

2. The equilibrated solution gave no evidence of a stable enol and treatment with acid did not produce furfural.

3. When trimethylxylose was treated with dilute alkali under the same conditions, it was transformed in part into the epimeric trimethyllyxose, a high iodine absorbing compound believed to be the monomethylenediol and saccharinic acid, the latter in small amount.

4. Methyl alcohol was found in the alkaline solution of trimethylxylose approximately in the proportion of one mole to each mole of methylated sugar decomposed. On treatment with dilute acids, two further moles of methyl alcohol was liberated per mole of sugar decomposed and furfural was formed. A mechanism is proposed for this reaction.

5. The gum formed consisted of trimethylxylose, trimethyllyxose and partially demethylated products in the proportion of 26 to 70 to 4 parts, respectively. Indirect evidence is advanced for the absence of ketose.

6. The conversion of normal trimethylxylose into normal trimethyllyxose confirms the identity of their ring structures.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

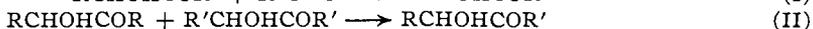
MIXED BENZOINS. VI. FURTHER EXAMPLES OF REVERSIBILITY. THE FORMATION OF ADDITION COMPOUNDS

BY JOHANNES S. BUCK AND WALTER S. IDE

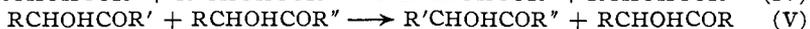
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In Part V¹ the reversibility of the benzoin condensation was demonstrated by means of the reaction $RCHOHCOR + R'CHO \longrightarrow RCHOHCOR' + R'CHOHCOR'$. This change took place under conditions comparable to those of the usual benzoin reaction. A scheme was formulated for the equilibrium conditions of a benzoin reaction mixture of any type. As noted in part V the scheme implied that a number of other transformations were possible, and most of these implications have now been investigated. Positive results were obtained in two of the possible reactions, namely



The results are tabulated. The remaining possibilities



were examined, but only negative results were obtained. The inability to isolate the expected product means either that it was formed in amounts

¹ Buck and Ide, *THIS JOURNAL*, 53, 2350 (1931).

too small to isolate by the methods available or that it was less stable under the conditions of the reaction than was the starting material. It must be borne in mind that continual destruction of material takes place in the reaction mixture, and that the reaction therefore cannot be forced beyond a certain point. Also, the fact that many aldehydes do not form simple benzoins greatly limits the choice of starting materials.

The transformation $RCHOHCOR' \rightarrow R'CHOHCOR$ was not investigated in the present work.

Experimental

The experimental work was carried out in a manner similar to that described in part V,¹ the starting materials being refluxed in aqueous-alcoholic potassium cyanide solution for a given time, determined by trial. The positive results are recorded in Tables I and II. Negative or indecisive results were obtained in all of the following cases.

Reaction (I).—Benzanisoin and *o*-chlorobenzaldehyde, benzpiperoin and furfural, benzanisoin and furfural, *o*-chlorobenzveratroin and benzaldehyde, *o*-chlorobenzveratroin and *p*-dimethylaminobenzaldehyde, *o*-chlorobenzveratroin and anisaldehyde, *o*-chloro-*p*'-dimethylaminobenzoin and piperoinal.

Reaction (II).—Benzoin and anisoin, piperoin and anisoin, furoin and anisoin, piperoin and furoin.

Reaction (III).—Benzanisoin, benzpiperoin, benzfuroin.

Reaction (IV).—Benzpiperoin and *o*-chloro-*p*'-dimethylaminobenzoin, benzanisoin and *o*-chlorobenzpiperoin, *o*-chlorobenzpiperoin and *p*-dimethylaminobenzoin.

Reaction (V).—Benzpiperoin and *o*-chlorobenzpiperoin, *p*-dimethylaminobenzanisoin and *o*-chlorobenzanisoin, *p*-dimethylaminobenzanisoin and benzanisoin.

Reaction (VI).—*p*-Dimethylaminobenzanisoin and anisaldehyde.

The above-cited examples do not, of course, exhaust all the possibilities,

TABLE I
REACTION (I)

Benzoin	Taken, g.	Aldehyde	Taken, g.	Product	Yield, g.	KCN, g.	Alco-hol, cc.	Heating, hours
<i>o</i> -Chloranisoin	5.54	Dimethylaminobenz-	5.96	<i>o</i> -Chloro- <i>p</i> '-dimethylaminobenzoin	3.33	4.0	40	2.5
Benzanisoin	4.84	Dimethylaminobenz-	5.96	Dimethylaminobenzoin	2.04	4.0	40	3.0
Benzpiperoin	5.12	<i>o</i> -Chlorobenz-	5.64	<i>o</i> -Chlorobenzpiperoin	3.13	4.0	40	1.5
Benzpiperoin	5.12	Dimethylaminobenz-	5.96	Dimethylaminobenzoin	1.93	4.0	40	2.0

TABLE II
REACTION (II)

Benzoin I	Taken, g.	Benzoin II	Taken, g.	Product	Yield, g.	KCN, g.	Alco-hol, cc.	Heating, hours
Benzoin	4.24	Piperoin	6.00	Benzpiperoin	0.98	5.0	50	3.2
Benzoin	4.24	Furoin	3.84	Benzfuroin	3.00	3.0	50	1.0

but they represent what, in the authors' opinion, are the ones offering the best prospects of success.

Note on the Formation of Addition Compounds.—There is a remarkable tendency among mixed and simple benzoin to form crystals containing equimolecular amounts of two different benzoin. The following pairs show this property clearly: (a) benzoin and benzpiperoin, (b) benzoin and anisoin, (c) benzoin and piperoin, (d) anisoin and piperoin, (e) piperoin and *p*-dimethylaminobenzoin. If equimolecular amounts of these are dissolved together in alcohol and allowed to crystallize, well-formed crystals are obtained in almost the theoretical yield. The crystal form differs from that of either of the components, and the solubility is generally somewhat less. The melting points are lower (about what would be expected for a mechanical mixture of the components) and are raised by the addition of either component. Repeated crystallization from alcohol fails to separate the constituent benzoin. It is evident that an additive compound is formed. If this were not so, oils or gums, or at any rate a mixture of crystals, would be obtained. Oils and gums are in fact painfully frequent outside of the above and perhaps a few other cases.

Molecular weight determinations in acetic acid and in benzene (both cryoscopic) gave values approximately the mean of the molecular weights of the component benzoin, indicating that the addition compounds do not persist in solution. No optical phenomena appear to be involved as solutions and liquors, even after several fractionations, show no rotation.

The bearing of the above observations on mixed benzoin work is important. Apart from complicating fractional crystallizations, these additive compounds interfere with certain preparations. Thus, in the preparation of benzpiperoin, if the reaction mixture (containing very little water) is refluxed for twenty to thirty minutes only, the addition compound of benzoin and piperoin is produced. It is evident that, on further heating, the reaction (II) [Table II] must take place, resulting finally in a mediocre yield of benzpiperoin. It is precisely in cases where such addition compounds have not been observed or cannot have been formed that the best yields of mixed benzoin are obtained, *e. g.*, with *p*-dimethylaminobenzoin.

The formation of addition compounds between certain benzoin is doubtless analogous to the formation of dimerides in the acyloin series. Dirscherl and Braun,² in discussing the dimerides of acetoin, attribute their existence to partial valency linkages. In the benzoin series such partial valency linkages must be very feeble, as no dimerides are known and the addition compounds do not persist in solution.

Summary

The reversibility of the benzoin condensation has been further demonstrated by means of two of the reactions previously mentioned.¹ The

² Dirscherl and Braun, *Ber.*, 63, 416 (1930).

formation of addition compounds between certain benzoines has been observed.

TUCKAHOE, NEW YORK

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

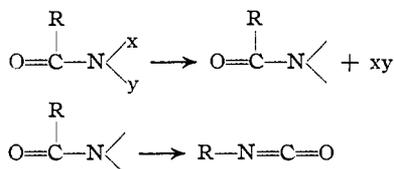
MOLECULAR REARRANGEMENTS INVOLVING OPTICALLY ACTIVE RADICALS. II. THE HOFMANN REARRANGEMENT OF OPTICALLY ACTIVE ACID AMIDES

BY EVERETT S. WALLIS AND S. C. NAGEL

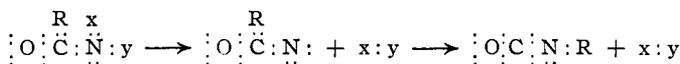
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It has long been known that aliphatic and aromatic acid amides are converted into amines by treatment with chlorine or bromine and an alkali. Hofmann discovered this reaction¹ and detected among the products an isocyanate. It has since been shown, however, that the first product formed is a halogen amide. Of the several theories which have been advanced to explain this rearrangement, perhaps the most fruitful has been the interpretation of Stieglitz and his students² developed from the suggestion of Tiemann³ that an acid amide is converted into an amine through the formation of an unstable intermediate univalent nitrogen compound. Their investigations have made it evident that the Lossen, Curtius and Hofmann rearrangements are fundamentally alike and they have proposed that all rearrangements of this character take place as follows



In terms of modern valence relationships Jones and Hurd⁴ suggested an interpretation of this mechanism based on the Lewis conception of chemical bonds and electrons:



From this interpretation it was assumed that the radical, R, in its wandering from the carbon atom to the nitrogen atom existed momentarily as a free radical, and that the ease of the rearrangement of such types of compounds depended upon the tendency of the radical, R, in the univalent

¹ Hofmann, *Ber.*, **15**, 407 (1882).

² Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); *ibid.*, **29**, 49 (1903); Stieglitz and Earle, *ibid.*, **30**, 399, 412 (1903); Stieglitz and Slossen, *Ber.*, **28**, 3265 (1895); *ibid.*, **34**, 1613 (1901); Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914).

³ Tiemann, *Ber.*, **24**, 4162 (1891).

⁴ Jones and Hurd, *THIS JOURNAL*, **43**, 2422 (1921).