

THE WOLFF REARRANGEMENT OF α -ACETOXY DIAZO KETONES

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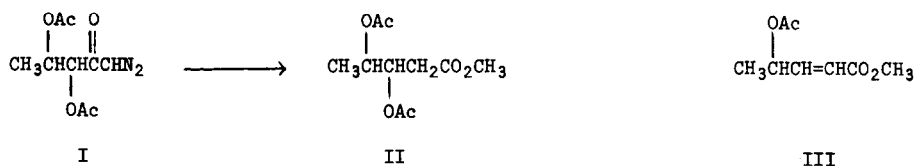
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The Wolff rearrangement of α -diazoketones to prepare homologous acids or their derivatives has not been generally applied to the preparation of β -acetoxy acids. We have attempted to use this reaction to accomplish such a transformation but find that the major products are those resulting from β -elimination from the rearranged acid or its derivatives.

Two examples of this reaction have been previously reported: (1,2). The photochemical rearrangement of methyl 2,3-di-O-acetyl-5-deoxy-5-diazo-L-threo-4-pentulonate in absolute methanol is reported to give the homologous ester in 61% yield.* The second example of this rearrangement is that of 1-diazo-1-desoxy-D-glucoheptulose pentaacetate in water with silver oxide as a catalyst. The product obtained in 70% yield, was reported to be 2-desoxy-D-glucoheptonolactone tetraacetate from its analysis and saponification equivalent.**

We have attempted to rearrange the α -diazoketone I to yield the homologous ester II. Rearrangement of diazoketone I in either water or methanol with silver oxide gave complex mixtures but the major recognizable product from the latter was the α,β -unsaturated ester III.



Diazoketone I was also subjected to photochemical rearrangement in absolute methanol in a Rayonet Srinivasan-Griffin reactor using 2500Å light. Analysis of the resulting mixture by gas chromatography showed three major products in the ratio of 3:10:8. The major product was

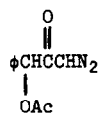
* We have repeated this reaction and find that in addition a small amount of unsaturated material is formed.

** It was also reported that a mole of acetic acid had been lost on lactonization. Other properties such as mutarotation and titration were reported to be anomalous. All of the data ascribed to this compound and to its hydrolysis product agree more satisfactorily with a β -elimination product.

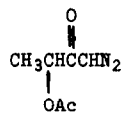
identical with that from the silver oxide catalyzed decomposition, compound III. Fractional distillation gave the minor component in a sufficiently pure state to be identified as the normal rearrangement product II. The NMR and infrared data for both of these compounds agree with the expected values. From later results the third is assumed to be the other geometrical isomer of the unsaturated ester III.

In order to study this reaction further we prepared as model compounds 3-acetoxy-3-phenyl-1-diazo-2-propanone (IV) and 3-acetoxy-1-diazo-2-butanone (V) from mandelic acid and lactic acid respectively.

Rearrangement of diazo ketone IV in absolute methanol with silver oxide, with UV light or with a sunlamp gave various mixtures of five principal products as determined by gas chromatography. These were identified as cis and trans methyl cinnamate, (VI and VII), cis and trans cinnamic acid (VIII and IX), and 3-acetoxy-3-phenylpropionate (X), in the percentage ratios listed in TABLE I.



IV



V

TABLE I

Rearrangement of 3-Acetoxy-3-phenyl-1-diazo-2-propanone IV in
Absolute Methanol

Catalyst	% Ratio				
	VI	VII	VIII	IX	X
Ag ₂ O	6	72	- ^a	- ^a	22
UV	30	17	20	6	27
Sunlamp	26	13	27	15	19

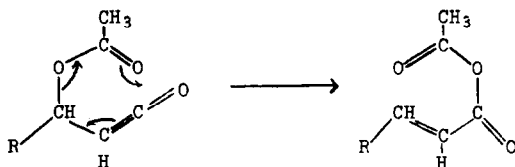
^a The acids were not isolated from this reaction.

These were identified by comparison of their retention times on gas chromatography with authentic samples. An authentic sample of methyl 3-acetoxy-3-phenylpropionate was prepared

by a Reformatsky reaction between benzaldehyde and methyl bromacetate followed by acetylation.

The rearrangement of diazo ketone V in absolute methanol catalyzed by silver oxide or ultraviolet light showed similar results. In both cases the reaction mixture showed four major components. Three of these were identified as crotonic acid, methyl crotonate (the major component), and methyl 3-acetoxybutyrate. The fourth product is assumed to be the other geometrical isomer of methyl crotonate.

The formation of cinnamic acid and crotonic acid in absolute methanol suggested to us that the elimination might in fact be an intramolecular process proceeding from the intermediate ketene. One can visualize this reaction taking place by the cyclic process shown;



This would lead to a mixed anhydride which could then react with the methanol to give acetic acid and the unsaturated methyl ester, or methyl acetate and the unsaturated acid.* In order to test this hypothesis we irradiated a solution of diazo ketone IV in dry tetrahydrofuran. The crude syrup exhibited bands in the infrared at 1810, 1780, and 1640 cm^{-1} suggesting the presence of acetic cinnamic anhydride but as yet we have not been able to isolate this compound. Its instability with respect to disproportionation has been reported (3).

* A similar rearrangement has been suggested for the formation of acetic cinnamic anhydride from the reaction of ketene and benzaldehyde (3).

REFERENCES

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