51. *Autoxidation Processes. Part VIII.* Steric Hindrance in Oxidation and Racemisation of α-Ketols.*

By Arnold Weissberger.

It has been shown in previous papers of this series that a relation exists between the rates of autoxidation, oxidation with Fehling solution, and racemisation of α-ketols R·CH(OH)·CO·R′ in alkaline solution, and the electrolytic dissociation constants of the carboxylic acids $R{\cdot}CO_2H$ and $R'{\cdot}CO_2H$. Table I shows for a series of α-ketols (one aliphatic, and the others benzoin and *p*-substituted benzoins) the autoxidation velocities k at 10° and at 20° in 79% ethyl-alcoholic solution in the presence of 0·05*N*-potassium hydroxide, the ketol concentration being 0·0057*M*. Col. 4 gives the values of the empirical relation between k_{20° and the dissociation constants (K and K') of the carboxylic acids, $k_{20^\circ}/(KK')^{1\cdot8}$ =const., the constancy being reasonably good. Of *m*-substituted benzoins, hitherto only piperonyloin and *mm*′-dimethoxybenzoin had been investigated. The ratio for the former, a *p*-substituted compound also, agrees with the average value for the other ketols in Table I; that for the latter (Table II) is rather lower. For the *m*-substituted benzoins in general there are three possibilities : they might give a value of the ratio identical with that of the *p*-compounds, or an average value somewhat different, or thirdly, they might obey no simple relation at all. The last had been shown to be the case with the *o*-substituted benzoins, and this failure was attributed to steric hindrance. To examine this interpretation is the main purpose of the present paper.

It was found that these steric effects played no part whatever in the *m*-compounds,

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* Part VII : Weissberger and Dym, *Annalen*, 1933, **502**, 74.

TABLE I.

	Benzoin.	$10^3k_{10^\circ}$.	$10^3k_{20^\circ}$.	$10^{10}\times KK'$.[‡]	$10^{-13}k_{20^\circ}/(KK')^{1\cdot 8}$.	$10^6(x-x')$.[§]
1.	(Butyroin)	0·93	2·1	2·25	49	—
2.	[*]*p'*-Dimethylamino-	2·6	9·7	6·2	36	—
3.	*p'*-Chloro-*p*-dimethylamino-	11·1	32	8·74	65	—
4.	*pp'*-Diethoxy-	15·6	49	—	74 [†]	—
5.	*pp'*-Dimethoxy-	17·4	61	10·2	93	8·1
6.	*pp'*-Di*iso*propyl-	38·4	98	27·04	26	—
7.	*pp'*-Dimethyl-	41·7	101	18·7	52	9·0
8.	3 : 4 : 3' : 4'-Di(methylenedioxy)-	42·4	108	20·2	48	9·8
9.	*p'*-Methyl-	54	140	28·6	34	10
10.	*p*-Methyl-	66	180	28·6	44	10·1
11.	Benzoin	97	270	43·6	30	12·1
12.	*p'*-Chloro-	258	674	61·4	41	21·3
13.	*p*-Chloro-	330	770	61·4	47	22·1
14.	*pp'*-Dichloro-	668	~1500	86·5	49	37·4

[*] The dash marks the ring adjacent to the carbonyl group.

[†] Calculated from K for *p*-methoxybenzoic acid.

[‡] From Landolt–Börnstein–Roth and International Critical Tables.

[§] See Part IX.

TABLE II.

	Benzoin.	$10^3k_{10^\circ}$.	$10^3k_{20^\circ}$.	$10^{10}\times KK'$.	$10^{-13}k_{20^\circ}/(KK')^{1\cdot 8}$.	$10^{-13}k_{10^\circ}/(KK')^{1\cdot 8}$.	$10^6(x-x')$.
15.	*mm'*-Dimethoxy-	108	300	79·4	12	3·9	13·7
16.	*mm'*-Diethoxy-	115	290	—	11	4·3	—
17.	*mm'*-Dichloro-	980	—	240·3	—	5·1	59·6

as shown in Table II, but are confined to the *o*-derivatives. The ratios with the k_{20° values are given only for the first two compounds, since *mm'*-dichlorobenzoin is too reactive to be investigated at 20°. For this substance, therefore, the ratio with the k_{10° value is given, together with the corresponding ratios for the other two substances. The value of the ratio for the three *m*-derivatives is constant, and is about one-third of that for the compounds in Table I. This difference will be discussed in a subsequent paper. The three derivatives with methoxyl, ethoxyl, and chlorine, however, all behave in the same way; the *autoxidation rates of the meta-substituted benzoins are linked without individual deviations to the dissociation constants of the carboxylic acids*, just as in the case of the para-substituted compounds.

If, however, the same substituents are introduced into the *o*-position, they cause large individual deviations from the relation in question, as appears from Table III. The values in col. 4 for the benzoins with ortho-substituents in *both* rings (Table III*a*) decrease as one goes from methyl through methoxyl to ethoxyl, *i.e.*, they fall with increasing volume of the substituents, as would be expected for a steric effect. The decrease for the dichloro-compound is so large as to require special discussion (see Part IX, succeeding paper). Table III*b*, which concerns the derivatives with only one substituent in the *o*-position, shows the same regularity, and further, shows that the *o*-effect of the substituent is larger if it is introduced into the ring next to the hydroxyl group than into the other nucleus.

TABLE III*a*.

	Benzoin.	$10^3k_{10^\circ}$.	$10^3k_{20^\circ}$.	$10^{10}\times KK'$.	$10^{-13}k_{20^\circ}/(KK')^{1\cdot 8}$.	$10^{-13}k_{10^\circ}/(KK')^{1\cdot 8}$.	$10^6(x-x')$.
18.	*oo'*-Dimethyl-	72	200	148·8	2·5	—	15·8
19.	*oo'*-Dimethoxy-	12·4	34	67·2	1·7	—	7·9
20.	*oo'*-Diethoxy-	3·6	9·8	74·0	0·42	—	7·7
21.	*oo'*-Dichloro-	510	1250	16900	0·0051	—	54·6

TABLE III*b*.

22.	*o'*-Methyl-	360	880	80·5	33	—	21·9
23.	*o*-Methyl-	170	460	80·5	17	—	20·0
24.	*o'*-Ethoxy-	88	218	56·8	15	—	9·8
25.	*o*-Ethoxy-	44	114	56·8	7·9	—	8·3
26.	*o*-Chloro-	295	735	858·0	0·39	—	22·9

These facts, *viz.*, that the relation between the dissociation constants and the rates of reaction holds in the para- and the meta- but not in the ortho-substituted benzoins, and that the deviations in the last series increase with the volume of the substituents, provide conclusive evidence that these deviations are caused by steric hindrance.

EXPERIMENTAL.

Measurements were made as described in the previous papers of this series.

Materials.—mm'-*Dichlorobenzoin.* A solution of potassium cyanide (0·5 g. in water, 3 c.c.) was added to *m*-chlorobenzaldehyde (10 g.) in ethyl alcohol (20 c.c.), heated at 60° for 5 hours (air being excluded), poured into ice-water which was kept *acid* by hydrochloric acid, shaken with ether, and the ethereal layer steam-distilled. The residue was dissolved in ether, dried (sodium sulphate), the ether removed, and the residue dissolved in a little ligroin. A part of this solution, on being cooled in solid carbon dioxide–ether, gave crystals; the rest, when seeded with these, crystallised at 0°. After repeated crystallisations from ligroin, 2·2 g. (22%) of a colourless product were obtained, m. p. 76° (sintering at 69°). The substance solidifying from the melt remelted sharply at 75—76°, and after seeding with this the main bulk also gave crystals of m. p. 75—76°. Investigation under the hot-stage microscope confirmed that the substance is polymorphous (Found : C, 59·9; H, 3·4; Cl, 24·9. Calc. : C, 59·8; H, 3·6; Cl, 25·2%). Klimont (Diss., Heidelberg, 1891) describes the compound as light yellow, m. p. 65—67°.

o-*Methylbenzoylphenylcarbinol* (o'-*Methylbenzoin*). We had previously prepared this compound (*Annalen*, 1931, **478**, 126) according to the method of McKenzie, Martin, and Rule (J., 1914, **105**, 1586) and obtained a product, m. p. 108—109°, which we believed to be the right substance as it had the properties given in the literature. When, however, we used *o*-bromotoluene prepared from purified *o*-toluidine, instead of Kahlbaum's material, we obtained a ketol of m. p. 74—75°, having the autoxidation velocities given in Table III*b*. This compound is the true *o*-methylbenzoylphenylcarbinol, whilst the compound of higher m. p. is the *p*-derivative. The isolation of the latter compound, from the *p*-bromotoluene present as an impurity, is evidently due to its readier formation and its greater ability to crystallise.

By the method of Weissberger *et al.* (*loc. cit.*), 58 g. of pure *o*-bromotoluene and 10·6 g. of benzaldehyde yielded 1·3 g. of crystals, which, after recrystallisation from ligroin, gave 0·8 g. (4%) of colourless crystals, m. p. 74—75° (Found : C, 79·7; H, 6·0. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%).

mm'-*Diethoxybenzoin.* This was similarly prepared, 43 g. of *m*-bromophenetole and 9·3 g. of *m*-ethoxybenzaldehyde affording 2·4 g. of uncrystallisable oil; its absorption of oxygen in the autoxidation showed that it contained more than 90% of the acyloin.

Benzoyl-o-*chlorophenylcarbinol* (o-*Chlorobenzoin*). 60 G. of bromobenzene and 14·5 g. of *o*-chlorobenzaldehyde yielded a product which, after crystallisation from ligroin, was colourless; 12·8 g. (50%), m. p. 82·5—83·5° (Found : C, 68·0; H, 4·6; Cl, 14·7. Calc. for $C_{14}H_{11}O_2Cl$: C, 68·15; H, 4·46; Cl, 14·4%).

We have redetermined the values of the necessary constants at 20° for most of the substances for which data were published before, using freshly prepared material. The new values agree with the earlier ones. The m. p.'s of the following compounds should, however, be corrected : *p*-methylbenzoylphenylcarbinol, 110—111°; benzoyl-*p*-tolylcarbinol, 118—119°; *p*-chlorobenzoylphenylcarbinol, 89·5—90·5°; benzoyl-*p*-chlorophenylcarbinol, 114—115°; benzoyl-*o*-ethoxyphenylcarbinol, 82—83°; *oo*'-dichlorobenzoin, 63—64°; benzoyl-*o*-tolylcarbinol 68·5—69·5°. Polymorphism seems to be the reason for the (small) deviations from the earlier values. In the case of the *o*-methylbenzoylphenylcarbinol, however, our former values for the autoxidation rate are in error for the reason given above.

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