ROTATORY POWER AND CHEMICAL CONSTITUTION.

Part I. The Preparation and Resolution of α-Benzyl-α-Caproic Acid and some Derivatives.

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In an earlier paper it was shown that the β-toluene sulphonyl derivative of cinchonicine had a much smaller positive rotatory power than the benzoyl derivative while the picryl derivative had a very large negative rotation and it was suggested that these changes were due to the effect of the substituents upon the intramolecular electrical field of force, and the consequent changes in the forces binding the electrons responsible for optical activity. Looking at these facts from another point of view we see that the dipole produced by the benzoyl group is weaker than that produced by the β-toluene sulphonyl group and this in turn weaker than the three dipoles formed by the three nitro groups in the picryl group and this change first lowers the rotatory power and finally changes its sign. The object of these experiments was to determine whether effects similar to those observed by Flurscheim in reactivity and strengths of acids and bases could also be observed in rotatory powers. Although molecular rotatory powers for one wave-length only are not suitable for absolute comparisons of optical activity yet when the substances examined possess no absorption bands in the neighbourhood of the wave-length used for the measurements, qualitative relationships may at least be hoped for. In this connection it must be pointed out that the high, negative rotation of picryl cinchonicine is possibly bound up with its possessing absorption bands in the visible region of the spectrum.

The effect of a substituent on reactivity is usually considered under three heads: the general polar effect and the electromeric effect both of which are regarded as transmitted through the chain of atoms and a space effect, similar to the general polar effect but transmitted through space. In spirane compounds where no asymmetric atoms in the normal sense of the word are present optical activity may be regarded as due entirely

to effects transmitted through space and the existence of optical activity in such cases shows that the direct or space effect is by no means negligible. The general polar effect of substituents upon rotatory power has been the subject of extensive work by Betti,\textsuperscript{2} Rule\textsuperscript{3} and others, who have obtained valuable results. The object of the experiments to be described was the search for an alternating effect similar to that observed by Olivier, Lapworth and Shoesmith and others in the reactivity of benzyl halides. For this purpose cinchonicine with its two optically active centres was unsuitable and so were all compounds in which the group whose effect was to be studied was bound to the optically active centre by an oxygen atom because it has been shown that an oxygen atom is generally a very effective barrier to alternating effects. It has, however, been found that in substances of the type $X.C_6H_4.CH_2.Y$ an alternating effect is transmitted to $Y$ and therefore it was expected that acids of the type $X.C_6H_4.CH_2.CH(R).COOH$ might show such an alternating effect. Reactivity measurements have shown that, in substances of the type $X.C_6H_4.CH_2.Y$ where $Y$ is a halogen, when $X$ is a halogen or the methyl group the reactivity is higher with $X$ para than with $X$ meta but that when $X$ is the nitro or carboxyl group the reactivity is lower with $X$ para than with $X$ meta. There is an exception to this; with trimethyl-amine in benzene para nitrobenzyl chloride reacts faster than does meta nitrobenzyl chloride\textsuperscript{4} with aromatic amines the meta compound reacts faster than the para. This discrepancy is not shown by all substituted benzyl halides when they react with aromatic and fatty tertiary amines because Jones and Preston\textsuperscript{5} found that with both dimethylaniline and tri-isoamylamine para xylyl bromide reacted faster than meta. The reaction studied by Norrish and Smith seems therefore to be exceptional. The compounds examined below were those of the type $X.C_6H_4.CH_2.CH(C_6H_9).COOH$ where $H$ was $H$, $Br$ meta and para, $COOH$ meta and para. It was expected that if the change from the meta position to the para position of the bromine atom produced any effect on the rotatory power then the opposite effect would be produced by the carboxyl group. No particular difficulty was observed in resolving $\alpha$-benzyl-$n$-caproic acid and the meta and para brom derivatives but the resolution of the meta and para carboxy compounds gave capricious results and the rotations observed were very small. The molecular rotations for the acids concerned are given below:—

\textsuperscript{2} *Gazzetta*, 1907, 37, 1, 62 and later papers.
\textsuperscript{3} *J.C.S.*, 1924, 125, 2168 and later papers.
\textsuperscript{4} Norrish and Smith, *J.C.S.*, 1928, 129.
\textsuperscript{5} *J.C.S.*, 1912, 101, 1930.