

Analysis of broccoli shows that the leaves and buds have materially the same composition and nutritive value. Both buds and leaves contain proteins somewhat in excess of that reported in spinach.⁶

The predominating organic acid in broccoli is citric acid. It also contains *l*-malic acid and small amounts of oxalic and succinic acids. The proportion of citric and malic acids is 3:2.

The organic acids of lettuce were found to be oxalic acid, 0.011%, *l*-malic acid, about 0.065%, and citric acid, about 0.048%.

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WELLCOME AND COMPANY]

MIXED BENZOINS. IV. DETERMINATION OF THE STRUCTURE OF MIXED BENZOINS BY THE BECKMANN REACTION¹

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The rigid determination of the structure of a number of mixed (unsymmetrically substituted) benzoins would allow important generalizations to be made as to the reactivity of various aromatic aldehydes, and would also contribute to the wider use of benzoins in synthetic work. Up to the present time a few mixed benzoins have been assigned structures, largely on the basis of their production (or the production of the isomer) by the Grignard reaction. Benzanisoin,^{2a} benzfuroin^{2b} and *p*-dimethylaminobenzoin³ have been so determined. In addition, the structure of benzfuroin has been deduced by a Beckmann reaction,⁴ that of *p*-dimethylaminobenzoin by an indirect method,⁵ and that of benzanisoin by synthesis from the desoxy compound.⁶ The structures of the three foregoing benzoins may therefore be taken as definitely settled, and the authors have taken these compounds as standards in this paper.

For determining the structure of mixed benzoins, the Grignard reaction, although probably trustworthy, is anything but convenient. Indirect

⁶ Werner, "Die Pflanzenstoffe, 1911, p. 180.

¹ Since submitting this paper, a note has appeared by Tiffeneau and Lévy, *Compt. rend.* 192, 287 (1931), in which the structures of some mixed benzoins are determined by fission with potassium hydroxide. The results with benzfuroin, benzpiperoin and benzanisoin agree with those of the present authors. Hörbye, Ref. 11, has determined the structures of benzpiperoin and benzanisoin by an oxidation method.

^{2a} McKenzie, Luis, Tiffeneau and Weill, *Bull. soc. chim.*, [4] 45, 414 (1929).

^{2b} Asahina and Terasaka, *J. Pharm. Soc. Japan*, 494, 219 (1923).

³ Jenkins, Bigelow and Buck, *THIS JOURNAL*, 52, 5198 (1930).

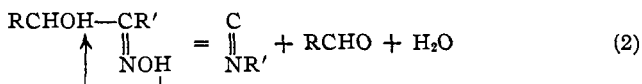
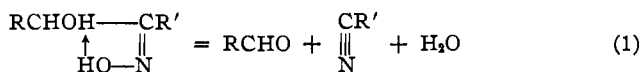
⁴ Werner and Detscheff, *Ber.*, 38, 69 (1905).

⁵ Jenkins, Buck and Bigelow, *THIS JOURNAL*, 52, 4495 (1930).

⁶ Meisenheimer and Jochelson, *Ann.*, 355, 249 (1907).

methods are of limited application. The authors therefore decided to examine further the reaction of Werner and Detscheff⁴ in order to work out a more facile and general method, and found that, with some modifications in technique, the reaction leaves little to be desired from a practical point of view. Seven mixed benzoin (the same as were used in Part III)⁷ were investigated, and structures assigned to them and to their oximes.

The Beckmann reaction, using benzenesulfone chloride, does not generally give an amide with benzoin oximes, but a mixture of an aldehyde and a nitrile or isonitrile. This is known as a Beckmann reaction of the second type and is formulated by Werner and Detscheff⁴ as follows



involving in the first case the elimination of water between the two adjacent hydroxyl groups and in the second case the wandering of a hydroxyl group and a radical, with the elimination of a molecule of water. The authors prefer to regard the reaction as taking place by the usual vicinal transposition of the first type, followed by the fission of the enol form of the amide. Oxime (1) would give the amide, RCHOHN=C(OH)R' (R-CHOHNHCOR'), which, after the manner of the von Braun fission,⁸ would (spontaneously) give RCHO and R'CN, as before. The alternative (improbable) fission between the N and C(OH) groups would give RCN and R'CHO, corresponding, on Werner and Detscheff's views, to the isomeric benzoin. If *trans* groups were concerned, then RCHO and R'N=C would be expected.

In the case of oxime (2) the normal product would be the amide RCHOH-C(OH)=NR' (RCHOHCONHR'), which might lose water between the two hydroxyl groups, giving RCHO and R'N=C.⁹ If *trans* groups were involved, RCHO and R'CN (corresponding to oxime (1)) would be formed. Fission between the C(OH) and N groups would give products never observed in this type of reaction.

The conception of the Beckmann reaction involving the transposition of vicinal groups has been attacked by several workers, notably by Meisen-

⁷ Buck and Ide, *THIS JOURNAL*, 53, 1536 (1931).

⁸ Von Braun and Müller, *Ber.*, 39, 2018 (1906), where, for example, benzylbenzamide, with phosphorus pentabromide gives benzyl bromide and benzonitrile.

⁹ In this connection the authors have found that mandelic anilide with phosphorus pentachloride gives phenylisonitrile. Werner and Piguet, *Ber.*, 37, 4309 (1904), have obtained mandelic anilide from β -benzoin oxime (*syn*-phenyl) by using benzenesulfone chloride with pyridine. The same oxime, using alkali in place of pyridine, gives benzaldehyde and phenylisonitrile.⁴

heimer (who, however, worked chiefly on benzil oximes). The matter cannot be regarded as settled, and the present authors prefer to interpret their results on the basis of vicinal transposition, or on Werner and Det-scheff's theory, both giving the same structure. The reason for so doing is the complete agreement of the structures so deduced with those found by other methods in the three cases cited above.

It will be seen that the aldehyde formed determines the structure of the parent benzoin, while the formation of a nitrile or of an isonitrile discriminates between the two oximes, the *syn*-phenyl oxime giving the isonitrile and the *anti*-phenyl oxime the nitrile. For practical purposes only the aldehyde need be isolated to determine the position of the carbonyl group in the benzoin. Either oxime, or indeed a mixture of the two, could be used for this purpose.

The benzoin examined in the present paper, together with the desoxy compounds derived from them (as main product) by reduction, are listed below (letters as in Part III, Ref. 7).

$\text{ClC}_6\text{H}_4\text{CHOHCOC}_6\text{H}_3(\text{OMe})_2$	A	$\text{ClC}_6\text{H}_4\text{CH}_2\text{COC}_6\text{H}_3(\text{OMe})_2$
$\text{ClC}_6\text{H}_4\text{CHOHCOC}_6\text{H}_4\text{OMe}$	B	$\text{ClC}_6\text{H}_4\text{CH}_2\text{COC}_6\text{H}_4\text{OMe}$
$\text{ClC}_6\text{H}_4\text{CHOHCOC}_6\text{H}_4\text{NMe}_2$	C	$\text{ClC}_6\text{H}_4\text{CH}_2\text{COC}_6\text{H}_4\text{NMe}_2$
$\text{ClC}_6\text{H}_4\text{CHOHCOC}_6\text{H}_3\text{O}_2\text{CH}_2$	D	$\text{ClC}_6\text{H}_4\text{CH}_2\text{COC}_6\text{H}_3\text{O}_2\text{CH}_2$
$\text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_4\text{OMe}$	E	$\text{C}_6\text{H}_5\text{COCH}_2\text{C}_6\text{H}_4\text{OMe}$
$\text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_3\text{O}_2\text{CH}_2$	G	$\text{C}_6\text{H}_5\text{CH}_2\text{COC}_6\text{H}_3\text{O}_2\text{CH}_2$
$\text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_4\text{NMe}_2$	H	$\text{C}_6\text{H}_5\text{CH}_2\text{COC}_6\text{H}_4\text{NMe}_2$

In the majority of cases the desoxy compound is formed by the replacement of the CHO group by CH_2 . The case of benzoin E shows that the reduction is not simple and that the hydrobenzoin or the isohydrobenzoin is involved¹⁰ and that it is not permissible to infer the structure of the benzoin from that of the desoxy compound produced by reduction.

It will be seen that, so far as they go, the results obtained support Hörbye's¹¹ view that the CHO group takes the position adjacent to the unsubstituted phenyl group. To this group may now be added the *o*-chlorophenyl group. The results are at variance with some of Staudinger's¹² views but support the contentions of Jenkins.^{3,5}

Experimental

Oximes.—Three general methods were used to prepare the oximes of the mixed benzoin. (1) The benzoin was allowed to stand in alcoholic solution at room temperature with hydroxylamine acetate and the product precipitated by gradual addition of water. (2) The benzoin was warmed on the bath with hydroxylamine and excess of sodium hydroxide, all in alcoholic solution, usually for three hours. The oxime was precipi-

¹⁰ Orékhoff and Tiffeneau, *Bull. soc. chim.*, [4] 37, 1410 (1925).

¹¹ Ch. Hörbye, "Dissertation," Dresden, 1917. Cf. Tiffeneau and Lévy, footnote.

¹² Staudinger, *Ber.*, 46, 3530, 3535 (1913).

tated by carbon dioxide. This method is useful when the benzoin is sparingly soluble in alcohol. (3) The benzoin, in pyridine solution, was warmed on the bath for three hours with hydroxylamine hydrochloride and the reaction mixture then gradually diluted with water.

The method was selected by trial, yield being the consideration. In no case was more than one oxime isolated, although the isomer was carefully sought for. When the yield was mediocre, the remainder of the material was recovered as a thick gum, probably containing unchanged starting material and decomposition products as well as the isomeric oxime. It is quite possible that the isomer could be obtained by other methods. All of the oximes obtained were of the α -(*anti*-phenyl) form, except that from *p*-dimethylaminobenzoin, which was the β -isomer. The oximes were recrystallized from alcohol, in which they are moderately soluble, until pure. As a rule, they are sparingly soluble in other solvents, except pyridine. The compounds are tabulated below.

TABLE I
OXIMES

Benzoin	No. in Pt. III	Form	No. of prep.	Yield, %
1-Chloro- α -hydroxybenzyl-3',4'-dimethoxyphenyl ketone (1-chlorophenyl-3',4'-dimethoxybenzoyl carbinol)	1	α	2	99
1-Chloro- α -hydroxybenzyl-4'-methoxyphenyl ketone (1-chlorophenyl-4'-methoxybenzoyl carbinol)	2	α	1	99
1-Chloro- α -hydroxybenzyl-4'-dimethylaminophenyl ketone (1-chlorophenyl-4'-dimethylaminobenzoyl carbinol)	3	α	3	80
1-Chloro- α -hydroxybenzyl-3',4'-methylenedioxyphenyl ketone (1-chlorophenyl-3',4'-methylenedioxybenzoyl carbinol)	4	α	2	81
α -Hydroxybenzyl-4'-methoxyphenyl ketone ¹ (phenyl-4'-methoxybenzoyl carbinol)	5	α	1	68
α -Hydroxybenzyl-3',4'-methylenedioxyphenyl ketone (phenyl-3',4'-methylenedioxybenzoyl carbinol)	6	α	1	50
α -Hydroxybenzyl-4'-dimethylaminophenyl ketone (phenyl-4'-dimethylaminobenzoyl carbinol)	7	β	2	57

M. p., °C.	Appearance	Formula	Nitrogen analyses Calcd.	Found	Structure of benzoin (p. s.)	No. of oxime
149	White rhombs	C ₁₆ H ₁₆ O ₄ NC1	4.35	4.53	A	A
144	Glittering crusts ^a	C ₁₆ H ₁₄ O ₂ NC1	4.80	4.97	B	B
156-158	Yellow rhombs	C ₁₆ H ₁₇ O ₂ N ₂ Cl	9.19	9.08	C	C
149	White rhombs	C ₁₆ H ₁₂ O ₄ NC1	4.58	4.64	D	D
140	Crusts of thin prisms	C ₁₅ H ₁₆ O ₂ N	5.44	5.47	E	E
158	Crusts of prisms ^a	C ₁₅ H ₁₃ O ₄ N	5.16	5.09	G	G
140	Glittering crusts ^a	C ₁₆ H ₁₈ O ₂ N ₂	10.36	10.60	H	H

^a Form obscure.

Beckmann Reaction.—The Beckmann reaction was carried out in alkaline (sodium hydroxide) solution, using benzenesulfone chloride as the transforming agent. The

chloride was added in portions to the alkali-oxime mixture, the whole being shaken vigorously and care being taken that the mixture remained alkaline. The temperature was not allowed to rise more than a few degrees. The reaction mixture was shaken until the chloride had disappeared, then cooled and the oily layer exhaustively extracted with ether, the extract dried over sodium sulfate and the ether driven off. The oil remaining was fractionated under low pressure, using a fine capillary. When benzaldehyde was present, this was removed at 10-mm. pressure, and the pressure then lowered to 0.5-1.0 mm. and the second product distilled off. This usually solidified in the receiver. In other cases (*o*-chlorobenzaldehyde) the oil was all fractionated at 0.5-1.0 mm. The fractions, which, however, were usually sharply separated, were redistilled if necessary under reduced pressure. Benzaldehyde was identified by its properties and by its conversion into benzoin (mixed melting point determinations). *o*-Chlorobenzaldehyde, after purification via the bisulfite compound, was identified by its properties and by mixed melting point determinations of its oxime with 2-chlorobenz-*anti*-aldoxime. The nitriles were identified by mixed melting point determinations with the authentic nitrile when this was available, but they were always hydrolyzed, by the Radziscewski¹⁸ method, to the amide and identified by properties and by mixed melting point determinations with the authentic amide.

It is doubtful whether an isonitrile odor (cf. Ref. 4) is of much significance. Its presence in the case of oximes D and E must be ascribed to a side reaction or (unlikely) to a trace of the other oxime. In the case of oxime H the odor was intense, but it was not possible to isolate the isonitrile. Werner and Detscheff⁴ encountered the same difficulty. The absence of any nitrile (obtained without difficulty from oxime C) is evidence for the formation of the isonitrile. This observation also answers the possible objection that the nitriles might be formed from the isonitriles by distillation, although this is unlikely at the temperatures to which

TABLE II
BECKMANN REACTION

Oxime	Taken, g.	1st Fraction		2d Fraction			
		Name	G.	%	Name	G.	%
A	20.0	<i>o</i> -Chlorobenzaldehyde	6.8	78	Veratronitrile	6.2	61
B	15.0	<i>o</i> -Chlorobenzaldehyde	7.0	96	Anisonitrile	6.7	98
C	20.0	<i>o</i> -Chlorobenzaldehyde	7.1	77	<i>p</i> -Dimethylaminobenzonitrile	7.9	83
D	20.0	<i>o</i> -Chlorobenzaldehyde	6.0	65	Piperonitrile	5.4	56
E	15.0	Benzaldehyde	5.8	94	Anisonitrile	7.2	93
G	12.0	Benzaldehyde	4.3	92	Piperonitrile	6.4	98
H	12.0	Benzaldehyde	4.1	86	[<i>p</i> -Dimethylaminophenylisonitrile]	0	0
Oxime		Isonitrile smell	Resin residue, g.		Reaction mixture		
A		—	Large		Brown-black, some dirt		
B		—	0.5		Light yellow, clean		
C		—	5.2		Green-black		
D		+	Large		Dark brown, much dirt		
E		+	2.2		Yellow		
G		—	0.3		Little color		
H		+++++	Large		Brown-black, much dirt		

¹⁸ Technique of Rupe and Majewski, *Ber.*, 33, 3401 (1900), using somewhat stronger peroxide.

they were exposed (the nitriles distil at about 120° below 1.0 mm.). In the case of oximes A, D and H much black, amorphous matter was formed in the reaction. Some of this was separated from the ether extract; the rest appeared as residue in the distilling vessel. The residue is not formed by decomposition during distillation, as can be seen by the small residues from oximes B and G. The results are given in tabular form.

Summary

The structures of seven mixed benzoin, obtained by the usual potassium cyanide condensation, have been determined by means of a second-type Beckmann reaction. The results, interpreted according to Werner's views of the Beckmann rearrangement, give structures in agreement with those determined by independent methods.

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CROTYL ETHERS OF PHENOL

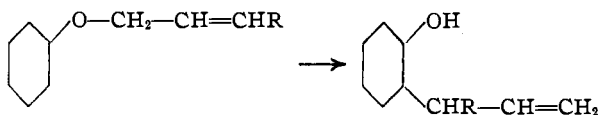
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When allyl aryl ethers are heated, rearrangement into *o*-allylphenols usually occurs with ease. The same has been shown to be true in some cases when substituted allyl aryl ethers undergo pyrolysis. Only the following groups seem to have received study in this connection: (1) crotyl, $\text{CH}_3\text{CH}=\text{CHCH}_2-$, with phenol,^{1,2} β -naphthol,² and hydroxynaphthoquinone;³ (2) cinnamyl, $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2-$, with phenol;⁴ (3) α -methylcrotyl, $\text{CH}_3\text{CH}=\text{CH}-\text{CH}(\text{CH}_3)-$, with phenol;⁵ (4) γ -methylcrotyl, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2-$, with phenol;⁶ (5) α,α -dimethylallyl, $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)_2-$, with phenol;⁷ (6) geranyl, $\text{CH}_2=\text{C}(\text{CH}_3)-(\text{CH}_2)_3-\text{C}(\text{CH}_3)=\text{CHCH}_2-$, with catechol.⁸

The first four groups undergo rearrangement of the type exemplified in the equation



¹ Claisen and Tietze, *Ber.*, **59**, 2350 (1926).

² Von Braun and Schirmacher, *ibid.*, **56**, 544-5 (1923).

³ Fieser, *THIS JOURNAL*, **48**, 3205 (1926).

⁴ Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 233 (1925).

⁵ Claisen and Tietze, *Ber.*, **58**, 277 (1925); Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 226 (1925).

⁶ Claisen and Tietze, Ref. 5; the reference by these authors in *Ber.*, **59**, 2349 (1926), gives a conflicting notation and evidently refers to $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)_2-\text{O}-\text{C}_6\text{H}_5$.

⁷ Claisen, Kremers, Roth and Tietze, *J. prakt. Chem.*, **105**, 67 (1922).

⁸ Kawai, *Sci. Papers Inst. Phys. Chem. Research*, **6**, 53 (1927).