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	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.

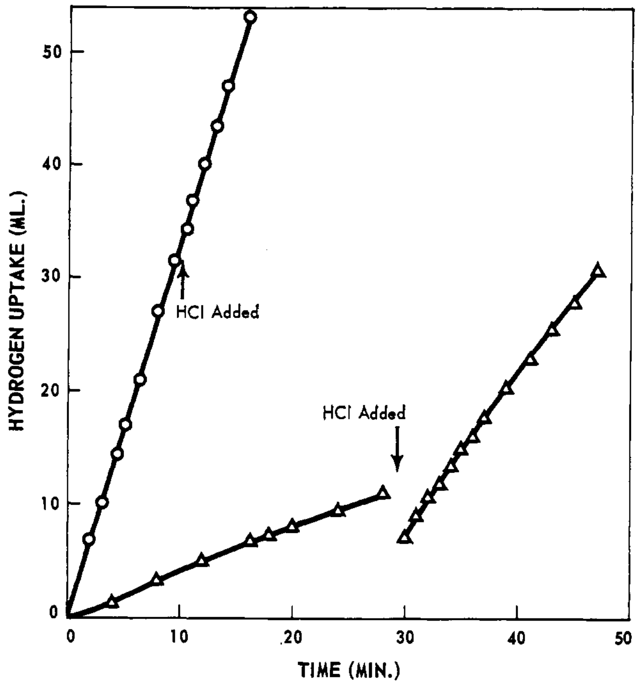

Fig. 1.—Effect of added hydrochloric acid upon hydrogenation of a relatively high concentration of cyclohexanone in acetic acid (O-O-O) and a relatively low concentration of cyclopentanone in acetic acid (Δ-Δ-Δ).

and that the rate of hydrogenation of adsorbed ketone is similar for all ketones.

At low ketone concentrations, rates of hydrogenation increased with increasing ketone concentration, especially for those ketones where unfavorable steric interactions would attend the conversion of the trigonal ketonic carbon atom to a tetrahedral carbon atom (cyclopentanone and cycloheptanone, compared to cyclohexanone). Furthermore, the rates of hydrogenation were found to be highly dependent upon the ketone structure at low ketone concentrations, as shown by the slow rate of hydrogenation of cyclopentanone and cycloheptanone, compared to cyclohexanone (*cf.* Table II). These results suggest that under these conditions the active sites of the catalyst are only partially occupied by ketone molecules, the least hindered ketone being adsorbed to the greatest extent.

TABLE II

RATES OF HYDROGENATION AT LOW KETONE CONCENTRATION BEFORE AND AFTER ADDITION OF CYCLOHEXANONE

Ketone	Solvent	Hydrogen uptake, ml./min.
Cyclopentanone	CF$_3$CO$_2$H	2.3 (6)
Cyclopentanone	CH$_3$CO$_2$H	0.4[a] (5)
Cycloheptanone	CH$_3$CO$_2$H	0.8[a] (3.0)

[a] Initial rates are given for hydrogenation of 0.25 ml. of ketone in 100 ml. of solvent in the presence of 50 mg. of prereduced platinum oxide. After approximately 30 min., 0.25 ml. of cyclohexanone was injected. The resulting increased rates are shown in parentheses. The conditions for the experiment involving trifluoroacetic acid were similar except that 0.5 ml. of cyclopentanone was used.

The concentration effects described in the preceding two paragraphs were inferred in part from the shape of plots of the rates of hydrogen uptake *vs.* time. Confirmatory evidence was obtained from experiments in which successive portions of ketone were injected during a hydrogenation, in order to increase the ketone concentration while holding other variables constant. In each case, the series of injections and rate measurements was completed before a large proportion of the ketone had been reduced. Accordingly, the total ketone concentration could be approximated as the sum of the concentrations due to the individual injections. The results, shown in Table III, indicate that at moderate concentrations of cyclohexanone in acetic acid the rate of hydrogenation is, in fact, unchanged upon injection of additional ketone. (It may be seen that this rate was reasonably reproducible in successive experiments. Accordingly, the difficulties sometimes involved in the comparison of successive experiments involving heterogeneous catalysis are not of major significance in our experiments.) Table III also illustrates the previously mentioned dependence of the rate of reduction of cyclopentanone upon the ketone concentration when the total ketone concentration is low. The observed rates are seen to be somewhat less than first order in ketone concentration.

TABLE III

EFFECT OF KETONE CONCENTRATION ON THE RATE OF HYDROGENATION[a]

Ketone	Total ketone added, ml.	Hydrogen uptake, ml./min.
Cyclohexanone[b]	0.25	1.66[c]
	0.50	1.75
	1.0	1.65 (3.21)[d]
Cyclopentanone[e]	0.25	0.10
	0.50	0.16
	1.0	0.24

[a] We are indebted to Mr. Robert Belloli, undergraduate research assistant, for performing these experiments. [b] Conditions: 25.0°, 5 ml. of acetic acid, 25 mg. of platinum oxide, 50-ml. erlenmeyer flask, constant-speed magnetic stirrer. [c] In separate experiments involving the same conditions, the rates were 1.53, 1.55, and 1.50 ml./min. [d] The higher rate (3.21 ml./min.) was obtained by replacement of the constant-speed stirrer with the variable-speed stirrer used to obtain the rates in Tables I and II. Increasing the stirring speed to approximately the maximum usable rate increased the rate of hydrogen uptake to the value shown, which is similar to that reported in Table I. [e] Conditions: 25.0°, 100 ml. of acetic acid, 50 mg. of platinum oxide, 500-ml. erlenmeyer flask, constant-speed magnetic stirrer.

Additional experiments were carried out to determine the effect of other variable factors in the hydrogenations. Rates of hydrogenation of 0.25 ml. of 2-methylcyclohexanone in trifluoroacetic acid in the presence of 25 mg. of prereduced platinum oxide were determined using 10-, 25-, and 50-ml. erlenmeyer flasks. The observed rates were 2.2, 6.7, and 7.6 ml./min., respectively. In view of these results, a 50-ml. flask was used for the experiments reported in Table I. It seems likely that the rate of hydrogen diffusion into the liquid layer was the limiting factor when the smallest flasks were used, although poor stirring and a resulting poor catalyst dispersal may have been a factor.

The effect of stirring speed is shown in Table III. The data in this table were obtained with a constant-speed magnetic stirrer, whereas all other experiments were performed with a variable-speed stirrer operating at a higher stirring rate (essentially the maximum usable rate). Slower hydrogen uptake was observed with the slower stirrer, although again it is not known whether the rate of hydrogen diffusion or the efficiency of catalyst dispersal was the factor involved. It should be noted that the data in Table II, Table III, and Fig. 1 were obtained by successive injections of small amounts of ketone (or hydrochloric acid) without interruption of the hydrogenation. Effects due to variations in stirring speed, catalyst activity, and other possible variables were "cancelled out" by this procedure; accordingly, these experiments are considered to be particularly definitive.

In an experiment designed to evaluate the effect of solvent upon the catalyst prereduction step, samples of platinum oxide were prereduced in 5 ml. of acetic acid and 5 ml. of trifluoroacetic acid, respectively. Then 5-ml. of the other acid was added *via* a hypodermic syringe to give in both cases a solvent containing 50% by volume of each acid. Finally 0.25 ml. of 2-methylcyclohexanone was hydrogenated. In both instances the rate was 3.2 ml./min., compared with rates of 1.9 and 6.1 ml./min., for reactions in acetic and trifluoroacetic acid under the same conditions (25-ml. flask). From these results it appears that the activity of the catalyst is not dependent upon the solvent in which it is prereduced. Accordingly, the influence of solvent upon ketone hydrogenation rates, observed in our study, occurs during the ketone reduction step.

Rates of reduction were shown in one instance to be roughly proportional to the amount of catalyst used. Finally, the effect of added hydrochloric acid upon the rate of hydrogenation in acetic acid was evaluated in several instances in order to test predictions based on Brewster's mechanism. The results are described in the next section.

Ketone Hydrogenations. Discussion.—Based on the results reported in Table I, trifluoroacetic acid appears to be the best solvent yet found for the platinum-catalyzed hydrogenation of ketones. For preparative hydrogenations in trifluoroacetic acid, a relatively high concentration of ketone should be used in order to avoid the slow rates observed in dilute solutions where the rate becomes dependent upon the ketone concentration. It is interesting that an organic chemist desiring to hydrogenate a few milligrams of ketone would perhaps choose the least effective conditions—hydrogenation on a relatively large volume of acetic acid.

The alcohol product from the hydrogenation of 2-methylcyclohexanone in trifluoroacetic acid was largely esterified. However, the trifluoroacetate esters obtained from reduction in trifluoroacetic acid are more readily hydrolyzed to the alcohol[5] than the corresponding acetates which may be formed during hydrogenations in acetic acid.

Our observations concerning the dependence of ketone hydrogenation rates upon the ketone concentration have some interesting implications, provided the protonated ketone is assumed to be the species reduced, as postulated by Brewster.[2] Consider first the zero-order hydrogenation of moderate concentrations of cyclohexanone in acetic acid. If it is further postulated that all of the ketone-adsorbing catalyst sites are occupied by ketone molecules under these conditions, two alternatives are possible. Either the adsorbed ketone molecules are all protonated or else the unprotonated adsorbed ketone molecules are not reduced at an appreciable rate. In the latter case addition of a strong acid should increase the proportion of protonated ketone molecules and lead to an increase in the hydrogenation rate. The results of such an experiment are shown in Fig. 1. Injection of 0.05 ml. of 37% hydrochloric acid into 0.7 ml. of hydrogenating ketone in 10 ml. of acetic acid did not change the rate of hydrogenation measureably, although a qualitative test using *p*-nitroaniline as an indicator showed that the acidity of the solution was markedly increased. In view of the low concentration of protonated ketone in acetic acid, this experimental result is perhaps surprising since it seems to imply that the catalyst sites are in fact occupied exclusively by protonated ketone molecules. At this point one might be led to question the original hypotheses involving hydrogenation *via* the protonated ketone and complete occupancy of the catalyst sites. Fortunately an additional critical experiment was possible. Under conditions of approximate first-order hydrogenation at low ketone concentrations, the catalyst hydrogenation sites must, according to the interpretation under consideration, be only partially occupied by protonated ketone molecules in order to account for the concentration dependence. Increasing the solvent acidity should increase the hydrogenation rate, since the proportion of occupied sites would be increased. The results of an experiment designed to test this point are also shown in Fig. 1. In striking contrast to the result observed in the previously described zero-order hydrogenation, injection of 0.4 ml. of 37% hydrochloric acid into a hydrogenating solution of 0.3 ml. of cyclopentanone in 100 ml. of acetic acid resulted in a 4- to 5-fold rate increase. (The break in the plot of hydrogen uptake is attributed to evolution of hydrogen chloride.) Under these conditions (dilute solution of ketone), the rate of hydrogenation of cyclohexanone was also increased by added hydrochloric acid, but not very markedly. Accordingly, the effect of added strong acid is not upon the rate of dissolution of hydrogen (as suggested by a referee), since the previously observed large increase in rate would then have been expected also in the case of cyclohexanone.

It may be concluded that our results support the previously postulated hydrogenation mechanism[2] involving a protonated ketone as the intermediate, although alternative interpretations are possible. The effectiveness of added strong acids as a hydrogenation promoter (*cf.* papers cited in ref. 2) is seen to be intimately connected with the type of rate dependence observed, which in turn is a function of both the ketone concentration and the presumed steric requirements of the adsorbed ketone molecule. The picture which has emerged is a satisfying one, in that previous results are well accommodated, and a number of new hydrogenation studies involving stereochemical effects, competitive hydrogenations, added ionic materials, and quantitative acidity correlations are suggested.

It is noteworthy that in the previous study[3] of ketone hydrogenation in acetic acid, a slow rate of hydrogenation of cyclopentanone compared to cyclohexanone and a decrease of the cyclopentanone hydrogenation rate with time were observed, in analogy with our results. However, the decreasing rate observed in a number of instances in the earlier study was at-

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[5] See ref. 8 for a simple hydrolysis procedure.

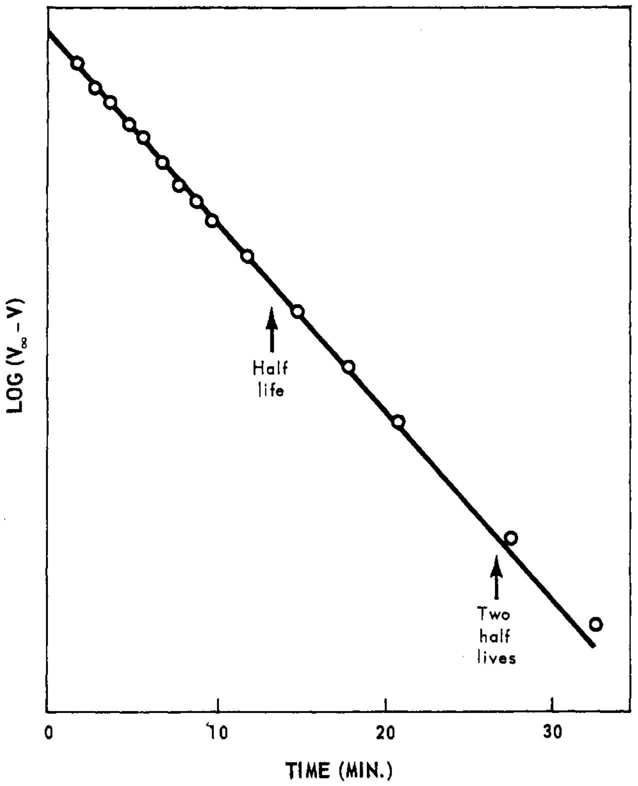


Fig. 2.—First-order rate plot for hydrogenation of 3-hexyl tosylate.

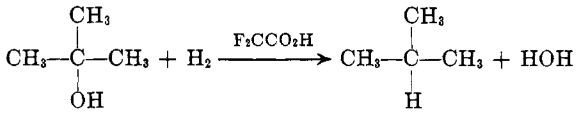
tributed to slow catalyst poisoning. In the present study catalyst poisoning was ruled out by the observation that the rate of hydrogen uptake during the hydrogenation of cyclopentanone and cycloheptanone at low concentration was increased greatly by the introduction of cyclohexanone (*cf.* Table II). Furthermore, injection of an additional quantity of the same ketone increased the hydrogenation rate, as expected if the rate is a function of the ketone concentrations. Interestingly, the previous study involved low ketone concentrations. Accordingly, the previous results can probably be reinterpreted as reflecting the limited tendency of some of the ketones to undergo adsorption on the catalyst, as postulated in our own study.

In solvents such as ethyl acetate and methanol, ketones were reduced quite slowly; furthermore, the rates seemed to be relatively independent of ketone structure.[3] It seems possible that these nucleophilic solvents compete effectively with ketone molecules for the catalyst sites. Since alkenes are reduced effectively in these solvents, indicating that carbon–carbon double bonds are effectively adsorbed in competition with solvent molecules, it is tempting to speculate that the enol form of the ketone is the species reduced in these solvents, at least in the case of the less readily adsorbed ketones.[6]

Finally it may be pointed out that the type of substrate concentration dependence observed in our studies appears to be paralleled in alkene reductions. Thus, various alkenes hydrogenate at similar zero-order rates in the presence of platinum, although competition studies show that the catalyst exhibits high selectivity toward less hindered alkenes.[6b] Our study suggests that the selectivity would lead to a dependence of the rate of hydrogenation upon the alkene structure at sufficiently low alkene concentrations. Indeed, a recent study[7] appears to provide an example of such behavior involving both the characteristic dependence of rate upon alkene structure and the concomitant dependence of rate upon alkene concentration, judged from the curved plots of hydrogen uptake *vs.* time. If our interpretation is correct, Brown and Brown's P-2 nickel boride catalyst adsorbs alkenes less strongly than platinum, facilitating the study of selectivity by the observation of hydrogenation rates rather than by the observation of products formed in competition experiments.

Hydrogenation of Tertiary Alcohols and Esters.—Studies in our laboratory had previously indicated that tertiary esters are in equilibrium with the corresponding alkenes in trifluoroacetic acid.[8] Although the concentration of olefin at equilibrium was small, it was thought that complete reaction of the ester might be obtained if the olefins were trapped by catalytic hydrogenation to the alkane. This was found to be the case; hydrogen uptake occurred according to a first-order rate law, as shown by the fact that a plot of log $(V_\infty - V)$ *vs.* time was a straight line, where V_∞ is the volume of hydrogen taken up at seven or more half-lives and V is the volume at earlier times. First-order hydrogen uptake indicates either that all alkene molecules formed underwent hydrogenation or that a constant fraction of the alkene molecules formed were hydrogenated before they underwent addition of trifluoroacetic acid to reform the tertiary ester.

It was also shown that *t*-butyl alcohol was hydrogenated (eq. 1) with a half-life of 50 min. at 23°. In this experiment 4 ml. of trifluoroacetic acid, 25 mg. of platinum oxide, and 0.2 g. of alcohol were employed. Actually it is likely that the *t*-butyl alcohol was converted to the trifluoroacetate by a rapid carbonium ion reaction prior to hydrogenation (*cf.* ref. 8).



$$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3 + H_2 \xrightarrow{F_3CCO_2H} CH_3-\overset{CH_3}{\underset{H}{C}}-CH_3 + HOH \quad (1)$$

The reaction just described might have some value in accomplishing the selective removal of a tertiary oxygen from a polyfunctional molecule and in studying the rates of carbonium-ion reactions as a function of the structure of the substrate.

Hydrogenation of Solvolyzing Tosylates.—It was previously shown that the solvolysis of hexyl tosylates in trifluoroacetic acid gave predominantly hexenes which then underwent addition of trifluoroacetic acid at a moderate rate.[9] In the present study hexenes were found to undergo rapid platinum-catalyzed hydrogenation in trifluoroacetic acid. The rate of reaction was

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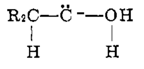
(6) Stereochemical implications need not be construed from such a mechanism since alkene hydrogenations are not always highly stereospecific; *cf.* (a) S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960); (b) S. Siegel and B. Dmuchovsky, *ibid.*, **84**, 3132 (1962). Furthermore if a hydride ion (instead of a hydrogen atom) is transferred from the catalyst surface, the following intermediate postulated by Brewster could be obtained from the enol.



$$\underset{H}{R_2C}-\ddot{C}-\underset{H}{O}H$$

(7) H. C. Brown and C. A. Brown, *ibid.*, **85**, 1003, 1005 (1963).

(8) P. E. Peterson and E. V. P. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

(9) P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 5834 (1960).

TABLE IV

RATES OF SOLVOLYSIS AND PER CENT ELIMINATION AT 25° FOR HEXYL TOSYLATES IN TRIFLUOROACETIC ACID[a]

Reactant	$k \times 10^4$ sec.$^{-1}$	Elimination, %
2-Hexyl tosylate	1.92 (2.2)	87.5 (83.5)
3-Hexyl tosylate	8.54 (7.5)	80.9 (84)

[a] Values were determined by hydrogenation; the values in parentheses were previously determined (gas chromatographic) from ref. 9.

constant (zero order in alkene concentration) until hydrogenation was almost complete, suggesting that, if the solvolysis of a tosylate in trifluoroacetic acid were carried out under hydrogenation conditions, the alkene product might be reduced essentially as fast as it was formed. Hydrogenation did, in fact, occur as expected provided freshly prepared tosylates were used. A first-order plot of the hydrogen uptake is shown in Fig. 2 for the hydrogenation of 3-hexyl tosylate. A single experiment yields both the rate constant for tosylate solvolysis and the per cent elimination. Results for the hexyl tosylates are given in Table IV. These reasonably precise results are in agreement with approximate values previously determined by a gas chromatographic method.

It is noteworthy that the sulfur-containing tosylates do not poison the catalyst. A slightly discolored tosylate which had stood at room temperature for several days did poison the catalyst, however, probably because traces of polymer were present as a result of an elimination reaction followed by acid-catalyzed polymerization. Traces of pyridine in the tosylate samples were also suspected of causing anomalous hydrogenation behavior.[10]

[10] P. E. Peterson and R. E. Kelly, Jr., unpublished work.

Terminal Benzoylation of Certain β-Keto Sulfones to Form Diketo Sulfones by Means of Sodium Hydride. Dibenzoylation of Dimethyl Sulfone[1]

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Received March 3, 1964

Benzoylations at the methyl groups of benzenesulfonylacetone and methyl phenacyl sulfone were effected with methyl benzoate by means of sodium hydride to form the corresponding terminal derivatives. The twofold terminal benzoylation of dimethyl sulfone to form the corresponding diketo sulfone was accomplished similarly. Sodium hydride appears not to produce initially the dicarbanion of the β-keto sulfone, which is the reactive intermediate in the analogous reaction employing potassium amide.

Benzoylation at the methyl group of benzenesulfonylacetone (I) has previously been accomplished through dicarbanion II, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia. Thus II condensed with methyl benzoate to form the terminal derivative III.[2]

$C_6H_5SO_2CH_2COCH_3$
I

$C_6H_5SO_2\bar{C}HCO\bar{C}H_2$
II

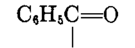
$C_6H_5SO_2CH_2COCH_2COC_6H_5$
III

Benzoylations at the methyl groups of keto sulfones I and IV have now been realized by means of sodium hydride in refluxing 1,2-dimethoxyethane (monoglyme) even though this reagent may not produce dicarbanions as intermediates.

$C_6H_5COCH_2SO_2CH_3$
IV

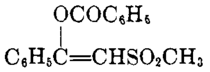
$C_6H_5COCH_2SO_2CH_2COC_6H_5$
V

The product from I was identified as methyl derivative III by comparison with an authentic sample prepared through II.[2] By analogy, the product from the benzoylation of IV was expected to be its methyl derivative V, not the possible methylene derivative VI or VII. In agreement with this, the product failed to give a positive enol test with ethanolic ferric chloride indicating that it was not VI, and its infrared spectrum was consistent with V, not VII. Its spectrum showed a band at 1690 cm.$^{-1}$ for the carbonyl group[3] and bands at 1330 and 1145 cm.$^{-1}$ for the sulfonyl group.[4] Had the product been the possible methylene derivatives VI, it should have given a positive enol test since VI is a β-diketone having an α-hydrogen; had the product been enol benzoate VII, it should have shown an infrared spectrum somewhat different from that observed.



$$\begin{array}{c} C_6H_5C{=}O \\ | \\ C_6H_5COCHSO_2CH_3 \end{array}$$

VI



$$\begin{array}{c} OCOC_6H_5 \\ | \\ C_6H_5C{=}CHSO_2CH_3 \end{array}$$

VII

Structure V was confirmed by its n.m.r. spectrum, which showed besides the aromatic proton resonance (intensity = 10) only a single peak located at τ 5.02 (intensity = 4), indicative of two identical methylene groups. No peak was observed in the region that may be ascribed to a terminal methyl group as in structure VI or VII. The n.m.r. spectrum of the parent compound IV showed peaks at τ 5.37 and 6.89, which were assigned to the methylene and methyl groups, respectively.[5]

The yields of diketo sulfones III and V from keto sulfones I and IV were 55 and 78%, respectively. The yield of III by the earlier potassium amide method was 60% based on the ester but the per cent conversion of I to III was only 30%.[2]

Since sodium hydride was found to effect the benzoylation of not only keto sulfone IV to form V but also of

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[1] Supported by the National Institutes of Health.

[2] W. I. O'Sullivan, D. F. Tavares, and C. R. Hauser, *J. Am. Chem. Soc.*, **83**, 3453 (1961).

[3] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 134.

[4] See ref. 3, p. 360.

[5] H.-D. Becker and G. B. Russell, *J. Org. Chem.*, **28**, 1896 (1963).