concentrated, and distilled, yield 67.7 g. (96%) of N-(*n*-propyl)-cyclohexylamine, b.p. 181° (745 mm.) (lit.[13] b.p. 185°), hydrochloride m.p. 247–249° (lit.[13] m.p. 248–250°).

Ten grams of the amine in 125 ml. of ether was added to 300 ml. of 1.21 *M* ethereal lithium aluminum hydride and refluxed with stirring for 6 hr. The work-up was as described above. There was recovered 8.7 g. (87%) of starting material, b.p. 180–181° (745 mm.), hydrochloride m.p. 248–249.5°. In similar experiments where the thiazanes derived from cyclohexanone, 4-*t*-butylcyclohexanone, acetophenone, and *p*-chlorobenzaldehyde were reduced with excess hydride, only the amino mercaptans described in Table II could be isolated in yields of 35, 25, 25, and 17%, respectively; no sulfur-free amines were found.

Acknowledgment.—This work was supported under National Institutes of Health Grant RG-8848.

[13] A. Skita and F. Keil, *Monatsh.*, **53**, 753 (1929).

A Study of Some Acetylation Reactions of Isopropenyl Acetate

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The rates of reaction and product distributions for the reaction of isopropenyl acetate with methyl isopropyl ketone, methyl isobutyl ketone, and methyl *t*-butyl ketone have been measured under standard conditions of temperature and catalyst. The reaction follows a complex kinetic pathway in which the initial products are kinetically controlled, and the ultimate products are thermodynamically controlled. The rates of reaction of isopropenyl acetate with *n*-butyl, *sec*-butyl, isobutyl, and *t*-butyl alcohol have also been measured. Most reasonably, ketene plays no important role in these reactions.

It has been well known for a number of years that isopropenyl acetate plus an acidic catalyst reacts smoothly with alcohols and enolizable aldehydes and ketones to produce the appropriate acetates and enol acetates, respectively.[1] Based on an unsupported statement that isopropenyl acetate is decomposed to ketene by acids and the fact that ketene is also an excellent acetylating agent, Hagemeyer and Hull[2] suggested that isopropenyl acetate acts as a ketene carrier, the implication being that ketene is the actual acetylating agent. Hauser and co-workers[3] have spoken of the reaction as an exchange without specifying the mechanistic details. One may infer from these statements that the mechanism of the acetylation reactions of isopropenyl acetate is not known. Since several exchange mechanisms may be written which do not directly involve ketene, for instance, a direct ester interchange with the alcohol or enol, one goal of the present study was to investigate the possible role of ketene in these reactions.

Several other facets of the enol acetylation reactions of isopropenyl acetate are of interest. It has been reported that ketones which may enolize in two different directions are prone to form the less highly substituted enol acetate in contrast to enol acetylations with acetic anhydride.[4] However, Hagemeyer and Hull[2] have reported methyl ethyl ketone to give 2-acetoxy-2-butene in 96% yield, while methyl isobutyl ketone produced 2-acetoxy-4-methyl-1-pentene in 92%. Subsequently, House and Kramar[5] showed that the various enol acetates of methyl isobutyl ketone were interconverted to a common equilibrium mixture by acid catalysis. In fact, this acid-catalyzed isomerization has been used in some instances to produce enol acetates which are not otherwise available.[6]

In view of these observations, it seemed highly desirable to carry out a quantitative study of the enol acetylation of a series of related ketones with isopropenyl acetate. As a corollary to this work, a similar study was carried out with a series of structurally related alcohols.

Experimental

Product Studies.—Isopropenyl acetate, methyl isopropyl ketone, methyl isobutyl ketone, methyl *t*-butyl ketone, and the various alcohols were all commercial products, distilled before use, and checked as pure by vapor phase chromatography (v.p.c.). *p*-Toluenesulfonic acid was purified by crystallization from benzene after first distilling off a large volume of benzene to azeotrope off water.

Each of the above ketones was treated with isopropenyl acetate plus a small amount of *p*-toluenesulfonic acid following the procedure of Hagemeyer and Hull.[2] All of the products produced agreed with the literature values regarding boiling point and index of refraction.[2,3,7]

The enol acetate of methyl *t*-butyl ketone has not been previously reported. The material produced here had b.p. 136–137°, $n^{25}\text{D}$ 1.4144.

Anal.[8] Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.38; H, 10.05.

V.p.c. of the product from methyl isopropyl ketone showed two product bands which were trapped and characterized by n.m.r. spectroscopy. Methyl isobutyl ketone gave three products, while methyl *t*-butyl ketone gave one product. The columns used for these three separations were 6 ft. of 20% 1,2,3-tris(2-cyanoethoxy)propane[9] on Chromosorb P at 70°, 12 ft. of the same packing at 75°, and 6 ft. of 20% Apiezon N on Chromosorb P at 130°, respectively.

The n.m.r. spectrum of each product was determined on a Varian A-60 in carbon tetrachloride with tetramethylsilane as an internal standard. The chemical shifts (τ units), integrated band intensities, and band multiplicities are given below. Weak, badly split bands are not listed.

Methyl *t*-butyl ketone gave 2-acetoxy-3,3-dimethyl-1-butene: 5.32 (two vinyl H, AB system, J = 2 c.p.s., $\Delta\nu$ = 11.2 c.p.s.), 7.91 (singlet, acetyl Me), 8.89 (singlet, three Me groups).

Methyl isopropyl ketone gave 2-acetoxy-3-methyl-1-butene: 5.32 (vinyl H, multiplet unresolved), 7.91 (singlet, acetyl Me), 8.95 (doublet, two alkyl Me, J = 6.5 c.p.s.); and 2-acetoxy-3-

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[1] R. N. Lacy, *Advan. Org. Chem.*, **2**, 213 (1960).

[2] H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1942).

[3] E. H. Mann, F. C. Frostick, and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3635 (1950).

[4] (a) R. B. Moffett and D. I. Weisblatt, *ibid.*, **74**, 2183 (1952); (b) H. Vanderhaeghe, E. R. Katzenellenbogen, K. Dobriner, and T. F. Gallagher, *ibid.*, **74**, 2811 (1952).

[5] H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

[6] H. Favre and A. J. Liston, *Can. J. Chem.*, **42**, 268 (1964).

[7] E. H. Man, F. C. Frostick, and C. R. Hauser, *ibid.*, **74**, 3228 (1952).

[8] Analysis was performed by Galbraith Laboratories, Knoxville, Tenn.

[9] A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959), footnote 24.

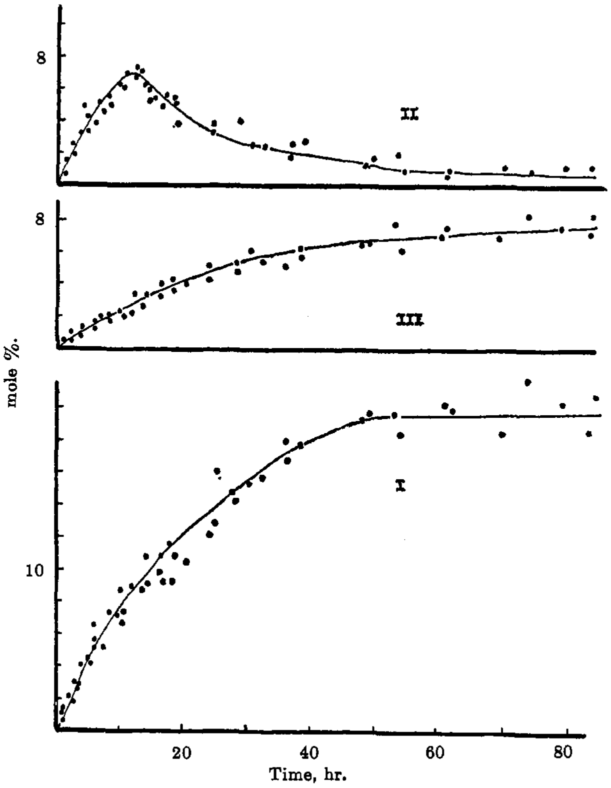


Figure 1.—The distribution of products for the reaction of isopropenyl acetate with methyl isobutyl ketone: I, 2-acetoxy-4-methyl-*trans*-2-pentene; II, 2-acetoxy-2-methyl-1-pentene; and III, 2-acetoxy-4-methyl-*cis*-2-pentene.

methyl-2-butene: 7.95 (singlet, acetyl Me), 8.21, 8.30, 8.48 (three methyls, broadened singlets).

Methyl isobutyl ketone gave 2-acetoxy-4-methyl-1-pentene: 5.36 (two vinyl H, AB system, $J = 1.5$ c.p.s., $\Delta\nu = 5.5$ c.p.s.), 7.95 (singlet, acetyl Me), 9.08 (doublet, two Me, $J = 6.5$ c.p.s.); 2-acetoxy-4-methyl-*trans*-2-pentene: 5.26 (vinyl H, two broad doublets, $J = 9$ c.p.s., long range $J = 1.2$ c.p.s.), 7.95 (singlet, acetyl Me), 8.21 (doublet, vinyl Me, long range $J = 1.2$ c.p.s.), 9.07 (doublet, $J = 9.07$ c.p.s., Me); and 2-acetoxy-4-methyl-*cis*-2-pentene: 5.14 (vinyl H, two broad doublets, $J = 9.5$ c.p.s., long range $J = 1$ c.p.s.), 8.00 (singlet, acetyl Me), 8.21 (doublet, vinyl Me, long range $J = 1$ c.p.s.), 8.99 (doublet, two Me, $J = 6.5$ c.p.s.).

Since the yields of products produced above were quite low, a series of experiments was carried out to determine the conditions for optimum yields. The results for isopropenyl acetate and methyl isobutyl ketone are given in Table I. The reactants were mixed and heated at such a rate that acetone just distilled through a 32-cm. column packed with steel sponge. The reactions were continued until no more acetone distilled over (runs II and III) or until acetone in excess of the required amount based on starting ketone had been collected (runs I, IV, and V). The reaction mixtures were then cooled and analyzed by v.p.c. It was established from mixtures of known composition that the v.p.c. band areas were proportional to the weight per cent of each component within ±3% in all cases.

TABLE I

THE YIELD OF THE REACTION OF ISOPROPENYL ACETATE AND METHYL ISOBUTYL KETONE UNDER DIFFERENT CONDITIONS

Run	Reactant,[a] moles	Catalyst, M	Run	Acetone distilled, mole	Reaction time, hr.	Yield, %	Ratio of the products[b] 1	2	3
I	0.4 I	0.09	1	0.23	5.5	80.0[c]	42	44	13
	0.2 K		2	0.25	6	97.5	43	44	14
II	0.2 I	0.09	1	0.18	2	78.5	64	7	29
	0.4 K		2	0.19	2	77.4	66	8	26
III	0.2 I	0.09	1	0.16	4	69.0[c]	59	12	29
	0.2 K		2	0.17	3.67	72.3	64	7	28
IV	0.48 I	0.09	1	0.24	8	94.4	40	45	15
	0.16 K		2	0.22	8	95.5	41	45	15
V	0.4 I	0.18	1	0.24	2.67	95.8	44	41	15
	0.2 K		2	0.26	3	98.4	46	40	14

[a] I = isopropenyl acetate; K = methyl isobutyl ketone. [b] Products by number as given in Table III. [c] The calculation of these yields was based on the analyses of the v.p.c. chromatogram of the washed reaction mixtures, where the rest of the yield data were obtained from the analyses of the reaction mixtures without being washed.

In three of the cases above, the v.p.c. yields were checked by direct distillation. The yield of enol acetates were *ca.* 10% lower owing to mechanical loss. Only a slight residue of evil-smelling sludge remained in the distillation pot.

The same procedure was followed in allowing 30 g. (0.3 mole) of isopropenyl acetate to react with 20 g. (0.2 mole) of methyl *t*-butyl ketone and 17.2 g. (0.2 mole) of methyl isopropyl ketone, respectively, in the presence of 0.09 M p-toluenesulfonic acid. The first reaction required 7.5 hr. to produce 11.1 g. of acetone (13.1 g. of distillate contaminated with 15% by weight of isopropenyl acetate). The yield of 2-acetoxy-3,3-dimethyl-1-butene was 68%. The second reaction required 5.5 hr. and produced 15 g. of acetone. The yield of products was 93.6%.

Kinetic Procedure.—All kinetic experiments were carried out in a constant-temperature bath operated at 74.8 ± 0.05° for the ketone experiments and 50.4 ± 0.03° for the alcohol experiments. All reactants were mixed at room temperature since no reaction was found to occur at this temperature. The sealed-ampoule technique was used throughout. Usually 15–30 points were obtained for each run. Experiments with the ketones were done in quadruplicate and with the alcohols in duplicate. The ketone runs were carried out until equilibrium was reached. The alcohol experiments were followed essentially to completion with the exception of those with *t*-butyl alcohol which were followed to *ca.* 50% completion.

At appropriate times, ampoules were withdrawn, chilled in Dry Ice–acetone, brought to room temperature, broken, and analyzed by v.p.c. During each of the reactions it was consistently noted that the amount of acetone was somewhat in excess of the amount of acetate product(s). With high injection-port temperatures and no attempt to clean the injection port between determinations, the excess of acetone rose to 13–16% during the first hour and, thereafter, remained essentially constant. By operating the injection port at 70° and cleaning the port after each determination the excess amount of acetone was greatly reduced. For the ketone experiments about 8–10% excess acetone appeared during the first 0.5 hr. of reaction time and remained nearly constant thereafter. In the alcohol experiments, the excess acetone was very slight initially but increased throughout the course of the reaction to 3–7% above the amount of ester formed.

The equilibrium values obtained for all of the ketone acetylations are given in Table II.

TABLE II

EQUILIBRIUM COMPOSITIONS

Methyl ketone[b]	Final composition, mole %[a] Isopropenyl acetate	Ketone	Acetone	Product[c]
Isopropyl	8.7	18.3	41.3	1, 0.3; 2, 31.3
Isobutyl	5.6	18.2	46.3	1, 20.7; 2, 1.2; 3, 7.8
t-Butyl	(a) 44.8	27.6	17.6	10.1
	(b) 28.0	37.7	22.8	11.9
	(c) 24.0	38.6	26.4	11.2
	(d) 12.7	55.7	20.7	11.0
	(e)[d] 24.1	38.8	23.3	13.9

[a] Products by number as given in Table III. [b] Composition of starting materials as given in Table III. [c] Average values found for all runs used in Table III. [d] The equilibrium composition for the reverse reaction, *i.e.*, the reactants were acetone and enol acetate of methyl *t*-butyl ketone (both 3.88 M) and the concentration of catalyst was 0.09 M. The conditions and results are comparable with case b.

In one duplicate set of experiments, the enol acetate of methyl *t*-butyl ketone was allowed to react with acetone under the same conditions as those above. The equilibrium values are given in Table II, and the rate data are discussed subsequently.

TABLE III

RATE DATA FOR THE REACTION OF A SERIES OF METHYL KETONES WITH ISOPROPENYL ACETATE[a]

Methyl ketone	Ketone, M	Isopropenyl acetate, M	Catalyst, M	$k \times 10^5$, l./mole min.	$R_0{}^b \times 10^4$, moles/l. min.	$R_p{}^b \times 10^4$, moles/l. min.
Isopropyl	4.18	4.18	0.09	12.0	20.6	
1. 2-Acetoxy-3-methyl-1-butene						1. 16.4
2. 2-Acetoxy-3-methyl-2-butene						2. 4.2
Isobutyl	3.90	3.90	0.09	17.5	35.3	
1. 2-Acetoxy-4-methyl-1-pentene						1. 22.1
2. 2-Acetoxy-4-methyl-*trans*-2-pentene						2. 9.9
3. 2-Acetoxy-4-methyl-*cis*-2-pentene						3. 3.3
t-Butyl	(a) 2.67	5.34	0.09	4.3	6.2	...
	(b) 3.92	3.92	0.09	6.4	9.8	...
	(c) 5.10	2.55	0.09	8.3	10.8	...
	(d) 3.92	3.92	0.18	16.0	24.6	...
2-Acetoxy-3,3-dimethyl-1-butene						
Acetone with *t*-butyl ketone enol acetate[c]				30.0	45.2	...

[a] At 74.8° with *p*-toluenesulfonic acid as catalyst. [b] R_0 is the intial rate of disappearance of ketone, and R_p is the initial rate of product formation. [c] Acetone, 3.88 M; enol acetate, 3.88 M; catalyst, 0.09 M.

Calculations from the Kinetic Data.—The reaction of isopropenyl acetate with methyl isobutyl ketone, methyl isopropyl ketone, and methyl *t*-butyl ketone followed the same general course. The amount of starting ketone and acetate decreased rapidly at first and then slowed. Concurrently, there was an initial rapid formation of products which slowed until equilibrium was reached. The formation of the three enol acetates from methyl isobutyl ketone as a function of time is shown in Figure 1. Since equal molar amounts of reactants were used, the results are given in mole per cent, a figure which is most readily available from the v.p.c. data. The results in Figure 1 combine the data for four runs, and the reproducibility of the method is amply indicated by the plot. Similar plots were obtained for the other ketones. The equilibrium values are given in Table II.

For those cases where more than one enol acetate product was formed, the relative initial rates of formation were calculated in the following fashion. During the first 6–10 hr. the mole per cent product *vs.* time plot (such as in Figure 1) closely followed a parabola. The data for each case were fitted by the method of least squares to a general equation of the type: $t = am + bm^2$, where t is the time in minutes, m is the mole per cent of product, and a and b are constants. It can readily be shown that the initial rate of product formation in mole per cent per minute is just $1/a$. The experimental conditions and various products are assigned by number in Table III. The parameters derived for the above equation are given in Table IV.

TABLE IV

Ketone	Product[a]	a	b
Methyl isopropyl	1	37.2	4.9
	2	151.5	4.3
Methyl isobutyl	1	55.0	1.4
	2	25.0	12.8
	3	156.0	63.0
Methyl *t*-butyl	Case a	83.5	9.5
	b	96.8	0.11
	c	37.2	4.56
	d	25.4	2.7
Acetone with the enol acetate of methyl *t*-butyl ketone		8.0	1.0

[a] Products by number as given in Table III.

Considering the final equilibrium values as complete reaction, it was found for all cases above that good second-order kinetics were followed for the first 30–50% reaction for the rate of disappearance of starting ketone; *i.e.*, the reactions were first order in ketone and first order in isopropenyl acetate. The rate constants for the disappearance of ketone were determined graphically from conventional second-order plots. A typical plot is shown in Figure 2, and the rate constants, initial reaction rates, and the initial rates of formation of each product are given in Table III. Of course, for those reactions where only one product was formed, it was assumed that the rate of product formation equalled the rate of ketone disappearance.

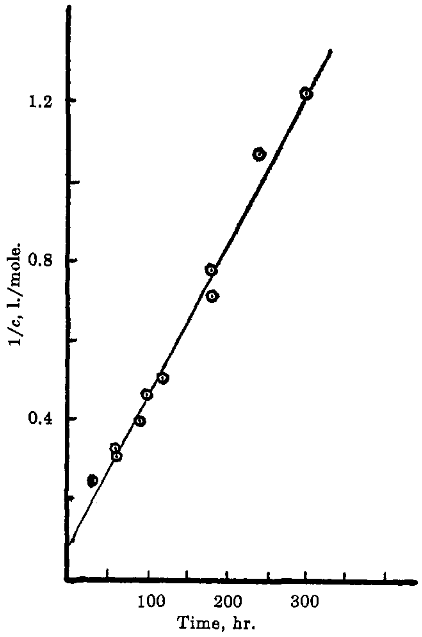


Figure 2.—The second-order rate plot for the reaction of isopropenyl acetate with methyl *t*-butyl ketone in a 2:1 molar mixture. The reaction was 0.09 M in *p*-toluenesulfonic acid, and the reaction temperature was 74.8°.

The rates of reaction of isopropenyl acetate with *n*-butyl, *sec*-butyl, isobutyl, and *t*-butyl alcohol were all found to follow second-order kinetics to upwards of 90% completion. The reaction conditions, rate constants, and initial reaction rates are given in Table V. A typical plot for duplicate runs with *n*-butyl alcohol is shown in Figure 3. All rate constants were determined graphically. Again, all concentrations are at 50.4°.

TABLE V

RATE DATA FOR THE REACTION OF A SERIES OF ALCOHOLS WITH ISOPROPENYL ACETATE[a]

Alcohol	ROH, M	Isopropenyl acetate, M	$k \times 10^5$, l./mole min.	$R^{t-0} \times 10^4$, moles/l. min.
n-Butyl	4.71	4.71	380	875
Isobutyl	4.68	4.68	400	876
sec-Butyl	4.70	4.70	50	110
t-Butyl	4.63	4.63	46	99

[a] At 50.4° with 0.09 M *p*-toluenesulfonic acid as catalyst.

The Decomposition of Isopropenyl Acetate by *p*-Toluenesulfonic Acid.—Isopropenyl acetate (20 g.) and *p*-toluenesulfonic acid (1 g.) were heated to reflux in a Podbelniak Minical column with an aniline trap attached at the top of the condenser. Since

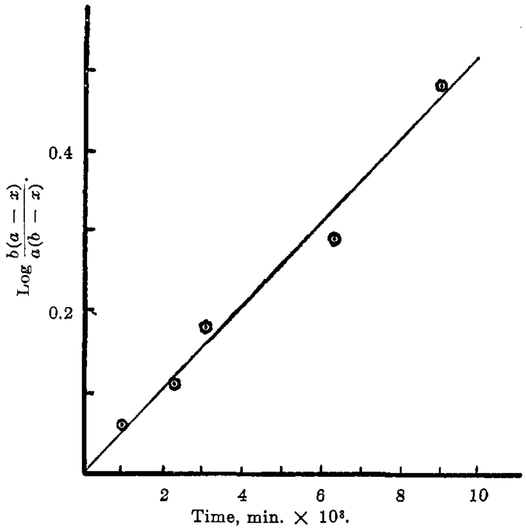


Figure 3.—The second-order rate plot for the reaction of equal molar amounts of *n*-butyl alcohol with isopropenyl acetate at 50.4° (0.09 *M* *p*-toluenesulfonic acid).

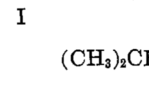
the receiver assembly constituted a closed system, all volatile materials had to pass through the aniline trap to escape to the atmosphere. Distillate was collected over a period of 10 hr. and, with the exception of the first few drops which boiled at *ca.* 58°, came over at 94°. The distillation was stopped when the material in the distillation pot was reduced to one-sixth of the original volume.

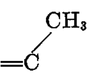
The distillate was light yellow but turned red on standing. Analysis by v.p.c. showed only a slight amount of acetone and a large amount of isopropenyl acetate. The residue in the pot gave five bands on v.p.c. The first band (minor) was acetone, and the third band (major) was isopropenyl acetate. The fourth band (trivial amount) was trapped and identified as acetic acid by its infrared spectrum. Bands 2 and 5 were very small and could not be trapped in sufficient quantities for identification.

The entrance to the aniline trap contained a tiny amount (less than 100 mg.) of yellow crystals which were washed with dilute hydrochloric acid. This material was identified as acetanilide by melting point, mixture melting point, and infrared spectrum.

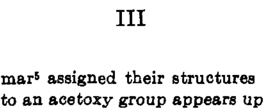
Discussion

The complexities of the enol acetylation reactions of isopropenyl acetate are brought out, in part, by a consideration of the data for the reaction with methyl isobutyl ketone. In keeping with the observations of House and Kramar,[5] three products were formed. These were isolated by v.p.c. trapping, and the structures, assigned by n.m.r. spectroscopy following the logic of House and Kramer,[5] were as follows in order of elution.[10] The formation of I, II, and III as a function


I


$(CH_3)_2CHCH_2\underset{OAc}{C}{=}CH_2$

II


III

of time is shown in Figure 1. Clearly, during the early portion of the reaction, kinetic factors are in control with the terminal olefin II produced most rapidly. After passing through a maximum, the amount of II declines, and thermodynamic control determines the final equilibrium composition. House and Kramar[5] have shown that the same equilibrium composition, consisting of 73% I, 5% II, and 22% III, resulted from the acid-catalyzed isomerization of each of the above at 100°. These values are close to the observed values obtained here at 74.5°, *i.e.*, 70% I, 4% II, and 26% III.

Similar results were obtained with methyl isopropyl ketone. Again the terminal olefin, while formed more rapidly at beginning of the reaction, was the minor final product.

Most reasonably, ketene itself plays no important role in the acetylation reactions of isopropenyl acetate, for when isopropenyl acetate and *p*-toluenesulfonic acid are heated together in the presence of an aniline trap only a trace of acetanilide was formed. While this trace may have arisen from ketene, it might well have been formed by the vapors of isopropenyl acetate. Consequently, no further consideration of a mechanism involving ketene will be given here.

The kinetic studies were plagued to a certain extent by an unknown side reaction which occurred both with the ketone and alcohol acetylations. It was consistently observed that acetone was produced in excess of the stoichiometric amount during the reaction. For the enol acetylations, this amounted to some 8–10% which was quite reproducible and which appeared, for the most part, early in the reaction. Perhaps owing to the lower temperature, the excess acetone amounted to only 3–7% in the alcohol acetylations and was produced gradually during the course of the reaction. In spite of a diligent search, we could not account for the acetyl moiety in the product. Distillation of preparative-size reactions left only a slight, evil-smelling residue. This side reaction was ignored in the kinetic calculations to be discussed subsequently since good, reproducible, second-order plots were obtained. The major effect of the side reaction appears to be reflected in the equilibrium constants calculated from the data in Table II. Thus, for methyl *t*-butyl ketone, values of 0.14, 0.26, 0.32, and 0.35 are given for various conditions as cited.

The acetylation of the various alcohols in Table V was inconveniently rapid at 75°, and the reaction was studied, therefore, at 54°. Good second-order kinetics were observed. As noted in Table V, the primary alcohols reacted appreciably faster than the secondary or tertiary alcohol. Certainly the simplest mechanistic picture for this reaction is that of an acid-catalyzed ester interchange in which the alcohol attacks some form of the conjugate acid of isopropenyl acetate. At least three conjugate acids of isopropenyl acetate, two involving O-protonation and one C-protonated form, can be written, and we have no idea as to which is the more likely. In any event, the observed rate differences can most reasonably be ascribed to steric

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[10] House and Kramar[5] assigned their structures on the basis that the olefinic hydrogen *trans* to an acetoxy group appears upfield from a hydrogen *cis* to the acetoxy group. Additional support for this contention is offered by the assignment of protons in vinyl acetate (N. S. Bhacca, L. F. Johnson, and J. N. Schoolery, "Catalog of NMR Spectra," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 65), and from the analysis of the spectra of *cis*- and *trans*-1-acetoxy-1-heptene [J. J. Riehl, J. M. Lehn, and F. Hemmert, *Bull. soc. chim. France*, 224 (1963)].

differences between the alcohols and the effect which these exert on the bimolecular step.

The enol acetylation reactions are more difficult to deal with. As the referees of an earlier form of this manuscript have pointed out, a variety of mechanisms for the enol acetylations can be written. These may involve the ketone, its enol, and the various conjugate acids of isopropenyl acetate, as well as both cyclic or noncyclic transition states and intermediates. If one evokes the criterion of simplicity, then it would seem to us that the most reasonable mechanism would be analogous to the ester interchange reaction in which the enol attacks the conjugate acid of isopropenyl acetate. While the data do not allow a clear-cut decision among the various possibilities, the following comments seem in order.

During the early stages of the reaction, before the reverse reaction has assumed importance, the observed rates follow second-order kinetics. The rate constants given in Table III are really "apparent" or "pseudo" second-order constants for they vary with the ratios of the starting materials as well as with the catalyst concentration.

Combining rate data and product analyses for the iodination and bromination of a series of ketones, Cardwell and Kilner[11] have concluded that in aqueous acid the relative rates of enolization fall in the order acetone > methyl isobutyl ketone > methyl isopropyl ketone > methyl *t*-butyl ketone. Furthermore, when alternative pathways for enolization exist, the internal enol is formed more rapidly than the external.

Extrapolation of results in aqueous acid to results obtained in the milieu of the enol acetylations is subject to some question. However, the rate values in Table III do show the same order of reactivity, *i.e.*, acetone > methyl isobutyl ketone > methyl isopropyl ketone > methyl *t*-butyl ketone. Regardless of whether the ketone reacts in the keto or enol form, there must, at some point, be a bimolecular collision, and this presumably would be subject to steric considerations which suggest the above order of reactivity. These expectations are, of course, substantiated by the alcohol acetylations.

The initial rapid formation of the terminal olefin is also reasonable. If the enol is the attacking species, then the hydroxyl group is less sterically hindered for the terminal enols as opposed to the internal enols. If the ketone takes part in the bimolecular step, then a proton must be removed from a position α to the carbonyl group in forming the ultimate enol acetate product. Following the considerations of House and Kramar,[5] it is reasonable that a terminal methyl hydrogen would be more accessible to the base than a more highly substituted internal position.

In summary, it is evident that in situations where more than one enol acetate may be formed both kinetic and thermodynamic control influence the course of the reaction and determine the product composition at a given time. In preparative reactions, the use of an excess of isopropenyl acetate does not greatly enhance the yield but is probably advisable to offset the side reaction which destroys some of the isopropenyl acetate. An increase in the amount of catalyst materially shortens the reaction time without decreasing the yield of product.

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Thermal Decomposition of β-Allyloxypropionyl Peroxide. Cyclization of the β-Allyloxyethyl Radical[1]

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Results of kinetics runs are reported for decompositions of β-allyloxypropionyl peroxide in toluene and *p*-xylene. The kinetics of decomposition in toluene are approximately first order, although very slight curvatures of first-order plots indicate a small amount of induced decomposition. β-Allyloxypropionyl peroxide decomposes somewhat more rapidly in *p*-xylene than in toluene, and the kinetic behavior is such as to suggest that there is more radical-induced decomposition in the former. Product studies are reported for decompositions of the β-allyloxypropionyl peroxide in *p*-xylene and in the same solvent containing excess galvinoxyl. The main product formed from the β-allyloxyethyl radical is 3-methyltetrahydrofuran, which indicates that this radical, like the 5-hexenyl radical, undergoes cyclization to give a five-membered ring.

It has been found recently that the 5-hexenyl radical cyclizes in solution to give the cyclopentylmethyl radical, whether the 5-hexenyl radical is generated by decomposition of 6-heptenoyl peroxide,[3] by reaction of 6-mercapto-1-hexene with triethyl phosphite,[4] or by the Kolbe electrolysis of 6-heptenoic acid.[5]

It is also known that 1-substituted derivatives of the 5-hexenyl radical undergo cyclization to give five-membered ring compounds as the only cyclic products. Thus, Brace has shown that the only cyclic products which are formed in the free-radical addition of 1-iodoperfluoropropane to 1,6-heptadiene have structures I and II.[6]

At the same time, it has been shown by Cadogan that free-radical additions to ethyl diallylacetate result in the formation of both the five- and six-membered

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