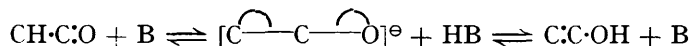


**141.** *Optical Activity in Relation to Tautomeric Change. Part VI. Comparison of the Rates of Racemisation and of Bromination of a Ketone. A Further Study under Conditions of Basic Catalysis.*

By SHING KONG HSÜ and CHRISTOPHER L. WILSON.

IT was shown in Part IV (Ingold and Wilson, J., 1934, 773) that the speed of racemisation of an enolisable ketone in which the  $\alpha$ -carbon atom is the centre of asymmetry is identical with its speed of bromination under equivalent conditions of acid catalysis. The example studied was 2-*o*-carboxybenzylindan-1-one. Ramberg and collaborators (*Arkiv Kemi, Min. Geol.*, 1934, **11**, B, Nos. 31, 41) have since examined the racemisation and bromination of  $\alpha$ -ethylsulphonyl- and  $\alpha$ -phenylsulphonyl-propionic acid, and Bartlett and Stauffer (*J. Amer. Chem. Soc.*, 1935, **57**, 2580) the racemisation and iodination of phenyl *sec.*-butyl ketone; in each case the rates were equal. These workers also used acid catalysts and their findings therefore simply confirm those of Part IV (*loc. cit.*).

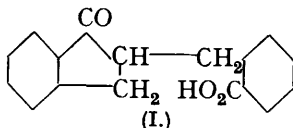
In this paper we break new ground by investigating base-catalysed reactions: the mechanism of both racemisation and halogenation must be different from those of the previous comparisons. We assume the mechanism for catalysis by a base (B) to be represented by the scheme:



It is very probable that the anion is the reactive entity in unimolecular bromination and since optical activity should be lost at this stage the two rates are likely to be equal. In these circumstances each of the velocities measures the speed of formation of the anion from the ketone under the existing catalytic conditions. On the other hand it should also be pointed out that, since an enolisable ketone is a  $\psi$ -acid, the reversible process represented on the right of the above scheme will have a much greater velocity than that represented on the left, so that the speed of ionisation of the ketone is likely to be substantially equal to its speed of enolisation. Thus it would also be correct to say that either of the measured velocities represents enolisation.

The correspondence between the rates of racemisation and bromination was demon-

strated with *d*-2-*o*-carboxybenzylindan-1-one (I). Dilute acetic acid was the solvent, and sodium acetate (*i.e.*, acetate ions) the catalyst. Experiment showed that the speed was principally controlled by the added catalyst and not by the solvent. Both reactions were unimolecular and comparable velocity constants are 0.0438 hr.<sup>-1</sup> for racemisation and 0.0471 hr.<sup>-1</sup> for bromination. Although the difference is larger than our experimental error (less than 1%), it is possible that some systematic imperfection of method has not been eliminated.



## EXPERIMENTAL.

**Preparation of Materials.**—2-*o*-Carboxybenzylindan-1-one was prepared and resolved in the manner previously described (Ingold and Wilson, *loc. cit.*). The optically active ketone had m. p. 195—205° and  $[\alpha]_D^{25} + 50^\circ$  (90% aqueous acetic acid,  $c = 1.33$ ). Glacial acetic acid was purified by Orton and Bradfield's method (J., 1924, 125, 960) and diluted to 16.00*N*. Crystalline sodium acetate and bromine were of AnalaR standard of purity.

**Racemisation of the *d*-Ketone.**—The experiments were conducted in a 2 dm. jacketed polarimeter tube maintained, by circulation of thermostat water, at a mean temperature of 25.00° ± 0.01°.

A 0.05*M*-solution of the active ketone in 16.00*N*-acetic acid containing 2.0% of crystalline sodium acetate lost activity as follows :

Time, <i>t</i> (hrs.)	0	2.42	4.70	7.42	9.7
Rotation ( $\alpha$ )	1.45°	1.305°	1.195°	1.05°	0.95°
Time, <i>t</i> (hrs.)	22.75	25.25	29.25	33.25	46.33
Rotation ( $\alpha$ )	0.54°	0.48°	0.40°	0.34°	0.195°

The logarithms of  $\alpha$  when plotted against time (*t*) give a straight line which corresponds with a unimolecular velocity constant of 0.0438 hr.<sup>-1</sup>

The "solvent reaction" was determined in a similar manner, the sodium acetate being omitted, but water added to the acetic acid to compensate for that present in the sodium acetate crystals used in the previous experiment. The figures were as follows :

Time, <i>t</i> (hrs.)	0	6.58	22.25	28.33	46.25	56.00	69.16
Rotation ( $\alpha$ )	1.44°	1.38°	1.25°	1.20°	1.06°	1.00°	0.90°
Time, <i>t</i> (hrs.)	78.67	94.83	101.67	143.42	150.50	171.00	
Rotation ( $\alpha$ )	0.84°	0.75°	0.73°	0.58°	0.55°	0.47°	

The reaction was again strictly unimolecular, the velocity constant being 0.00649 hr.<sup>-1</sup>

**Bromination.**—A 0.05*M*-solution (50 c.c.) of the ketone in 16.00*N*-acetic acid in which 2.0% of crystalline sodium acetate had been dissolved was treated at 25.00° ± 0.01° with bromine, delivered from a previously calibrated capillary pipette. At determined intervals of time 5 c.c. samples of the solution were run into 50 c.c. of water in a stoppered bottle, potassium iodide added, and the iodine titrated with *N*/50-thiosulphate. Chloroform (5—6 c.c.) was added towards the end of the titration to liberate iodine adsorbed by the precipitated organic material.

Details of two experiments involving different concentrations of the halogen are in the following tables. Column 2 contains the amounts of *N*/50-thiosulphate required for a 5 c.c. sample of the reaction mixture. Column 3 gives the concentration (*M*) of brominated (*x*) ketone.

[Br] ~ 0.01 <i>M</i> . [Ketone] = 0.05 <i>M</i> .			[Br] ~ 0.005 <i>M</i> . [Ketone] = 0.05 <i>M</i> .								
Time, <i>t</i> (mins.).	Titre (c.c.)	$x(M) \times 10^5$ .	Time, <i>t</i> (mins.).	Titre (c.c.)	$x(M) \times 10^5$ .	Time, <i>t</i> (mins.).	Titre (c.c.)	$x(M) \times 10^5$ .	Time, <i>t</i> (mins.).	Titre (c.c.)	$x(M) \times 10^5$ .
0	4.81 *	0	115	2.63	436	0	2.72 *	0	90	1.02	340
15	4.56	50	135	2.28	506	15	2.43	58	105	0.77	390
35	4.15	132	155	1.96	570	45	1.87	170	120	0.51	442
55	3.70	222	175	1.67	628	62	1.53	238	135	0.32	480
75	3.35	292	195	1.38	686	75	1.30	284			
95	2.98	366									

\* Extrapolated.

A plot of  $\log(0.05 - x)$  against *t* gives straight lines over the major portion of the reaction. Slight deviations from linearity are observable in the latter stages of halogenation, due, no doubt,

to the decrease in the concentration of the catalyst caused by the hydrogen bromide liberated. The initial slopes give first-order constants of  $0.0473 \text{ hr.}^{-1}$  (for  $[\text{Br}] = 0.01M$ ) and  $0.0470 \text{ hr.}^{-1}$  (for  $[\text{Br}] = 0.005M$ ) indicating that the reaction velocity is independent of halogen concentration.

The authors are grateful to Professor C. K. Ingold, F.R.S., for his interest and help.

UNIVERSITY COLLEGE, LONDON.

[Received, March 18th, 1936.]

---