents on the rearrangement of α-benzyloxystyrene is also being studied.

Acknowledgment.—We wish to express our appreciation to the Research Corporation of New York for financial support of this investigation. We also wish to thank Mr. J. A. Wheat of the National Research Council of Canada for a generous gift of (−)-2,3-butanediol from which the active 2-butanol was prepared.

Experimental[7]

α-2-Butoxystyrene (IV).[8]—To a mixture of 29.3 g. (0.14

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[7] Analyses were performed by B. Nist and by A. Elek. The melting points are corrected, whereas boiling points are not.

[8] This procedure was adapted from the general procedure of M. Tiffeneau, *Compt. rend.*, **145**, 813 (1907).

mole) of mercuric oxide, 20.0 g. of 2-butanol[9] ($[\alpha]^{25}\mathrm{D}$ $-2.89°$, l 1, neat) and 68.6 g. (0.27 mole) of iodine in a glass stoppered bottle cooled in an ice-bath was added slowly with stirring a solution of 28.2 g. (0.27 mole) of styrene in 50 ml. of peroxide-free anhydrous ether.[10] The addition required 10 to 15 minutes. The stopper was inserted into the bottle and then coated with paraffin and further secured with wire. After shaking for four hours while cooled in an ice-bath, the solution was filtered and the precipitate was washed with a little ether. To the combined ether extracts was added a solution of potassium iodide, and small portions of sodium bisulfite were added with shaking until the dark color of iodine was discharged. The ether layer was separated, washed with water and dried over anhydrous potassium carbonate. After the solvent had been removed under reduced pressure, the residue was dissolved in 140 ml. of ethanol containing 30.0 g. of potassium hydroxide and the solution was heated to reflux for three hours. After the addition of 400 ml. of water, the solution was extracted with three 100-ml. portions of ether. After drying over potassium carbonate, the ether solution was distilled in a nitrogen atmosphere giving 27.8 g. (59%) of α-2-butoxystyrene, b.p. 106–110° at 14 mm., $n^{25}\mathrm{D}$ 1.5120, d^{25} 0.940, $[\alpha]^{25}\mathrm{D}$ $+12.50°$ (l 0.5, neat).[11]

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.2. Found: C, 81.2; H, 9.2.

When optically active alcohol was not used, the following procedure was found to be more convenient. To a mixture of 100 ml. of 2-butanol, 44 g. (0.2 mole) of mercuric oxide and 92 g. (0.4 mole) of iodine was slowly added 42 g. (0.4 mole) of styrene with stirring while cooled in an ice-bath. The above procedure was repeated except that pentane was used instead of ether for the extraction. Distillation gave 45 g. (64%) of α-2-butoxystyrene, b.p. 109–111° at 15 mm., $n^{22}\mathrm{D}$ 1.5136.

α-Phenethoxystyrene.—To a mixture of 30.5 g. (0.25 mole) of α-phenethyl alcohol ($[\alpha]^{25}\mathrm{D}$ $-5.18°$, l 1, neat),[12] 68.6 g. (0.27 mole) of iodine and 35.8 g. (0.17 mole) of mercuric oxide was added 28.2 g. (0.27 mole) of styrene in 50 ml. of anhydrous ether, and the subsequent procedure was as outlined above. On distillation there was obtained 28.6 g. (47%) of α-phenethoxystyrene, b.p. 116–117° at 0.6 mm., $n^{25}\mathrm{D}$ 1.5735, d^{25} 1.043, $[\alpha]^{25}\mathrm{D}$ $+19.58°$ (l 0.5, neat).[13]

α-Neopentoxystyrene (IX).—To a mixture of 28.4 g. (0.32 mole) of neopentyl alcohol,[14] 83.8 g. (0.33 mole) of iodine and 35.8 g. (0.17 mole) of mercuric oxide was added 34.3 g. (0.33 mole) of styrene in 50 ml. of ether, and the above procedure was then followed. On distillation there was obtained 44.2 g. (76%) of α-neopentoxystyrene, b.p. 120–121° at 18 mm., $n^{25}\mathrm{D}$ 1.5061, d^{25} 1.174.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.7; H, 9.4.

β-Methylvalerophenone (VI).—2-Methyl-1-butanol ($[\alpha]^{25}\mathrm{D}$ $-5.40°$, l 1, neat)[15] was converted to 2-methyl-1-butyl chloride ($[\alpha]^{25}\mathrm{D}$ $+1.46°$, l 1, neat, $n^{25}\mathrm{D}$ 1.4092).[16] The Grignard reagent was prepared in the usual fashion and then carbonated with Dry Ice[17] giving 3-methylpentanoic acid (62%), b.p. 88–91° at 13 mm., $n^{25}\mathrm{D}$ 1.4142, d^{25} 0.923, $[\alpha]^{25}\mathrm{D}$ $+7.67°$ (l 1, neat).[18]

3-Methylpentanoic acid was converted to the acid chloride, which was then treated with benzene and aluminum chloride giving β-methylvalerophenone,[19] b.p. 119–122° at 10 mm., $n^{25}\mathrm{D}$ 1.5082, $[\alpha]^{25}\mathrm{D}$ $+17.50°$ (l 1, neat), d^{25} 0.964.

Purification of β-Methylvalerophenone.—The semicarbazone from 5.3 g. (0.03 mole) of IV was prepared by the procedure of Shriner and Fuson.[20] It was dissolved in a solution of 434 ml. of acetic acid, 192 ml. of water and 5.4 g. of pyruvic acid, and carbon dioxide was bubbled through the mixture for one hour to displace the air. The mixture was warmed gently until all of the semicarbazone had dissolved, and the solution was then allowed to stand for 20 hours. The solution was diluted with 400 ml. of water and continuously extracted with pentane for 60 hours. On distillation, 2.5 g. (47%) of β-methylvalerophenone was obtained, b.p. 118–120° at 10 mm., $[\alpha]^{25}\mathrm{D}$ $+17.39°$ (l 1, neat).[21]

Pivalalacetophenone.—A mixture of 11.0 g. (0.13 mole) of pivalaldehyde, 12.2 g. (0.12 mole) of acetophenone, 57 ml. of 95% alcohol, 15 ml. of water and 13 ml. of 10% sodium hydroxide solution was shaken for 48 hours. After diluting with 100 ml. of water, the solution was extracted with three 40-ml. portions of benzene. The benzene solution was washed with water until neutral, then with 40% sodium bisulfite solution, and again with water. After drying over calcium chloride, the solution was distilled giving 11.6 g. (52%) of pivalalacetophenone, b.p. 98–99° at 0.8 mm., $n^{25}\mathrm{D}$ 1.5248.

γ,γ-Dimethylvalerophenone (X).—A solution of 4.5 g. (0.024 mole) of pivalalacetophenone in 15 ml. of absolute ethanol was hydrogenated at atmospheric pressure using one-half teaspoon of W-4 Raney nickel.[22] Hydrogen takeup ceased after 1.16 equivalents had been consumed. After filtration through Filter-cel, the solvent was removed, and the residue was dissolved in pentane and dried over anhydrous calcium sulfate. Distillation gave 3.8 g. of material boiling from 80–96° at 0.3 mm. This product was oxidized to remove the alcohol formed, by adding it dropwise to a solution of 15 ml. of water, 1.7 ml. of concentrated sulfuric acid and 2.5 g. of sodium dichromate, followed by heating for 2 hours. The mixture was steam distilled, and the distillate was extracted with pentane. The pentane solution was dried with anhydrous potassium carbonate and distilled giving 1.1 g. (24%) of γ,γ-dimethylvalerophenone, b.p. 76–77° at 0.2 mm., $n^{25}\mathrm{D}$ 1.5041.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 81.5; H, 9.3.

The 2,4-dinitrophenylhydrazone had m.p. 203–205°.

Anal. Calcd. for $C_{19}H_{22}N_4O_4$: C, 61.6; H, 6.0; N, 15.1. Found: C, 61.4; H, 6.3; N, 15.1.

Rearrangement of α-2-Butoxystyrene (IV).—α-2-Butoxystyrene (6.04 g.) was introduced into a glass tube which was sealed after the liquid had been degassed at approximately 1μ pressure. It was heated at 190–200° for 210 min. in a Carius furnace. Distillation of the product gave 1.30 g. of IV, b.p. 105–112° at 13 mm., 3.55 g. (59 or 76% based on unrecovered starting material) of β-methylvalerophenone, b.p. 119–124° at 13 mm., and 0.45 g. of a red residue. The semicarbazone had m.p. 180.8–181.1°.[23]

Rearrangement of Optically Active α-2-Butoxystyrene.—2-Butoxystyrene (8.0 g., $[\alpha]^{25}\mathrm{D}$ -13.56, l 1, neat) and 0.5 g. of diphenylamine were introduced into a tube which was sealed after degassing. It was heated at 195–205° for 60 minutes in a Carius furnace. The resultant material was transferred to a distilling flask with the aid of a little pen-

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[9] The maximum rotation reported by R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 49 (1911), was $[\alpha]^{22}\mathrm{D}$ 13.6°.

[10] The ether was distilled from lithium aluminum hydride immediately before use.

[11] The maximum rotation of the α-2-butoxystyrene was calculated based on the rotation of the 2-butanol used and its maximum rotation of 13.6°. The values thus obtained varied from run to run, and had a range of 37.7 to 54.0°.

[12] A. J. H. Housea and J. Kenyon, *J. Chem. Soc.*, 2260 (1930), reported the maximum rotation to be $[\alpha]^{19}\mathrm{D}$ 42.88°.

[13] Although the rearrangement of this ether gave the known β-phenylbutyrophenone in excellent yield, it was not possible to obtain a satisfactory analysis for this compound.

[14] Prepared by the procedure of J. B. Conant, C. N. Webb and W. C. Mendum, THIS JOURNAL, **51**, 1249 (1929).

[15] The 2-methyl-1-butanol was obtained by the distillation of fusel oil, and was kindly supplied by Dr. R. W. Young. The maximum reported rotation is $[\alpha]^{25}\mathrm{D}$ $-6.04°$ (F. C. Whitmore and J. H. Olewine, *ibid.*, **60**, 2569 (1938).

[16] The procedure of H. C. Brown and C. Groot, *ibid.*, **64**, 2563 (1942), was used. They reported $[\alpha]^{25}\mathrm{D}$ $+1.33°$, $n^{20}\mathrm{D}$ 1.4126 for the chloride obtained from less pure 2-methyl-1-butanol.

[17] A. I. Vogel, "Practical Organic Chemistry," 2nd ed., Longmans, London, 1951, p. 355.

[18] A rotation of $[\alpha]^{19}\mathrm{D}$ $+8.92°$ (l 2, neat) was reported by P. van Romburgh, *Rec. trav. chim.*, **5**, 222 (1886), for 3-methylpentanoic acid obtained by the oxidation of the hexyl alcohol from the essence of *Camomille romaine.*

[19] The method used by H. Stenzel and Fr. Fichter, *Helv. Chim. Acta*, **20**, 846 (1931), for the preparation of inactive β-methylvalerophenone was employed.

[20] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

[21] The hydrolysis procedure is that of W. F. McGuckin and E. C. Kendall, THIS JOURNAL, **74**, 5813 (1952).

[22] A. A. Pavlic and H. Adkins, *ibid.*, **68**, 1471 (1946).

[23] Reference 18 reported m.p. 179–180°.

tane, and then was distilled giving thirteen fractions. Fraction IV, 0.40 g., b.p. 106–107° at 13 mm., $[\alpha]^{25}\mathrm{D}$ −8.17° (*l* 1, neat), had the highest rotation. The infrared spectrum, by comparison with synthetic mixtures, showed this fraction to contain 70% IV, indicating $[\alpha]^{25}\mathrm{D}$ −11.7°, or 86% of the original rotation. The fractions were combined, and the β-methylvalerophenone was isolated and purified *via* the semicarbazone as described above. Distillation gave 0.5 g. of β-methylvalerophenone, b.p 124–126° at 13 mm., $n^{25}\mathrm{D}$ 1.5089, $[\alpha]^{25}$ +0.16° (*l* 1, neat). The infrared spectrum of this sample was identical with that of a synthetic mixture.

Another tube was prepared as described above, containing 6.4 g. of IV ($[\alpha]^{25}\mathrm{D}$ −13.56°, *l* 1, neat) and 0.5 g. of diphenylamine, and was heated at 205–215° for 80 minutes. Treatment similar to that described above gave 0.5 g. of β-methylvalerophenone, b.p. 123–125° at 14 mm., $[\alpha]^{25}\mathrm{D}$ +0.04° (*l* 1, neat).

A third tube was prepared as above, containing 2.62 g. of IV ($[\alpha]^{25}\mathrm{D}$ −40.00°, *l* 1, neat) and 0.22 g. of trinitrobenzene and was heated at 195–205° for 250 minutes. The above procedure was then used, giving 0.45 g. of β-methylvalerophenone, b.p. 110–117° at 10 mm., $[\alpha]^{25}\mathrm{D}$ 0.00° (*l* 1, neat).

Study of β-Methylvalerophenone under the Conditions of Rearrangement.—α-2-Butoxystyrene (1.37 g.), 1.37 g. of β-methylvalerophenone ($[\alpha]^{25}\mathrm{D}$ +17.50°, *l* 1, neat) and 0.05 g. of diphenylamine were put into a tube which was evacuated and sealed. The tube was heated for 155 minutes at 200°. The product was distilled giving 1.58 g. of β-methylvalerophenone, b.p. 129° at 14 mm., $[\alpha]^{25}\mathrm{D}$ +9.90° (*l* 1, neat), $n^{25}\mathrm{D}$ 1.5093.

Rearrangement of α-2-Butoxystyrene in the Presence of Chloroanil.—Chloranil (0.05 g.) and 3.05 g. of IV were introduced into a tube, and 2.95 g. of IV was introduced into another tube. The tubes were degassed and sealed. After heating for 57 minutes at 200–210°, the contents were separately distilled at 10 mm. under identical conditions. The tube containing chloranil gave 2.0 g., b.p. 88–121°, and 0.5 g. of residue; the other gave 2.2 g., b.p. 91–124°, and 0.35 g. of residue. The infrared spectra of both samples were taken, and the two spectra appeared nearly identical.

Initiation of the Rearrangement of Di-*t*-butyl Peroxide.—α-2-Butoxystyrene (10 g.) and 1.0 g. of di-*t*-butyl peroxide were introduced into a flask fitted with a total condensation, partial take-off head and a nitrogen supply. The flask was immersed in an oil-bath maintained at 125–135°. As a control, approximately 1 ml. of α-2-butoxystyrene was put in a test-tube, and then heated, under nitrogen, in the same oil-bath. Small aliquots were removed from both the control and reaction solutions at 2- to 3-hour intervals, and the infrared spectra were taken. The material which distilled from the reaction mixture was collected in a test-tube immersed in a Dry Ice–acetone-bath. The heating bath was removed after 10.5 hours. Figure 1 shows the catalytic effect of the peroxide. One ml. of distillate was obtained, and it was shown to be predominantly *t*-butyl alcohol by its infrared spectrum. The reaction mixture was distilled giving 5.5 g. of β-methylvalerophenone, b.p. 122–126° at 14 mm., $n^{25}\mathrm{D}$ 1.5085. A considerable amount of higher boiling residue was also obtained.

Rearrangement of α-Phenethoxystyrene.—α-Phenethoxystyrene (0.98 g., $[\alpha]^{25}\mathrm{D}$ +19.58°, *l* 0.5, neat) was heated in a sealed evacuated tube at 200° for 180 min. The tube was then cooled and the pale orange solid was recrystallized from 95% ethanol giving 0.95 g. of β-phenylbutyrophenone, $[\alpha]^{25}\mathrm{D}$ +0.01° (*l* 1, *c* 7.90, acetonitrile), m.p. 72.4–73.0°.[24]

Rearrangement of α-Neopentoxystyrene (IX).—α-Neopentoxystyrene (2.4 g.) was heated in a sealed evacuated tube at 230–240° for 420 min. A positive pressure was noted on opening the tube. The product was distilled giving 0.84 g. of material having b.p. 94° at 1 mm., $n^{25}\mathrm{D}$ 1.5057. The infrared spectrum of this material was identical with that of a synthetic sample of γ,γ-dimethylvalerophenone. The 2,4-dinitrophenylhydrazone had m.p. 203–205°, and a mixture of the dinitrophenylhydrazones of the rearranged and synthetic material had m.p. 203–204°.

The Rate of Rearrangement of α-2-Butoxystyrene in Heptane.—A solution of 2.89 g. of IV in heptane (total volume 50.0 ml., *c* 0.328 *M*) was prepared and portions of this solution were added to seven tubes which were evacuated and sealed. They were then heated at 178–179°, and tubes were withdrawn and the contents analyzed at regular intervals. The concentration of the ketone was determined from the infrared spectrum of the solution using a 0.05-mm. fixed cell. A straight line was obtained by plotting the logarithm of the ratio of the intensity of the 8.90 μ ether band to that of the 8.33 μ ketone band, against the composition of synthetic mixtures. The concentrations could thus be determined, and the results are shown in Fig. 2.

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[24] E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904), reported m.p. 74°.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY AND THE UNIVERSITY OF MARYLAND]

Cyclic Dienes. XIII. Substituted 1,2-Dimethylene-4-cyclohexenes[1,2]

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Through the pyrolysis of diacetates, 4-methyl-1,2-dimethylene-4-cyclohexene, which is isomeric with pseudocumene, was synthesized in an 89% yield, and 4,5-dimethyl-1,2-dimethylene-4-cyclohexene, which is isomeric with durene, was synthesized in a 77% yield. The structures of these trienes were proved by analysis, ultraviolet absorption and conversion to known derivatives by isomerization and intermediate Diels–Alder adducts.

The pyrolysis of esters has been used in these laboratories to produce in excellent yields and in high purity a series of strained dienes with double bonds exocyclic to five- and six-membered rings.[6–9] In order to determine more exactly the mildness of this synthetic procedure for introducing unsaturation by the pyrolysis of esters, the method was applied to the synthesis of 1,2-dimethylene-4-cyclohexene, which is isomeric with *o*-xylene. It was found that this highly strained triene could be prepared by the pyrolysis of a diacetate in a 92% yield that was completely free of *o*-xylene.[10] Since this synthesis indicated that this pyrolytic method was highly unusual, it was of interest to show that the procedure was general by preparing other isomers of aromatic compounds.

For this reason, the synthesis of 4,5-dimethyl-1,2-dimethylene-4-cyclohexene (I), which is isomeric

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[1] Previous paper in this series, THIS JOURNAL, **77**, 1043 (1955).

[2] Presented before the Washington Section of the American Chemical Society, College Park, Md., May, 1952.

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[6] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[7] W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 2251 (1954).

[8] W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 5421 (1954).

[9] W. J. Bailey and C. W. Liao, *ibid.*, **77**, 990 (1955).

[10] W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).