sented some theoretical reasons for the existence of surface cracks on heteropolar crystals. Both theoretical and experimental evidence can be adduced showing that cracks of the same kind also exist in the interior of these crystals. Different authors[7] have discussed the possibility of clearing up the discrepancy mentioned at the beginning of this paper on these grounds. Most of them came to the conclusion that the existence of internal cracks would make it necessary to introduce corrections which would make the stated discrepancy still worse. It appears to me, however, that no effect is to be expected at all, at least, not if the cracks are of the nature which I have proposed in my paper. The opening of the cracks and the resulting decrease of the average density of the crystal is, indeed, exactly compensated for by the contraction of one or more surface planes bounded by the cracks. The interior structure of the blocks which are formed in this manner, is hardly affected, and it is these blocks, which constitute the major part of the crystal. Their structure, therefore, determines the interference pattern of the reflected x-rays and this will be the same as that given by an ideal crystal except for the intensity and the width of the reflected lines.

[1] J. A. Bearden, *Proc. Nat. Acad. Sci.*, **15,** 528–533 (1929).

[2] A. P. R. Wadlund, *Phys. Review,* **32,** 841 (1928).

[3] E. Baecklin, *Upsala Dissertation,* 1928.

[4] F. Zwicky, *Proc. Nat. Acad. Sci.*, **15,** 816 (1929).

[5] F. Zwicky, *Ibid.*, **15,** 253 (1929).

[6] O. K. de Foe and A. H. Compton, *Phys. Review,* **25,** 618 (1925).

[7] See for instance, A. H. Compton, *J. Frank. Inst.*, **208,** 605 (1929).

THE PROBLEM OF PREPARING OPTICALLY ACTIVE FREE RADICALS

BY EVERETT S. WALLIS

FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY

Communicated January 31, 1930

In carrying out certain investigations on the Beckmann rearrangement Jones and Wallis[1] studied the nature of the products formed by the rearrangement of certain optically active acid azides, and optically active hydroxamic acids. *d*-Benzylmethylacetazide, $C_7H_7(CH_3)HCCON_3$, was found to give on rearrangement an optically active isocyanate, $C_7H_7(CH_3)HCNCO$, which could be converted into an optically active amine hydrochloride, and by treatment with aniline into an optically active monosubstituted urea. These experiments together with certain other facts taken from a survey of the properties of optically active compounds described in the literature led them to suggest that it was very probable that in the rearrangement the optically active radical, if existing as a free radical, did so in such a way as to maintain a configuration required to produce an optically active rearrangement product, that is, it was a positive radical which is of the nature of a carbonium ion, and that in its wandering from the carbon atom to the nitrogen atom it leaves behind the electron which it shared with the carbon atom.

These investigations suggested to the author two problems: 1. A study of the Beckmann rearrangement in the presence of free radicals; 2. The possibility of preparing an optically active free radical. The results obtained from a study of the first problem have been published.[2] I now wish to report on certain investigations which of necessity had to be carried out before any answer could be given to the second problem.

The first step in the preparation of an optically active free radical involves the preparation of certain derivatives of an optically active tertiary carbinol, and since derivatives of tertiary carbinols of the aliphatic series do not form free radicals, we are limited in our choice to tertiary carbinols of the aromatic series containing an asymmetric carbon atom. A survey of the literature shows that no derivatives of tertiary carbinols of this type have hitherto been resolved. Therefore any method of resolution of these compounds should be of interest.

For these investigations I chose phenylbiphenyl-α-naphthyl carbinol, $C_6H_5(C_6H_5C_6H_4)(C_{10}H_7)COH$. This carbinol in the form of its chloride was prepared by the method of Schlenk[3] and had a melting point of 196.5–197°C. The carbinol was also prepared and melted at 162°C.

Several attempts were made to resolve the carbinol itself by combining it directly with brucine, quinine, camphor sulphonic acid, etc., but only negative results were obtained. Experiments were carried out in an attempt to make the carbinol in the form of its chloride combine with silver salts of optically active acids, but this method of approach proved unsatisfactory. Attempts to prepare the half ester of phthalic acid and the carbinol also failed so that method of resolution with an alkaloid could not be used. The chloride did combine with the sodium salt of optically active amyl alcohol as was first reported by Schmidlin[4] but fractional crystallization gave only a very small amount of the optically active amyl ether and this method was abandoned.

Phenylbiphenyl-α-naphthylchlormethane, however, was found to combine with thioglycollic acid according to the following equation

$$C_6H_5(C_6H_5C_6H_4)(C_{10}H_7)CCl + HSCH_2COOH \longrightarrow$$
$$HCl + C_6H_5(C_6H_5C_6H_4)(C_{10}H_7)C\text{-}SCH_2COOH,$$

giving a stable thioglycollic acid derivative which combined with brucine and was easily resolved, giving the thioglycollic acid derivative of the optically active tertiary carbinol.

Preparation of d,l-Phenylbiphenyl-α-naphthylmethylthioglycollic Acid.—

$$C_6H_5(C_6H_5C_6H_4)(C_{10}H_7)C\text{–}SCH_2COOH,$$

10.90 g. of thioglycollic acid were refluxed with 47.8 g. phenylbiphenyl-α-naphthylchlormethane in 100 cc. dry toluene. The reaction began at a temperature of about 70°C., and hydrogen chloride gas came off as the by-product of the reaction. After the end of the reaction, which usually took about one hour, the solution was allowed to cool, and the white crystalline precipitate which separated was collected at the pump. This was washed with petrol ether, and after two crystallizations from hot toluene gave a white crystalline material which contained one molecule of toluene of crystallization and melted sharply at 116–116.5°C. Yield, 51 g. Analysis for sulphur. Carius method. 0.2006 g. of substance. gave 0.0851 g. $BaSO_4$. Calc., S: 5.79 per cent. Found, 5.82 per cent.

Resolution of Phenylbiphenyl-α-naphthylmethylthioglycollic Acid.—85 g. of the racemic material were dissolved in 200 cc. of dry acetone and added while still warm to 90 g. brucine suspended in 400 cc. of acetone. Solution took place immediately. The mixture was filtered, and allowed to cool overnight without stirring. A large amount of a white material separated. This was collected at the pump, and fractionally crystallized from a hot chloroform petrol ether solution. After four crystallizations no further change in the optical activity or the melting point of the solid could be detected. Forty g. of brucine salt were obtained which melted sharply at 215°C.

1.2124 g. of this material dissolved in 25 cc. of chloroform solution gave a rotation of -1.64 in a 2-dc. tube at 20°C. $[\alpha]_D^{20} = -16.91$.

Preparation of l-Phenylbiphenyl-α-naphthylmethylglycollic Acid.—39 g. of the brucine salt were suspended in ether and decomposed with dilute sulphuric acid. The ether layer was washed free from the sulphate ion and then dried with anhydrous sodium sulphate. This solution was concentrated to about 150 cc. and the acid slowly precipitated by addition to petrol ether. The white material which precipitated was collected at the pump, and recrystallized from warm toluene-petrol ether solution. The dry product melted at 109–110°C.

1.0242 g. dissolved in 25 cc. of dry ether solution gave a rotation of -1.06 at 25°C. in a 2-dc. tube. $[\alpha]_D^{25} = -12.93°$.

1.002 g. dissolved in 25 cc. of carbon tetrachloride solution gave a rotation of -1.09 at 20°C. in a 2-dc. tube. $[\alpha]_D^{20} = -13.63°$. Analysis for sulphur. Carius method.

0.1412 g. of substance gave 0.0722 g. $BaSO_4$. Cal. S: 6.95 per cent. Found, 6.90 per cent.

Conclusions.—A method of resolution of tertiary carbinols of the aromatic series containing an asymmetric carbon atom has been described by means of which an optically active derivative of phenylbiphenyl-α-naphthyl carbinol has been prepared. Investigations are now in progress with a view of converting this compound into an optically active triarylmethyl. The results of these experiments will be reported at a later date and should be of interest not only in connection with the Beckmann rearrangement but also should contribute further valuable information on such important questions as the Walden Inversion and the constitution of the triaryl methyls in general.

[1] Jones and Wallis, *J. Am. Chem. Soc.*, **48**, 169 (1926).

[2] Wallis, *Ibid.*, **51**, 2982 (1929).

[3] Schlenk, *Ann.*, **394**, 196 (1912).

[4] Schmidlin, *Ber.*, **45**, 3188 (1912).

THE IMPLANTATION OF ADDITIONAL HYPOPHYSEAL RUDIMENTS IN URODELE EMBRYOS

By Raymond F. Blount

Osborn Zoölogical Laboratory, Yale University

Communicated February 5, 1930

A series of experiments has been performed in which additional hypophyseal rudiments have been implanted in urodele embryos. The object of the transplantation has been to produce a continuous excess of a secretion similar in character and mode of excretion to that of the normal gland. The transplants have been from embryos of the same age, which, by developing concomitantly with the normal gland, bring about a condition comparable to spontaneous hypersecretion which occasionally occurs in animals. This cannot be done by methods formerly used, such as periodic injection, feeding, or by grafting adult glands in late stages. Recently Allen ('29)[1] has grafted pituitary anlagen from the embryo into the larvae of frogs. Since the age of the graft and the age of the host are widely different, neither the method nor the results of this work are directly comparable to those of the present.

Embryos of Amblystoma punctatum were used for the majority of the transplantations, although for some of the work those of A. tigrinum and the axolotl were used. The operations were performed before the invagination of the pituitary rudiment (Harrison's Stages 25–31).[2]

The operations were of two types. The first consisted in removing the ectoderm and underlying neural tube from the region immediately anterior to the stomodeum of one animal and placing it in an opening prepared in