the theoretical values within about 0.02% for carbon and 0.01% for hydrogen (see table), a degree of accuracy quite adequate for distinguishing between alternate formulas even in difficult cases.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED MARCH 21, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HOWARD UNIVERSITY, WASHINGTON, D. C., AND HAMPTON INSTITUTE, HAMPTON, VA.]

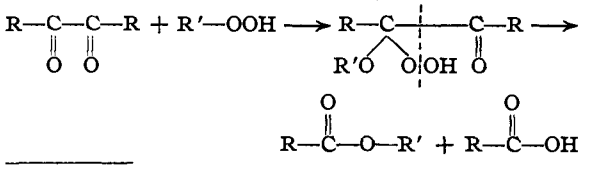
The Action of Ethylhydroperoxide on Alpha Diketones—Mechanism

BY R. P. BARNES AND ROSCOE E. LEWIS

In connection with our work on alpha diketones we have had many occasions to use the alkaline hydrogen peroxide cleavage reaction of Weitz and Scheffer.[1] This reagent which is a specific cleavage reagent for all alpha diketones seems particularly interesting in view of the fact that the most highly hindered alpha diketones cleave with ease when subjected to it.

Mesitylbenzylglyoxal[2] resists all reagents which involve a 1,2-addition to the carbonyl adjacent to the mesityl group, yet it is cleaved quantitatively by this reagent. Dimesityl diketone[3] resists all reagents which involve addition to carbonyl except strongly alkaline hydroxylamine, zinc in alcoholic potassium hydroxide, and alkaline hydrogen peroxide. The explantion of the fact that dimesityl diketone yields to these drastic treatments is that one of the twinned carbonyls activates the other and hence reduction is effected, presumably by way of 1,2-addition.

To test the mechanism of this cleavage reaction as proposed by Weitz and Scheffer,[1] which according to them involves a 1,4-addition of OH groups to the ends of the system of twinned carbonyls, the use of an unsymmetrical reagent occurred to the authors. If this reaction goes according to the mechanism proposed by its authors, either a symmetrical or an unsymmetrical reagent would yield two molecules of acid; if, on the other hand, it should go by way of a 1,2-addition to a carbonyl, it would yield one molecule of an acid and one molecule of an ester



(1) Weitz and Scheffer, *Ber.*, **54**, 2327 (1921).
(2) R. P. Barnes, THIS JOURNAL, **57**, 937 (1935).
(3) Kohler and Baltzly, *ibid.*, **54**, 4015 (1932).

Ethylhydroperoxide was made according to Baeyer and Villiger[4] and the following compounds were subjected to treatment with this reagent in alkaline solution with the indicated results.

	Substance	Cleavage products
I	$C_6H_5COCOC_6H_5$	Benzoic acid and ethyl benzoate
II	p-$CH_3OC_6H_4COCOC_6H_4OCH_3$-$p$	Anisic acid and ethyl anisoate
III	$C_6H_5COCOC_6H_4OCH_3$-p	Anisic and benzoic acids; ethyl benzoate and anisoate
IV	$C_6H_5CH_2COCOC_6H_5$	Benzoic and phenylacetic acids
V	$C_6H_5CH_2COCOC_6H_2(CH_3)_3$	Benzoic and trimethylbenzoic acids

(I) and (II) cleave cleanly and rapidly yielding the corresponding acid and ester; (III) cleaves less rapidly producing a mixture of benzoic and anisic acids and a mixture of ethyl benzoate and anisoate. The latter is explained by the fact that neither carbonyl is hindered and hence addition takes place to either carbonyl with the corresponding cleavage products. (IV) and (V) (in enolic modification) cleave still more slowly with the result that exposure of the esters to the hot alkaline solution effects complete hydrolysis.

Experimental Part

Treatment of the Alpha Diketone with Alkaline Ethylhydroperoxide.—In each case 1.0 g. of the alpha diketone was dissolved in methyl alcohol to which 20 cc. of approximately 15% ethylhydroperoxide was subsequently added. The solution was made slightly alkaline with 20% sodium hydroxide and warmed on the water-bath. When the color of the solution faded it was poured into 100 cc. of cold water to check further hydrolysis. The solution was extracted with ether. The alkaline solution was acidified with hydrochloric acid, yielding acid; the ethereal solution was evaporated and the residual ester refluxed for thirty minutes with hydrochloric acid, whereupon the ester was

(4) Baeyer and Villiger, *Ber.*, **34**, 738 (1901).

hydrolyzed. All products were identified by their melting points and mixed melting points with known pure samples.

Benzil (I) yielded 0.4 g. of benzoic acid from the alkaline solution and 0.4 g. of benzoic acid from the ester hydrolysis.

4,4'-Dimethoxybenzil (II) yielded 0.5 g. of anisic acid from the alkaline solution and 0.3 g. of anisic acid from the ester hydrolysis.

4-Methoxybenzil (III) yielded 0.8 g. of a mixture of benzoic and anisic acids from the alkaline solution and 0.1 g. of the mixed acids from the hydrolysis of the esters.

Phenylbenzylglyoxal (IV) yielded 0.7 g. of a mixture of phenylacetic and benzoic acids from the alkaline solution and 0.2 g. of unchanged material from the ethereal solution.

Mesitylbenzylglyoxal (V) yielded 0.8 g. of a mixture of phenylacetic and trimethylbenzoic acids from the alkaline solution and 0.2 g. of unchanged material from the ethereal solution.

Summary

A simple mechanism for the alkaline peroxide cleavage of alpha diketones is herein presented.

WASHINGTON, D. C. RECEIVED APRIL 18, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Polyazines. I. The Structure of the Dimethyl Aziethane of Curtius and Thun[1]

BY B. G. ZIMMERMAN AND H. L. LOCHTE

Curtius and Thun[2] in the course of their study of the reactions of ketones with hydrazine hydrate obtained a compound to which they assigned the formula, $\begin{matrix} CH_3C{=}N \\ | \quad | \\ CH_3C{=}N \end{matrix}$. This insoluble microcrystalline compound which gradually decomposes on heating to 270° without melting is obtained in the reaction between equimolecular amounts of hydrazine hydrate and diacetyl. Although Diels[3] and Diels and Pflaumer[4] encountered the same substance in their work, they apparently were not interested in its structure and dismissed it with the statement that their substance was identical with that of Curtius and Thun.

The low solubility and high melting point of the compound makes the Curtius and Thun formula very unlikely and indicates that the compound should be classed as a polyazine formed by polycondensation or "C polymerization"[5] of the two bifunctional compounds involved. A closer study shows that it is an unsymmetrical polyazine of the type $H_2N{-}N{=}C(CH_3)[C(CH_3){=}N{-}N{=}C(CH_3)]_nC(CH_3)O$ with a moderately high value of n.

Ebullioscopic molecular weight determinations, using benzene as solvent, with freshly prepared and recrystallized substance yield an apparent molecular weight of only 300 to 400; but these values probably have little significance since the apparent molecular weight increases rapidly with concentration. Staudinger[6] recently reported similar difficulties in his work with polymers. Since the solubility of our polyazine decreases rapidly with age or with repeated recrystallization ebullioscopic molecular weight determinations on such aged samples are impossible.

Analyses of freshly prepared and recrystallized material show definitely the unsymmetrical structure of the polyazine and indicate a value of 6–10 for n.

Material which becomes insoluble upon repeated recrystallization or other treatment decomposes without melting on heating to 300°.

Analyses of such samples indicate a much higher value of n and can no longer be employed to differentiate between the unsymmetrical and one of the symmetrical structures possible.

Experimental Part

Diacetyl Monohydrazone.—Prepared according to the method of Diels and Pflaumer,[4] the melting point of this compound was found as reported at 67.5° (corr.). After standing in a desiccator for nine months the white crystalline compound had changed to a yellow microcrystalline powder decomposing slowly without melting on heating to 250°.

Monoacetyl Derivative of Diacetyl Hydrazone.—This compound, also prepared according to Diels and Pflaumer,[4] is colorless and melts at 163.4° (corr.). It hydrolyzes readily in hot alkaline solution yielding the yellow polyazine.

Diacetyl Dihydrazone and Polyazine.—Three grams of diacetyl, 12 g. of hydrazine hydrate, and 12 g. of sodium carbonate in 50 cc. of water were refluxed for five hours. Two products were isolated, a white crystalline material

(1) Presented at a Sectional Meeting of the American Chemical Society at Waco, Texas, April 25, 1936.

(2) Curtius and Thun, *J. prakt. Chem.*, [2] **44**, 175 (1891).

(3) Diels, *Ber.*, **35**, 350 (1902).

(4) Diels and Pflaumer, *ibid.*, **48**, 223 (1915).

(5) Carothers, THIS JOURNAL, **51**, 2550 (1929); *Chem. Rev.*, **8**, 358 (1931); *Trans. Faraday Soc.*, **32**, 39 (1936).

(6) Staudinger and co-workers, *Ber.*, **68**, 2313–2357 (1935).