

LXXXI.—*The Alkaline Hydrolysis of ω -Bromo- and ω -Chloro-nitrostyrenes.*

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THERE appears to be in the literature no definite statement that the influence of a group may be transmitted through a mixed aliphatic aromatic conjugated system, as it undoubtedly is through certain conjugated purely aromatic or aliphatic compounds. Some evidence of the effect of ω -substituents in styrene derivatives is available as far as nitration is concerned. Both cinnamic acid and ω -nitrostyrene (Priebs, *Annalen*, 1884, **225**, 347) give negligible quantities of meta- in comparison with ortho-para-substitution products, and Flürscheim (*J. pr. Chem.*, 1902, **66**, 19) has shown that ω -bromostyrene yields *p*- and *o*-nitro-derivatives. These instances contrast with the nitration of α -nitro- β -phenylethane (Holleman and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79) and of salts of β -phenylethylamine (Goss, Hanhart, and Ingold, *J.*, 1927, 250), in which about 13% of the *m*-nitro-derivative is produced. It is difficult to believe that a saturated aliphatic chain can transmit the effect of a group already present better than an unsaturated conjugated chain.

The problem of the transmission of the influence of one group in a styrene throughout the molecule has been attacked from the reverse point of view, namely, by comparing the activating effects of the nitro-group in different positions in the nucleus on the ω -halogen atom in the *trans-o*-, *m*-, and *p*-nitro- ω -halogenostyrenes.

The reaction involved was that of aqueous-alcoholic potassium hydroxide and the halogenonitrostyrenes at different temperatures, the amounts of potassium bromide (or chloride) produced when the isomerides were subjected to identical and simultaneous treatment being compared. Probably some other reaction than the two already mentioned occurs, as the ω -halogeno-*p*-nitrostyrenes give an intense red colour with alcoholic potassium hydroxide in the cold.

Nef (*Annalen*, 1899, **308**, 268) has shown that the action at 130—135° of alcoholic potassium hydroxide on ω -bromostyrene is to give phenylacetylene and β -ethoxy- α -phenylethylene. These

reactions, although quite distinct, are both due to the mobility of the bromine atom.

In the higher-melting bromonitrostyrenes (which have been called the *trans*-forms), the reactivity of the bromine atom is in the order ortho > para > meta. The order for the chloro-analogues is similar, being para > ortho > meta. It is thus seen that the nitro-group has a greater effect when it is in the ortho- or para-position than when it is in the meta-position, and it follows that its effect is transmitted through the side chain in apparently the same way as it is through the benzene nucleus. Otherwise it is difficult to explain why the nitro-group should have a greater activating influence in the para-position than in the meta-position, in which (if the usual formulæ for benzene are adopted) it is nearer the halogen atom.

This research, however, has brought to light two unexpected facts which must be taken into consideration. The first is that the *cis*- and *trans*- ω -bromo-*p*-nitrostyrenes have a difference of activity of the order of that separating the *trans*-*m*- and *trans*-*p*-compounds. The unsubstituted *cis*- and *trans*- ω -bromostyrenes also present marked differences in activity. Now since ω -bromo-*p*-nitrostyrene is only about 1.25 times as much attacked by the alkali as the *m*-nitro-isomeride (when a total conversion of between 3 and 4% has been brought about; see Table I), it is possible that the great difference in activity of the geometrical isomerides of the same substance may, if the *cis*- changes into the *trans*-form during the reaction, prevent the results obtained being true criteria of the effects of the differently situated nitro-groups. Although possible, this is not probable because the unsubstituted *cis*- and the *cis*-*p*-nitro- ω -bromostyrenes, which are more reactive than the *trans*-forms, only show a tendency to change into the geometrical antimerides in bright light.

cis- ω -Chloro-*m*-nitrostyrene has not been isolated in a pure condition, nor its reactivity investigated. *trans*- ω -Chloro-*m*-nitrostyrene is more reactive at low and less reactive at high temperatures than ω -chlorostyrene (doubtless a mixture of the *cis*- and *trans*-forms) (see Table II and the discussion of results). This phenomenon may be due to the more reactive, geometrically isomeric ω -chlorostyrene being produced at high temperatures, whereas the *trans*-*m*-nitro-derivative may remain in the *trans*-form. In any event, the surprisingly great difference in reactivity of the geometrical isomerides of the same substance encourages the seeking of other and more cogent evidence of the transmission of group influences through a styrene molecule.

Light has been of great assistance in changing *cis*- ω -bromo-*p*-nitrostyrene into the otherwise less accessible *trans*-form.

E X P E R I M E N T A L.

Nitro- ω -bromostyrenes.—The three nitrocinnamic acids (these are best obtained, the *o*- and *m*-compounds from the nitrobenzaldehydes by the Perkin reaction, and the *p*-compound from ethyl cinnamate by nitration and subsequent hydrolysis), when made into a thin paste with glacial acetic acid and treated at 100° with bromine (1 mol.), were converted within a few hours almost quantitatively* into the $\alpha\beta$ -dibromo- β -nitrophenylpropionic acids. These were heated in 30% aqueous sodium acetate (5 mols.) for 4–6 hours and the nitro- ω -bromostyrenes were then isolated by distillation in steam. Each of these was separated by distillation in a vacuum into a high-boiling (which solidified almost completely) and a low-boiling form. The latter in ethereal or benzene solution, when exposed in a silica vessel to sunlight or the ultra-violet light from a 1000-watt mercury lamp, was largely converted into the high-melting form, which was obtained pure by crystallisation from alcohol. When exposed in the solid state to light, these bromo-nitrostyrenes acquire a much deeper yellow colour. They all have pleasant odours.

*The ω -bromo-*o*-nitrostyrenes* (yield, about 20%). The *cis*-form (collected up to 165°/21 mm.) does not solidify at 0°. The *trans*-form boils at 165–167°/21 mm. and separates from alcohol in light yellow prisms, m. p. 39° (Reich and Chang, *Helv. Chim. Acta*, 1920, 3, 240, record m. p. 70°; which is possibly a misprint for 40°) (Found: Br, 35.2. Calc.: Br, 35.1%).

*The ω -bromo-*m*-nitrostyrenes* (yield, about 35%). The solid form boils at 150°/18 mm. and separates from alcohol in very light yellow needles, m. p. 77° (Wollring, *Ber.*, 1914, 47, 110, records m. p. 78–79°: Reich and Koehler, *Ber.*, 1913, 46, 3733, give m. p. 59°). The *cis*-form suffers only a slight conversion into the high-melting form through the action of light.

*The ω -bromo-*p*-nitrostyrenes* (yield, more than 50%). The mixture melts at 40–60° and mostly consists of the low-melting form, contrary to the statement of Reich and Chang (*loc. cit.*, p. 239) that the use of aqueous sodium acetate gives the high-melting form. *trans- ω -Bromo-*p*-nitrostyrene* boils at 182°/21 mm. and separates from alcohol or light petroleum in minute, very pale yellow needles, m. p. 160° (Reich and Chang, *loc. cit.*, record m. p. 123°), unchanged by sublimation in a cathode ray vacuum (Found: Br, 34.8; *M*, by Rast's method, 224. Calc.: Br, 35.1%; *M*, 228).

* The difficulty in brominating these acids reported in the literature (Müller, *Annalen*, 1882, 212, 122; Beilstein's "Handbuch," 3rd edn., II, p. 1414) was due to the selection of an unsuitable solvent.

cis- ω -Bromo-*p*-nitrostyrene, which cannot be obtained pure from the mixture described above, is produced unaccompanied by the *trans*-form when $\alpha\beta$ -dibromo- β -*p*-nitrophenylpropionic acid is heated with alcoholic instead of aqueous sodium acetate (Reich and Chang, *loc. cit.*). It crystallises from light petroleum (b. p. 40—60°) in thick, yellow prisms, m. p. 49°, b. p. 168—170°/21 mm. (Found; *M*, by Rast's method, 236).

*The Action of Light on cis- ω -Bromo-*p*-nitrostyrene.*—A dilute benzene solution, 5 mm. deep, of the pure *cis*-form (m. p. 49°) was exposed in a clear silica test-tube to bright sunlight for 4 hours, and after removal of the benzene the melting point was 95—140°. Similarly, a mixture of the two forms (m. p. 40—60°) in benzene solution was converted in bulk into a mixture, m. p. 115—150°, after 30 hours' exposure to sunlight. From such a mixture the pure *trans*-form is easily obtained by crystallisation from alcohol. Photo-conversion in solutions in glass vessels is also quite rapid, and the solid *cis*-form is unstable to sunlight. When spread in thin layers, the pure *cis*-form has its melting point raised from 49° to 45—70° after 2 hours' exposure to sunlight. It had previously been noted that it was impossible to obtain the pure *cis*-form by crystallisation in bright light.

ω -Bromostyrene.—The two forms, m. p. -7° and $+7^\circ$ respectively, have been isolated by Dufraisse (*Compt. rend.*, 1920, **171**, 960), who found that exposure to light changed both forms into a mixture, m. p. 2° , containing a large proportion of the higher-melting isomeride. Our experiments, probably partly owing to different lighting conditions, gave one form, m. p. -5° to -2.5° , b. p. 105°/18 mm., and another form, m. p. 2.2° , b. p. 120°/29 mm. These mixtures must have contained relatively large amounts of the *cis*- and *trans*-forms respectively, because the lower-melting form remained almost colourless, whereas that melting at 2.2° soon became deep yellow and finally brown even in the dark. This behaviour is characteristic of the two forms isolated by Dufraisse (*loc. cit.*). The low-melting isomeride is converted into the mixture, m. p. 2.2° , by the action of light. This mixture, m. p. 2.2° , and the mixture, m. p. -5° to -2.5° , were examined from the point of view of comparative mobility of the bromine atom (see Table I).

Nitro- ω -chlorostyrenes.—Into an ice-cold solution of the nitrocinnamic acid in sodium carbonate a slow stream of carbon dioxide is passed, and a cold solution of sodium hypochlorite is gradually added, during 8 hours. The product is then steam-distilled, the styrene derivative being obtained in the high-melting form without a trace of the low-melting isomeride (yield, 5—15%). All these chloronitrostyrenes have pleasant odours.

ω -Chloro-*o*-nitrostyrene forms very pale yellow needles, m. p. 58° (Lipp, *Ber.*, 1884, 17, 1070, records m. p. 58—59°). ω -Chloro-*m*-nitrostyrene crystallises from alcohol in short, thick, yellow prisms, m. p. 83° (Found : Cl, 19.4. $C_8H_6O_2NCl$ requires Cl, 19.4%), which rapidly deepen in colour on exposure to light. ω -Chloro-*p*-nitrostyrene crystallises from alcohol, in which it is much less soluble than the two preceding isomerides, in very pale yellow, minute needles, m. p. 128° (Found : Cl, 19.4%).

ω -Chlorostyrene is best prepared by taking advantage of the formation of $\alpha\beta$ -dichloro- β -phenylpropionyl chloride by the interaction of cinnamic acid and phosphorus pentachloride (Clarke, *J.*, 1910, 97, 894). The acid chloride was isolated, the acid decomposed with sodium acetate, and the styrene fractionated, a colourless oil, b. p. 92—93°/22 mm., which slowly became pale yellow, being obtained (yield, 60%).

TABLE I.

Hydrolysis of the ω -Bromostyrenes.

Bromostyrene.	Experiment. Temp. Time (hours).					
	I.	II.	III.	IV.	V.	VI.
	14°.	17°.	17—24°.	41—41.3°.	39.3—41.3°.	40.7—42.0°.
	24.	18.	117.5.	16.	5.	16.
	Percentage conversion.					
<i>o</i> -Nitro-	99.5	99.5	—	—	—	—
<i>m</i> - "	3.30	3.62	4.69	—	—	—
<i>p</i> - " , m. p. 160° ...	4.15	4.45	30.8	48.8	18.7	—
Unsubs., m. p. 2.2° ...	—	4.37	11.3	12.41	—	13.9
" , m. p. -2.5° ...	—	—	15.07	17.9	—	18.74
<i>p</i> -Nitro-, m. p. 49°	—	—	—	98.51	98.1	—

Procedure.—The bromostyrene (0.001—0.002 g.-mol.) was dissolved in cold alcohol and after the correct temperature had been attained, 5.0 c.c. of 7*N*-potassium hydroxide were added. The product was worked up on a macro-scale as described for the chloro-compounds. The amount of alcohol (98.6%) required to dissolve 0.002 g.-mol. of ω -bromo-*p*-nitrostyrene was about 180 c.c. The comparisons were made under identical conditions of concentration and temperature, and were carried out simultaneously. The results recorded in Table I are discussed after Table II.

TABLE II.

Hydrolysis of the ω -Chlorostyrenes.

Chlorostyrene.	Experiment. Temp. Time.			
	I. 40.3—41.3°.	II. 41—41.3°.	III. 81°.	IV. 81°.
	20 hrs.	20 hrs.	125 mins.	125 mins.
	Percentage conversion.			
Unsubs.	5.65	5.7	37.95	36.3
<i>o</i> -Nitro-	33.6	34.3	101.4	100.2
<i>m</i> - "	11.7	12.1	23.6	24.2
<i>p</i> - "	64.9	68.0	100.7	100.5

Procedure.—0.001 G.-mol. (0.1835 g. of the chloronitrostyrene; 0.1385 g. of ω -chlorostyrene) was made up to 100 c.c. in alcohol. 10 C.c. of this solution were treated with 10 c.c. of alcohol and 10 c.c. of 2*N*-potassium hydroxide. The comparison of the four substances in each experiment was made at the same time, either in a thermostat or at the boiling point (81°). After the reaction had finished, the product was washed out by water and a little alcohol into a large boiling-tube, nitric acid and silver nitrate were added, and the silver chloride was coagulated by heating the mixture nearly to the boiling point in a beaker of water. By having the level of the water in the beaker above that of the solution in the tube and by keeping the temperature below that of boiling water, the sudden disastrous evolution of acetaldehyde, generated by the action of nitric acid on the alcohol, was prevented. The silver chloride was estimated after Pregl. It is advisable, before drying, to wash the filter tube with hot alcohol to remove traces of precipitated styrene. This is particularly necessary when working with the very sparingly soluble ω -chloro-*p*-nitrostyrene. The alcohol used throughout these micro-experiments was methylated spirit, consisting of ethyl alcohol (91.6%), water (6.4%), and methyl alcohol (2%).

The experiments were carried out in the dark or in diffused daylight. The chlorostyrenes are too non-reactive at the ordinary temperature for the decomposition to be measurable. Even at the ordinary temperature, however, the solution containing the para-compound became red on standing. On boiling, the ortho-compound gave a very pale yellow solution, but the unsubstituted and the *m*-nitro-chlorostyrene remained colourless.

Discussion of the Results.—From the results in Table I for the *trans*- ω -bromostyrenes it is seen that (1) the *o*-nitro-compound is extraordinarily reactive, (2) at the temperatures investigated, the *p*- is more reactive than the *m*-nitro-compound; the ratios of the conversion in experiments (I) and (II), in which only a small percentage conversion was obtained, are respectively 1.26 and 1.23 to 1, (3) the order of activity of the bromine atom is ortho > para > unsubstituted > meta. It must be remembered, however, that the unsubstituted bromostyrene (m. p. 2.2°) contained some of the more reactive *cis*-form.

The *cis*-*p*-nitro- is far more reactive than the *trans*-*p*-nitro-compound (see experiments IV and V), and the unsubstituted bromostyrene (m. p. -2.5°), which contains much of the *cis*-form, is more reactive than the mixture, m. p. 2.2°, which is richer in the *trans*-form (experiments IV and VI).

For the ω -chlorostyrenes (Table II) the order of activity of the halogen atom is, at about 41°, para > ortho > meta > unsubstituted,

and at 81°, (para and ortho) > unsubstituted > meta. An explanation of the inversion of the order for the *m*-nitro- and the unsubstituted ω -chlorostyrene is suggested on p. 606. It is also possible that two reactions occur simultaneously between the alkali and the nitro- and the unsubstituted styrene. A similar phenomenon is noticeable, though to a less extent, in the *m*- and *p*-nitro- ω -bromostyrenes (see experiments I, II, and III in Table I), where increase in temperature from 17° to 17–24° increases the activity of the *p*-far more than that of the *m*-isomeride.

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