water, the reaction would be second order; but heretofore this has never been actually demonstrated. By using acetone as a solvent and having present only enough water to react with the methyl acetate, we were able to demonstrate the second order course of the reaction under these conditions.

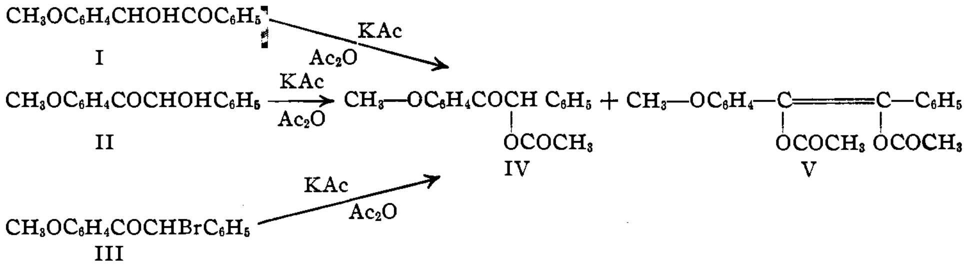
ATLANTA, GA. RECEIVED OCTOBER 31, 1940

NOTES

Interconversion of Mixed Benzoins

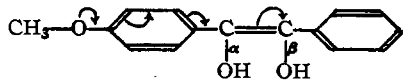
BY R. P. BARNES AND V. J. TULANE

In view of the ease with which it has been found possible to prepare diacetates of ene-diols from benzoin and non-enolic α-bromo ketones,[1,2] we made pure anisbenzoin (I), benzanisoin (II) and anisoyl phenyl bromo-methane (III), and acetylated[1] each of these compounds. In each instance there was obtained a mixture of the monoacetate (IV) and the diacetate (V). The anisbenzoin melted sharply at 89°, the benzanisoin at 106°. Since the mono-acetate was the same in each instance and since it hydrolyzed to benzanisoin, it is reasonable to conclude that it resulted by way of a partial hydrolysis of the diacetate.

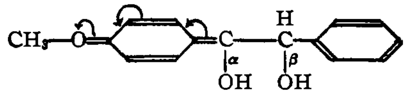


When an alcoholic solution of the diacetate was boiled for a few minutes with a few cubic centimeters of concd. hydrochloric acid an odor of ethyl acetate was produced and on cooling, the 106°-melting benzoin separated out. Thus the diacetate upon hydrolysis goes by way of the unstable ene-diol to the more stable high-melting benzanisoin in acid solution.

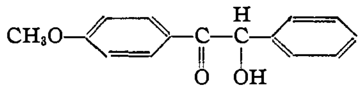
In this case of the ene-diol of anisbenzoin or benzanisoin there is obviously a directing influence. We believe that this influence can be explained in terms of the CH_3O– group. This ene-diolic modification contains a completely conjugated system, and since the CH_3O– group possesses a strong tendency toward electron release,[3,4] its mesomeric effect will give rise to a condition of electronic strain in the attached aromatic nucleus with the result that the para-carbon atom will be negatively charged and the two intermediate carbon atoms (α and β) charged positively and negatively, respectively. Thus there is created a seat for a proton on the β-carbon from the anisyl group



This molecule combines with a proton at the β-carbon



with subsequent ejection of a proton from the α-hydroxyl and regeneration of the stable benzanisoin



This mechanism lends support to the view that benzanisoin must be the stabler isomer (lower

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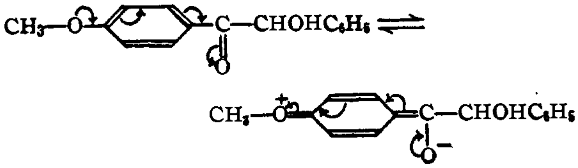
[1] R. P. Barnes and Victor J. Tulane, THIS JOURNAL, **62**, 894 (1940).

[2] R. P. Barnes, Charles I. Pierce and Chappelle C. Cochrane, *ibid.*, **62**, 1084 (1940).

[3] R. Robinson and co-workers, *J. Chem. Soc.*, 401 (1926).

[4] C. K. and E. H. Ingold, *ibid.*, 1310 (1926).

energy content) since it gives rise to benzanisoin and since there is the possibility for resonance between the CH$_3$O– group and the carbonyl in this molecule whereas anisbenzoin does not have this possibility



Experimental Part

Acetylation Products (IV) and (V).—Separate solutions of 5.0 g. each of anisbenzoin, benzanisoin, and anisoylphenylbromomethane in 25 cc. of acetic anhydride are refluxed gently with equal weights of freshly fused potassium acetate for thirty minutes. Each solution turns slightly yellow. After cooling they are worked up as described,[1] producing a cream-colored granular solid. Repeated fractional crystallizations from methyl alcohol yield in each case approximately 1.0 g. of the monoacetate, melting sharply at 83°, and 1.0 g. of the diacetate, melting at 127°.

Anal. Calcd. for $C_{17}H_{16}O_4$: —OCH$_3$, 10.9. Found: 11.2. Calcd. for $C_{19}H_{18}O_5$: —OCH$_3$, 9.5. Found: 9.7.

Both the mono and the diacetate on dissolving in alcohol and on gentle refluxing with concd. hydrochloric acid hydrolyze completely in thirty minutes to benzanisoin, melting and mix melting sharply with an authentic sample at 106°. The odor of ethyl acetate is observed.

DEPARTMENT OF CHEMISTRY
HOWARD UNIVERSITY
WASHINGTON, D. C.

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The Photolysis of the Aliphatic Aldehydes. IX. Glyoxal and Acetaldehyde

BY F. E. BLACET AND ROBERT W. MOULTON

A study of vapor phase mixtures of glyoxal and acetaldehyde has been made in an attempt to throw light on the primary photochemical process for glyoxal, as well as on the reaction

$$CH_3CHO + HCO \longrightarrow H_2 + CO + CH_3CO \quad (1)$$

which has been postulated as a part of the mechanism of acetaldehyde decomposition.[1]

Experimental Method

The photochemical technique was very similar to that previously described.[2] In a number of experiments glyoxal was mixed with carbon dioxide instead of with acetaldehyde. λ 3660 Å. was the principal radiation employed, since it is absorbed by glyoxal but not by acetaldehyde. The gaseous products were analyzed by well-known micro methods. Glyoxal was prepared by oxidizing ethylene with selenium dioxide in the presence of phosphorus pentoxide in a manner similar to that described by Riley and Friend.[3]

Experimental Results

Experiments with pure glyoxal gave a gaseous product which consisted of 97% CO and 3% H$_2$. This is in very good agreement with 97% CO, 2.5% H$_2$ and 0.5% unsaturated compounds reported by Norrish and Griffiths.[4] No unsaturated hydrocarbons were detected in our work. The percentages of carbon monoxide reported in the accompanying tables are based upon the sum of the two gases found, hence the per cent. of hydrogen in each case is the difference between 100 and the figure given for carbon monoxide.

Table I gives the percentages of carbon monoxide obtained in the photolysis of a series of glyoxal and acetaldehyde mixtures in which the ratio of these two substances was varied. Since it was evident that some polymerization was taking place during the runs, the reporting of ratios and percentages beyond two significant figures would not be justified.

Table II gives the results of a similar study in which carbon dioxide was substituted for acetaldehyde. In Fig. 1 the carbon monoxide to hy-

TABLE I

DATA OBTAINED FROM GLYOXAL–ACETALDEHYDE MIXTURES

Pressure, mm. (CHO)$_2$	Pressure, mm. CH$_3$CHO	CH$_3$CHO/(CHO)$_2$	% CO	Ratio CO/H$_2$
75	0	0	97	32
64	210	3.3	90	9.0
60	600	10	73	2.7
36	440	12	66	2.0
50	650	14	79	3.8
45	705	16	88	7.3

TABLE II

DATA OBTAINED FROM GLYOXAL–CARBON DIOXIDE MIXTURES

Pressure, mm. (CHO)$_2$	Pressure, mm. CO$_2$	Ratio CO$_2$/(CHO)$_2$	% CO	Ratio CO/H$_2$
75	0	0	97	32
100	216	2.2	89	8.1
75	465	6.2	79	3.8
56	555	10	66	2.0
40	510	13	77	3.3
50	685	14	86	6.1
40	555	14	90	9.0
40	630	16	90	9.0

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[1] (a) Blacet and Volman, THIS JOURNAL, **60**, 1243 (1938). (b) Leighton, *J. Phys. Chem.*, **42**, 749 (1938). (c) Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[2] Blacet and Taurog, THIS JOURNAL, **61**, 3024 (1939).

[3] Riley and Friend, *J. Chem. Soc.*, 2342 (1932).

[4] Norrish and Griffiths, *ibid.*, 2829 (1928).