tion of air and the following replacement with dry nitrogen was repeated several times while keeping the tube immersed in an acetone–Dry Ice mixture. The tube was then maintained at polymerization temperature (65°). After the lapse of a given period of time, the contents of the tube were poured into pentane (10:1 excess) containing a trace of phenyl-β-naphthylamine as an inhibitor against oxidation or further polymerization. The precipitated polymer was washed thoroughly with pentane and dried *in vacuo*. In such case that gelation occurred during polymerization, the insoluble gel was separated by centrifugation.

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Reductions with Metal Hydrides. XVII. Reduction of 1,3-Thiazanes[1a]

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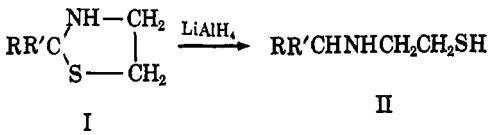
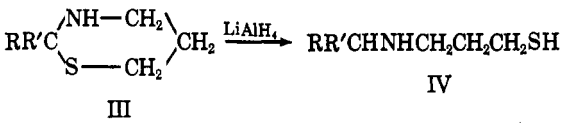
Reduction of 2-substituted 1,3-thiazanes (1-thia-3-azacyclohexanes) with lithium aluminum hydride gives N-substituted 3-aminopropyl mercaptans, $RNHCH_2CH_2CH_2SH$. Contrary to earlier implications, even 2-aryl-substituted thiazanes appear to exist largely as such rather than as the tautomeric Schiff bases.

In a previous publication[1] we described the reduction of thiazolidines (I) to β-alkylaminoethyl mercaptans (II) by means of lithium aluminum hydride.



I II

The present paper reports the extension of the reduction reaction to 1,3-thiazanes (III) which are reduced to γ-alkylaminopropyl mercaptans (IV). Apart from



III IV

the intrinsic interest of ascertaining whether the six-membered heterocyclic rings were hydrogenolyzed as easily as the five-membered ones, the present study serves to answer two questions which had arisen in connection with earlier work. One refers to the structure of the thiazanes (III) which had been suggested[2] to exist in tautomeric equilibrium with substantial portions of the Schiff bases, $RR'C{=}NCH_2CH_2CH_2SH$, in cases where R = phenyl. The other point has to do with the overreduction of the β-alkylaminoethyl mercaptans (II), with excess hydride, to ethylamines $RR'CHNHCH_2CH_3$.[1] In connection with ascertaining possible mechanisms of this hydrogenolysis, it was of interest whether the next higher homologs (IV) would be similarly hydrogenolyzed.

Thiazanes (III) were readily obtained from aldehydes or ketones by treatment with the previously described[3] 3-amino-1-propanethiol. The compounds synthesized and their properties are listed in Table I.

Since it had been previously suggested[2] on the basis of the appearance of a strong infrared absorption band at 1650 cm.$^{-1}$ that the condensation product of benzaldehyde and 3-mercaptopropylamine existed principally in the Schiff base rather than the thiazane form, the infrared, ultraviolet, and n.m.r. spectra of this compound were recorded. The infrared spectrum showed no band at 1650 cm.$^{-1}$, but only weak absorption at 1600 cm.$^{-1}$ (probably a phenyl band) in either a KBr pellet or chloroform solution. The ultraviolet spectrum in absolute ethanol was structureless, as reported previously.[2] As Schiff bases ArC(R)=NR are known[4] to have a strong absorption band ($\epsilon \sim 17{,}000$) at 2470 Å. the Schiff base structure would seem to be excluded.[5] The n.m.r. spectrum corroborates the thiazane structure: singlet (1) at τ 8.63 (NH), quintet (2) at 8.36 (central methylene), broad multiplet (4) at 7.10–6.83 (methylenes next to N and S), singlet (1) at 4.95 (benzylic hydrogen), and multiplet (5) at 2.75 (phenyl). The signal position for the benzylic hydrogen is close to that in 2-phenylthiazolidine (τ 4.54) and remote from that of the PhCH=N— proton in the Schiff base structure (τ 3.2[6]). Of course, the n.m.r. spectrum does not entirely exclude a rapidly equilibrating mixture of thiazane and Schiff base with the equilibrium shifted toward the former structure, but if such an equilibrium does exist, the infrared and ultraviolet spectra indicate that it must lie very far on the side of the thiazane.

The characteristic C=N absorption in the infrared was also missing in the spectra of 2-phenyl-2-methyl-1,3-thiazane (from acetophenone) and of 2-(*p*-chlorophenyl-1,3-thiazane (from *p*-chlorobenzaldehyde). The thiazane derived from cyclohexanone is known[2] not to exist in the Schiff base form.[7]

Reduction of the thiazanes with lithium aluminum hydride proceeded smoothly to give the corresponding amino mercaptans IV, except in the case of the 3-

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(3) S. D. Turk, R. P. Louthan, R. I. Cobb, and C. R. Bresson, *J. Org. Chem.*, **27**, 2846 (1962).

(4) G. E. McCasland and E. C. Horswill, *J. Am. Chem. Soc.*, **73**, 3923 (1951).

(5) Only in the case of the *o*-chlorobenzaldehyde condensation product with 3-amino-1-propanethiol did we, on one occasion, obtain a product which showed a *small* infrared band at 1650 cm.$^{-1}$ and some ultraviolet absorption. However, in a second preparation, the material did not show these characteristics. Because of this lack of reproducibility of properties, the compound is not reported here.

(6) From the n.m.r. spectrum of $C_6H_5CH{=}NCH_2CH_2OH$ which, on the basis of infrared and ultraviolet spectroscopic evidence, has the previously proposed Schiff base structure: *cf.* E. D. Bergmann, *Chem. Rev.*, **53**, 325 (1953).

(7) Since the condensation product of benzaldehyde and 3-amino-1-propanethiol was reported in ref. 2 to have a structureless ultraviolet spectrum (the spectrum is actually reproduced in the paper), it seems puzzling how the Schiff base structure could have been assigned with any confidence on the basis of the infrared spectrum.

TABLE I

THIAZANES (III)

R	R′	Yield, %	$n^{20}D$	B.p. (mm.) or m.p., °C.	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
C_2H_5	H	82	1.5155	68 (9)	54.91	9.98	10.67	55.19	9.99	11.07
Cyclohexylidene		68	1.5400	127–128 (13)			[a]			
4-*t*-Butylcyclohexylidene[b]		87	1.5220	108 (0.13)	68.66	11.08	6.16	69.00	11.05	6.19
3-Cholestanylidene[b]		91	...	135–136	78.36	11.62	3.05[c]	78.62	11.71	3.07
C_6H_5	H	69	...	134–136 (5) 65.5–67			[d]			
C_6H_5	CH_3	83	1.5827	98.5 (0.19)	68.34	7.82	7.25[e]	68.36	8.07	7.39
4-ClC_6H_4	H	74	...	87–87.5	56.19	5.66	6.56	56.12	5.54	6.47
C_2H_5	H′	67	1.5003	96–99 (6)	60.32	10.76	8.80	60.04	10.97	9.15

[a] Lit.[2] b.p. 118–120° (13 mm.), $n^{20}D$ 1.5303. [b] Configuration unknown. [c] Calcd: S, 6.97. Found: S, 6.96. [d] Lit.[2] b.p. 142–144° (8 mm.), m.p. 64–65.5°. [e] Calcd.: S, 16.59. Found: S, 16.71. [f] N-Ethyl compound.

TABLE II

LITHIUM ALUMINUM HYDRIDE REDUCTION OF 2-SUBSTITUTED 1,3-THIAZANES TO AMINO MERCAPTANS, RR′CHNHCH$_2$CH$_2$CH$_2$SH (IV)

R	R′	Yield, %	B.p., °C. (mm.)	$n^{20}D$	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
C_2H_5	H	53	70 (9.5)	1.4749	54.08	11.35	10.51	54.08	11.34	10.71
Cyclohexylidene		55	103 (4)	1.5042	62.37	11.05	8.08	62.45	11.21	8.25
4-*t*-Butylcyclohexylidene[a]		59	108.(0.16)	1.4961	68.06	11.86	6.11	68.11	11.99	6.17
C_6H_5	H	56	112.5 (0.28)	1.5537	66.25	8.34	7.73	66.40	8.40	7.44
p-ClC_6H_4	H	51	124 (0.1)	1.5619	55.67	6.54	6.49	55.97	6.99	6.50
C_6H_5	CH_3	66	101.5 (0.17)	1.5430	67.64	8.77	7.17	67.61	8.77	7.36
C_2H_5	H[b]	78	88–91 (11)	1.4748	59.57	11.87	8.69	59.65	11.82	8.90

[a] Stereochemistry of starting material and product unknown. [b] N-Ethyl compound.

cholestanone derivative where a pure crystalline amino mercaptan could not be obtained. The seven amino mercaptans obtained in the pure state are listed in Table II; all were liquids and were characterized as such rather than as the hydrochloride derivatives since it was found, in accordance with earlier observations,[8] that these salts were readily oxidized to disulfide dihydrochlorides by air on attempted recrystallization. For purposes of characterization, the reduction product of 2-ethyl-1,3-thiazane (III, R = C_2H_5; R′ = H), 3-propylaminopropyl mercaptan, $C_3H_7NHCH_2CH_2CH_2SH$, was deliberately oxidized to the corresponding disulfide in quantitative fashion by means of iodine. The dihydrochloride of the disulfide had the same melting point as an authentic sample[8,9] and the corresponding mixture melting point was undepressed. The structure of the reduction product of the thiazane derived from cyclohexanone (III, R, R′ = cyclohexylidene), $C_6H_{11}NHCH_2CH_2CH_2SH$, was also confirmed by synthesizing an authentic sample from 3-cyclohexylamino-1-propanol,[10] $C_6H_{11}NHCH_2CH_2CH_2OH$, by treatment with hydrochloric acid and thionyl chloride (to form 3-cyclohexylamino-1-propyl chloride hydrochloride, $C_6H_{11}NHCH_2CH_2CH_2Cl\cdot HCl$) followed by sodium hydrogen sulfide, NaSH. The compound so prepared had the same refractive index and infrared spectrum as the reduction product listed in Table II.

In connection with the mechanism of reduction it is of interest that the N-substituted thiazane, N,2-diethyl-1,3-thiazane, was reduced as smoothly as thiazanes having H on nitrogen. This observation will be discussed in more detail in a later paper.

In the case of the reduction product from 2-cyclohexylidenethiazolidine, it was observed[1] that, with excess $LiAlH_4$, overreduction of the mercaptan $C_6H_{11}NHCH_2CH_2SH$ to the ethylamine $C_6H_{11}NHCH_2CH_3$ occurred readily. No corresponding hydrogenolysis occurred in the case of the higher homologs studied in the present investigation; in particular, no compounds of structure $RR'CHNHCH_2CH_2CH_3$ could be isolated in the reduction of the thiazanes derived from cyclohexanone, 4-*t*-butylcyclohexanone, 3-cholestanone, acetophenone, and *p*-chlorobenzaldehyde. Since material recoveries of the corresponding 3-mercaptopropylamines were poor when a large excess of hydride was used (possibly owing to difficulty of decomposing the metal complexes formed), a control experiment was performed in which N-propylcyclohexylamine was subjected to the conditions of the hydride reduction. In this case, 87% of the amine was recovered; thus, since no N-propylcyclohexylamine was isolated in the reduction of 2-cyclohexylidene-1,3-thiazane, it may be safely concluded that none was formed and the "overreduction" is characteristic of mercapto*ethyl*amines, $RR'NHCH_2CH_2SH$.[1]

After this work had been completed, a report appeared[11,12] indicating that 5,6-dihydro-1,3-thiazines can be reduced to 1,3-thiazanes by means of sodium borohydride without further hydrogenolysis of the thiazanes. Since thiazolidines are reduced to β-amino mercaptans by either lithium aluminum hydride or sodium borohydride, it would appear that the reduction of 1,3-thiazanes is somewhat less facile than that of thiazolidines.

(8) D. Plant, D. S. Tarbell, and C. Whiteman, *J. Am. Chem. Soc.*, **77**, 1572 (1955).

(9) The authentic sample was kindly supplied by Professor Tarbell.

(10) M. Freifelder, M. B. Moore, M. R. Vernsten, and G. R. Stone, *J. Am. Chem. Soc.*, **80**, 4320 (1958).

(11) J. C. Getson, J. M. Greene, and A. I. Meyers, *J. Heterocyclic Chem.*, **1**, 300 (1964).

(12) See, however, D. M. Green, A. G. Long, P. J. May, and A. F. Turner, *J. Chem. Soc.*, 766 (1964).

Experimental

All melting and boiling points are uncorrected. Elemental analyses are by Midwest Microlabs. N.m.r. spectra were recorded on a Varian HR-60 high-resolution instrument at 60 Mc.p.s. Infrared spectra were recorded on Perkin-Elmer Infracord and Model 21 instruments.

3-Amino-1-propanethiol.[3]—The starting material was prepared in 53% yield from 3-chloropropylamine hydrochloride and sodium hydrogen sulfide on a 2.3-mole scale, m.p. 108–110° (lit.[3] m.p. 109–110°).

2-Ethyl-1,3-thiazane (III, R = C_2H_5; R′ = H).—To a solution of 12.8 g. (0.22 mole) of propionaldehyde in 100 ml. of dry ether contained in a flask equipped with a reflux condenser was added 18.2 g. (0.2 mole) of 3-amino-1-propanethiol. A brisk reaction ensued which was moderated by immersing the flask in ice–water. After the reaction subsided, the reaction mixture was refluxed for 3 hr. The water formed collected at the bottom of the flask. Anhydrous sodium sulfate (2–3 g.) was added after cooling, the reaction mixture was filtered, and the sulfate was rinsed with ether. Concentration and distillation gave 21.6 g. (82%) of product boiling at 73–74° (10 mm.). Redistillation gave the material listed in Table I.

1-Thia-5-azaspiro[5.5]undecane.—The preparation of this compound from 3-amino-1-propanethiol and cyclohexanone is typical of all the preparations listed in Table I except the first and last. To 14.3 g. (0.147 mole) of freshly distilled cyclohexanone and 12.1 g. (0.133 mole) of 3-amino-1-propanethiol in 125 ml. of benzene was added a catalytic amount of *p*-toluenesulfonic acid and the solution was boiled for 3 hr. employing a reflux condenser equipped with a Dean–Stark trap. The theoretical amount of water having separated, the light yellow solution was cooled and washed twice with 10% aqueous sodium hydroxide followed by two portions of water. The solvent was distilled and the residue was distilled under vacuum, b.p. 99–100° (6 mm.), yield 15.5 g. (68%). The properties of the redistilled material are reported in Table I as are the yields, properties, and analyses of other thiazanes prepared in the same manner.

In the case of 3-cholestanone, a 10% excess of 3-amino-1-propanethiol was employed. The product crystallized from ethanol in fine, shiny white needles.

Spectral Data.—The n.m.r. spectra of the 3-cholestanone, cyclohexanone, and benzaldehyde derivatives were compatible with the assigned structures. The benzaldehyde derivative showed peaks at τ 8.63 (singlet, NH), 8.36 (quintet, CH_2), 6.83, 7.10 (multiplets, CH_2 next to heteroatoms), 4.95 (singlet, CH), and 2.75 (multiplet, C_6H_5). The position of the benzylic CH is similar to that in 2-phenylthiazolidine (τ 4.54) and different from that in N-benzylidene-2-amino-1-ethanol (τ 3.21). The infrared spectra of all compounds were compatible with the assigned structures. In particular, the infrared spectra of the pure benzaldehyde, *p*-chlorobenzaldehyde, and acetophenone derivatives were transparent in the 1650-cm.$^{-1}$ region. In contrast, N-benzylidene-2-amino-1-ethanol, $C_6H_5CH{=}NCH_2CH_2OH$, had a very intense band at 1645 cm.$^{-1}$. This compound also had strong ultraviolet absorption at 2485 Å. (ϵ 15,000), whereas 2-phenyl-1,3-thiazane and 2-phenylthiazolidine had only end absorption.

2,3-Diethyl-1,3-thiazane.—A solution of 9.17 g. (0.07 mole) of 2-ethyl-1,3-thiazane and 6.3 ml. (0.078 mole) of ethyl iodide in 100 ml. of absolute ethanol containing, in suspension, 8.9 g. (0.084 mole) of anhydrous sodium carbonate was gently refluxed with stirring for 18 hr. The solution was then cooled, filtered, concentrated, and diluted with ether. The solid (sodium iodide?) which separated was filtered and the filtrate was concentrated and distilled, yield 7.5 g. (67%), b.p. 88–103° (17 mm.). The properties of the redistilled material are listed in Table I.

Reductions.—The preparation of 3-(N-propylamino)propane-1-thiol, n-$C_3H_7NHCH_2CH_2CH_2SH$, is described as typical. To a stirred solution of 7.5 g. (0.057 mole) of 2-ethylthiazane in 100 ml. of sodium-dried ether contained in a three-necked flask equipped with stirrer, addition funnel, and reflux condenser was added, dropwise, 12.5 ml. (0.016 mole) of 1.29 *M* ethereal lithium aluminum hydride over a period of 15 min. The solution became turbid immediately and a white solid precipitated toward the end of the addition. After additional stirring (15 min.) the solid disappeared; up to this time 370 cc. (0.0165 mole) of hydrogen (measured at STP) had been collected. An additional 12.5 ml. of hydride solution (1.29 *M*) was then added over 15 min. and stirring was continued for an additional 45 min.; during this stage 0.05 mole of hydrogen was evolved. Refluxing of the reaction mixture for 45 min. produced hardly any additional gas. The reaction mixture was cooled, decomposed with 5 ml. of water, and stirred for 0.5 hr., 300 cc. (0.0135 mole) of hydrogen being evolved. The reaction mixture was filtered with the aid of Celite and the residual salts were washed thoroughly with ether. The water layer was separated and discarded. The ether layer was dried over sodium sulfate, concentrated, and distilled to give 4.0 g. (53%) of product, b.p. 69° (9 mm.). The properties of the redistilled material are listed in Table II.

The hydrochloride, prepared in quantitative yield by treatment of the base in ether with ethereal hydrogen chloride, melted at 230–238° (with previous softening) after crystallization from absolute ethanol–ethyl acetate.

The freshly distilled amino thiol (1.42 g., 10.7 mmoles) was dissolved in 50 ml. of benzene and layered with 50 ml. of water. The thoroughly stirred suspension was titrated with standard (0.5138 *N*) iodine in benzene to a faint yellow end point; 20.3 ml. (10.4 mmoles) of iodine were consumed. This titration indicated that the thiol was pure and essentially uncontaminated by disulfide. In a slightly larger scale experiment, 1.86 g. of thiol in 25 ml. of benzene and 75 ml. of water was oxidized with iodine until a faint yellow color persisted. The aqueous layer was separated and the benzene layer was washed with water. The water layer was made basic with aqueous sodium hydroxide and extracted with chloroform, the chloroform layer being cleared once with water. Distillation of the chloroform gave an oil which was dissolved in absolute ethanol and treated with ethanolic hydrogen chloride. The hydrochloride which crystallized was collected and recrystallized twice from absolute ethanol, m.p. 257.5° dec., lit.[8] m.p. 262–263°. The mixture melting point with an authentic sample,[9] m.p. 255.5–256° uncor., was 255.5–256° and the infrared spectra of the two specimens were superimposable.

Other amino thiols listed in Table II were prepared in a manner analogous to that described above. In general, it was found that little distillation residue was obtained when the thiols were distilled promptly, but a residue, probably disulfide, was obtained when the ethereal solutions were left overnight prior to distillation.

3-Cyclohexylamino-1-propanethiol.—3-Cyclohexylamino-1-propanol was prepared as described[10] from 3-aminopropanol and cyclohexanone by hydrogenation over palladium on charcoal, yield 94%, m.p. 67–71° (lit.[10] m.p. 71–73°). To a solution of 52 g. (0.33 mole) of the amino alcohol dissolved in 500 ml. of chloroform was added an excess of ethereal hydrogen chloride. The hydrochloride precipitated and was collected: first crop, 47 g., m.p. 149–151°; second crop, 14 g., m.p. 147–150°; combined yield 95%. To a suspension of 60 g. (0.31 mole) of the hydrochloride in 500 ml. of heptane was slowly added 35 ml. (0.485 mole) of thionyl chloride with stirring. After 1 hr. with stirring and 3 hr. at reflux the mixture was cooled and the precipitated 3-cyclohexylaminopropyl chloride hydrochloride was collected, yield 54.5 g. (77%), m.p. 230–235° dec.

A solution of 21 g. (0.525 mole) of sodium hydroxide in 125 ml. of methanol was saturated with hydrogen sulfide. The solution was then placed under an atmosphere of nitrogen and warmed to 50–60° and there was added, over 0.5 hr., a solution of 54 g. (0.26 mole) of 3-cyclohexylaminopropyl chloride hydrochloride in 250 ml. of methanol. The elevated temperature was maintained for an additional 0.5 hr. and the solution was then cooled, diluted with 450 ml. of ether, and filtered. The filtrate was concentrated and the residual dark red liquid was distilled to give 13.5 g. (30%) of 3-cyclohexylaminopropanethiol boiling at 104–106° (4.5 mm.). Upon redistillation the material boiled at 96.5° (2.5 mm.), $n^{20}D$ 1.5043, and was identical in infrared spectrum with the material obtained by reduction of 2-cyclohexylidene-1,3-thiazane (Table II). The n.m.r. spectrum of the compound was compatible with the assigned structure.

Control Experiment with N-(n-Propyl)cyclohexylamine.—The amine was prepared by reductive amination. Redistilled cyclohexanone (49 g., 0.5 mole) was mixed with n-propylamine (29.5 g., 0.5 mole); the mixture was cooled, thoroughly shaken, and left overnight at room temperature. It was then diluted with 50 ml. of ethanol and hydrogenated at 50 p.s.i. using 4 g. of 10% palladium on charcoal as catalyst. The requisite amount of hydrogen was taken up in 1 hr. The solution was filtered,

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.

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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°, $n^{25}D$ 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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