The reaction is shifted in the direction of the ketal by continuous removal of the ketal as an azeotrope with an excess of the alcohol used. The equilibrium also can be shifted in the direction of the ketal by decreasing the temperature and even at temperatures of 30 to 60° the reaction is rapid and this method of ketal preparation is effective.

This reaction has been used for the preparation of acetone dimethyl and diethyl acetals from 2,2-dimethyl-4-methylol-1,3-dioxolane and butanone dimethyl acetal from 2-ethyl-2-methyl-4-methylol-1,3-dioxolane. The reaction also provides a convenient method for the methanolysis of isopropylidene derivatives of diols, as the by-product ketal can be easily removed as its azeotrope with methanol at 61°.

EXPERIMENTAL

Effect of temperature on the equilibrium. Samples A and B of 15 ml. each were taken from a common stock solution composed of 0.25 mole of 2,2-dimethyl-4-methylol-1,3-dioxolane, 1.0 mole of methanol, and 1 drop of sulfuric acid. For a period of 10 min. sample A was kept at 62° and B at 0°. At the end of this time, the solutions were made basic by the addition of 5 ml. of a stock solution of sodium methylate in methanol. By infrared spectroscopy the per cent of dioxolane converted to acetone dimethyl acetal was determined for each sample: A, 17%; B, 21%. The conversion was estimated by computing the initial and final concentrations of acetone dimethyl acetal calculated from its absorption coefficient determined in solutions of similar composition with an authentic sample. The precision is about 5%.

Preparation of acetone dimethyl acetal. A solution composed of 1 mole of 2,2-dimethyl-4-methylol-1,3-dioxolane, 15 moles of methanol, and 1 drop of sulfuric acid was distilled through a 3-foot column packed with 1/8-in. helices and equipped with an automatic distillation head. The pressure was 220 mm. and the overhead temperature was 32–35°. (At atmospheric pressure methanol and acetone dimethyl acetal form an azeotrope, b.p. 61–62°, the composition of which is 45% and 55% by weight respectively.) With a reflux ratio of 20 to 30, 156 g. of a mixture of methanol and acetone dimethyl acetal was collected. The distillate contained 0.72 mole of acetone dimethyl acetal. Following the procedure described by Bond and Klar,[4] the azeotrope solution was washed with 13–15% aqueous sodium hydroxide solution, dried with potassium carbonate, and distilled to give pure acetone dimethyl acetal, b.p. 80° (760 mm.), n_D^{25} 1.3748 (lit.[2] b.p. 78–80°, n_D^{20} 1.3746).

Using 1 mole of 2,2,4-trimethyl-1,3-dioxolane, 6 moles of methanol, and 0.5 g. *p*-toluenesulfonic acid a 52% yield of acetone dimethyl acetal was obtained.

Preparation of butanone dimethyl acetal. A solution composed of 1 mole of 2-ethyl-2-methyl-4-methylol-1,3-dioxolane, 14 moles of methanol, and 1 drop of sulfuric acid was distilled. (At atmospheric pressure methanol and butanone dimethyl acetal distill as an azeotrope, b.p. 64.5°, 18.5% acetal by weight.) The pressure was 220 mm. and the overhead temperature was 33–36°. After 325 ml. of distillate was collected with a reflux ratio of 20, the distillation was stopped. After adding 150 ml. of xylene to the distillate, it was washed three times with 10% sodium hydroxide solution, dried with potassium carbonate, and distilled at atmospheric pressure. A 25-ml. (0.18 mole) fraction of butanone dimethyl acetal was collected, b.p. 106–107° (760 mm.), n_D^{24} 1.3918 (lit.[3] n_D^{24} 1.3915).

The undistilled residue of the reaction solution was made basic with sodium methylate and distilled. The distillate was 0.65 mole of 2-ethyl-2-methyl-4-methylol-1,3-dioxolane and the residue was 0.33 mole of glycerine which had the same infrared spectrum as a pure sample.

Preparation of acetone diethyl acetal. In the manner already described, a solution composed of 1 mole of 2,2-dimethyl-4-methylol-1,3-dioxolane, 15 moles of ethanol, and 0.5 g. of *p*-toluenesulfonic acid was slowly distilled at 100 mm. pressure. A 385-ml. fraction of distillate (b.p. 33–36°) was collected which was shown by infrared spectroscopy to be 6.8% (vol.) of acetone diethyl acetal. No attempt was made to separate the acetone diethyl acetal from the ethanol.

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[4] G. C. Bond and L. A. Klar, U. S. Patent **2,827,495** (1958).

Preparation of 2,2-Dialkyl-4-pentenoic Acids

KENT C. BRANNOCK, HERMAN S. PRIDGEN,
AND BENJAMIN THOMPSON

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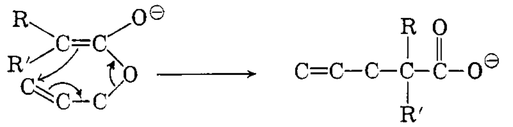
The rearrangement of the enolate anions of allyl esters, where either *R* or *R'* is aryl, is well known.[1]



It has also been reported that allyl acetate gives 4-pentenoic acid on treatment with sodium.[2] In the present investigation, however, treatment of allyl acetate with sodium hydride gave allyl acetoacetate as the only identifiable product.

A more favorable case for rearrangement to occur was that of an allyl ester of an acid having only one hydrogen atom in the α-position, as such compounds do not ordinarily undergo the acetoacetic ester condensation. Treatment of allyl isobutyrate and methallyl isobutyrate with sodium hydride gave 2,2-dimethyl-4-pentenoic acid and 2,2,4-trimethyl-4-pentenoic acid, respectively. When sodium methoxide or potassium *tert*-butoxide was used instead of sodium hydride, no rearrangement products were obtained.

EXPERIMENTAL

2,2-Dimethyl-4-pentenoic acid. A mixture of sodium hydride, 36 g. (1.5 moles), dispersed in mineral oil and 200 ml. of toluene was heated to 110°, and allyl isobutyrate, 192 g. (1.5 moles), was added dropwise over a 3.5-hr. period. Heating was continued for 1 hr. at 110°. The reaction mixture

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[1] (a) R. T. Arnold and S. Searles, Jr., *J. Am. Chem. Soc.*, **71**, 1150 (1949); (b) R. T. Arnold, W. E. Parham, and R. M. Dodson, *J. Am. Chem. Soc.*, **71**, 2439 (1949); (c) R. T. Arnold, U.S. Patent **2,526,108** (1950); (d) P. N. Craig, U.S. Patent **2,618,637** (1952); (e) R. T. Arnold and G. E. Ullyot, U.S. Patent **2,650,231** (1953).

[2] Heou-Feo Tseou and Yih-Teh Yang, *J. Chinese Chem. Soc.*, **5**, 224 (1937); *Chem. Zentr.*, **108**, II, 3309 (1937).

became quite thick and difficult to stir as the reaction proceeded. The mixture was cooled and 25 ml. of methanol was added to decompose any unused sodium hydride. Then 600 ml. of 7% hydrochloric acid solution was added. The organic phase was separated and distilled to give, after removal of toluene and other low-boiling materials, 126 g. (66%) of 2,2-dimethyl-4-pentenoic acid, b.p. 82–83° (4 mm.), n_D^{20} 1.4337; reported[3] b.p. 104–108° (20 mm.)

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4; neut. equiv. 128. Found: C, 65.7; H, 9.5; neut. equiv. 129.

2,2,4-Trimethyl-4-pentenoic acid. Under the conditions described above, methallyl isobutyrate and sodium hydride gave 2,2,4-trimethyl 4 pentenoic acid in 68% yield, b.p. 78–81° (1.5–2 mm.), n_D^{20} 1.4421.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.6; H, 9.9; neut. equiv. 142. Found: C, 67.2; H, 9.9; neut. equiv. 143.

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(3) R. F. Brown and N. M. Van Gulick, *J. Am. Chem. Soc.*, 77, 1092 (1955).

Catalytic Interaction of 2-Vinylpyridine and Hydrogen Sulfide[1]

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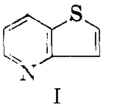
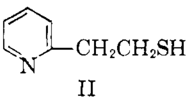
Moore and Greensfelder[2] have described the synthesis of benzothiophene in 60% yield from styrene and hydrogen sulfide using a flow apparatus, a ferrous sulfide–alumina catalyst, and a temperature of 600–625°. Besides benzothiophene and unchanged starting materials other substances identified in the effluent were hydrogen, a tar-like polymer, and small amounts of benzene, ethene, and probably ethane. By use of similar conditions we have been able to isolate, albeit in only 1.6% yield, a compound which appears to be the previously unknown thieno[3,2-*b*]pyridine (I) from 2-vinylpyridine and hydrogen sulfide. Other products identified in the gases condensable above −70° from



I



II

the reaction effluent were ethyl mercaptan, diethyl sulfide, pyridine, thiophene, sulfur, and hydrogen sulfide, but not unchanged 2-vinylpyridine. A material balance showed that at least half of the nitrogen atoms in the influent were retained on the column, perhaps as polymeric or strongly adsorbed[3] species. The formation of the products can be rationalized by the assumption that hydrogen sulfide adds to 2-vinylpyridine to form the intermediate 2-(2-pyridyl)ethyl mercaptan (II) which undergoes hydrogenolysis (by hydrogen sulfide) to ethyl mercaptan, pyridine, and sulfur and dehydrocyclization to I. In addition, condensation of ethyl mercaptan with 2-vinylpyridine followed by hydrogenolysis and subsequent dehydrocyclization could account for the formations of diethyl sulfide and thiophene, respectively.

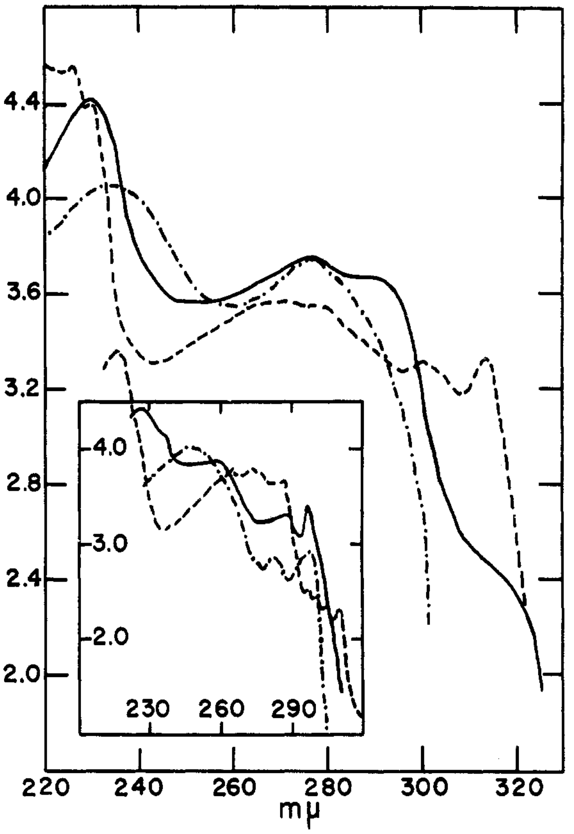


Fig. 1. Comparison of ultraviolet spectra. Large graph: ——— thieno[3,2-*b*]pyridine; – – – – quinoline; –·–·–· 2-vinylpyridine. Inset graph: ——— benzothiophene; – – – – naphthalene; –·–·– styrene.

Structure I was assigned to the faintly yellow liquid obtained from fractional distillation of the crude reaction product on the basis of its b.p. (82–84°/2 mm., estimated b.p. 240°/760 mm.; *cf.* quinoline,[4] b.p. 239°), its ultraviolet absorption spectrum (nearly a composite of the spectra of quinoline[5] and 2-vinylpyridine,[6] *cf.* the spectrum

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(1) Abstracted from the M.S. thesis of David D. Reed, University of Oregon, June 1957. Further details concerning the apparatus used may be obtained by consultation of this thesis.

(2) R. J. Moore and B. S. Greensfelder, *J. Am. Chem. Soc.*, 69, 2008 (1947).

(3) In preliminary chromatographic studies conducted in this laboratory the unusually strong adsorbability of aromatic nitrogen heterocycles (as compared to the corresponding arenes) on alumina has been noted.

(4) R. L. Shriner, R. C. Fuson, D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., J. Wiley & Sons, New York, 1956, p. 297.

(5) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, J. Wiley & Sons, New York, 1951.

(6) R. P. Mariella, L. F. A. Peterson, and R. C. Ferris, *J. Am. Chem. Soc.*, 70, 1494 (1948).