Solvents of Low Nucleophilicity. IV. Addition of Acetic, Formic, and Trifluoroacetic Acid to Branched Alkenes[1]

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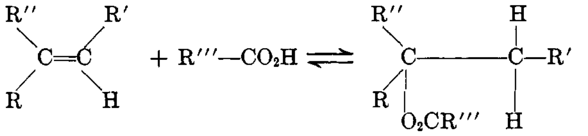
Approximate equilibrium constants for the addition of acetic, formic, and trifluoroacetic acid to 1-methylcycloalkenes and 2-methyl-2-butene were determined for 0.1 M solutions of alkene at 35°. The previously noted failure of formic and acetic acid to add to branched alkenes was due to the presence of alkene at equilibrium and, in the case of formic acid, to the low solubility of alkenes of higher molecular weight in the acid. The addition of trifluoroacetic acid to branched alkenes, followed by hydrolysis of the resulting tertiary trifluoroacetates, was found, in agreement with a previous report, to be an advantageous method for preparing tertiary alcohols. A basic fore column useful for gas chromatographic analysis of acidic solutions is described.

In previous work[3] trifluoroacetic acid was found to add to unbranched alkenes in Markovnikov fashion at moderate temperatures. The resulting secondary trifluoroacetates were stable under the reaction conditions. In the work reported here, the addition of trifluoroacetic, formic, and acetic acid to branched olefins to give the less stable tertiary esters was studied (eq. 1).



(1)

$$K_1 = \frac{[\text{ester}]}{[\text{alkene}]} \qquad K_{-1} = \frac{[\text{alkene}]}{[\text{ester}]}$$

(excess acid assumed to be present)

Most of our work involved studies of the equilibrium constants for addition of the various acids to the branched olefins. Because of the rapidity with which some of the equilibria were established, the quantitative analysis of some of the equilibrium mixtures was difficult, but we obtained gas chromatographic results (*cf.* Table I) in which there is essentially the same variation of equilibrium constant with alkene structure in the three different solvents. Furthermore, the gas chromatographic equilibrium constants are supported in several instances by independent titrimetric and preparative experiments. Accordingly, we believe that our work provides a sound basis for the planning of further experiments involving the addition of carboxylic acids to branched alkenes.

Acetic Acid.—Equilibrations in acetic acid were carried out, starting from the olefins and also from the corresponding tertiary acetates, in the presence of p-toluenesulfonic acid monohydrate. After several days (which was required for complete equilibration in some cases at least) the amount of alkene present in 1-μl. aliquots was determined by gas chromatography.

Formic Acid.—In the case of the formic acid reactions at 35°, equilibrium was approached only from the olefin side, except for equilibrations involving the 2-methyl-2-butyl system. Equilibrium was complete after a few minutes as indicated by the constancy of olefin concentrations obtained by gas chromatography and by titrimetric analysis using iodine monobromide (Hanus solution).[4] Titrimetric analysis was of limited but still useful accuracy because of reaction of some of the tertiary esters with iodine monobromide. The gas chromatographic values are subject to a different possible error: the equilibria were established so rapidly that changes in the olefin concentration due to changes in temperature may have occurred in the syringe or injection port. This error was minimized by keeping the injection port near 35° as described in the Experimental section. The approximate agreement between the equilibrium constants determined by the two methods indicates that our results, although inexact, are free of gross errors.

Trifluoroacetic Acid.—Equilibrium in trifluoroacetic acid was established at a rate too fast to measure. Accordingly, the gas chromatographically measured olefin concentrations are perhaps subject to a greater error than in the case of the formic acid reactions. However, the important feature of the results, shown in Table I, is the relatively small concentration of alkene present at equilibrium in the case of all alkenes except 1-methylcyclooctene, for which addition is unfavorable because of steric interactions in the product. The favorable equilibrium constants suggested the possibility of preparing tertiary trifluoroacetates and (by hydrolysis) alcohols *via* addition of trifluoroacetic acid to branched alkenes. Further study showed that relatively unstable trifluoroacetate esters were readily obtained, provided distillations were carried out at room temperature. However, the preparation of tertiary alcohols by basic hydrolysis of the undistilled trifluoroacetate esters was found to be the preferable procedure when the alcohols were desired. Similar findings are reported in a patent[5] whose abstract appeared during the last phases of our work. Yields of alcohols obtained *via* addition of trifluoroacetic acid to the alkene are shown in Table II. As far as we know, the trifluoroacetic acid method for accomplishing the indirect hydration of branched alkenes is the only one which is reasonably free of difficulties due to unfavorable equilibrium constants or solubility problems.

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(1) (a) Gas chromatographic equipment used in this study was purchased in part with funds from a National Science Foundation Grant (NSF G20904) and in part with a grant-in-aid from the Allied Chemical Corp. (b) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962; Organic Abstracts, p. 70 Q.

(2) This paper is based on the M.S. research of E. V. P. Tao.

(3) (a) P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 5834 (1960); (b) P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 1505 (1962); (c) P. E. Peterson and G. Allen, *J. Am. Chem. Soc.*, **85**, 3608 (1963).

(4) Titrimetric experiments indicated that 2-methyl-2-butene and 2-methyl-2-butyl formate approached equilibrium with half-lives of 1 to 2 min., but other compounds may have reacted even more rapidly.

(5) Esso Research and Engineering Co., German Patent 1,112,057 (Appl. 1954); *Chem. Abstr.*, **56**, 5834 (1962).

TABLE I

EQUILIBRIUM CONSTANTS FOR ADDITION OF ACIDS TO BRANCHED ALKENES AT 35°

Alkene	Acetic acid[a] K	Acetic acid[a] $\frac{1}{K_{-1}}$	Formic acid K, gas chromatographic	Formic acid K, titrimetric	Formic acid Recovery, %[b]	Trifluoroacetic acid K, gas chromatographic	Trifluoroacetic acid Recovery, %[b]
2-Methyl-2-butene	0.78	0.78	>10	>10	97	88	96
1-Methylcyclopentene	0.12	0.14	1.7	1.3	86	9.7	87
1-Methylcyclohexene	0.32	0.19	6.0	6.9	88	61	92
1-Methylcycloheptene	0.06	0.02	1.5	0.3	83	1.7	92
1-Methylcyclooctene	0.0	0.0	0.05	0.03		0.2	

[a] K and K_{-1} are the gas chromatographically determined equilibrium constants for the reactions starting from alkene and from tertiary acetate, respectively. In the absence of experimental error, the values for K and $1/K_{-1}$ would be equal. See eq. 1 for the definition of K and the Experimental section for the method of measurement. [b] The "recovery" figures are calculated from the total quantity of volatile products eluted from the gas chromatograph, determined by comparison with standard samples. As indicated in the Experimental section, these figures serve as a check on the equilibration method and on the gas chromatographic procedure.

TABLE II

YIELDS OF ALCOHOLS

Alcohol	Yield, %
2-Methyl-2-butanol	42
1-Methylcyclopentanol	50
1-Methylcycloheptanol	43
1-Methylcyclooctanol[a]	

[a] The distillate was alkene, but the pot residue was 1-methylcyclooctanol as shown by the infrared spectrum, which was identical with that of an authentic sample prepared from cyclooctanone and methylmagnesium iodide.

Discussion

The tendency of the acids in our study to add to alkenes may be seen from Table I to parallel the order of acid strength, although the correlation may be accidental. Previously, Altschul[6] noted a similar correlation for equilibrations in acidified dioxane as shown by the equilibrium constants for the reaction of isobutene with benzoic acid (1.47) and *p*-nitrobenzoic acid (3.57). It may be noted (*cf.* eq. 1) that during the addition reaction an O–H bond is broken and an O–C bond is formed. If there is any generality to the correlation of acid strength with equilibrium constants, the correlation may be expressed by stating that the O–H bond strength is somewhat more strongly affected by electron availability in the acid moiety than is the O–C bond strength in the corresponding ester. The failure of acetic acid to add to various branched olefins at equilibrium might have been inferred from the previous success achieved in equilibrating exocyclic and endocyclic olefins in acetic acid–toluenesulfonic acid.[7] Our study differs from the previous one in that 0.1 M alkenes solutions were used (approximately 1%), instead of the 10% solutions used previously, and in the assurance that ester–alkene equilibration occurred, achieved by allowing the reaction to proceed to equilibrium starting both from the ester and the alkene.[8] It appears that esters cannot be prepared in good yield from branched olefins and acetic acid simply because of an unfavorable equilibrium constant.[9]

In the case of formic acid and trifluoroacetic acid the equilibrium tends to lie on the side of the ester for most of the branched alkenes. The solubility of 1-methylcycloheptene and 1-methylcyclooctene was so low in formic acid, however, that 0.1 M solutions could not be employed. Accordingly, the low yield of formates achieved by shaking branched alkenes with formic acid[10] is due to the fact that only a small portion of the alkene dissolves; the amount of ester in equilibrium with the dissolved alkene may represent only a small yield based on the total alkene present.

Inspection of Table I reveals that the equilibrium constants in the three acid solvents exhibit similar variations as a function of alkene structure. Furthermore, the variation is essentially that expected based on the assumption that eclipsed hydrogens and other steric interactions in the esters are the most important factors affecting the relative tendency of the various alkenes to react with acids (*cf.* ref. 7). Interestingly, such steric interactions should be approximately independent of acid structure since the $-CO_2-$ group, which perhaps accounts for most of the effect, is common to all carboxylic acids.

Interest in the stereochemistry of the addition of electrophilic reagents to alkenes has been revived by the finding of predominant *cis* addition in certain instances.[11] It is clear from the reversible character of the addition of acids to branched alkenes that stereochemical studies in these systems could be carried out only with exacting care to distinguish between rate and equilibrium controlled products. The latter type of product is clearly the one which will result from ordinary preparative procedures.

The results of our study likewise emphasize the need to consider possible reversible addition of acids to akenes in studies of the stereochemistry of cyclization reactions (*cf.* 12). If concerted stereospecific polyene ring closures occur, such reactions must proceed faster

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(6) (a) R. Altschul, *J. Am. Chem. Soc.*, **68**, 2605 (1946); (b) *cf.* also "Methoden der Organischen Chemie," (Houben-Weyl), Vol. VIII, 4th Ed., E. Müller, Ed., George Thieme Publishers, Stuttgart, Germany, 1952, p. 535.

(7) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Am. Chem. Soc.*, **82**, 1750 (1960).

(8) Based on the gas chromatographically determined quantities of ester reported in ref. 7, equilibrium was probably achieved; the amounts of ester present indicate that the equilibrium constants for the addition were somewhat greater in the 10% solutions equilibrated at 25° than in our study.

(9) (a) Under strictly anhydrous conditions even more alkene might be present than we observed, since traces of water in our solvent probably caused the formation of some alcohol along with the acetates (*cf.* ref. 7). (b) The yields of 1-methylcyclohexene and 1-methylcyclohexyl acetate in the cleavage of bicyclo[4.1.0]heptane with acetic acid-toluenesulfonic acid probably represent the equilibrium mixture [R. T. LaLonde, *J. Org. Chem.*, **27**, 2276 (1962)]. (c) For an instance of possible equilibrium control in the addition of acetic acid to dienes see Glidden Co., British Patent 859,657 (Jan. 25, 1961); *Chem. Abstr.*, **55**, 17,507 (1961).

(10) C. Barkenbus, M. B. Naff, and K. E. Rapp, *J. Org. Chem.*, **19**, 1316 (1954).

(11) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2248, 3645 (1963).

(12) (a) G. Stork and A. W. Burgstahler, *ibid.*, **77**, 5068 (1955); (b) P. A. Stadtler, H. Eschenmoser, H. Schinz, and G. Stork, *Helv. Chim. Acta*, **40**, 2091 (1957).

than the competing addition–elimination reactions, since the intermediates in addition–elimination reactions could cyclize in a nonstereospecific manner. Concerted acid-catalyzed cyclizations, if they can be realized experimentally, will accordingly occur under milder conditions than addition–elimination reactions.

Experimental

Chemicals.—The 1-methylcycloalkenes were obtained from the Aldrich Chemical Co. with the exception of 1-methylcyclooctene which was prepared by dehydration of 1-methylcyclooctanol,[13] obtained from cyclooctanone and methylmagnesium iodide.[14] 2-Methyl-2-butene (99%) was obtained from Matheson Coleman and Bell. The preparation of the other 1-methylcycloalkanols *via* the corresponding trifluoroacetates is described in another portion of the Experimental section. Reagent grade acetic acid and toluenesulfonic acid monohydrate were used without further purification. Formic acid (98%) was dried according to the published method[15] by distilling through a 3-ft. jacketed column packed with glass helices. The center cut was stored in a closed three-neck flask with fittings for dispensing acid by pumping in air through a drying tube. Trifluoroacetic acid (Allied Chemical Co.) was distilled through a Vigreux column, and sodium trifluoroacetate (Columbia Organic Chemicals Co.) was added to give a 0.125 *M* solution. The various tertiary alcohols were acetylated by the published method[16] to give the tertiary acetates containing some unreacted tertiary alcohol, as shown by gas chromatography on a Dow-Corning 550 silicone oil column.

Equilibrations.—The amount of alkene or ester required to give a 0.1 *M* solution was weighed in a 10-ml. volumetric flask and diluted to the volume of the flask with one of the following solvents: acetic acid, 0.0145 *M* in toluenesulfonic acid monohydrate; formic acid; or trifluoroacetic acid, 0.125 *M* in sodium trifluoroacetate. In the case of 1-methylcycloheptene and 1-methylcyclooctene, 0.05 *M* solutions of alkene in formic acid were used because the solubility of these alkenes appeared to be insufficient to allow the preparation of 0.1 *M* solutions. The solutions were allowed to come to equilibrium in a constant temperature bath maintained at 35.0 ± 0.05° according to a Bureau of Standards calibrated thermometer. Equilibrium was established in a few days in the acetic acid solutions, in 15 min. or less in the formic acid solutions, and at a rate too fast to measure in the trifluoroacetic acid solution. Samples (2-ml. for titration or 1-μl. for gas chromatography) were withdrawn for analysis as described in one of the following sections.

Gas Chromatography.—An F. and M. Model 609 flame ionization gas chromatograph fitted with a disk integrator and a 6-ft. column of Haloport F coated with 5% dimer acid–silicone oil 550 was employed in the gas chromatographic analyses in the case of the acetic acid equilibrations. Originally it was hoped that this packing would allow each of the carboxylic acid solvents to be eluted as a relatively sharp peak which might not interfere with analysis of most of the esters and alkenes. In practice, acetic acid did give a well-shaped peak, but, at the high sensitivity setting used for the analysis of the dilute solutions employed in this study, the tail of the acetic acid peak prevented a rapid return to a level baseline. Accordingly, only the 2-methyl-2-butyl system could be analyzed for all components (alkene, ester, and alcohol), since the components in this case were eluted before the acetic acid peak. In the other analyses of acetic acid solutions, one of the earlier versions of a short basic fore column (described in detail in later portions of the Experimental) was used to absorb acetic acid. Only relatively low temperatures could be employed with this fore column. Accordingly, only the alkene peak was obtained. Equilibrium constants were based on the alkene concentrations determined by comparing the area of the alkene peak with that of a standard solution of the alkene in acetic acid.

Analyses of the formic and trifluoroacetic acid solutions were carried out with the aid of an improved basic fore column. The fore column was "S-shaped" and contained firebrick coated with potassium carbonate and Carbowax 20 M. (The preparation of the packing is described in the next section.) The 6–12-in. fore column was attached by tubing connectors to a 6-ft. Dow-Corning 550 silicone oil column. In a preliminary investigation 1-μl. samples of the appropriate compounds in the *t*-amyl series were injected, and the resulting peak areas (1000-16 sensitivity) were divided by the densities to give area counts per milligram. The basic fore column converted the formate partially to the corresponding alcohol, as shown by the presence of a well-shaped peak having the retention time of *t*-amyl alcohol, and converted the trifluoroacetate entirely to alcohol. It is possible that adsorbed water or water of hydration present in the fore column hydrolyzed the esters. Results of the calibration study (compound and counts per milligram) were as follows: *t*-amyl alcohol, 1300; *t*-amyl acetate, 1620; *t*-amyl trifluoroacetate, 779 (eluted as alcohol); *t*-amyl formate, 1250 (formate peak) plus 203 (alcohol peak). Based on these results, formates and alcohols give similar area counts per milligram. In subsequent determinations this relationship was assumed for the other (unavailable) alcohol–formate pairs.

In gas chromatographic analyses of equilibrations in formic and trifluoroacetic acid, 1-μl. samples of a freshly mixed solution of alkene in the acid at 35° were injected into the chromatograph. The injection port was maintained at approximately 35 ± 10° by means of Dry Ice cooling of the injection port when necessary. (Separate experiments indicated that equilibration occurred to some extent in the injection port; a high injection port temperature resulted in larger alkene peaks and a low injection port temperature gave smaller alkene peaks than those obtained at 35°. Presumably, no further reaction occurred after the samples evaporated in the injection port, as judged by the agreement of the gas chromatographic results with results determined by titration of formic acid equilibrations.) The improved fore column used in the formic and trifluoroacetic acid equilibrations permitted the observation of both alkene and alcohol peaks in the case of trifluoroacetic acid and of alkene, alcohol, and formate peaks in the case of formic acid, except for the reactions of 1-methylcyclooctene. Column bleeding and the resultant baseline instability made analysis for cycloheptanol at the equilibrium concentration (approximately 0.03 *M*) moderately difficult at 150°. Accordingly, measurements in the cyclooctyl system were limited to the alkene peak.

Gas chromatographic equilibrium constants reported in Table II were calculated from the observed values by these equations.

$$K_{\mathrm{F_3CCO_2H}} = \frac{[\text{alcohol}]}{[\text{alkene}]}$$

$$K_{\mathrm{HCO_2H}} = \frac{[\text{alcohol}] + [\text{formate}]}{[\text{alkene}]}$$

The quantities in brackets represent molar concentrations, determined by comparison of the peak area with that of a standard sample of similar concentration in acetic acid. As has been mentioned, it was assumed that alcohols and formates gave the same area response on a weight basis. The "recoveries" of products were calculated by dividing the sum of the molar concentrations of all products observed during the gas chromatographic analysis of an equilibrium mixture by the initially employed alkene concentration. These values, reported in Table I, show that polymerization was not appreciable during the time (less than 30 min.) required to chromatograph several duplicate samples. After several hours polymerization did occur in some experiments involving trifluoroacetic acid as shown by the clouding of the solutions due to separation of insoluble polymer. The yields reported are probably not significantly different from 100%, the discrepancies between 100% and the observed values indicating the accuracy limitations of the gas chromatographic method.

Basic Packing for Fore Column.—Anhydrous potassium carbonate (36 g.) was dissolved in 180 ml. of water, and the solution was added to 90 g. of 60–80-mesh firebrick. The water was removed by means of a rotary evaporator. A solution of Carbowax 20 M (12.6 g.) in 250 ml. of absolute ethanol was added, and the packing was again dried on a rotary evaporator. Gas chromatography using a dimer acid–silicone oil column showed that the packing in a 6- to 12-in. fore column effectively removed acetic acid. Packing emptied from a fore column after use showed a sharp division between the acidic and basic portions as shown by tests with wet pH paper. Omission of the Carbowax 20 M led to a basic packing which gave skewed peaks.

Preparation of Tertiary Alcohols.—In a representative example, 1-methylcyclohexene (19.2 g.) was dissolved in a cooled mixture of 40 ml. of trifluoroacetic acid and 2 ml. of 0.125 *M* sodium

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[13] F. K. Signaigo and P. L. Cramer, *J. Am. Chem. Soc.*, **55**, 3326 (1933).

[14] H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[15] P. D. Bartlett, C. E. Dills, and H. G. Richey, Jr., *ibid.*, **82**, 5414 (1960).

[16] J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

trifluoroacetate in trifluoroacetic acid. (The sodium trifluoroacetate is not essential and was added only to ensure the absence of adventitious traces of strong acid which could cause polymerization.) Ether (50 ml.) and 40% potassium hydroxide (150 ml.) were added with continued cooling of the mixture. The erlenmeyer flask containing the two-phase mixture was stoppered, and the mixture was magnetically stirred at room temperature for 24 hr. The ether layer was separated, and the water layer was extracted with three additional small portions of ether. (Gas chromatography showed that only one extraction was necessary.) Drying the ether layers (magnesium sulfate) and distilling gave 14.2 g. (62%) of 1-methylcyclohexanol, b.p. 78–79° (41 mm.). The low yields may be associated with the difficulty of thoroughly drying ether solutions of alcohols.

Solvents of Low Nucleophilicity. V. Platinum-Catalyzed Hydrogenation of Ketones, Tertiary Alcohols and Esters, and Tosylates in Acidic Solvents Including Trifluoroacetic Acid[1a]

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The platinum-catalyzed hydrogenation of acyclic and cyclic ketones in trifluoroacetic acid at atmospheric pressure occurs at approximately three times the rate for comparable hydrogenations in acetic acid at relatively high ketone concentrations where rates in some instances are approximately zero order in ketone concentration. At lower ketone concentrations, the rates become strongly dependent upon the ketone concentration and structure. Under these conditions, hydrogenations in acetic acid are subject to acid catalysis, especially in the case of ketones for which adsorption on the catalyst surface may be attended by unfavorable steric interactions. Tertiary alcohols and esters are hydrogenated in trifluoroacetic acid, probably *via* a reversibly formed alkene intermediate. The rates of solvolysis of secondary tosylates in trifluoroacetic acid can be followed by hydrogenation of the alkene formed during the solvolysis.

Ketone Hydrogenations. Introduction.—The platinum-catalyzed hydrogenation of ketones has not been studied very extensively, although one attempt to systematize the existing information may be mentioned. Brewster advanced the hypothesis that the reduction of carbonyl groups in acidic media proceeds *via* transfer of a hydride ion from the catalyst surface to the carbonyl carbon of the protonated ketone, while reduction in neutral solvents proceeds *via* transfer of a hydride ion to the carbonyl oxygen.[2] The former process presumably leads to axial alcohols starting from 2-substituted cyclohexanones, while the latter gives predominantly equatorial alcohols. Since the experimental evidence upon which the proposal is based is quite limited, the Brewster hypothesis must be regarded primarily as a stimulus for further studies, particularly in regard to the effect of the solvent acidity upon ketone hydrogenations. Recently the hydrogenation of ketones and alkenes in a variety of solvents in the presence of a supported platinum catalyst was studied.[3] Ketones were found to be reduced slowly in certain neutral solvents (methanol, ethyl acetate), whereas alkenes were reduced readily in all solvents. These results, which will be discussed in a later section, also serve to emphasize the role of the solvent in ketone hydrogenations.

Ketone Hydrogenations. Results.—The present work involved hydrogenation of ketones in acetic and trifluoroacetic acid at atmospheric pressure in the presence of prereduced Adams catalyst (platinum oxide).[4] Our initial efforts were prompted by the observation that trifluoroacetic acid appeared to be a particularly effective solvent for ketone hydrogenations. In the course of optimizing the procedure used for hydrogenations in trifluoroacetic acid we recognized that hydrogenation rates were in some but not all instances dependent upon the ketone concentration.

Specifically in the case of cyclohexanones we found that at high ketone concentrations the rates of hydrogen uptake were approximately independent of the ketone concentration (zero order in ketone). The acyclic ketones appeared to approach zero-order behavior, although not so closely. Cyclic ketones other than cyclohexanones exhibited some decrease of the rate with time, indicative of a concentration dependence, but the fact that at higher ketone concentrations all ketones underwent hydrogenation at similar rates (*cf.* Table I) may indicate that initially a zero-order behavior was approached. A convenient (though not necessarily correct) interpretation of these observations is that at higher ketone concentrations all active sites of the catalyst are occupied by ketone molecules

TABLE I

RATES OF HYDROGENATION OF KETONES IN ACETIC AND TRIFLUOROACETIC ACID

Ketone	Hydrogen uptake, ml./min.[a] CF_3CO_2H	Hydrogen uptake, ml./min.[a] CH_3CO_2H
Cyclopentanone	6	2.4
Cyclohexanone	10.5	3.5
Cycloheptanone	4.7	2.5
Cyclooctanone	5.7	1.8
Acetone	10	1.5
4-Heptanone	10	1.8
2-Methylcyclohexanone	9.4	3.1

[a] Initial rates are given. Conditions: 25.0°, atmospheric pressure, 0.25 ml. of ketone, 5 ml. of solvent, 25 mg. of prereduced platinum oxide, 50-ml. erlenmeyer flask, magnetic stirrer.

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(1) (a) Support from the General Chemical Division, Allied Chemical Corp. is gratefully acknowledged. (b) National Science Foundation undergraduate research participant.

(2) J. Brewster, *J. Am. Chem. Soc.*, **76**, 6361 (1954).

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

(4) The usual laboratory apparatus was refined by the use of a jacketed hydrogen buret and a jacketed hydrogenation flask maintained at 25.0° by circulating water and also by the inclusion of a sensitive butyl tartrate manometer which permitted precise adjustment of the mercury leveling bulb, following a coarse leveling of the mercury manometer. Another useful feature of the apparatus was a serum cap through which samples could be injected by means of a hypodermic syringe without interrupting the hydrogenation.