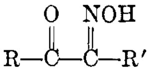
TABLE I

SECOND ORDER BECKMANN REARRANGEMENTS OF α-OXIMINO KETONES IN ALCOHOLS[a]



$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle NOH}{\overset{\|}{C}}{-}R'}$$

α-Oximino Ketone			Products and Yields[b]	
R	R′	Alcohol	Ester	Nitrile
C_6H_5	CH_3	CH_3OH	$C_6H_5CO_2CH_3$ (54%)	[c]
		C_2H_5OH	$C_6H_5CO_2C_2H_5$ (73%)	[c]
C_6H_5	C_6H_5	C_2H_5OH	$C_6H_5CO_2C_2H_5$ (75%)	C_6H_5CN (81%)
$C_6H_5CH_2$	C_6H_5	C_2H_5OH	$C_6H_5CH_2CO_2C_2H_5$ (43%)	C_6H_5CN (52%)
$C_6H_5CH{=}CH$	H	C_2H_5OH	$C_6H_5CH{=}CHCO_2C_2H_5$ (57%)	[c]

[a] In all cases the base was the sodium alkoxide corresponding to the alcohol and the acylating agent was acetic anhydride. [b] All yields are based on starting α-oximino ketone not recovered. [c] Not isolated.

ucts Industries, Rochester, N. Y. 1,3-Diphenyl-1-oximino-2-propanone has been described previously.[1b] 1-Oximino-4-phenyl-3-buten-2-one was prepared by the method of Foulds and Robinson[5] using butyl instead of isoamyl nitrite. It melted at 137–139° (lit.,[6] m.p. 143–144°).

Rearrangements. Two typical experiments are described below. The other rearrangements were carried out and products worked up in essentially the same manner.

Rearrangement of α-benzil monoxime in ethanol. A solution of sodium ethoxide in ethanol was prepared by dissolving 12.0 g. (0.52 g.-atom) of sodium in 1500 ml. of ethanol, and 112.5 g. (0.50 mole) of α-benzil monoxime was dissolved in it. During 30 min. 55.0 g. (0.54 mole) of acetic anhydride was added dropwise with stirring. The temperature rose steadily to a maximum of 55°, then dropped to 30° during the next 30 min. The ethanol was evaporated under reduced pressure, and the residue was taken up in 500 ml. of ether. The solid which failed to dissolve (sodium acetate) was removed by filtration and washed with ether. The filtrate was washed with two 200-ml. portions of 5% sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of the ether under reduced pressure left a mixture of solid and liquid. The mixture was taken up in 200 ml. of hexane, and the solid, which failed to dissolve, was recovered by filtration, washed with hexane, and dried. The filtrate separated into two layers. The upper (hexane) layer was removed, and the lower layer was washed with several small portions of hexane until it crystallized. The solid recovered by filtration amounted to 40.0 g. and that from the filtrate to 2.5 g. The 42.5 g. of solid was shown to be unchanged α-benzil monoxime by melting point and mixed melting point.

The hexane solution was evaporated under reduced pressure, and the liquid residue was distilled *in vacuo.* Three fractions were obtained: I, 12.0 g., b.p. 81.5–82.5° (19 mm.), n_D^{25} 1.5257; II, 25.0 g., b.p. 82.5–101° (19 mm.), n_D^{25} 1.5162; and III, 24.0 g., b.p. 101–102° (19 mm.), n_D^{25} 1.5041. Fraction I gave an infrared spectrum identical with that of benzonitrile and Fraction III a spectrum identical with that of ethyl benzoate. Fraction II was estimated from its index of refraction to contain 56% benzonitrile and 44% ethyl benzoate. Total recoveries thus were 26.0 g. (81%) of benzonitrile and 35.0 g. (75%) of ethyl benzoate.

Rearrangement of 1-oximino-4-phenyl-3-buten-2-one. A solution of sodium ethoxide in ethanol was prepared by dissolving 10.0 g. (0.435 g.-atom) of sodium in 1000 ml. of ethanol, and 52.5 g. (0.30 mole) of 1-oximino-4-phenyl-3-buten-2-one was added. Some solid, probably sodium salt of the oxime, remained in suspension. Then 43.0 g. (0.42 mole) of acetic anhydride was added with stirring during 30 min., the temperature being kept at 20–30° by cooling. After stirring 15 min. more the mixture was filtered and the solvent was evaporated under reduced pressure. The residue was taken up in 250 ml. of ether, and the ether solution was filtered, washed with 100 ml. of 5% sodium bicarbonate solution, dried over magnesium sulfate, and evaporated. The liquid residue was distilled under reduced pressure to give 35.0 g. of ethyl cinnamate, b.p. 142–146° (19 mm.), containing a little solid. On redistillation there was obtained 30.0 g. (57%) of pure ethyl cinnamate, b.p. 114° (2.6 mm.), n_D^{28} 1.5555. The infrared spectrum of this material was identical with that of authentic ethyl cinnamate.

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(5) R. P. Foulds and R. Robinson, *J. Chem. Soc.*, **103**, 1768 (1913).

(6) L. Claisen and O. Manasse, *Ber.*, **22**, 529 (1889).

The Preparation of Three Ketone Acetals by Alcohol Interchange with Dioxolanes

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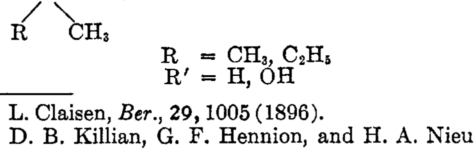
The usual methods for the preparation of ketals are the reaction of an ortho ester with a ketone[1] and the addition of two moles of an alcohol to a substituted acetylene.[2] Recently a method for the preparation of ketals directly from simple ketones and alcohols was reported.[3] The success of this method is dependent upon the use of a low reaction temperature (<−20°) because the amount of the ketal formed is inversely related to the temperature of the reaction mixture. Each of the above methods requires either an uncommon reagent or inconvenient temperatures.

Two ketals have now been prepared by using readily available dioxolanes and methanol.



R = CH_3, C_2H_5
R′ = H, OH

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(1) L. Claisen, *Ber.*, **29**, 1005 (1896).

(2) D. B. Killian, G. F. Hennion, and H. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 1384 (1934).

(3) N. B. Lorette, W. L. Howard, and J. H. Brown, Jr., *J. Org. Chem.*, **24**, 1731 (1959).

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

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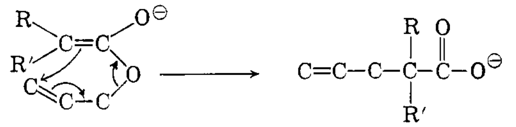
The rearrangement of the enolate anions of allyl esters, where either *R* or *R'* is aryl, is well known.[1]



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

(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).