250. *Aliphatic Substitution and the Walden Inversion. Part II.*

By E. D. HUGHES, F. JULIUSBURGER, A. D. SCOTT, B. TOPLEY, and J. WEISS.

IN Part I (J., 1935, 1525) it was shown that, when *d-sec.*-octyl iodide is racemised by sodium iodide in acetone solution, the inversion process involved is also the process of substitution of iodine by iodine. This result is in accord with a theory of aliphatic substitution developed by various authors (see Part I, *loc. cit.*; also Bergmann, Polanyi, and Szabo, *Trans. Faraday Soc.*, 1936, **32**, 843). In principle, the method consisted of a direct comparison of the rate of substitution (followed by means of a radioactive halogen indicator) with the rate of optical inversion in a solution of the same composition; the two rates agreed within the error of the substitution measurements.

A similar comparison has now been made for the analogous reaction between *d*-α-phenylethyl bromide and lithium bromide in anhydrous acetone solution. The experimental procedures were similar, and the method of calculating the results was the same, as described in Part I.

EXPERIMENTAL.

The Racemisation. (By E. D. HUGHES and A. D. SCOTT.)—The rate of racemisation of *d*-α-phenylethyl bromide has not been previously measured. No change in rotation could be detected in acetone solution in the time necessary and under the conditions employed. Under the influence of lithium bromide, however, racemisation took place rapidly and completely, the product being *r*-α-phenylethyl bromide. The lithium bromide concentration does not change during the racemisation, and the reaction is formally of the first order. The first-order constant increases with the lithium bromide concentration but notably less than linearly (cf. Part I). We have made measurements at three different temperatures. The Arrhenius equation takes the form $\log_e k = 21{\cdot}27 - 17{,}100/RT$. The results are summarised in Table I as second-order velocity constants calculated from the expression $k = (2{\cdot}303/2Bt).\log_{10}\alpha_0/\alpha_t$, where B is the molar concentration of lithium bromide and α_0 and α_t are respectively the rotations initially and after reaction for t seconds.

TABLE I.

Expt.	Temp.	*B*.	$k \times 10^3$.	Expt.	Temp.	*B*.	$k \times 10^3$.
1 and 2	30·2°	0·200	0·795	5 and 6	40·45°	0·198	2·00
3 and 4	30·2	0·102	0·963	7	15·2	0·204	0·180

Preparation of r-*α-Phenylethyl Bromide.*—A benzene solution (500 c.c.) of *r*-α-phenylethyl alcohol (100 g.; prepared from phenylmagnesium bromide and acetaldehyde) was cooled, and slowly saturated with hydrogen bromide. Reaction took place rapidly, as shown by the appearance of cloudiness followed by separation into two clear layers. The benzene layer was separated from the water and dried over anhydrous sodium sulphate. The solvent was removed in a vacuum below 35°, and the bromide was finally distilled from a little anhydrous potassium carbonate; b. p. 88°/12 mm.; yield almost quantitative (Found: C, 52·0; H, 5·0; Br, 42·8. Calc.: C, 51·9; H, 4·9; Br, 43·2%).

d-α-Phenylethyl bromide was prepared from *l*-α-phenylethyl alcohol (Pickard and Kenyon, J., 1911, **99**, 45; Houssa and Kenyon, J., 1930, 2260; Ott, *Ber.*, 1928, **61**, 2139) as described above. The alcohol used had $[\alpha]_D^{20°} - 37{\cdot}4°$; the bromide obtained had $[\alpha]_D^{20°} + 12{\cdot}6°$. Holmberg (*Ber.*, 1912, **45**, 997) obtained a dextrorotatory bromide ($\alpha_D^{14°} + 1{\cdot}50°$) by the action of phosphorus pentabromide on a lævorotatory alcohol ($\alpha_D^{17°} - 4{\cdot}40°$) in ethereal solution. The same author observed complete racemisation when an active alcohol was treated with hydrogen bromide in the absence of a solvent. It is not clear whether the rotations recorded are specific rotations.

The purification of materials and the method employed in the racemisation experiments were as described in Part I.

In Table II, A is the molar concentration of organic bromide and N_i is the total rate of inversion (in mols./l./sec.) calculated by means of the equation $N_i = (A/2t) . \log_e \alpha_0/\alpha$. The significance of the other terms has already been defined. Two experiments are given in detail, and the results of the other five are summarised.

TABLE II.

Expt. 1. Temp., 30·2°;
$A = 0{\cdot}200$; $B = 0{\cdot}200$.

t.	*a*.	$N_i \times 10^5$.	*t*.	*a*.	$N_i \times 10^5$.
0	0·645°	—	1645	0·385°	3·14
418	0·565	3·20	1808	0·370	3·08
616	0·530	3·20	1867	0·360	3·13
939	0·475	3·27	2006	0·340	3·20
1198	0·435	3·30	2195	0·320	3·20
1438	0·405	3·24	2360	0·300	3·25
				Mean	3·20

Expt. 2. Temp. 30·2°;
$A = 0{\cdot}200$; $B = 0{\cdot}200$.

t.	*a*.	$N_i \times 10^5$.	*t*.	*a*.	$N_i \times 10^5$.
0	0·645°	—	1663	0·380°	3·19
295	0·585	3·26	1862	0·360	3·14
767	0·510	3·07	1915	0·350	3·20
833	0·490	3·12	2199	0·330	3·05
993	0·470	3·20	2390	0·310	3·07
1144	0·445	3·25	2575	0·290	3·11
1353	0·415	3·27	3175	0·265	3·19
1475	0·405	3·16		Mean	3·16

Expt.	Temp.	*A*.	*B*.	$N_i \times 10^5$ (mean).	Expt.	Temp.	*A*.	*B*.	$N_i \times 10^5$ (mean).
3	30·2°	0·200	0·102	1·98	6	40·45°	0·197	0·198	7·94
4	30·2	0·200	0·102	1·95	7	15·2	0·201	0·204	0·740
5	40·45	0·197	0·198	7·64					

The Substitution (Exchange) Reaction. (By F. JULIUSBURGER, B. TOPLEY and J. WEISS.)—The apparatus was as already described (Part I, *loc. cit.*). Solutions of lithium bromide and *dl*-α-phenylethyl bromide in acetone were mixed at 30·2°, the mixture being 0·2*M* with respect to each reactant. It was verified by special experiments that the hydrolysis of the organic bromide could be kept below 1% if the water used for precipitating it from the acetone solution at the end of the reaction period (21 minutes) and for washing the carbon tetrachloride layer was ice-cold. The precipitate produced by warming the organic bromide solution with alcoholic silver nitrate contained, besides silver bromide, a certain amount of a solid organic substance (? silver benzoate), which was destroyed by heating for ¼ hour with fuming nitric acid. The samples of silver bromide from the lithium bromide and from the organic bromide were heated to incipient fusion and finely ground before comparison of their activities on the Geiger–Müller counter.

The results, calculated by equation (4) of Part I, are given below, N_s being the *total* rate of the reversible substitution, expressed in mols./l./sec.

Expt.	1	2	3	4	5	6	7	Mean
$N_s \times 10^5$	3·53	3·06	3·28	3·99	4·03	3·70	2·84	3·49 ± 0·37

Discussion.—The absolute rate of the inversion is N_i = 3·18 (± 0·05) × 10^{-5} at 30·2° and in a solution 0·2*M* with respect to each reactant. This agrees, within the experimental error of the radioactive method, with the absolute rate of the substitution reaction at the same temperature and concentrations of reactants, and we conclude that all, or at least 90% of, the molecular acts of substitution lead to stereochemical inversion in this reaction.

SUMMARY.

By means of the radioactive bromine isotope, the velocity in acetone solution of the substitution of bromine for bromine in α-phenylethyl bromide has been compared with the rate of racemisation of the *d*-bromide by lithium bromide under identical conditions. The absolute rates of the two processes are the same within the experimental uncertainty of 10%. The temperature coefficient of the inversion has been determined.

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