solid product was filtered off and washed free of alkali; yield: 1.4 g. crude. Two recrystallizations from ethanol gave 0.75 g., m.p. 190–190.5°. The liquors were evaporated to dryness, the residue was dissolved in hexane and run through a column of alumina to give, first, 0.11 g. of a compound not yet identified, m.p. 57–58°, and then 0.32 g., m.p. 189–90°. The total yield of XII was 1.07 g. (68%); mol. wt. (Rast), 396 (calcd. 382).

Anal. Calcd. for $C_{23}H_{30}O$ (382.52): C, 87.91; H, 7.91. Found: C, 86.72; H, 7.89.

Ultraviolet spectrum in ethanol: λ_{max} mμ (log ε): 228 (5.11), 233 (5.13), 283 sh (4.08), 292 (4.16), 301 sh (4.06). Infrared absorption shows a broad band at 1000–1100 cm.$^{-1}$ indicating the —C—O—C— group. N.m.r.: 143, 148, and 157 c.p.s. due to six methyl groups; 307 c.p.s. (two CH_2 groups); 436–490 c.p.s. (eight aromatic hydrogen atoms).

3,4-Diethyl-2,5-hexanedione (XIII).—A 400-g. sample (4.64 moles) of 2-pentanone and lead dioxide, 530 g. (2.22 moles), were heated together at reflux temperature for 27 hr. The lead oxide was removed by filtration and washed with ether. The filtrate and washings were dried over calcium chloride and distilled to give 10 g. of recovered pentanone and then 50.7 g. (13.4%) of XIII, b.p. 112–115°/20 mm., n^{20}_D 1.446.

Anal. Calcd. for $C_{10}H_{18}O_2$ (170.24): C, 70.57; H, 10.55. Found: C, 72.18; H, 10.81.

2,5-Dimethyl-3,4-diethylfuran (XIV).—A 93.0-g. sample (0.546 mole) of XIII, 70 g. (0.69 mole) of acetic anhydride, and 7.0 g. of anhydrous zinc chloride were warmed together slowly until an exothermic reaction began. The reaction was moderated by cooling with water, and finally the mixture was heated at reflux temperature for 3 hr. (A shorter time may be desirable, since charring seemed to increase with time.) After making alkaline by addition of 50 ml. of 40% sodium hydroxide, the furan was distilled with steam. The layers in the distillate were separated, the aqueous layer was extracted with ether and the extract added to the crude furan layer. After drying over calcium chloride, vacuum distillation gave 40.2 g. (48.5%) of XIV, b.p. 67–69°/17 mm., n^{20}_D 1.458.

Anal. Calcd. for $C_{10}H_{16}O$ (152.23): C, 78.89; H, 10.60. Found: C, 77.93; H, 10.48.

1,4-Dimethyl-2,3-diethyl-1,4-epoxy-1,4-dihydronaphthalene (XV).—Using method B described above for the preparation of VIII, 36.4 g. of XIV gave 26.2 g. (57.5%) of XV, b.p. 152–154°/18 mm. Recrystallization from hexane gave 22.5 g. (49.4%) of XV, m.p. 50–52°. Another recrystallization gave m.p. 51.6–52.3°.

Anal. Calcd. for $C_{16}H_{20}O$ (228.32): C, 84.20; H, 8.76. Found: C, 84.16; H, 8.76.

Ultraviolet spectrum in ethanol: λ_{max} mμ (log ε): 250 (2.89), 265 (2.92), 272.5 (3.00), 280 (2.92). Infrared absorptions at 1250–1300 (—C—O—C—) and 680–880 cm.$^{-1}$ (Ar C—H deformation).

1-Chloromethyl)-4-methyl-2,3-diethylnaphthalene (XVI).—Dry hydrogen chloride was passed into a solution of 2.08 g. (8.76 mmoles) of XV in 30 ml. dry methanol. After 20 min. the solution, now dark in color, was refrigerated, the crystals were filtered off and washed with cold methanol; yield: 1.8 g. (84.5%). Recrystallization from hexane gave 1.2 g. (56.4%) of pure XVI, m.p. 72.5–73°.

Anal. Calcd. for $C_{16}H_{19}Cl$: Cl, 14.32. Found: Cl, 13.85.

Ultraviolet spectrum in ethanol: λ_{max} mμ (log ε): 230 sh (4.80), 235.5 (4.98), 293 (3.86), 329 sh (2.87).

Acknowledgment.—We thank the American Chemical Society for the Petroleum Research Fund Grant, No. 1032-B5, which supported this research.

Catalytic Hydrogenation of α,β-Unsaturated Ketones. III. The Effect of Quantity and Type of Catalysts[1,2]

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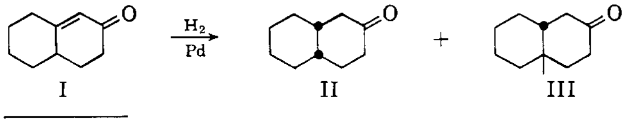
Received July 12, 1962

The relative amounts of *cis*- and *trans*-β-decalone obtained on hydrogenation of Δ^{1,9}-octalone-2 using varying amounts of 10% palladium–charcoal catalyst has been determined in acidic, basic, and neutral media. In all cases, a sharp change in the per cent of *cis* isomer formed was observed at a palladium–substrate ratio of 1:100. This corresponded to the point of inflection of the rate *vs.* quantity of catalyst curve. The effect of platinum and rhodium as catalysts was also determined.

In line with other work on the hydrogenation of α,β-unsaturated ketones,[1] it was considered important to study the effect of the quantity of catalyst on the stereospecificity of the reaction. To do this a series of hydrogenations of Δ^{1,9}-octalone-2 (I) using a wide variety of catalyst–substrate ratios were run. The amounts of *cis*-β-decalone (II) obtained in acidic, basic and neutral medium hydrogenations using different weights of 10% palladium on charcoal to hydrogenate 250 milligrams of I are shown in Fig. 1. It is of interest to note that the stereospecificity in acid medium shows a maximum at a palladium–octalone ratio of 1:100 while in neutral and basic media a minimum in the percent of II obtained occurs at the same point.



I II III

Fig. 2 shows the per cent of II obtained using fifty milligrams each of different percentages of palladium on charcoal in the hydrogenation of I. The results shown here are not so clear as those in Fig. 1. Young and Hartung have stated that varying the metal to carrier ratio of palladium-on-charcoal catalysts can also vary the number of palladium atoms in a given cluster, the spacing between these clusters and, possibly, even the crystalline lattice structure of the metal as well.[3] It is possible, then, that the activity of the catalyst as well as its stereospecificity could be effected by changing any of these variables. In the case where the weight of catalyst was varied the metal to carrier ratio remained constant and the above mentioned variables were eliminated. The following discussion will concern itself only with this latter type of system.

The rates of the various reactions are shown in Fig. 3. These rates represent the volume of hydrogen taken up in the time between five and fifteen minutes after the initiation of the reaction keeping the hydrogen pressure and the stirring rate constant. The re-

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(1) Part II in this series; R. L. Augustine and A. D. Broom, *J. Org. Chem.*, **25**, 802 (1960).

(2) Support for this work by the National Institutes of Health through Research Grant RG9696 from the Division of General Medical Sciences, U. S. Public Health Service, is gratefully acknowledged.

(3) J. G. Young and W. H. Hartung, *J. Org. Chem.*, **18**, 1659 (1953).

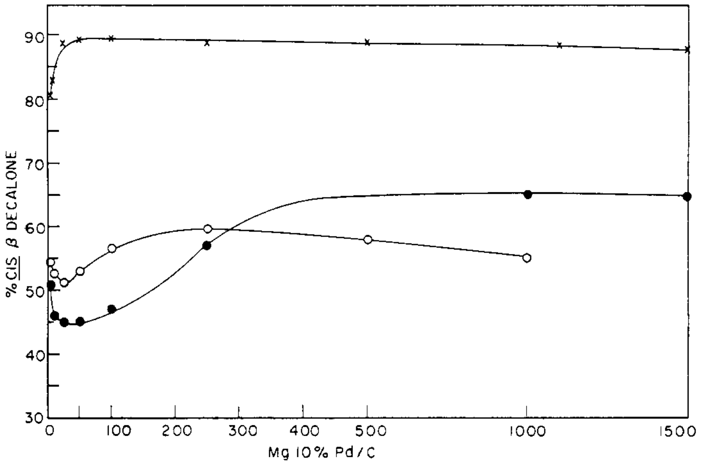


Fig. 1.—Per cent of *cis*-β-decalone formed on hydrogenation of 250 mg. of $\Delta^{1,9}$ octalone-2 with varying weights of 10% palladium-charcoal as the catalyst.

x Acidic medium
○ Basic medium
● Neutral medium

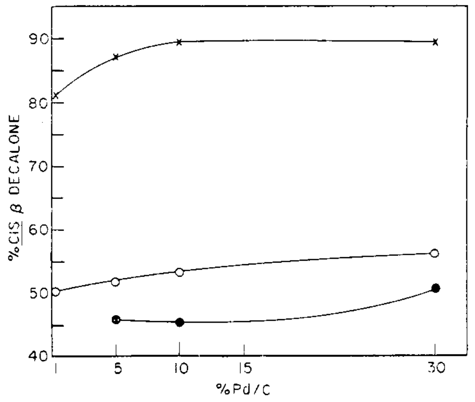


Fig. 2.—Per cent of *cis*-β-decalone formed on hydrogenation of 250 mg. of $\Delta^{1,9}$-octalone-2 with 50 mg. of varying percentages of palladium-charcoal as the catalyst.

x Acidic medium
○ Basic medium
● Neutral medium

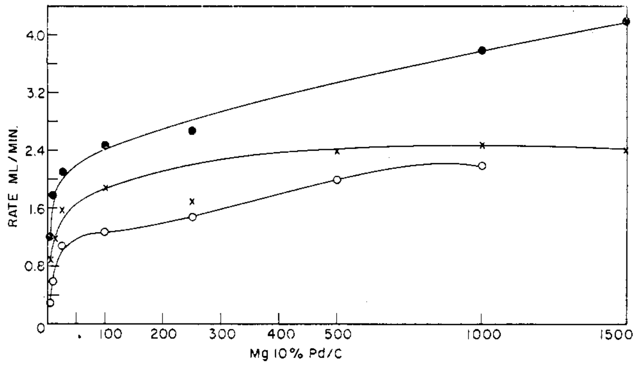


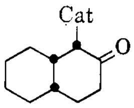
Fig. 3.—Rate of hydrogen uptake on hydrogenation of 250 mg. of $\Delta^{1,9}$-octalone-2 with varying weights of 10% palladium-charcoal as the catalyst.

x Acidic medium
○ Basic medium
● Neutral medium

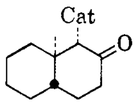
actions were run at room temperature which was 20° ± 2° over the entire sequence of reactions. Even though these measurements were crude, they give approximately the same shape curve as that reported by Watt[4] for the hydrogenation of allyl alcohol using varying quantities of palladium. He reports a transition in the curve corresponding to 20 mg. of palladium catalyst with 1 ml. of allyl alcohol in 11 ml. of neutral solution. Csuros[5] and Erdey-Grúz and Szabó[6] also mention a dependency of the rate of hydrogenation on the quantity of palladium catalyst used. They observed, however, both a minimum and a maximum in the velocity–quantity of catalyst curve. The position of these minima and maxima were particular to the compound being hydrogenated. No such curves corresponding to hydrogenation in acidic or basic medium could be found in the literature. It should be noted that in all three rate curves, the point of transition corresponds to the point of maximum or minimum formation *cis*-β-decalane as shown in Fig. 1.

From examination of the neutral curves of Fig. 1 and Fig. 3, it appears that the hydrogen availability to the catalyst surface is the primary factor involved, particularly in those instances above the inflection point. This concept was proven by Watt[4] and used recently by House to explain similar data.[7]

Examination of molecular models of I shows that the difference between the steric hindrance to *cis* and *trans* adsorption is very slight with the *trans* adsorption being somewhat more favored. Thus, one can say that as the amount of catalyst increases above the inflection point, the amount of hydrogen available is spread over a larger surface area of catalyst, decreasing the probability of interaction with I. This permits equilibration between the *cis* and *trans* half-hydrogenated states (IV and V)[8] or the *cis* and *trans* adsorbed octalone thus resulting in decreased stereospecificity of the reaction. This same concept can be used to explain the increase in selectivity with decrease in amount of catalyst in the hydrogenation of substituted isopropylidenebicycloheptenes reported by DePuy and Story.[9]



IV



V

At very low catalyst ratios hydrogen diffusion is no longer the limiting factor, but, instead, the actual surface area of the catalyst. Thus, one may ascribe the effect observed to a lessening of the number of "active sites" available for reaction between the substrate and the hydrogen, both of which are in plentiful supply to the catalyst. It is possible then that the change in stereospecificity observed could be due to a crowding of substrate molecules on the catalyst surface combined with a rapid reaction which does not allow for any desorption of the substrate before hydrogenation takes place.

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(4) G. W. Watt and M. T. Walling, Jr., *J. Phys. Chem.*, **59**, 7 (1955).

(5) Z. Csuros, *Chem. Abstr.*, **42**, 3726 (1948).

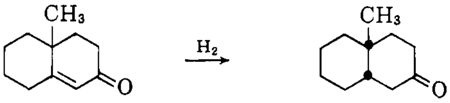
(6) T. Erdey-Grúz and J. Szabó, *ibid.*, **45**, 10009 (1951).

(7) H. O. House, R. G. Carlson, J. Muller, A. W. Noltes, and C. D. Slater, *J. Am. Chem. Soc.*, **84**, 2614 (1962).

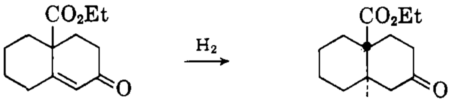
(8) J. F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **83**, 3874 (1961).

(9) C. H. DePuy and P. R. Story, *ibid.*, **82**, 627 (1960).

These results point out a discrepancy reported in the interpretation of the hydrogenation data given for the 10-substituted β-octalones. Hydrogenation of 10-methyl-$\Delta^{1,9}$-octalone-2 (VI) reportedly gives the *cis*-decalone,[10] whereas the 10-carbethoxy compound (VII) yields the *trans* compound.[11] McQuillan[12] has explained this by stating that the large size of the carbethoxy group hinders that adsorption on the catalyst surface which would lead to the formation of the *cis* isomer, but the smaller methyl group does not hinder this adsorption as much, thereby permitting the *cis* isomer to be formed. If this were the case, the even smaller 10-hydrogen of I would offer even less hindrance resulting in the formation of exclusively *cis*-β-decalone. The present data repudiates this as does the examination of molecular models mentioned earlier in which it appears that *trans* adsorption is somewhat more favored for I. The hydrogenations of the 10-substituted octalones is currently being re-examined in this laboratory.



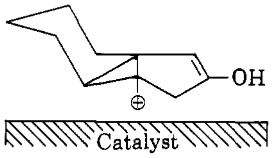
VI



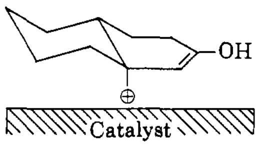
VII

It was considered possible that the change in the amount of the *cis* isomer formed using increasing quantities of catalyst could have been due to a preferential strong adsorption of the *trans*-β-decalone on the catalyst thereby removing some of this material from the reaction mixture when the catalyst was filtered. This consideration was dismissed by treating the catalysts from two duplicate runs in different ways. In one run, the catalyst was filtered, washed with a small amount of acetone, and the filtrate worked up as described in the Experimental. In the second run, the catalyst, after filtration, was refluxed with acetone, filtered, and the acetone added to the original filtrate which was then worked up as usual. The per cent of *cis*-β-decalone obtained in each run was the same.

In acid medium the situation is much the same as that in neutral medium providing one introduces the concept of hydride ion transfer from the catalyst surface to an initially formed carbonium ion adsorbed stereospecifically on the catalyst surface to account for the preponderance of *cis*-β-decalone formed.[13] At low catalyst quantities every adsorption of the carbonium ion on the "active sites" of the catalyst results in an immediate hydride ion transfer. This rapid reaction would not allow for any equilibration between the *cis* and *trans* adsorbed ions (VIII and IX) and would be, effectively, a kinetic controlled process. Above the inflection point, the quantity of hydrogen available has decreased sufficiently to permit equilibration between the two ions to occur before hydride ion transfer is accomplished.



VIII



IX

The data for hydrogenation in basic medium approximates that obtained in neutral medium except for the presence of a maximum as well as a minimum in the % *cis*-β-decalone curve but not in the rate curve. Two theories have been put forth concerning the effect of base on catalytic hydrogenation. It has been suggested, on one hand, that base modifies the adsorption characteristics of the catalyst.[14] On the other hand, the hydrogenation of α,β-unsaturated ketones in basic medium has been presumed to proceed through the initial formation of the enolate anion which is subsequently hydrogenated.[15] Since the quantity of base remained constant in the present instance, it could spread out more over the large quantities of catalyst affecting changes such as enolization in varying degrees.

The percentages of *cis*-β-decalone formed on the hydrogenation of I using various other catalysts and conditions are listed in Table I. The rates of hydrogenation of α,β-unsaturated ketones using a variety of catalysts and conditions have been published by Rylander,[16] but, while the stereochemistry of many products formed using platinum as the hydrogenation catalyst is known, similar data using rhodium has not been reported.

Examination of Table I shows that the use of platinum as catalyst has the same effects in acidic, basic, and neutral medium as does palladium but the differences are less pronounced. The use of acetic acid as the solvent gives less of the *cis* isomer than the use of ethanol, but the addition of hydrogen chloride to the acetic acid gives more of an increase in the formation of this compound. It can therefore be assumed that the same mechanism is operative with platinum as with palladium.

TABLE I

Catalyst	Solvent	*cis*-β-Decalone, %
PtO_2	Ethanol	62.7
PtO_2	Ethanol–acid	77.5
PtO_2	Ethanol–base	58.1
PtO_2	HOAc	55.8
PtO_2	HOAc–HCl	84.8
5% Rh/C	Ethanol	69.6
5% Rh/C	Ethanol–acid	86.9
5% Rh/C	Ethanol–base	82.5
2% Pd/$SrCO_3$	Ethanol	32.8

The gas–liquid chromatograph of the product mixture obtained in the hydrogenation of I in an acetic acid–hydrochloric acid solvent using a platinum catalyst shows the presence of small amounts of the *cis*- and *trans*-decalins and the *cis*- and *trans*-β-decalols in about the same ratio as the *cis*- and *trans*-β-decalones present. This indicates that the reaction occurs stepwise with saturation of the double bond occuring

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[10] W. G. Dauben, J. B. Rogan, and E. J. Blanz, Jr., *J. Am. Chem. Soc.*, **76**, 6384 (1954).

[11] W. G. Dauben, R. C. Tweit, and R. L. MacLean, *ibid.*, **77**, 48 (1955).

[12] F. J. McQuillan and W. O. Ord, *J. Chem. Soc.*, 2902 (1959).

[13] R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958).

[14] G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947).

[15] A. L. Wilds, J. A. Johnson, Jr., and R. E. Sutton, *ibid.*, **72**, 5524 (1950).

[16] E. Breitner, E. Roginski, and P. N. Rylander, *J. Org. Chem.*, **24**, 1855 (1959).

first followed by the hydrogenation of the carbonyl group and hydrogenolysis of the resulting alcohol. This was shown to be the case in the hydrogenations reported by Rylander.[16] In all of the hydrogenations run here, this was the only instance of alcohol or hydrocarbon formation noted.

Use of rhodium on charcoal as the catalyst showed an increase in the % of the *cis* isomer formed on going from neutral to acidic medium but the effect is even less pronounced than that in the case of platinum. In basic medium, though, the effect is considerably different from that with palladium or platinum. Hernandez and Nord[17] have shown evidence, however, to the effect that rhodium hydrogenates by a different mechanism than does palladium. However, Yao and Emmett,[18] after reinvestigation of the work, state that the differences observed were better interpreted by difference in the activity of the palladium and rhodium catalysts used. This difference could also conceivably account for the change in stereospecificity observed here.

Apology should be made at this time for two typographical errors which appeared in the first paper of this series.[13] In Table I of that article the data for the % of *cis* and *trans* isomers formed using 2% palladium–strontium carbonate as the catalyst should be reversed and the solvent used with the 30% palladium–charcoal should have read ethanol–aqueous hydrochloric acid. Other differences between the data recorded in this table and Table I of the current article can be attributed to a difference in concentration of I, a different catalyst to substrate ratio, and a considerably more efficient separation of the isomers in the analysis procedure in the present instance.

Experimental

Apparatus.—The hydrogenations were carried out in an atmospheric pressure hydrogenator which was, effectively, a manifold to which wasat tached a gas buret filled with mercury connected to a leveling bulb, an 80-cm. mercury U-tube manometer, a small U-tube manometer filled with water and capable of being isolated from the rest of the system by means of a stopcock, a 100-ml. round-bottomed reaction flask stirred by means of a magnetic stirrer, and a three-way stopcock leading to an aspirator and a hydrogen cylinder.

The catalysts used were obtained from Engelhard Industries, Newark, New Jersey.

Rates of Hydrogenation.—The rates of hydrogenation were determined by measuring the amount of hydrogen taken up in the time interval between 5 and 15 min. after the reaction was started. The hydrogen pressure was kept constant at atmospheric pressure by raising the level of the mercury at a rate equal to that of hydrogen absorption by observing the relative heights of the water in the two arms of the water manometer during the operation. The rate of stirring the reaction mixture was kept constant throughout all of the runs. The temperature was 20° ± 2° for all determinations.

$\Delta^{1,9}$-Octalone-2.—A solution of 100 g. of cyclohexanone and 100 g. of morpholine in 1 l. of benzene was refluxed overnight with the water formed collected in a Dean–Stark water separator. After the water was entirely removed the solvent was evaporated and the residue distilled giving 198.5 g. (1.2 moles) of 1-morpholinocyclohexene, b.p. 123–127° (12 mm.). To a solution of this enamine in 1 l. of pure dioxane was added slowly 85.5 g. (1.2 moles) of freshly distilled methyl vinyl ketone and the resulting solution stirred at room temperature for 1 hr. and refluxed for 4 hr., after which time 1 l. of water was added and refluxing continued for an additional 10 hr. The solution was cooled, poured into an additional 1.5 l. of water and extracted with four 500-ml. portions of ether. The ether extracts were washed with 3 N hydrochloric acid, saturated aqueous sodium bicarbonate, water, and saturated sodium chloride solution and dried over magnesium sulfate. The solution was filtered, the ether removed, and the residue distilled giving 114.0 g. of $\Delta^{1,9}$-octalone-2 (I), b.p. 140–145° (1.2 mm.). This was shown by g.l.c. analysis to be an 85:15 $\alpha,\beta:\beta,\gamma$ unsaturation mixture[19]. After three recrystallizations at −80° from 700 ml. of petroleum ether (b.p. 60–110°) a mixture which contained about 3% of the β,γ unsaturated isomer, $\Delta^{9,10}$-octalone-2 could be obtained.[20]

Hydrogenation.—Into a 100-ml. round-bottomed flask was placed the catalyst, the solvent, a magnetic stirring bar, and 250 mg. of the 97:3% octalone mixture prepared above. The solvent was 20 ml. of 95% ethanol for neutral runs, 18 ml. of 95% ethanol, and 2 ml. of 3.0 N aqueous hydrochloric acid for acid runs, and 18 ml. of 95% ethanol and 2 ml. of 2.6 N aqueous sodium hydroxide for basic runs. The flask was attached to the hydrogenation apparatus and the apparatus evacuated and filled with hydrogen three times. The hydrogen pressure was equalized with the atmosphere and the magnetic stirrer turned on and kept at a constant setting for all runs to make constant any diffusion effect on the reaction. After hydrogen uptake had ceased, the flask was removed from the apparatus and the catalyst removed by filtration. In acidic and basic runs the filtrate was neutralized. Most of the ethanol was removed by distillation and the residue poured into water and extracted with ether. The ether extracts were evaporated and the residue subjected to gas–liquid chromatographic analysis as described below. In one instance a duplicate run using 1 g. of 10% palladium–charcoal the catalyst, after being removed from the reaction mixture, was refluxed with 25 ml. of acetone for 30 min. The catalyst was again removed by filtration and the acetone filtrate combined with the original filtrate and the total treated as described above. No difference in the per cent of the *cis*-β-decalone was detected using this modified procedure.

Gas–Liquid Chromatographic Analysis.—A 0.8-μl. sample was subjected to g.l.c. analysis by passing it through a 6-ft. $^1/_8$-in. outside diameter stainless steel column containing 20% water soluble UCON on Chromosorb W. The temperature was programmed from 75° to 150° at 2.3°/min. Helium was the eluent gas at a flow rate of 30 cc./min. The retention times for *trans*-β-decalone and *cis*-β-decalone, were 17 and 19.5 min., respectively. Peak areas were measured using the peak height times peak width at half-height method. Over-all precision including duplicability of chromatograms and reproducibility of hydrogenation data was within ± 1%.

Acknowledgment.—The author is indebted to Dr. R. T. Conley for many stimulating discussions on this subject.

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(18) Hsien-Cheng Yao and P. H. Emmet, *J. Am. Chem. Soc.*, **81**, 4125 (1959).

(19) D. J. Baisted and J. S. Whitehurst, *J. Chem. Soc.*, 4089 (1961).

(20) P. Rosen, private communication (1960).