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# THE DETERMINATION OF THE ABSOLUTE CONFIGURATIONS OF SOME PHENYLALLENECARBOXYLIC ACIDS

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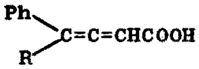
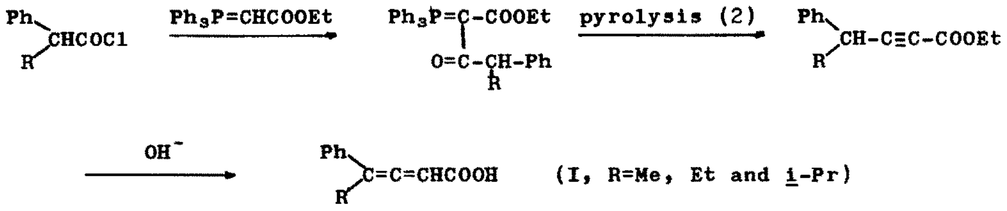
We wish to report the synthesis, resolution and the determination of the absolute configurations of some phenylallenecarboxylic acids (I).



$$\mathrm{(Ph)(R)C{=}C{=}CHCOOH}$$

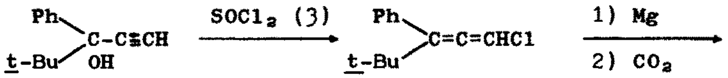
(I, R=H, Me, Et, *i*-Pr and *t*-Bu)

Phenylallenecarboxylic acid (I, R=H) was prepared according to the known procedure (1), and the other acids (I, R=Me, Et and *i*-Pr) were synthesized by the method outlined in the folowing chart.



(I, R=Me, Et and *i*-Pr)

Phenyl-*t*-butylallenecarboxylic acid (I, R=*t*-Bu), too, could be obtained by the same reactions, but the following route was found to be more convenient.



(I, R=*t*-Bu)*

These racemic acids were resolved via the cinchonidine salts. The (+)-isomers were obtained excepting the case of R=Et which gave the (-)-enantiomer.

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* The attempt to prepare the optically active acid starting from the active chloroallene failed due to the complete racemization.

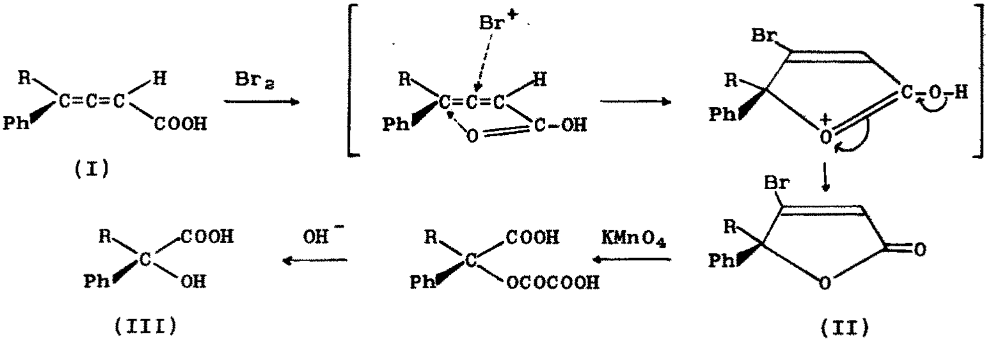
All attempts of resolution by the use of other bases such as brucine, strychinine, quinine and cinchonine gave unsatisfactory results. The melting points and the optical rotations (in methanol) of these acids are summarized in Table I.

TABLE I

Physical Properties of Phenylallenecarboxylic Acids (I)

| R | H | Me | Et | i-Pr | t-Bu |
|---|---|---|---|---|---|
| m.p. | 109-110 | 101-102 | 96-98 | 88.5-89.5 | 125 |
| $[\alpha]_D$ | +420 | +318 | -280 | +205 | +177 |

These allenic acids (I), on treatment with 1 mole of bromine in carbon tetrachloride, gave neutral materials (70-90% yield) with loss of hydrogen bromide. The elemental analyses, I.R.- and N.M.R. spectra indicated their bromolactone structures (II).



The optically active allenic acids (I) resulted in the optically active crotonolactones (II). Their properties are listed in Table II. The rotations were determined in methanol unless otherwise indicated. As illustrated in the

TABLE II

Physical Properties of Crotonolactones (II)

| R | H | Me | Et | i-Pr | t-Bu |
|---|---|---|---|---|---|
| m.p. | 88.5-89.5 | 99-101 | 61-62 | oil | 65-66 |
| $[\alpha]_D$ | +149* | +118 | -190 | +260 | +64 |

Asterisk indicates the value in n-hexane.

reaction scheme, the stereospecific cyclization may be rationalised assuming the carboxyl group participation in the attack of bromine cation. The proposed mechanism is considered to be analogous to that of the bromination of some $\gamma,\delta$-unsaturated acids (4). The structures of II were also confirmed by the following degradation. Permanganate oxidation of II in acetone-water, and successive hydrolysis in an alkaline solution resulted in the corresponding hydroxy acids (III, 40% yield). Moreover, all the hydroxy acids (III) were obtained in optically active state, when the active crotonolactones (II) were used. The melting points and the rotations (in ethanol) of the active acids (III) together with the literature values were listed in Table III. The high optical purity of the resulting III indicates the highly stereospecific nature of the brominative cyclization reaction. The hydrolysis of ester intermediate has already been shown to proceed with retention of configuration in these hydroxy acids (6), and the absolute configurations of III (R=H, Me and Et) are shown to be S(+) (7). Therefore, the absolute configurations of S(+) can be assigned to II and I (R=H, Me and Et). The fact that the intermediate cyclic compounds (II) can be isolated in optically pure state in the conversion of allenic compounds (molecular dissymmetry) into the asymmetric carbon compounds (III) of known absolute configurations makes unambiguous our assignment of the configurations of II and I. As the optical active hydroxy acids (III, R=*i*-Pr and *t*-Bu) have not been reported yet, the configurations were determined by their optical rotatory properties. Recently, Klyne and the co-workers have studied the O.R.D. of the derivatived of mandelic acids (8). They have attri-

TABLE III

Physical Properties of Hydroxy Acids (III)

| R | H | Me | Et | *i*-Pr | *t*-Bu |
|---|---|---|---|---|---|
| m.p. | 130.0-131.5 | 115-116 | 126-128 | 108-109 | 110-112 |
| $[\alpha]_D$ obs. | +151 | +36.5 | -32 | +33* | -50* |
| $[\alpha]_D$ lit. | +149.7 (5a) | +37.7 (5b) | +32.7 (5c) | | |

Asterisks indicate the values in methanol.

buted the Cotton-effect of III (R=H, Me and Et) in the 220-230 mμ region to the n ⟶ π* transition of the carboxyl group, and (S)-configurations have been related to the positive sign of the Cotton-effects. We have observed the (+)-Cotton-effects of III (R=i-Pr and t-Bu: C.D. maxima, 224 mμ ; $\Delta\varepsilon$ 12.5 and 222 mμ ; $\Delta\varepsilon$ 6, respectively) in the same region as III (R=H, Me and Et). It is to be noted that III (R=t-Bu) which has negative $[\alpha]_D$ exhibits (+)-Cotton-effect at 220 mμ region indicating the limited validity of simple application of the Brewster's rule (9).

Thus, all the hydroxy acids (III) derived from the (+)-phenylallenic acids (I) are shown to have (S)-configuration and accordingly the absolute configuration of the (+)-allenic acids (I) are established to be (S).

The studies on the optical rotatory properties of the phenylallenecarboxylic acids (I) will be reported in near future.

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