The compound was identified as bis(β-carboxy-β-ethylbutyl) sulfite, m.p. 142–144° (from ethyl ether–petroleum ether (b.p. 45–60°)).

Anal. Calcd. for $C_{14}H_{26}O_7S$: C, 49.69; H, 7.71; S, 9.48. Found: C, 49.65; H, 7.65; S, 9.51.

The organic layer was dried over sodium sulfate and distilled; 8.5% of *α,α-diethyl-β-propiolactone* (I) was isolated, b.p. 65°–70° (7 mm., air bath).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.43. Found: C, 65.59; H, 9.44.

Compound I was identical with an authentic sample of α,α-diethyl-β-propiolactone.[2] Its structure was confirmed by conversion of I into the known α,α-diethyl-β-hydroxypropionic acid[2,4,9] (m.p. 60–62°); the infrared spectrum of I shows a typical band at 1815 cm.$^{-1}$

The cyclization reaction with thionyl chloride and pyridine occurred also with α-phenyl-α-*n*-propyl-β-hydroxypropionic acid[2,4]: the corresponding β-lactone[2] (b.p. 110–115°/0.5 mm., air bath) was isolated in 5.3% yield. In this case, no formation of a sulfite derivative was noted. The lactone shows a typical band at 1815 cm.$^{-1}$ α-Phenyl-α-*n*-propyl-β-propiolactone was hydrolized to the known α-phenyl-α-*n*-propyl-β-hydroxypropionic acid[10] (m.p. 104–107°).

The method described allows the preparation of β-lactones directly from β-hydroxycarboxylic acids, though in low yields.

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[10] E. Testa, L. Fontanella, G. F. Cristiani, and F. Fava, *Ann.*, 619, 47 (1958).

α-Oximino Ketones. VIII. The Second Order Beckmann Rearrangement in Alcohols

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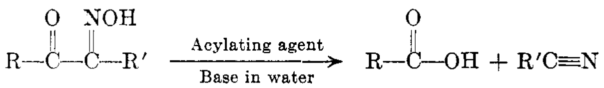
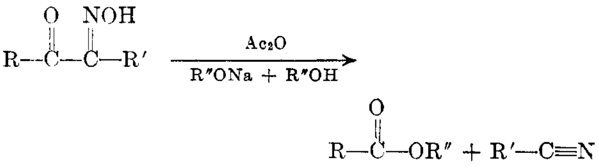
Received March 3, 1960

When α-oximino ketones possessing the *anti* configuration are treated with strong acids or acid chlorides, or when they are dissolved in aqueous base and treated with acylating agents, they are cleaved to nitriles and carboxylic acids, a reaction which has been termed a "second order" Beckmann rearrangement.[1] Recent work in this laboratory has shown that when a salt of 2,6-dioximinocyclohexanone in alcoholic base is treated with an acid anhydride, it is cleaved to ethyl 5-cyano-2-oximinovalerate.[2]



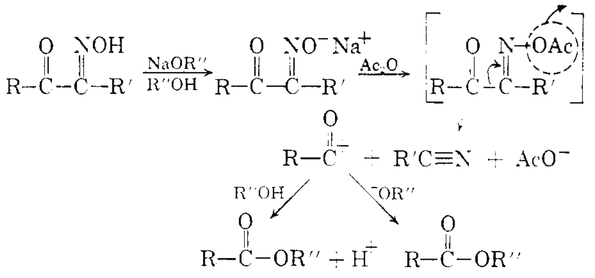
$$R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}R' \xrightarrow[\text{Base in water}]{\text{Acylating agent}} R{-}\overset{\overset{O}{\|}}{C}{-}OH + R'C{\equiv}N$$

It has been found now that formation of esters is characteristic of simple α-oximino ketones as well as of 2,6-dioximinocyclohexanone when the second order Beckmann rearrangement is carried out in alcohols. The yields of esters obtained by the action of acetic anhydride on solutions of four α-oximino ketones in alcoholic sodium alkoxides are reported in Table I. No attempt was made to isolate the low molecular weight nitrile products obtained when R′ was hydrogen or a methyl group, but when R′ was the phenyl group benzonitrile was obtained as expected. The tendency of the anhydride to react with the oxime instead of the alcohol can be explained on the basis discussed previously,[2] namely that the oxime anion is much more effective in attacking anhydride than the neutral alcohol molecule.



$$R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}R' \xrightarrow[R''ONa\ +\ R''OH]{Ac_2O} R{-}\overset{\overset{O}{\|}}{C}{-}OR'' + R'{-}C{\equiv}N$$

The fact that esters are obtained when the second order Beckmann rearrangement is carried out in alcohols provides additional confirmation for the mechanistic interpretation of the reaction presented previously.[1b] Thus if the rearrangement involves first formation of the acylated α-oximino ketone and second concurrent departure of the acetate anion and shift of the electron pair between the oxime carbon and the carbonyl carbon to form a nitrile and an oxocarbonium ion, it would be expected when the solvent is an alcohol that the oxocarbonium ion would attack the alcohol or combine with the alkoxide anion to form an ester, and that is exactly the result observed. The alternative hypotheses that the reaction is initiated by attack of the alkoxide ion on the carbonyl carbon or involves concurrent attack at the carbonyl carbon and departure of the acetate ion have been considered in earlier work[3] and rejected on the basis of the fact that treatment of an α-acyloximino ketone in alcohol with an amine or other weak base leads to formation of the same ester product obtained when alkoxide is used.



EXPERIMENTAL[4]

α-Oximino ketones. 2-Oximino-1-phenyl-1-propanone and α-benzil monoxime were purchased from Distillation Prod-

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[1] (a) A. H. Blatt and R. P. Barnes, *J. Am. Chem. Soc.*, 56, 1148 (1934); (b) A. F. Ferris, *J. Org. Chem.*, 25, 12 (1960). References to earlier work are given in these papers.

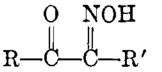
[2] A. F. Ferris, G. S. Johnson, F. E. Gould, and H. Stange, *J. Org. Chem.*, 25, 1302 (1960).

[3] A. F. Ferris, G. S. Johnson, and F. E. Gould, *J. Org. Chem.*, 25, 496 (1960).

[4] All melting points and boiling points are uncorrected.

TABLE I

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



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

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).

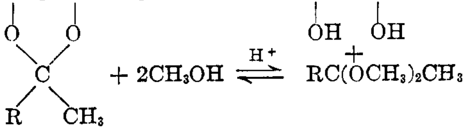
The Preparation of Three Ketone Acetals by Alcohol Interchange with Dioxolanes

N. B. LORETTE AND W. L. HOWARD

Received February 15, 1960

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).