

CCXXXI.—*The Preparation and Hydrolysis of the
Isomeric β -Tolyloethyl Bromides.*

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IN a recent paper (Shoesmith and Slater, J., 1924, **125**, 2278), comprising one of a series of investigations on the polar and other factors which govern the reactivity of halogens in substituted halogenated benzenoid derivatives, the transmission of a powerful alternating influence from the methyl group of the tolyl radical

to halogen (a) directly attached to the same benzene nucleus and (b) removed by one carbon atom from the nucleus was demonstrated by the great difference in reactivity of the halogens in the isomeric iodotoluenes, $\text{CH}_3\cdot\text{C}_6\text{H}_4\text{I}$, and ω -bromoxylenes, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$, and by the manner in which the order of ease of replacement of the bromine atoms in the latter case is dependent on the reagent used.

The interesting problem as to how far the influence of the methyl group extends beyond the benzene ring has now been investigated, the isomeric β -tolylethyl bromides having been prepared and submitted to the action of hydrolysing and reducing agents. The compounds are very different from the ω -bromoxylenes and very similar to one another in chemical and physical properties. They are quite stable towards aqueous alcohol at 76° and towards an aqueous acetic acid solution of hydrogen iodide. Differences in the rate of hydrolysis by aqueous-alcoholic sodium hydroxide have been observed and the order is : unsubs. (1.25) > *m*(0.83) > *p*(0.7) > *o*(0.6), but the differences are exceedingly small. (The figures in brackets denote the reciprocal of the time taken for half hydrolysis of the bromide at 76° , *i.e.*, an approximate rate of hydrolysis; compare Shoosmith and Slater, J., 1926, 214.) There appears to be a very slight residuum of alternating effect, and all the substituted compounds are slightly more difficult to hydrolyse than β -phenylethyl bromide—the reverse of the case in the corresponding benzyl bromides.

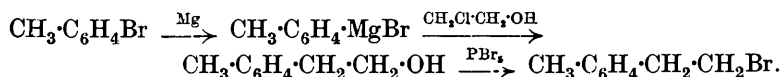
The *o*-isomeride is the most difficultly hydrolysable. The anomalous position of *o*-isomerides has been repeatedly stressed (as has also the fact that this is not due to steric influences; Shoosmith and Slater, J., 1926, 215). Olivier has arrived independently at the same conclusion (*Rec. trav. chim.*, 1926, 45, 452, 710). As yet no satisfactory explanation has been given of the factors governing the reactivity of ortho-substituted benzyl bromides, save that there is here present an influence which renders them less reactive to hydrolysing and more reactive to reducing agents (*e.g.*, hydrogen iodide) than would be expected from any of the various theories put forward to explain enhanced and subdued reactivity.

It may now with certainty be concluded that those influences the effect of which was demonstrated so clearly in the isomeric ω -bromoxylenes are only feebly transmitted through the α -carbon atom of the side chain in the β -tolylethyl bromides, a conclusion of special interest in view of recent observations (Ing and Robinson, J., 1926, 1656; Goss, Hanhart, and Ingold, this vol., p. 250) that a very appreciable general effect due to positively charged nitrogen

is transmitted through two singly bound carbon atoms directly attached to the benzene nucleus.

EXPERIMENTAL.

The isomeric β -tolylethyl bromides were prepared according to the general scheme:



The Isomeric β -Tolylethyl Alcohols.—Grignard's method (*Compt. rend.*, 1905, **141**, 44) was modified in several important particulars. To the bromotoluene (64 g., carefully freed from traces of possible phenolic impurities) in 250 c.c. of dry ether, 9 g. of magnesium were added and, when the vigorous reaction ended, dry, freshly distilled ethylene chlorohydrin (10 g.), dissolved in an equal volume of dry ether, was slowly dropped in. After the vigorous reaction had abated, the ether was distilled away and the residue was heated under 14 mm. pressure at a temperature not exceeding 180—200° for 2 hours to remove toluene, ditolyl, etc.; it was then mixed with ice and after 30 minutes the decomposition was completed by the addition of the calculated quantity of sulphuric acid in ice-water. The ethereal extract of this solution was dried, the ether distilled away, and the residue heated for about 10 minutes with aqueous-alcoholic potash. Extraction with ether, drying, and distillation, finally in a vacuum, then gave the β -tolylethyl alcohol in 20—24% yield, and no improvement could be effected. The alcohols had b. p.'s: *o*-isomeride, 115—116°/13 mm. (compare Grignard, *loc. cit.*); *m*-isomeride, 115—117°/13 mm. (Braun, Grabowski, and Kirschbaum, *Ber.*, 1913, **46**, 1266); and *p*-isomeride, 116.5—118°/14 mm. (Grignard).

The Isomeric β -Tolylethyl Bromides.—As hydrogen bromide has no effect on these alcohols, the bromides were prepared by adding phosphorus pentabromide (60 g.) to 15 g. of the respective β -tolylethyl alcohols, dissolved in 50 c.c. of dry benzene, the reaction being controlled by shaking in ice-water and completed by heating for 1 hour at a temperature not exceeding 50°. The mixture was then poured on excess of ice, and the bromide was extracted with ether, dried over sodium sulphate, and distilled in a vacuum. The distillate was washed with water to remove final traces of phosphoryl bromide, dried, and redistilled. The bromides all boiled, as expected, at a lower temperature than the corresponding alcohols. They had b. p.'s: *o*-compound, 99—100°/10 mm.; *m*-compound, 101—103°/11 mm.; and *p*-compound, 103.5—105°/11 mm. They con-

tained hydrolysable bromine: *o*-isomeride, 39.4; *m*-isomeride, 39.8; and *p*-isomeride, 40.3% ($C_9H_{11}Br$ requires hydrolysable Br, 40.2%). They are stable, sweet-smelling, non-pungent, non-lachrymatory oils, thus differing sharply from the corresponding ω -bromoxylenes.

β -Phenylethyl bromide was prepared from freshly distilled, commercial β -phenylethyl alcohol in a similar manner and, for comparative purposes, to make quite sure that only the *ethyl* bromides are formed by the action of phosphorus pentabromide on the alcohols, a sample was prepared by a method suggested to us by Professor Lapworth. A mixture of β -phenylethyl alcohol (20 g.) and constant-boiling hydrobromic acid (50 c.c.) was boiled under reflux for 4 hours. The bromide so formed was washed with water until free from halogen acid, dried, and distilled. The samples obtained by the two methods had identical boiling points, 89–89.5°/12 mm., estimations of hydrolysable bromine showed they were pure, and later the rate of hydrolysis showed they were identical.

Behaviour towards Hydrogen Iodide.—All the bromides were stable to hydrogen iodide in aqueous acetic acid at 100° for 4 hours. For comparative purposes, some unpublished observations, made in collaboration with Dr. R. H. Slater, on ω -bromo-*m*- and -*p*-xylenes are given in order to stress the differences observed in the two cases. These figures were obtained in a similar manner, but at 110° (experience has shown that slightly different results are obtained at the two temperatures); *t*, *w*, and *x* have the usual significance.

TABLE I.

<i>t</i> (hrs.).	ω -Bromo- <i>m</i> -xylene.		ω -Bromo- <i>p</i> -xylene.*	
	<i>w</i> .	<i>x</i> .	<i>w</i> .	<i>x</i> .
1	0.1239	69	0.1208	44
2	0.1245	87	0.1217	66
3	0.1225	100	0.1286	75

* The *p*-isomeride is not reduced by hydrogen iodide in glacial acetic acid at 25°. Its reduction at 110° shows the powerful reducing action of the aqueous acetic acid reagent at this temperature.

Hydrolysis of the Isomeric β -Tolylethyl Bromides.—The bromides were stable to aqueous alcohol at 76° for 4 hours. Comparative hydrolysis figures were obtained as follows: The bromide (approx. 0.50 g.) was dissolved in 75 c.c. of absolute alcohol, 25 c.c. of *N*/10-sodium hydroxide were added, and the volume was made up to 103 c.c. Aliquot portions (20 c.c.) were heated in a thermostat at 76° (b. p. of carbon tetrachloride) for definite times, and the amount

of hydrolysis which had taken place was estimated by titrating the unused alkali with standard hydrochloric acid. The results are in Table II.

TABLE II.

<i>t</i> (hrs.).	<i>o</i> -Isomeride. <i>w</i> = 0.501.	<i>m</i> -Isomeride. 0.506.	<i>p</i> -Isomeride. 0.500.	β -Phenylethyl bromide. 0.453.
$\frac{1}{2}$	<i>x.</i>	<i>x.</i>	<i>x.</i>	<i>x.</i>
1	38	45	46	56
2	54	63	56	68
4	69	75	71	81
6	82	86	83	89
6	85	90	87	93

The order of reactivity with *N*/30-alcoholic potassium hydroxide at 25° was exactly the same.

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