the collecting tubes were removed after hydrolysis. From this reaction 4.3 g. of *n*-hexane and approximately 0.08 mole of ethane were isolated.

Physical constants, yields and identification data for the ketones are shown in Table III.

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

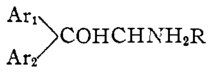
Rearrangement with Nitrous Acid of the Diastereoisomeric 1-*p*-Anisyl-1-phenyl-2-aminopropanols. The *cis* Effect of Methyl and Phenyl Groups[1]

BY DAVID Y. CURTIN[2] AND MALCOLM C. CREW

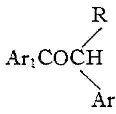
RECEIVED JULY 1, 1954

The rearrangement with nitrous acid of *erythro*- and *threo*-1-*p*-anisyl-1-phenyl-2-aminoethanol has been shown to give mixtures of the two possible ketones, *p*-anisyl α-phenylethyl ketone and phenyl α-*p*-anisylethyl ketone. Ultraviolet analysis was used to determine the relative amounts of the two products. The results have been interpreted in terms of a steric factor (the *cis* effect of the phenyl and methyl groups) and an electronic effect (the *p*-anisyl/phenyl migration ratio in the absence of the steric effect). The magnitudes of these quantities (11 and 1.5, respectively) are in agreement with values suggested by other work.

A number of racemic amino alcohols of the general type (A) have been shown to rearrange stereospecifically to the ketone (B) or (C) (when treated with nitrous acid) in such a way that the non-migrating aryl and R groups are *trans* to each other in the transition state.[3]

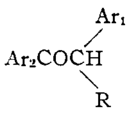


(A)



$\mathrm{Ar_1COCH(R)Ar_2}$

(B)



$\mathrm{Ar_2COCH(Ar_1)R}$

(C)

R = $\mathrm{C_6H_5, CH_3, C_6H_5CH_2-}$

In each of the rearrangements above, a single racemic ketone was isolated from the rearrangement of any racemate and since none of the isomeric ketone which might have been formed in small amount was found, no estimate of the magnitude of the steric effect could be made.

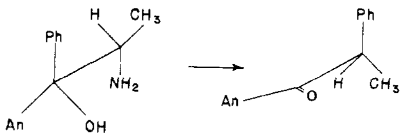
For this reason it was desired to carry out a careful study of the amounts of products obtained from such a rearrangement with the hope of estimating the magnitude of the steric effect.

dl-*erythro*- and *threo*-1-*p*-anisyl-1-phenyl-2-aminopropanol (*erythro*- and *threo*-I)[4] were chosen as suitable for this purpose.

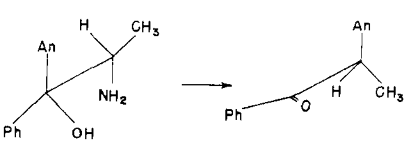
erythro-I was synthesized by the reaction previously employed by Tiffeneau, Levy and Ditz of α-aminopropiophenone hydrochloride with *p*-anisylmagnesium bromide[5] while *threo*-I was prepared by the reaction which had been carried out by the same workers of *p*-methoxy-α-aminopropiophenone hydrochloride with phenylmagnesium bromide.[5] The configurations are assigned by analogy with other such Grignard additions.[6]

The rearrangements of *erythro*- and *threo*-I were carried out at 0° in 50% glacial acetic acid to which was added aqueous sodium nitrite solution. The rearrangement of *erythro*-I was found to lead to *p*-anisyl α-phenylethyl ketone (II) (formed with phenyl migration) which could be isolated in a yield of 42% in agreement with the work of Tiffeneau, Levy and Ditz.[5] Rearrangement of *threo*-I gave phenyl α-*p*-anisylethyl ketone (III) (formed with *p*-anisyl migration) in a yield of 40%. The total neutral fraction from each rearrangement was subjected to ultraviolet analysis. Each amino alcohol (*erythro*- and *threo*-I) was then recrystallized four more times, rearranged and the products analyzed. The results of the ultraviolet analyses are given in Table I.

It is clear that the *erythro*-isomer rearranges with predominant phenyl migration and that the *threo*-



erythro-I II (+ III)



threo-I III (+ II)

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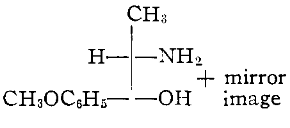
[1] From the Ph.D. Dissertation to be submitted to Columbia University by Malcolm C. Crew. Presented in part at the Thirteenth National Organic Chemistry Symposium of the American Chemical Society, Ann Arbor, Michigan, June, 1953.

[2] University of Illinois, Urbana, Illinois.

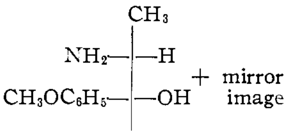
[3] (a) P. I. Pollak and D. Y. Curtin, THIS JOURNAL, **72**, 961 (1950); (b) D. Y. Curtin and P. I. Pollak, *ibid.*, **73**, 992 (1951); D. Y. Curtin, E. E. Harris and P. I. Pollak, *ibid.*, **73**, 992 (1951); (c) A. McKenzie and A. K. Mills, *Ber.*, **62**, 284 (1929); (d) A. McKenzie and A. D. Wood, *Ber.*, **71**, 358 (1938); (e) A. K. Mills, private communication to C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 507.

[4] The designations *erythro*- and *threo*-I will be used as shown below.



$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{H}- & | & -\mathrm{NH_2} \\ \mathrm{CH_3OC_6H_5}- & | & -\mathrm{OH} \\ & \mathrm{C_6H_5} & \end{array} + \text{mirror image}$$

erythro-I



$$\begin{array}{rcl} & \mathrm{CH_3} & \\ \mathrm{NH_2}- & | & -\mathrm{H} \\ \mathrm{CH_3OC_6H_5}- & | & -\mathrm{OH} \\ & \mathrm{C_6H_5} & \end{array} + \text{mirror image}$$

threo-I

[5] M. Tiffeneau, J. Levy and E. Ditz, *Bull. soc. chim.*, [5] **2**, 1848 (1935).

[6] (a) D. Y. Curtin, E. E. Harris and E. K. Meislich, THIS JOURNAL, **74**, 2901 (1952); (b) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952).

TABLE I

ANALYSIS OF THE NEUTRAL FRACTION FROM THE REARRANGEMENTS OF THE AMINO ALCOHOLS (*erythro*- AND *threo*-I)

Isomer rearranged	Phenyl migration (ketone II), %		p-Anisyl migration (ketone III), %	
	Original starting material	After further purification	Original starting material	After further purification
erythro-I	86.2 ± 0.7	88.0 ± 0.2	13.8 ± 0.3	12.0 ± 0.2
threo-I	8.6 ± 0.3	5.8 ± 0.3	91.4 ± 0.3	94.2 ± 0.3

isomer, on the other hand, rearranges with predominant p-anisyl migration as would be expected if the course of the reaction is primarily determined by steric factors.[3]

It can be seen that there is a detectable change in the product composition when repurified amino alcohol was employed. It is likely, then, that the Grignard reaction was not entirely stereospecific but that each amino alcohol I when initially rearranged contained about 3% of the diastereoisomeric racemate.

It is apparent that even the repurified amino alcohols gave mixtures on rearrangement and that the rearrangement of the *erythro*-isomer is less specific than that of the *threo*. While this could conceivably be explained by inhomogeneity of the starting materials, another explanation appears more likely. It will be noted that in the rearrangement of *threo*-I both steric and electronic influences favor migration of the p-anisyl group while in the rearrangement of the *erythro*-isomer the steric factor which favors phenyl migration is opposed by electronic effects favoring p-anisyl migration. If increments in the free energy of activation due to the steric and electronic effects are assumed to be additive, this situation can be described by the equations below where S is the ratio of p-anisyl to phenyl migration in the absence of electronic effects and E is the same ratio in the absence of steric effects.

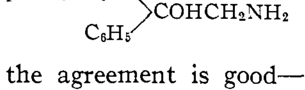
$$\text{For } erythro\text{-I } \frac{k_{\text{anisyl}}}{k_{\text{phenyl}}} = \frac{S}{E} = 7.33 \pm 0.14$$

$$\text{For } threo\text{-I } \frac{k_{\text{anisyl}}}{k_{\text{phenyl}}} = SE = 16.3 \pm 0.9$$

Solution of these two equations for S and E gives the following results.

$$S = 10.9 \pm 0.3$$
$$E = 1.49 \pm 0.04$$

A certain amount of reassurance that this is the correct interpretation is found in a comparison of the value of E above with the value of 1.5 obtained by Curtin and Crew[7] in a study of the rearrangement of 2-amino-1-p-anisyl-1-phenyl-ethanol (IV) for the p-anisyl/phenyl migration ratios. It is



$$\left.\begin{matrix} p\text{-CH}_3\text{OC}_6\text{H}_4 \\ \text{C}_6\text{H}_5 \end{matrix}\right\rangle \text{COHCH}_2\text{NH}_2 \quad \text{IV}$$

seen that the agreement is good—in fact better than might have been expected since the effect of substitution of a methyl group on the carbon containing the leaving group has been shown to have a considerable effect on the relative rates of the p-anisyl and phenyl analog in the solvolysis of certain arylsulfonate esters.[8]

The significance of S may now be considered. If the rate of rotation around the carbon–carbon single bonds of the diazonium ion from *erythro*-I, for example, is assumed to be very fast compared to rearrangement then it can be shown that the steric factor, S, is a function only of the difference in free energy between the two transition states for the rearrangement step and is independent of the relative populations of the conformations of the initial molecule.[9]

Such a free energy difference is probably not due alone to steric strain but is a composite effect which includes steric inhibition of resonance, di-

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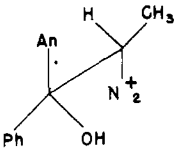
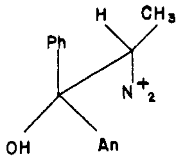
(7) D. Y. Curtin and M. C. Crew, THIS JOURNAL, **76**, 3719 (1954).

(8) See S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1141 (1952); S. Winstein, C. R. Lindegren, H. Marshall and L. I. Ingraham, *ibid.*, **75**, 147 (1953); W. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

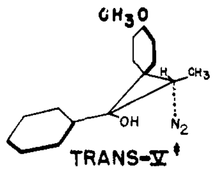
(9) This may be seen readily by an examination of the free energy diagram for the system as shown below.

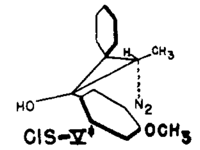


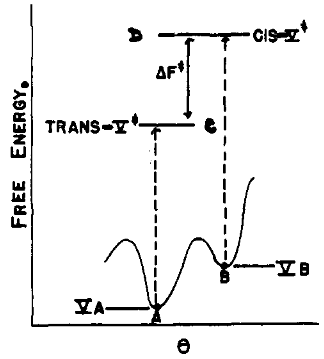
VA



V B







[Here V is regarded as an equilibrium mixture of the two species (Va and Vb) and the free energy is plotted against the angle of rotation. It is seen that a molecule Va (at point a on the diagram) can proceed directly to the transition state (*trans*-V‡) for p-X-C_6H_4 migration (with free energy indicated by line c) with activation free energy $\overline{ac}$ or can rotate to Vb (point b on the curve) and then proceed to the transition state *cis*-V‡ for phenyl migration (at line d). Since by the transition state theory the free energy change from a to d follows classical thermodynamics and is path independent, the difference in the free energy of activation (which determines the difference in rate) between the rearrangement with p-X-C_6H_4 migration and that with phenyl migration is the distance $\overline{cd}$. A similar argument with a molecule Vb shows that the difference between the rate of p-X-C_6H_4 migration and that of C_6H_5 migration is again the distance $\overline{cd}$. It follows then that molecules with conformation Vb rearrange with the same p-XC_6H_4/C_6H_5 ratio as molecules Va, and that the migration ratio is determined only by the difference between free energies of the *cis*- and *trans*- transition states.[10]]

(10) We are indebted to Professor L. P. Hammett, who pointed out this conclusion in 1950.

pole–dipole interactions and entropy differences resulting from unequal restriction of vibrational and rotational motions in passing to the two transition states. Because of the difficulties in separating these factors experimentally, they have been grouped together and their combined effect (which is to destabilize the *cis*-transition state with respect to the *trans*) is called the "*cis* effect."[11]

It is of interest to make a comparison of the *cis* effect obtained in the present case with other related examples. Although the preparation of *cis*- and *trans*-propenylbenzene recently has been reported,[12] no measurement of the free energy difference appears to have been made.

If it be assumed that the effects on the free energy of an olefin of two substituents attached to the same carbon are additive, the free energy difference between *cis*- and *trans*-propenylbenzene may be estimated to be equal to the sum of the free energy differences of the α-methylpropenylbenzenes (found by Cram[13] to be about 0.52 kcal./mole at 100°) and the 2-butenes (shown by extrapolation of the data of Voge and May[14] to be about 0.52 kcal./mole at 100°) or about 1 kcal./mole.[15] This value agrees as well as could be expected with the value of 1.4 kcal. calculated from $\bar{S}$ for the difference between the transition states (A) and (B) in the present work.

These values are rather smaller than the 70-fold difference in rates of rearrangement of N-benzoylephedrine and N-benzoyl-ψ-ephedrine would suggest.[16] Aside from the obvious difficulties of comparing *cis* effects of such dissimilar pairs of transition states, it should be noted that the free energy difference indicated by the factor of 70 includes not only the difference in the transition states but the difference in initial states, that is, the difference in free energy between N-benzoylephedrine and N-benzoyl-ψ-ephedrine in the reaction medium.

Experimental[17]

***dl-erythro*-1-*p*-Anisyl-1-phenyl-2-aminopropanol** (*erythro*-I) was prepared by the method of Tiffeneau, Levy and Ditz[5] by the action of *p*-anisylmagnesium bromide (from 150 g., 0.804 mole, of *p*-bromoanisole) on α-aminopropiophenone hydrochloride (25 g., 0.13 mole) in ether. After the addition was complete the mixture was refluxed for 5 hours and decomposed with a slightly alkaline mixture of ice, ammonium chloride and ammonium hydroxide. The amino alcohol was extracted with ether and the dried solution treated with dry hydrogen chloride which precipitated the hydrochloride salt of *erythro*-I. The crude salt was recrystallized from absolute ethanol to yield 19.5 g. (50% yield) of crystals, m.p. 247–248° dec. The reported m.p.[5] is 265°.

The free base was recovered from the hydrochloride by dropwise treatment of an aqueous solution with 10% sodium hydroxide until no further precipitation was observed. The *erythro*-I, obtained in 92% yield from the hydrochloride, melted at 86–86.5° (reported[5] m.p. 90°). This sample was used for the first nitrous acid rearrangement.

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.7; H, 7.4; N, 5.4. Found: C, 74.9; H, 7.5; N, 5.4.

α-Amino-*p*-methoxypropiophenone hydrochloride was prepared by the reduction with the hydrogen (50 p.s.i.) catalyzed with palladinized charcoal[18] of α-oximino-*p*-methoxypropiophenone.[19] The yield was 75% of amine hydrochloride, m.p. 225–226^c (reported[20] m.p. 226°).

***threo*-1-*p*-Anisyl-1-phenyl-2-aminopropanol** (*threo*-I) was prepared by the same procedure used for the *erythro*-isomer above except that the time of heating was 90 minutes. The yield was 20% of amine hydrochloride, m.p. 235.5–236° (reported[5] 255°).

The hydrochloride was converted to the free base by dropwise addition of a 10% solution of sodium hydroxide to an aqueous solution. The yield of *threo*-I, m.p. 83–83.5°, was 18% base on the amino ketone hydrochloride. The reported m.p. was 84°.[5]

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.7; H, 7.4; N, 5.4. Found: C, 74.8; H, 7.2; N, 5.3.

Admixture with *erythro*-I above depressed the m.p.

***p*-Anisyl α-phenylethyl ketone (II)** was prepared by the method of Bruzau[20] from hydratropic acid chloride, anisole and aluminum chloride. After four recrystallizations from hexane it melted at 53.5--55° (reported[20] m.p. 58–60°).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 80.2; H, 6.6.

The 2,4-dinitrophenylhydrazine of II melted at 71–75°.

Anal. Calcd. for $C_{22}H_{20}N_4O_5$: C, 62.9; H, 4.8; N, 13.3. Found: C, 63.1, 63.2; H, 4.9, 4.8; N, 13.6, 13.4.

Phenyl α-*p*-Anisylethyl Ketone (III).—To a solution of 2.4 g. (0.104 mole) of metallic sodium in 100 ml. of absolute ethanol was added 23.6 g. (0.104 mole) of solid phenyl *p*-methoxybenzyl ketone.[21] The mixture was heated with stirring until the solid dissolved and then 71 g. (0.50 mole) of methyl iodide was added slowly. The solution was then heated under reflux for one-half hour and allowed to stand overnight. Evaporation of solvent, addition of water and extraction of the product with ether gave, after evaporation of the ether, an oil which was purified by precipitation of part of the unreacted phenyl *p*-methoxybenzyl ketone from methanol and distillation of the remaining oil. A yield of 9.4 g. (44%) of III, m.p. 50–58°, was observed. The m.p. after repeated recrystallization from hexane was 58–59.5°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 80.0; H, 6.4.

The 2,4-dinitrophenylhydrazone melted at 151–152°.

Anal. Calcd. for $C_{22}H_{20}O_6N_4$: C, 62.9; H, 4.8; N, 13.3. Found: C, 63.6, 63.5, 63.2, 63.0; H, 4.8, 4.7, 5.0, 4.7; N, 13.4, 13.2, 13.3.

Rearrangement of *erythro*-I.—A solution of 1.00 g. (3.9×10^{-3} mole) of the amino alcohol (*erythro*-I) in 70 ml. of 50% acetic acid at 0° was treated dropwise with 0.85 g. (12.3×10^{-3} mole) of sodium nitrite in 5 ml. of water. The mixture was stirred for 38 hours at 1–2°. Excess nitrous acid was decomposed with 10% aqueous sulfamic acid (starch–potassium iodide test negative). The solution was then diluted with 75 ml. of water and extracted with 150 ml. of ether. Removal of the ether after drying with sodium carbonate gave 0.816 g. (87%) of an oil part of which was dissolved in 95% ethanol and diluted to a concentration of 20.4 mg./l. This solution was used for ultraviolet analysis described below. The remaining oil when triturated with hot pentane crystallized and the solid obtained, after recrystallization from benzene–hexane, yielded 0.27 g. of the ketone II, m.p. and mixed m.p. with authentic material 54–54°. None of the isomeric ketone III was isolated.

The amino alcohol (*erythro*-I) after four more recrystallizations from hexane melted at 86–87° and was submitted to rearrangement with nitrous acid as described above.

Rearrangement of *threo*-I.—The rearrangement of *threo*-I carried out as above gave an 85% yield of an oil part of which

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(11) D. Y. Curtin, Abstracts of the Thirteenth National Organic Chemistry Symposium of the American Chemical Society, Ann Arbor, Michigan, June, 1953, p. 40; *Record Chem. Progress* (*Kresge-Hooker Sci. Lib.*), **15**, 111 (1954).

(12) R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, THIS JOURNAL, **75**, 4094 (1953).

(13) D. J. Cram, *ibid.*, **71**, 3883 (1949).

(14) H. H. Voge and N. C. May, *ibid.*, **68**, 550 (1946).

(15) The correction from 100 to 0° is negligible even if ΔH is as high as 3 kcal. per mole.

(16) L. H. Welsh, THIS JOURNAL, **71**, 3500 (1949).

(17) All melting points are corrected unless otherwise indicated. Analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Middle Village, New York.

(18) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 989.

(19) W. H. Hartung, J. C. Munch, E. Miller and F. S. Crossley, THIS JOURNAL, **53**, 4149 (1931).

(20) Mme. Bruzau, *Ann. chim.*, [11] 1, 257 (1934).

(21) S. Teich and D. Y. Curtin, THIS JOURNAL, **72**, 2481 (1950).

was diluted with ethanol as before and submitted to ultraviolet analysis. Trituration of the oil with pentane and recrystallization from aqueous methanol and hexane–benzene yielded 0.32 g. of the ketone III, m.p. and mixed m.p. 58–59°.

A second rearrangement was carried out as above with amino alcohol, m.p. 84.5–85°, which had been recrystallized four more times from hexane–benzene. Again the neutral fraction was analyzed as described below.

Ultraviolet Analyses.—The quantitative results were obtained with a Beckman DU spectrophotometer. Determination of the extinction coefficients of solutions of known concentrations of ketones II and III (between 15 and 30 mg./l.) showed that Beer's law holds in this region. The extinction coefficients of the unknown mixtures measured at four wave lengths together with the corresponding extinction coefficients of the authentic ketones (II and III) were used to set up four pairs of simultaneous equations which were solved for the concentrations of II and III. Weights were assigned to the values so obtained[22] and the weighted averages together with the calculated probable errors are shown in Table I.

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[22] H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, p. 487 ff.

URBANA, ILLINOIS

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

Pyrolysis of Esters. II. Direction of Elimination in Pyrolysis of Tertiary Esters[1,2]

BY WILLIAM J. BAILEY,[3] JOHN J. HEWITT[4] AND CHARLES KING[5]

RECEIVED APRIL 29, 1954

Pyrolysis of three tertiary esters, *t*-amyl acetate, dimethylisopropylcarbinyl acetate, and 1-methylcyclohexyl acetate, produced only the least highly alkylated olefin. A method is outlined for the isomerization of an internal double bond to the terminal position.

We have shown[1] that in the pyrolysis of esters of secondary alcohols the elimination follows the Hofmann rule, which predicts the formation of the least highly alkylated olefin. The pyrolysis of simple alkyl esters, however, in contrast to other elimination reactions, does not give a mixture of products but appears to produce only a single olefin. Thus, the only product isolated from the pyrolysis of methylisopropylcarbinyl acetate was 3-methyl-1-butene.

The esters previously studied, however, were all derived from secondary alcohols. In order to show that this selectivity is general, several tertiary esters were pyrolyzed. Pyrolysis conditions were again selected so that much less than 100% of the acetic acid was eliminated in order to make sure that no carbonization that could cause isomerization took place. It was previously shown[6] that carbonization in the pyrolysis tube would cause isomerization of double bonds but that, if carbonization was avoided, the pyrolysis of esters could be used to synthesize 1,2-dimethylene-4-cyclohexene, an isomer of *o*-xylene. These mild conditions also appeared to produce the maximum selectivity in the direction of elimination. Pyrolysis of dimethylisopropylcarbinyl acetate (I), where the choice is between a primary and a tertiary hydrogen, produced only 2,3-dimethyl-1-butene (II). Since the properties of 2,3-dimethyl-2-butene differ markedly from those of II, it is certain that the product of this pyrolysis was at least 98% pure. The pyrolysis of *t*-amyl acetate (III), in which the competition of abstraction is between primary and secondary hydrogens, yielded only 2-methyl-1-butene (IV). Because of the moderate difference in physical properties of IV and 2-methyl-2-butene (V) and the limit of accuracy of the method used to determine the purity, it can only be said that the IV obtained by pyrolysis was at least 95% pure. In accordance with the observation of Rehberg and Fisher,[7] these tertiary esters decompose at a temperature at least 50° lower than the isomeric secondary esters.

In an effort to determine the strength of the driving force to produce only the least highly alkylated olefin, a case was found where the predicted olefin would be slightly strained. It has been shown that a double bond is more stable endocyclic to a cyclohexane than exocyclic to it.[8] It appeared that derivatives of the tertiary alcohol, 1-methylcyclohexanol (VI), would provide a suitable test. Mosher[9] had shown that dehydration of VI with iodine produced only 1-methylcyclohexene, and the fact that no formaldehyde was obtained on ozonolysis indicated the absence of any methylenecyclohexene (IX). The tertiary alcohol VI, which was prepared from cyclohexanone and methylmagnesium iodide, was acetylated with acetic anhydride and magnesium to produce 1-methylcyclohexyl acetate (VIII). Pyrolysis of VIII at 450° produced only the methylenecyclohexane (IX). Since the properties of the isomeric VII are moderately close to those of IX, the purity of IX was proved by independent synthesis. Cyclohexanecarboxylic acid (X) was reduced with lithium aluminum hydride to produce hexahydrobenzyl alcohol (XI), which was acetylated to give hexahydrobenzyl acetate (XII). Pyrolysis of XII at 530° produced pure IX. The infrared absorption spectrum of this methylenecyclohexane

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[1] Previous paper in this series, THIS JOURNAL, **77**, 75 (1955).

[2] Presented in part before the Division of Organic Chemistry at the 120th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

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[6] W. J. Bailey, J. Rosenberg and L. H. Young, THIS JOURNAL, **76**, 2251 (1954); W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

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